

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE**  
**ENGINEERING AND TECHNOLOGY**

**ENVIRONMENTALLY FRIENDLY COMPONENTS  
FOR ENERGY STORAGE DEVICES**



**Ph.D. THESIS**

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**Department of Polymer Science and Technology**

**Polymer Science and Technology Programme**

**SEPTEMBER 2019**



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**İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**ENERJİ DEPOLAMA CİHAZLARINDA ÇEVRE DOSTU BİLEŞENLERİN  
KULLANIMI**

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## ABBREVIATIONS

|                                    |                                           |
|------------------------------------|-------------------------------------------|
| <b>1D</b>                          | : One dimensional                         |
| <b>3D</b>                          | : Three dimensional                       |
| <b>AC</b>                          | : Active carbon                           |
| <b>ALD</b>                         | : Atomic layer deposition                 |
| <b>BE</b>                          | : Battery-like electrode                  |
| <b>BET</b>                         | : Brunauer-Emmette-Teller                 |
| <b>CAs</b>                         | : Carbon aerogels                         |
| <b>CBE</b>                         | : Capacitor and battery-like electrode    |
| <b>CC</b>                          | : Constant current                        |
| <b>CE</b>                          | : Capacitor-like electrode                |
| <b>CNF</b>                         | : Carbon nanofiber                        |
| <b>CNT</b>                         | : Carbon nanotube                         |
| <b>Cp</b>                          | : Peanut-shell derived carbon particles   |
| <b>Cs</b>                          | : Commercial carbon particles             |
| <b>CVD</b>                         | : Chemical vapor deposition               |
| <b>DFT</b>                         | : Density Functional Theory               |
| <b>EDX or EDAX</b>                 | : Energy dispersive x-ray spectroscopy    |
| <b>EIS</b>                         | : Electrochemical Impedance Spectroscopy  |
| <b>ELDCs</b>                       | : Electrochemical double layer capacitors |
| <b>FTIR</b>                        | : Fourier-transform infrared spectroscopy |
| <b>GCD</b>                         | : Galvanostatic charge-discharge          |
| <b>HER</b>                         | : Hydrogen evolution reaction             |
| <b>LC</b>                          | : Liquid crystal                          |
| <b>LiB</b>                         | : Lithium ion battery                     |
| <b>NaB or SIB</b>                  | : Sodium ion battery                      |
| <b>NF</b>                          | : Nanofiber                               |
| <b>NLDFT</b>                       | : Non Localized Density Functional Theory |
| <b>OER</b>                         | : Oxygen evolution reaction               |
| <b>SC</b>                          | : Supercapacitor                          |
| <b>SEI</b>                         | : Solid electrolyte interface             |
| <b>SEM</b>                         | : Scanning electron microscope            |
| <b>SME</b>                         | : Single main material                    |
| <b>SSA</b>                         | : Specific surface area                   |
| <b>XRD</b>                         | : X-ray diffraction                       |
| <b>Ag</b>                          | : Silver                                  |
| <b>BF<sub>4</sub></b>              | : Tetrafluoroboranium                     |
| <b>BF<sub>x</sub>O<sub>y</sub></b> | : Boron fluoride oxide                    |
| <b>C</b>                           | : Carbon                                  |
| <b>CO</b>                          | : Carbon monoxide                         |
| <b>CO<sub>2</sub></b>              | : Carbon dioxide                          |
| <b>Co<sub>3</sub>O<sub>4</sub></b> | : Cobalt(II, III) oxide                   |
| <b>Cu</b>                          | : Copper                                  |

|                                                             |                                    |
|-------------------------------------------------------------|------------------------------------|
| <b>DMC</b>                                                  | : Dimethyl carbonate               |
| <b>DMF</b>                                                  | : N, N-Dimethylformamide           |
| <b>EC</b>                                                   | : Ethylene carbonate               |
| <b>Fe(CN)<sub>6</sub></b>                                   | : Ferricyanide                     |
| <b>Fe<sub>2</sub>O<sub>3</sub></b>                          | : Iron(III) oxide                  |
| <b>Fe<sub>3</sub>O<sub>4</sub></b>                          | : Iron(II, III) oxide              |
| <b>H<sub>2</sub></b>                                        | : Hydrogen                         |
| <b>HCl</b>                                                  | : Hydrochloric acid                |
| <b>K</b>                                                    | : Potassium                        |
| <b>KCl</b>                                                  | : Potassium chloride               |
| <b>KOH</b>                                                  | : Potassium hydroxide              |
| <b>Li</b>                                                   | : Lithium                          |
| <b>Li/O</b>                                                 | : Lithium oxygen battery           |
| <b>Li/S</b>                                                 | : Lithium sulfur battery           |
| <b>Li<sub>2</sub>O</b>                                      | : Lithium oxide                    |
| <b>Li<sub>2</sub>S</b>                                      | : Lithium sulfide                  |
| <b>LiCoO<sub>2</sub></b>                                    | : Lithium cobalt oxide             |
| <b>LiPF<sub>6</sub></b>                                     | : Lithium hexafluorophosphate      |
| <b>Mn</b>                                                   | : Manganese                        |
| <b>Mn(CH<sub>3</sub>COO)<sub>2</sub></b>                    | : Manganese acetate                |
| <b>MnO<sub>2</sub></b>                                      | : Manganese(IV) oxide              |
| <b>MnO<sub>x</sub></b>                                      | : Manganese oxide                  |
| <b>MoO<sub>x</sub></b>                                      | : Molybdenum oxide                 |
| <b>MoS<sub>2</sub></b>                                      | : Molybdenum disulfide             |
| <b>Na</b>                                                   | : Sodium                           |
| <b>Na<sub>x</sub>Fe[Fe(CN)<sub>6</sub>]·nH<sub>2</sub>O</b> | : Prussian blue                    |
| <b>Ni</b>                                                   | : Nickel                           |
| <b>NMP</b>                                                  | : N-Methyl-2-pyrrolidone           |
| <b>O<sub>2</sub></b>                                        | : Oxygen                           |
| <b>PAN</b>                                                  | : Polyacrylonitrile                |
| <b>PANi</b>                                                 | : Polyaniline                      |
| <b>PB</b>                                                   | : Prussian blue                    |
| <b>PEDOT</b>                                                | : Poly(3,4-ethylenedioxythiophene) |
| <b>PEO</b>                                                  | : Polyethylene                     |
| <b>PPy</b>                                                  | : Polypyrrole                      |
| <b>Pt</b>                                                   | : Platinum                         |
| <b>PVA</b>                                                  | : Polyvinyl alcohol                |
| <b>PVDF</b>                                                 | : Polyvinylidene fluoride          |
| <b>PVP</b>                                                  | : Polyvinylpyrrolidone             |
| <b>RuO<sub>2</sub></b>                                      | : Ruthenium(IV) oxide              |
| <b>S<sub>8</sub></b>                                        | : Octasulfur                       |
| <b>Sb</b>                                                   | : Antimony                         |
| <b>Si</b>                                                   | : Silicon                          |
| <b>Si/C</b>                                                 | : Silicon/Carbon                   |
| <b>SiO<sub>2</sub></b>                                      | : Silicon dioxide                  |
| <b>Sn</b>                                                   | : Tin                              |
| <b>SnCl<sub>4</sub></b>                                     | : Tin(IV) chloride                 |
| <b>SnCl<sub>4</sub>·5H<sub>2</sub>O</b>                     | : Tin(IV) chloride pentahydrate    |
| <b>SnMo</b>                                                 | : Tin-Molybdenum                   |

|                         |   |                                      |
|-------------------------|---|--------------------------------------|
| <b>TEATFB</b>           | : | Tetraethylammonium tetrafluoroborate |
| <b>Ti</b>               | : | Titanium                             |
| <b>TiO<sub>2</sub></b>  | : | Titanium dioxide                     |
| <b>ZnCl<sub>2</sub></b> | : | Zinc chloride                        |





## SYMBOLS

|                         |                              |
|-------------------------|------------------------------|
| <b>CV</b>               | : Cyclic voltammetry         |
| <b>d</b>                | : Diameter                   |
| <b>E</b>                | : Energy                     |
| <b>I</b>                | : Current                    |
| <b>k</b>                | : Fitting pre-factor         |
| <b>La</b>               | : In-plane crystal size      |
| <b>Lc</b>               | : Crystal thickness          |
| <b>m</b>                | : Mass                       |
| <b>P</b>                | : Power                      |
| <b>Q</b>                | : Capacity                   |
| <b>Rb</b>               | : Bulk resistance            |
| <b>Rct</b>              | : Charge transfer resistance |
| <b>Rd</b>               | : Ion diffusion resistance   |
| <b>Rs</b>               | : Electrolyte resistance     |
| <b>S/N</b>              | : Signal-to-Noise            |
| <b>t</b>                | : Time                       |
| <b>U</b>                | : Potential/Voltage          |
| <b>X<sub>G</sub></b>    | : Graphitic domains          |
| <b>Z</b>                | : Impedance                  |
| <b>β</b>                | : Full width at half maximum |
| <b>θ</b>                | : Scattering angle           |
| <b>λ</b>                | : Wavelength                 |
| <b>μm</b>               | : Micrometer                 |
| <b>μm<sup>2</sup></b>   | : Square micrometer          |
| <b>A</b>                | : Ampere                     |
| <b>Å</b>                | : Angstrom                   |
| <b>A/g</b>              | : Ampere per gram            |
| <b>C/g</b>              | : Coulomb per gram           |
| <b>cm</b>               | : Centimeter                 |
| <b>cm<sup>-1</sup></b>  | : Reciprocal centimeter      |
| <b>cm<sup>2</sup>/g</b> | : Square centimeter per gram |
| <b>F/g</b>              | : Farad per gram             |
| <b>g</b>                | : Gram                       |
| <b>Hz</b>               | : Hertz                      |
| <b>kHz</b>              | : Kilohertz                  |
| <b>kV-DC</b>            | : Kilovolt – direct current  |
| <b>kW</b>               | : Kilowatt                   |
| <b>KW/kg</b>            | : Kilowatt per kilogram      |
| <b>kW/kg</b>            | : Kilowatt per kilogram      |
| <b>kW/L</b>             | : Kilowatt per liter         |
| <b>kWh</b>              | : Kilowatt hour              |

|                           |                                     |
|---------------------------|-------------------------------------|
| <b>L</b>                  | : Liter                             |
| <b>M</b>                  | : Moll                              |
| <b>m<sup>2</sup>/g</b>    | : Square meter per gram             |
| <b>mA/g</b>               | : Milliampere per gram              |
| <b>mAh</b>                | : Milliampere hour                  |
| <b>mAh/cm<sup>2</sup></b> | : Milliampere per square centimeter |
| <b>mAh/g</b>              | : Milliampere hour per gram         |
| <b>mg/cm</b>              | : Milligram per centimeter          |
| <b>mg/cm<sup>2</sup></b>  | : Milligram per square centimeter   |
| <b>MHz</b>                | : Megahertz                         |
| <b>ml</b>                 | : Milliliter                        |
| <b>ml/h</b>               | : Milliliter per hour               |
| <b>ml/h/nozzle</b>        | : Milliliter per hour per nozzle    |
| <b>mm</b>                 | : Millimeter                        |
| <b>MPa</b>                | : Megapascal                        |
| <b>mV</b>                 | : Millivolt                         |
| <b>mV/s</b>               | : Millivolt per second              |
| <b>MW</b>                 | : Megawatt                          |
| <b>nm</b>                 | : Nanometer                         |
| <b>° C/min</b>            | : Degree Celsius per minute         |
| <b>Pa</b>                 | : Pascal                            |
| <b>V</b>                  | : Volt                              |
| <b>V/sec</b>              | : Volt per second                   |
| <b>W</b>                  | : Watt                              |
| <b>W/kg</b>               | : Watt per kilogram                 |
| <b>Wh/kg</b>              | : Watt hour per kilogram            |
| <b>Wh/L</b>               | : Watt hour per liter               |
| <b>Ω</b>                  | : Ohm                               |
| <b>Ω/cm<sup>2</sup></b>   | : Ohm per square centimeter         |

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## **ENVIRONMENTALLY FRIENDLY COMPONENTS FOR ENERGY STORAGE DEVICES**

### **SUMMARY**

Fibrous materials with diameter below one micrometer and large aspect (length-to-diameter) ratio are considered as 1D nanomaterials, so called nanofibers. Their unique network structure gives them high surface-to-volume ratio and remarkable properties which can be controlled according to the choice of material(s) they are made of. Therefore, they meet the requirements in wide range of application areas, including filtration, functional textiles, tissue engineering, energy storage, etc. Regarding the area of energy storage systems, nanofibrous materials can be used as main constituents, namely electrodes and/or separators. Nanofibrous electrodes can improve the properties of the energy storage devices from many aspects. Firstly, nanofibers can be made of one unique or a combination of materials that can provide high electrical conductivity and electrochemical activity that would lead to high capacity and stable cycling life. Besides, their morphology can be shaped so that the fiber itself can be porous, hollow or act as a particle holder. The network nature of nanofibrous mats gives them flexibility and makes them suitable for stand-alone applications. An added value is the fact that the porosity of nanofibrous mats allows easier absorption of electrolyte and its penetration through the whole electrode thickness, which in turn allows production of thick electrodes with high mass loading. Thick and free-standing (without binder or conductive additives) electrodes are industrially feasible, since they reduce production cost and provide high volumetric performances of energy storage devices. Such thick nanofibrous electrodes are good candidates to replace conventional film-based electrodes in either batteries or supercapacitors. Moreover, combining electrodes made of materials with capacitive and redox behavior into one device, results in a hybrid device with fused electrochemical performance.

In that regard, this thesis deals with development of nanofibrous electrodes and their application in both, batteries and supercapacitors. More precisely, the thesis can be divided into two main parts where porous carbonaceous fibrous electrodes, polymer/particle nanofibers and thick carbon nanofibers were developed and used as electrodes in battery and supercapacitor cells. The use of environmentally friendly materials was emphasized in the first two parts, by developing carbonaceous electrodes for battery and polymer/particle electrodes for supercapacitor applications. On the other side, the possibility to produce high mass loading fibrous electrodes via industrially feasible spinning technique was investigated in the second part. At the end, the potential application of different types of composite CNF electrodes in various supercapacitor cell configurations were investigated.

Since, the main focus of the thesis is the development of nanofibrous materials, two production methods, namely electrospinning and solution blowing, are used and discussed. Among them, solution blowing is preferred due to its high production rates and safe use without the need for high voltage power supply. Solution blowing

technique is especially emphasized because it enables large scale production of thick layers of nanofibers, which is of outmost importance for their industrial implementation in energy storage devices. In terms of materials, the first part of the thesis emphasizes the usage of environmentally friendly carbon precursors, which, found as side products or waste, have the potential to be reused. In the second part, the accent is on the use of doping elements as electrochemically active materials. Deep understanding of the structural differences of all developed materials was performed via microscopic analysis, Fourier Transform Infrared (FTIR), Raman Spectroscopy, X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analysis. Whilst, the electrochemical performances of the fibrous electrodes were determined via cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and/or galvanostatic charge/discharge tests.

The focus of the thesis in the first part lays in the development of porous fibrous electrodes from environmentally friendly materials. For that purpose activated and mesoporous carbon nanofibers (CNF) were produced. Lignin was the main carbon precursor of choice due to its abundance in nature and aromatic structure. The fibers were obtained from lignin/poly(vinyl alcohol) polymer blends via electrospinning technique. Potassium hydroxide (KOH) was used as pore-formation and activation agent. In order to investigate its role in the formation of porous structure, it was applied in-situ before fiber production and after carbonization, so that two types of CNF were produced. SEM and BET analysis showed that activation of already carbonized nanofibers results in spongy CNFs with enhanced microporosity compared to non-activated CNF. On the other hand, in-situ addition of the activating agent promotes more uniform and mesoporous fibrous network. It also helps the formation of more ordered carbonaceous structure, which favors the electrochemical performances of the electrode. FTIR analysis emphasized that iodine acts as dehydration agent accelerating the formation of aromatic structure. Overall, it can be concluded that CNF with micro and mesoporous structure can be successfully produced from natural lignin. Furthermore, the developed CNF were used as free-standing anodes in a half cell lithium and sodium ion batteries and their rate capability and cycling stability were tested. Among the two porous CNF, the microporous one showed highest capacity. However, the mesoporous CNF was highlighted by its high cycling stability in both lithium and sodium ion cells even after 1000 charge-discharge cycles.

The perspective of the abundant bio-materials and the possibility to be reused was further extended in the second part of the thesis. In this regard, 4<sup>th</sup> chapter of the thesis depicts the formation of carbon nanoparticles using biowaste carbon precursor. Here, peanut shells were the material of choice due to its high cellulose content and fibrous structure. The formation of carbon particles was done by pretreatment of ground peanut shells with activating agent (in this case zinc chloride,  $\text{ZnCl}_2$ ) and then their carbonization. Microscopic and structural analysis showed that the obtained carbon particles (Cp) are micro-sized ( $\sim 20 \mu\text{m}$ ) with high specific surface area ( $1167 \text{ m}^2/\text{g}$ ) and highly disordered carbonaceous structure. Such particles were ball milled in order to reduce their size and make them more uniform in shape. Further analysis of ball milled Cp, revealed that the grinding process not only changed their size ( $\sim 580 \text{ nm}$ ) but also affected their porosity. Ball milling promoted the mesoporosity of the particles without changing the overall surface area significantly. Moreover, ball milled Cp showed slightly more disordered c-structure with large interlayer space and more (C=O) functional groups, which favors

reversible ion diffusion and improved capacity. The electrochemical behavior of the particles was investigated via cyclic voltammetry in a 3-electrode electrochemical system in aqueous electrolyte. Pseudocapacitive behavior of Cp electrodes was detected in a potential window between -1 to 0.3 V vs Ag. The improved electrochemical performances of the smaller Cp were also confirmed with CV analysis. At last, the performances of symmetric supercapacitor cell was also investigated. The potential of this bio-waste carbon particles as supercapacitor electrodes was analyzed and confirmed.

Further on, the developed bio-waste carbon particles were used as electrochemical component into an original electrode architecture for symmetric supercapacitor cells. To obtain freestanding electrodes, PVDF nanofibers containing ultra-high amount of carbon nanoparticles were produced via solution blowing technique. Composite nanofiber production parameters such as polymer concentration, solvent ratio, and carbon concentration were optimized in order to obtain defectless fibers with the largest possible amount of carbon particles. It was found that 10wt% polymer solution, 60wt% carbon content and 50:50wt% DMF/acetone mixture are the optimal parameters. In the second part of the 5<sup>th</sup> chapter, the produced fibrous materials were used in a symmetrical supercapacitor cell with aqueous and organic electrolytes. Aqueous supercapacitor cells with high electrode mass loading showed areal capacitance up to 1120 mF/cm<sup>2</sup>. Moreover, fibrous electrodes with increased electrical conductivity showed high rate capability and high cycling stability losing only 9% of its capacity after 10,000 cycles. The cycling stability of the electrodes is even more emphasized in organic supercapacitors where the cells retain 96.4% of their capacitance. The proposed biowaste derived composition and fibrous architecture was proven to be promising electrodes due to high areal capacitance and stability.

The second part of the thesis, starting with Chapter 6, discusses the development of flexible and thick carbon nanofiber electrodes for symmetric supercapacitor application. Free-standing CNF mats with average diameter of 335 nm are produced via solution blowing technique. Their microstructure and porosity were firstly analyzed. Later on, the electrochemical performances of CNF were investigated in order to determine the most suitable aqueous electrolyte and the maximum operating voltage window at it. The results showed that in basic aqueous electrolyte (pH14) CNF can operate in a maximum voltage window of 1.4 V, without evolution of oxygen or hydrogen. Then, CNF electrodes with high mass loading and thicknesses up to 1.2 mm were tested in symmetric supercapacitor cells with 6M KOH solution as an electrolyte. It was found that electrodes with mass loading up to 25 mg/cm<sup>2</sup> can deliver energy and power values comparable to those of commercial supercapacitor cells. Moreover, it can be cycled up to 10000 cycles without capacity loss, at current of 2 A/g. Further increase of the mass loading, results in lower cycling stability. Electrochemical impedance spectroscopy showed that the capacity loss of the thicker electrodes is a result of decreased ion diffusion during cycling. Post-mortem analysis of the electrodes revealed that lower ion diffusion appears due to crystal-like products formed as a result of side reactions with the electrolyte.

The structure of carbon nanofibers doped with several different active materials and their performances in aqueous supercapacitor cells was focus in the last chapter of the thesis. Solution blowing was again used as fiber formation method for the development of doped carbon nanofibers. Tin (Sn), manganese (Mn), molybdenum disulfide (MoS<sub>2</sub>) and Prussian blue (PB) were used as doping materials and were

embedded into CNF either through precursor salts or nanoparticles. Structural analysis on the doped CNF showed that the type of doping agent significantly affects the carbonaceous structure obtained. On the other side, electrochemical analysis of individual CNF electrodes, showed that the carbonaceous matrix is dominant and defines their properties in the electrochemical system. Symmetric supercapacitor cells were assembled in order to investigate the effect of doping materials on the electrochemical behavior and cycling stability of the electrodes. Impedance analysis of the cells showed that doping elements, even though does not contribute to the capacity, it can prevent the formation of side products during cycling, which in turn improves the ionic diffusivity and keeps the internal resistance low. This effect was most emphasized when Sn and MoS<sub>2</sub> nanoparticles were embedded into CNF. At the end, one doped and one neat CNF were matched and used as a pair of positive and negative electrodes for an asymmetric supercapacitor cell. Among the four doped CNF developed, SnMo CNF was chosen as a pair for neat CNF because their overall voltage range (1.6 V) is the highest one. Besides its high cycling stability, the asymmetric cell showed enhanced specific energy, when compared to the symmetric cells, as a result of its extended voltage window.

In summary, the research conducted in this thesis demonstrates development of various nanofibrous materials with controllable morphology. It demonstrates the possibility to use biowaste as main material for their production. It points out the feasibility to produce such fibers via an industrially scalable technique, namely solution blowing. Further on, it investigates the structure and properties of the fibers and shows their potential application in battery, supercapacitor and hybrid energy storage systems.

The dissertation presented here as a collection of research papers. As a result the redundancy of introductory information would be noticed because the papers are intended to be sufficiently independent. A short summary of each is provided bellow to help readers navigate through this dissertation.

## ENERJİ DEPOLAMA CİHAZLARINDA ÇEVRE DOSTU BİLEŞENLERİN KULLANIMI

### ÖZET

Nanolifler; çapları bir mikrometrenin altında ve yüksek en-boy oranına sahip lifli yapılarda 1D nanomalzemelerdir. Nanoliflerin nano boyuttaki ağsı yapısı yüksek yüzey alanı oluşturmakla birlikte kullanılan malzemeye göre farklılık gösteren birçok önemli özellik elde edilmektedir. Bu üstün özellikler sayesinde nanolifler filtrasyon, fonksiyonel tekstiller, doku mühendisliği ve enerji depolama gibi birçok uygulama alanında kullanılabilir. Özellikle enerji depolama alanında nanolifler elektrot ve/veya separatör olarak tüm temel elemanlarda kullanılabilir. Nanolif elektrotlar sahip oldukları üstün özellikleriyle enerji depolama cihazlarında birçok yönden performansın artmasını sağlayabilmektedir. Öncelikle, nanolifler yüksek elektrik iletkenliği ve elektrokimyasal aktivite sağlayan bir veya birden fazla malzemenin bir araya gelmesiyle oluşturularak, enerji depolamada yüksek kapasite ve stabil çevrim ömrü sağlayabilmektedir. Ayrıca nanolifler gözenekli, kanallı morfolojik yapıda veya küçük partikülleri lif üzerinde taşıyabilecek şekilde şekillendirilebilirler. Nanolifli yüzeylerin ağsı yapısı sayesinde esneklik kazanarak bağımsız uygulamalar için uygun hale getirilebilir. Buna ek olarak, nanolifli yüzeylerin yüksek gözenekliliği, farklı kalınlıklardaki elektrotlarda elektrolitin tüm yüzey boyunca daha kolay emilmesini sağlayarak yüksek aktif malzeme içeren kalın elektrotların üretilebilmesine olanak vermektedir. Enerji depolamada kalın ve destek malzemesiz (iletken malzeme, yapıştırıcı...) elektrotlar hem üretim maliyetini azalttığı hem de enerji depolama cihazlarında hacimsel enerji kapasite değerini arttırdığı için endüstriyel açıdan oldukça avantajlıdır. Bu tür yapıştırıcı veya aktif karbon katkı malzemesi kullanılmadan elde edilen nano lifli elektrotlar, pillerde ya da süper kapasitörlerde geleneksel film yapıdaki elektrotların yerine kullanılacak gelecek vadede önemli malzemelerdir. Ayrıca, kapasitif ve redoks özellik gösteren malzemelerden yapılmış elektrotların bir arada kullanılmasıyla birleşik elektrokimyasal performansa sahip hibrit sistemlerde elde edilebilir.

Bu kapsamda, bu tezde pillerde ve süperkapasitörlerde kullanılacak nanolif yapıları elektrotlar geliştirilmektedir. Yapılan çalışma temel olarak iki kısma ayrılmaktadır; polimer/parçacıklı nanolifler ve kalın yapıda karbon nanolif yüzeylerden, yüksek gözenekli elektrotlar geliştirilmesi ile pillerde ve süperkapasitörlerde elektrot olarak kullanılmasıdır. İlk iki bölümde, çevre dostu malzemelerden yararlanılarak üretilmiş elektrotların pillerde ve polimer/parçacıklı nanoliflerin süperkapasitörlerdeki uygulamaları incelenmiştir. İkinci bölümde ise yüksek aktif malzeme içeren nanolif elektrotların ticari miktarlarda eldesi için endüstriyel düzeyde nanolif üretim teknikleri araştırılmıştır. Son bölümde ise farklı yapıdaki kompozit CNF (karbon nanolif) elektrotların çeşitli hücre konfigürasyonlarındaki süperkapasitörlerde potansiyel uygulamaları incelenmiştir.

Yapılan çalışmada nanolifli malzemeleri ve özelliklerini geliştirmek için elektrolif çekim ve çözeltiden üfleme nanolif üretim yöntemleri kullanılmış ve karşılaştırılmıştır. Bu iki yöntem arasından çözeltiden üfleme nanolif üretim yöntemi ve elektroüretimden farklı olarak yüksek voltajlı bir güç kaynağına ihtiyaç duyulmadan güvenli kullanımı ve yüksek üretim hızı nedeniyle tercih edilmiştir. Çözeltiden üfleme nanolif üretim yöntemi, enerji depolama araçlarının endüstriyel uygulamaları için yüksek ölçekte üretim ve kalın nanolif katmanları eldesi gerektiğinden özellikle incelenmiştir. Malzemeler açısından ele alındığında, tezin ilk bölümünde karbon öncü maddesi olarak kullanılabilecek çevre dostu ve tekrar kullanılabilir yan ürün veya atık ürünler ele alınmıştır. İkinci bölümde ise katkı malzemelerinin elektrokimyasal aktif malzeme olarak kullanılmasından bahsedilmektedir. Geliştirilen tüm malzemelerin yapısal farklılıklarının derinlemesine araştırılması ve anlaşılması için, mikroskobik analiz, Fourier Transform Infrared (FTIR), Raman Spektroskopisi, X-ışını difraksiyonu (XRD) ve Brunauer-Emmett-Teller (BET) yüzey alanı analizi yapılmıştır. Diğer taraftan, nanolif yapıdaki elektrotların elektrokimyasal performanslarının ölçümü için çevrimsel voltametri (CV), elektrokimyasal impedans spektroskopisi (EIS) ve/veya galvanostatik şarj/deşarj testleri uygulanmıştır.

Tezin ilk bölümü gözenekli ve lifli yapıdaki elektrotların çevre dostu malzemelerden üretilmesi açıklanmaktadır. Bu amaçla, aktive edilmiş ve mezogözenekli karbon nanolifler (CNF) üretilmiştir. Lignin doğada bol miktarda bulunması ve aromatik yapısından ötürü öncül karbon malzemesi olarak kullanılmaktadır. Lifler lignin/polivinil alkol polimer karışımından elektroüretim yöntemiyle elde edilmiştir. Potasyum hidroksit (KOH), gözenekli yapının oluşmasını sağlayan aktive edici malzeme olarak kullanılmıştır. Lif üretiminden önce ve karbonizasyon işleminden sonra in-situ uygulama ile aktive edici malzemenin gözenekli yapı oluşmasındaki rolü elde edilen iki farklı CNF ile incelenmiştir. SEM ve BET sonuçları göstermiştir ki; karbonizasyon işlemi sonucunda aktive edilen CNF'lar aktive edilmemiş CNF'lere göre daha gelişmiş mikrogözenekli süngerimsi yapı göstermektedirler. Öte yandan, aktifleştirme ajanının in-situ yöntemiyle eklenmesi, daha düzgün ve mesogözenekli lifli ağı destekleyen ve elektrotun elektrokimyasal performansını arttıran daha düzenli karbonlu yapının oluşumuna yardımcı olmuştur. FTIR sonuçlarında iyot, aromatik yapının oluşumunu hızlandıran dehidrasyon ajanı olarak görev yaptığı görülmüştür. Sonuç olarak, mikro ve meso gözenekli yapıya sahip karbon nanolifler doğal ligninden başarılı bir şekilde elde edilmiştir. Ayrıca, geliştirilen CNF, lityum ve sodyum iyon pillerde yapıştırıcı ve katkı malzemesi kullanılmadan nanolif formda anot olarak kullanılmış ve bu pillerin farklı parametrelerin uygulanmasıyla değişen pil kapasitesi ve çevrim stabilitesi test edilmiştir. İki farklı gözenekli yapıdaki CNF arasından, mikro gözenekli olan yapı en yüksek kapasite değeri göstermiştir. Bununla birlikte, mezo gözenekli CNF, hem lityum hem de sodyum iyon hücrelerinde 1000 şarj-deşarj döngüsünden sonra bile yüksek döngüsel stabilitesi ile dikkat çekmiştir.

Tezin ikinci kısmında, biyo-malzemeler bol miktarda bulunmaları ve yeniden kullanım potansiyelinden dolayı birçok araştırmacı tarafından derinlemesine incelenmiştir. Bu bağlamda, tezin dördüncü kısmında biyo-atıkların öncül karbon malzemesi olarak kullanılarak karbon nanoparçacıkların üretilmesi anlatılmıştır. Burada yerfıstığı kabukları yüksek selüloz içeriği ve lifli yapısından dolayı karbon öncül malzemesi olarak tercih edilmiştir. Karbon parçacıkların oluşumu, öğütülmüş yer fıstığı kabuklarında aktive edici malzeme (bu işlemde çinko klorür,  $ZnCl_2$ ) ile ön

işlem uygulandıktan sonra karbonizasyon işleminden geçirilmesiyle meydana gelmektedir. Yapılan mikroskopik ve yapısal analizler göstermiştir ki, elde edilen karbon parçacıkları (Cp) yüksek yüzey alana ( $1167 \text{ m}^2/\text{g}$ ) ve oldukça düzensiz yapıya sahip mikro-boyutlu ( $\sim 20 \text{ }\mu\text{m}$ ) karbon yapılarıdır. Daha düşük boyutlara ve daha düzenli yapılara sahip olmasını sağlamak için ise bu parçacıklar bilyalı öğütücü ile parçalanmıştır. Öğütülmüş karbon parçacıklarına yapılan analizlerde öğütme işleminin sadece parçacık boyutunu ( $\sim 580 \text{ nm}$ ) değiştirmemiş aynı zamanda da gözenekliliğini de arttırdığı görülmüştür. Bilyalı öğütme işlemi, toplam yüzey alanını önemli ölçüde değiştirmeden parçacıkların mezogözenekliliğini arttırmıştır. Buna ek olarak, öğütülmüş karbon parçacıkları geniş katman boşluklu düzensiz c-yapıları ve daha yüksek fonksiyonelleştirilmiş (C=O) yapıları içermekte bu da tekrarlanabilir iyon difüzyonunu ve daha yüksek kapasiteye sağlamaktadır. Parçacıkların elektrokimyasal özellikleri sulu elektrolit kullanılarak 3-elektrotlu elektrokimyasal sistemde çevrimsel voltametri ile incelenmiştir. Cp elektrotlarının psodökapasitif davranışı incelendiğinde, Ag'ye karşı -1 ila 0.3 V arasındaki potansiyel aralıkta olduğu tespit edilmiştir. Daha küçük karbon parçacıkların gelişmiş elektrokimyasal performansı aynı zamanda CV (döngüsel voltametri) analizi ile de desteklenmiştir. Son olarak, simetrik süperkapasitör hücrelerinin performansı da incelenmiş ve biyo-atıklardan elde edilen karbon parçacıkların süperkapasitör elektrotlarda potansiyeli analiz edilip, açıklanmıştır.

Bunun yanında, biyo-atıklardan geliştirilen karbon parçacıkları, simetrik süperkapasitör hücreleri için elektrokimyasal bileşen olarak elektrotların tasarımında kullanılmıştır. Desteksiz nanolif elektrot eldesi için çözeltilerden üfleme yöntemi ile ultra-yüksek miktarda karbon nanoparçacığı içeren PVDF nanolifleri üretilmiştir. Polimer konsantrasyonu, çözücü oranı ve karbon konsantrasyonu gibi kompozit nanolif üretim parametreleri, mümkün olan en çok miktarda karbon parçacıkları ile hatasız lifler elde etmek için optimize edilmiştir. Optimum parametreler, 10wt% polimer çözeltisi, 60wt% karbon ve 50:50wt% DMF/aseton karışımı olarak bulunmuştur. Beşinci bölümün ikinci kısmında üretilen lifli malzemeler sulu ve organik elektrolit içeren simetrik süperkapasitör hücrelerinde kullanılmıştır. Yüksek aktif madde yüklenmiş elektrotların kullanıldığı sulu elektrolitli süperkapasitörler  $1120 \text{ mF}/\text{cm}^2$ 'ye kadar alan kapasitansı göstermiştir. Ayrıca, artırılmış elektrik iletkenliğe sahip lifli elektrotlar 10,000 çevrim sonunda bile kapasitelerinin sadece %9'unu kaybederek yüksek çevrim stabilitesi ve yüksek pil kapasitesi göstermişlerdir. Organik süperkapasitörlerde hücreler kapasitanslarının %96,4'ünü korudukları için elektrotların çevrimsel stabilitesi daha da öne çıkmaktadır. Önerilen biyolojik atık türevi kompozisyon ve lifli yapının yüksek alan kapasitansı ve kararlılığa sahip olması nedeniyle geliştirilmesi ve kullanımı umut verici elektrotlar olduğu kanıtlanmıştır.

Tezin ikinci kısmında, Bölüm 6'da simetrik süperkapasitör uygulamaları için geliştirilen nanolifli yapıdaki örnek ve kalın elektrotların geliştirilmesi tartışılmıştır. Desteksiz (yapıştırıcı ve iletken madde katkısız) karbon nanolif (CNF) yüzeyler 335 nm çap ortalamasında çözeltilerden üfleme yöntemi kullanılarak üretilmiştir. Öncelikler bu malzemelerin mikro-yapıları ve gözenekliliği analiz edilmiştir. Daha sonra en uygun sulu elektrolit belirlenmesi ve çalışılabilir uygun maksimum voltaj aralığının belirlenmesi için CNF elektrotların elektrokimyasal performansı incelenmiştir. Sonuçlar, karbon nanolif elektrotların (CNF) bazik sulu elektrolitte (pH14), oksijen veya hidrojen çıkışı olmadan, maksimum 1.4 V'lik bir voltaja kadar çalışabileceğini göstermiştir. Sonrasında, 6M KOH çözeltisinin elektrolit olarak kullanıldığı simetrik

süperkapasitörlerde 1,2 mm üzeri kalınlığa sahip ve yüksek aktif madde yüklemiş karbon nanolif (CNF) elektrotların performansı test edilmiştir. Sonuç olarak kütle yoğunluğu  $25 \text{ mg/cm}^2$ 'e kadar olan elektrotların enerji ve güç değerleri açısından ticari süperkapasitörlerle karşılaştırılabilir olduğu görülmüştür. Ayrıca 2 A/g akımda 10,000 çevrim üzerinde dahi kapasite kaybı yaşanmadığı belirlenmiştir. Bir diğer sonuç ise, aktif madde miktarının arttırılmasıyla daha düşük çevrim stabilitesi elde edilmesidir. Elektrokimyasal impedans analizi sonucunda belirlenen daha kalın elektrotlardaki kapasite kaybının çevrim sırasında iyon difüzyonun azalmasından olduğu sonucuna varılmıştır. Elektrotların post-mortem analizi, elektrolit ile gerçekleştirilen yan reaksiyonların ürünü olan kristal benzeri yapıların düşük iyon difüzyonuna sebebiyet verdiğini ortaya koymuştur.

Tezin son bölümünde birçok farklı aktif madde ile katkılanmış karbon nanoliflerin yapıları ve sulu elektrolitli süperkapasitör hücre içerisindeki performansları ele alınmıştır. Katkılanmış nanokarbon liflerinin üretilmesinde lif üretim tekniği olarak çözelti üfleme tekniği kullanılmıştır. Katkılama malzemesi olarak kullanılan Kalay (Sn), Manganez (Mn), Molibden disülfür ( $\text{MoS}_2$ ) ve Prussian mavisi (PB) karbon nanoliflerin yapısına ya öncül tuzlar kullanılarak ya da doğrudan nanoparçacıklar kullanılarak katılmıştır. Karbon nanoliflerin yapısal analizi gerçekleştirildiğinde doplanan farklı katkı maddelerinin karbon yapısında önemli değişikliklere neden olduğu ortaya çıkmıştır. Diğer taraftan, elde edilen kompozit karbon nanolif elektrotlar üzerinde yapılan elektrokimyasal analizler göstermiştir ki; karbon matrix yapı elektrokimyasal sistemde baskın ve belirleyicidir. Katkılama malzemelerinin elektrokimyasal özelliğe ve çevrim stabilitesi üzerine etkisini incelemek üzere simetrik süperkapasitör hücreleri hazırlanmıştır. Katkılama malzemelerinin empedans analizleri sonucunda; katkılama malzemelerinin her ne kadar kapasiteye yarar sağlamasalar da çevrim sırasında yan ürünlerin oluşmasını engelleyerek iyonik difüzyonu iyileştirmiş ve iç direncin küçük kalmasına katkı sağladığı belirlenmiştir. Bu etki Sn ve  $\text{MoS}_2$  nanoparçacıklar ile katkılanmış CNF yapılarında en çok göze çarpmaktadır. Son olarak ise, katkılanmış CNF ve sade CNF yapılarının eşleştirilerek oluşturulan pozitif ve negatif bir elektrot çifti asimetrik süperkapasitör hücre için kullanılmıştır. Katkılanarak oluşturulan dört CNF yapısı içerisinde, genel voltaj aralığı (1.6 V) en yüksek olan SnMo CNF yalın CNF'e çift olarak seçilmiştir. Genişletilmiş voltaj aralığı sayesinde asimetrik hücrelerin, simetrik hücrelere göre yüksek çevrim stabilitelerinin yanında daha fazla spesifik enerji verdiği görülmüştür.

Özetle, bu tezde gerçekleştirilen çalışmalarda kontrol edilebilir morfolojilere sahip farklı fonksiyonlarda nanolif malzemeler geliştirilmiştir. Farklı özelliklere sahip nanolif yapıların kontrol edilebilir bir biçimde endüstriyel ölçekte üretilebilirliği incelenmiştir. Ayrıca, liflerin yapı ve özellikleri araştırılarak pil, süperkapasitör ve hibrit enerji depolama sistemlerindeki potansiyel uygulamalarını araştırılmıştır.

## **1. INTRODUCTION**

### **1.1 Purpose of Thesis**

The dependence on fossil fuels and the greenhouse gas emission, demand renewable energy sources, such as solar, wind and biomass. Whilst, such energy sources require energy storage systems that 1) can store the surplus energy generated and 2) will enable its use on demand, during power shortages, peak hours of demand, blackouts, etc. There is also a demand for rechargeable energy storage systems for consumable electronics and transportation vehicles. In all these sectors, Li-ion batteries are the dominant technology, followed by sodium-sulfur and the well-known lead-acid technology [1]. Lead-acid technology is gradually leaving the market due to its high mass and low weight-to-energy ratio and hazardous lead contamination during their recycling. The application of sodium-sulfur technology, which provides long discharge periods and operation at high temperatures, will not increase due to the spontaneous inflammation of its components (sodium metal) in contact with air and moisture. On the other hand, despite the increased demand, large-scale application of high capacity Li-ion batteries are still expensive due to the geographically constrained lithium resources and the high cost of the materials used in production of their constituent parts [2]. Implementation of high capacity electrodes is still limited due to their mechanical integrity decay during cycling which decrease their potential for long-lasting energy efficiency. Additionally, the low power values of the batteries forces combination of several already available energy storage systems in order to meet the need for balanced power/energy demand for long-lasting large applications.

Nanofibrous electrodes are novel products that find application in several different application areas. The production of such electrodes, with industrially scalable devices, such as solution blowing allows high production rates, hence reduced nanofiber production cost, and a safer working environment. On the other hand, due to their 1D structure nanofibrous materials can enhance the surface area of the electrode, when compared to the conventional film-like electrodes. This feature

contributes to faster and more efficient electrochemical reactions, as a result of the improved interaction between the electrolyte and the electrodes and make the active material into the electrode more accessible for the ions from the electrolyte. This in turn enables increasing the thickness of the electrode and thus enhancing the energy density of the energy storage device. The area of application of such electrodes includes standard battery, supercapacitor and hybrid cells, flexible and semi-flexible energy storage devices for wearables, e-textiles, medical devices, etc.

In that regard, the purpose of this thesis can be summarized as development of novel fibrous materials with tailored morphology via industrially scalable production methods and their application as electrodes for energy storage devices.

## **1.2 Literature Review**

### **1.2.1 Nanofibers**

Nanofibers, as one branch of the nanomaterials tree, are fibrous structures with high aspect ratio and nanoscale diameter which according to one definition can be in the range between 10 -100 nm, while in another it can go up to 1000 nm [3]. Either way, they are 1D structures which can be made of organic or inorganic materials. They are usually used as a fibrous network – called nanofiber mat - with high surface area and porosity which makes them suitable for a wide range of applications. In the last decade, nanofibrous materials showed potential for development of high performance and efficiency products in several areas, but has been mostly emphasized in the filtration technology. Their application in both, air and liquid, filtration systems is expected to grow in the upcoming years. Although a high impact on the global nanofiber market will also provide their application in biosensors, followed by energy, electronics and medical [4]. It is expected nanofiber market annual grow rate to be 25% in the period from 2018 to 2025, or from 1.26 billion US\$ in 2017 to 7.24 billion US\$ in 2025 [5].

Additional value to nanofibrous materials gives, the wide range of material nanofibers can be made and the morphologies that can be achieved (porous, hollow, core-shell, etc.). Another important point for their industrial application is the production methods. There are three general methods nanofibers can be produced, namely electrospinning, solution blowing and centrifugal spinning [6], [7]. These

methods use specific forces that shape the polymer solutions or melts into fibrous structures. In the case of electrospinning, electrical force is used for attenuation of the polymer jets [8], while compressed air and centrifugal forces are used in solution blowing and centrifugal spinning, respectively [7].

The electrospinning apparatus (Figure 1.1-a) consists of a high-voltage supply, grounded collector, and spinneret components that produce the nanofibrous structure [8]. The principle is based on the interaction of a charged fluid, such as a polymer solution or melt, with a strong electrical field (10–80 kV DC). The induced electrical charge in the viscoelastic fluid and the strong electric field forms a structure called a Taylor cone at the nozzle tip. When the electrical forces overcome the surface tension and viscosity of the fluid, the jet is ejected from the tip of the nozzle. The solvent evaporates during the motion of the fluid jet towards the collector, leaving a solid nonwoven fiber mat on the collector.

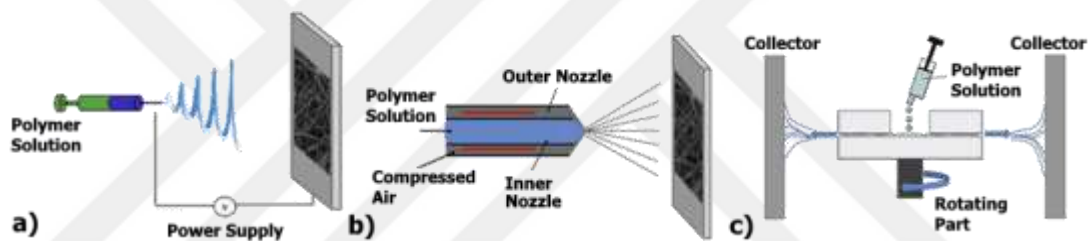


**Figure 1.1 :** Schematic representation of different nanofiber production methods: a) electrospinning, b) solution blowing, c) centrifugal spinning [8].

Solution blowing and centrifugal spinning technique are alternatives to electrospinning, offering higher production rate and safer conditions for nanofiber production [7]. In the melt/solution blowing system (Figure 1.1-b), the polymer solution or melt is extruded through a nozzle into a stream of high-pressure air under high pressure. The drag of the air on the surface of the polymer jet causes the elongation and eventual solidification of the nanofiber. By controlling the process parameters, such as the air pressure, temperature, feeding rate, and nozzle-collector distance, all of which affect the polymer rheology, fibers with a large range of diameters can be produced. On the other hand, the centrifugal spinning system uses a spinneret filled with a polymer solution or melt (Figure 1.1-c). The spinneret rotates in order to produce the centrifugal force necessary to overcome the surface tension of the polymer fluid to form a jet. The polymer jet further elongates into a fiber, guided by the centrifugal and frictional forces between the jet surface and the air. Processing

parameters that influence the final fiber morphology include the angular velocity applied, nozzle diameter, and the spinneret-collector distance.

While these three methods offer production of large amounts of nanofibers, there are also techniques, such as phase inversion, template synthesis or lithography with which nanofibers with well controlled properties and diameters below 100 nm can be easily produced [7]. However, the major drawback of such techniques is their scalability. On the other hand, all of the three main nanofiber production techniques can be used for large-scale production. Moreover, all of them are/can be industrially applied. However, not all have the same advantages on an industrial level. Though industrial scale electrospinning devices are already on the market [9], their maximum production rates are 40 ml/h in batch mode. Additionally, the high voltage demand (up to 100 kV) adds safety concerns and low cost effectiveness (energy consumption of 1.4 kWh, without peripherals [10]). Pilot version solution blowing system with 8 nozzle spinneret (tested in TEMAG Labs) can increase the production rates for at least 2,5 times (up to 100 ml/h), which when working with 4 bar air pressure consumes approximately 1.04 kWh. Which means with solution blowing system, we can produce 2.5 times larger amount of fibers with 25% lower energy consumption then when using electrospinning line. The solution blowing same system when using multi (64) nozzles spinneret with a specially designed nozzle geometry reduces compressed air consumption and thus enabling more cost-effective nanofiber production.

### **1.2.2 Energy storage**

Based on the mechanism the energy is captured, energy storage technologies can be divided as mechanical, electrochemical and/or electrical, chemical, thermal and thermochemical [11]. Among them, electrochemical and/or electrical storage can be highlighted as technology that enables reversible energy storage, pollution control and greenhouse reduction. It offers high volumetric and gravimetric power and energy (Figure 1.2), hence it is suitable for wide range of applications. Due to the fast response time and moderate to high power rating of the different electrochemical energy storage systems, they can be used where power needs to be bridged, where power quality needs to be maintained and for optimization of energy uses and decoupling the timing of generation and consumption of electrical energy [11].

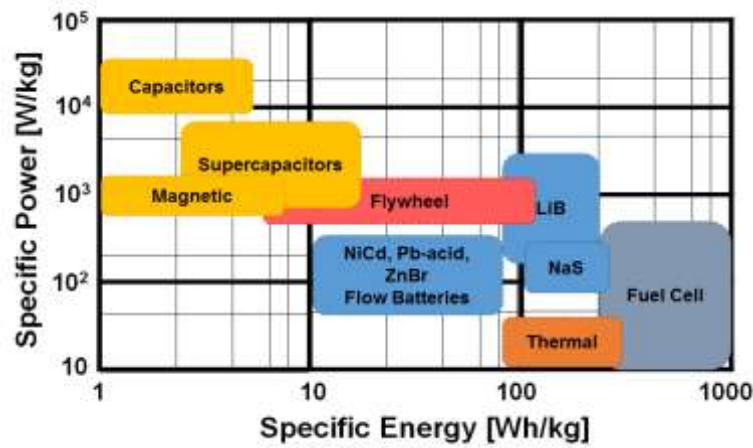


**Figure 1.2 :** Specific power and energy of different energy storage technologies (Adapted from [11]).

Batteries and supercapacitors represent electrochemical and electrostatic groups of energy storage devices widely used today in areas such as consumer electronics, transportation, industry and storage of energy from renewable sources. Today's renewable energy sources, such as solar or wind power require rechargeable energy storage units that will have the capacity to accumulate their excess power and to be able to deliver it depending on demand. By preventing power shortages during peak hours' demand and blackouts they will enable better power management and power grid stabilization. Long lasting and high capacity energy storage systems will also enable integration of renewable power sources and will reduce the need for additional investment in upgrading networks [1]. The decreased price of LiB, its increased competition with fuel cells and the planned deployment of microgrids in the next years, will have huge impact on the application of rechargeable batteries as energy storage units [12]. This would lead to an increased battery energy storage by 1.48 kW in the period from 2019 to 2023 [13]. On the other hand, manufacturing sector requires extra energy supply during peak production hours at reduced cost. Energy storage devices that can be added into the existing electrical system will enable fast energy supply. Supercapacitors with their high power characteristics will be most beneficial for this sector. Additionally, advanced supercapacitors with higher energy performances will provide better utility of transportation vehicles and consumer electronics. Therefore, it is expected that 30% of the total supercapacitor market be for automotive industry, followed by the consumer electronics segment which will account for 23% in next period up to 2022 [14]. Strict environmental

regulations, long cycling life and decreases in price will contribute to an increased supercapacitor market, which is expected to reach 6.98 billion US\$ by 2026 [15].

### 1.2.2.1 Supercapacitors

As energy storage devices, supercapacitors consist of two conductor electrodes separated with an insulating material and an electrolyte as ion source. Depending on the mechanism in which they store the electrical charges, supercapacitors may be ideal and non-ideal [16]. Ideal supercapacitors or electrochemical double layer capacitors (ELDCs) store electrical charge through electrostatic mechanism as a consequence of reversible electrostatic accumulation of charges on the surface of the electrode [17]. When electrodes are polarized, positive and negative charges move towards the surface of the negative and positive electrode, respectively, forming a neutral double layer at the electrode/electrolyte interphase. This is a typical non-faradaic charge-storage mechanism during the discharge process of supercapacitors (**Figure 1.3-b**), while during charging there is diffusion of ions into the electrolyte, as shown in **Figure 1.3-a**. On the other hand, non-ideal supercapacitor or a capacitor with pseudocapacitive electrodes uses faradaic charge-storage mechanism [16]. Here, the charges pass across the double layer and the charge-storage is pseudocapacitive. The pseudocapacitive behavior includes fast and reversible faradaic reactions and electrochemical conversion of the active material used.

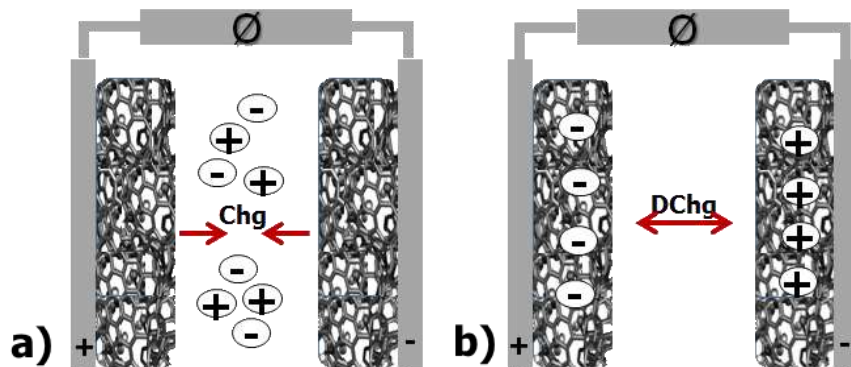


**Figure 1.3** : Schematic diagram of the working mechanism of supercapacitor.

The ability of the supercapacitor to store electrical charge is named capacitance, and is measured in farads (F) [16]. The capacitance of both types' supercapacitors is linear to the width of their potential window (Figure 1.4-a), therefore their CV-curve is almost rectangular. On the other hand, their charge/discharge behavior shows linear voltage-time relationship, which leads to formation of triangle-like charge-

discharge profiles (Figure 1.4-b). Therefore, distinction of the type of electrode used is necessary in order to apply the appropriate approach for calculating their capacitance [18]. Supercapacitor performances are characterized through their power and energy storage capability. In that regard, supercapacitors exhibit very high power densities due to their fast charge-storage mechanisms. The short time needed for the ions to move from/to the electrodes allows specific powers in the range between 3 and 50 kW/kg [19]. On the other hand, they have limited capability for storing charge since their electrodes attract charges only superficially. Thus, the specific energy of commercial supercapacitors is in the range from 2 to 12 Wh/kg and further development of new electrodes is necessary.

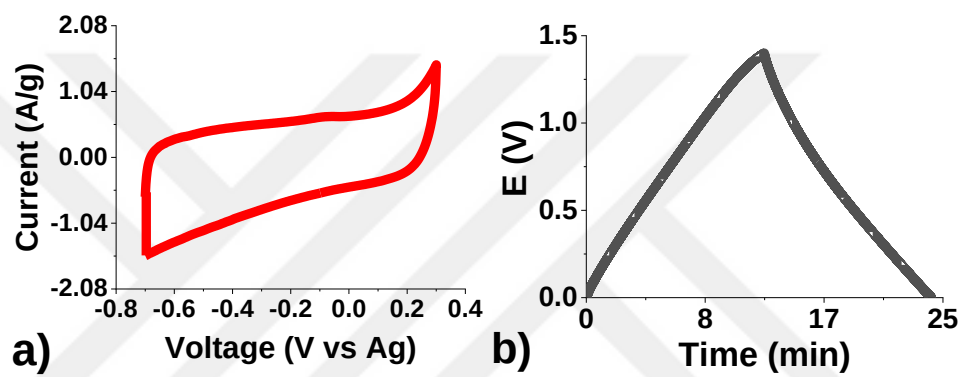


**Figure 1.4 :** a) Cyclic voltammogram and b) charge-discharge profile of active carbon electrode in 3-electrodes electrochemical system with aqueous electrolyte.

Regarding the materials, the electrodes of ideal supercapacitors use activated carbonaceous materials with well-defined high surface area, pore size and distribution [17]. Such materials can be porous carbon nanostructures, templated carbons, carbon aerogels, carbon nanofibers, carbon nanotubes or graphene [20]. For pseudocapacitive behavior composite structures are used which also contain conductive polymers, metal oxides or heterotopic dopants. As ion source, supercapacitors may use aqueous or organic solutions or ionic liquids as electrolytes. Their choice depends on the electrode material used and as well on the performances that need to be met.

#### 1.2.2.2 Secondary batteries

Rechargeable batteries are electrochemical cells composed of two electrodes, anode and cathode, separated by a membrane and an electrolyte which allows movement of ions from anode to cathode and vice versa (Figure 1.5-a). They store the electrical energy as chemical potential through reversible electrochemical redox reactions. The

working mechanism includes flow of cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , etc.) from one to another electrode during the charge/discharge cycles. When charging, metal ions move from the cathode towards the anode, and on the opposite direction when discharging the battery [8].

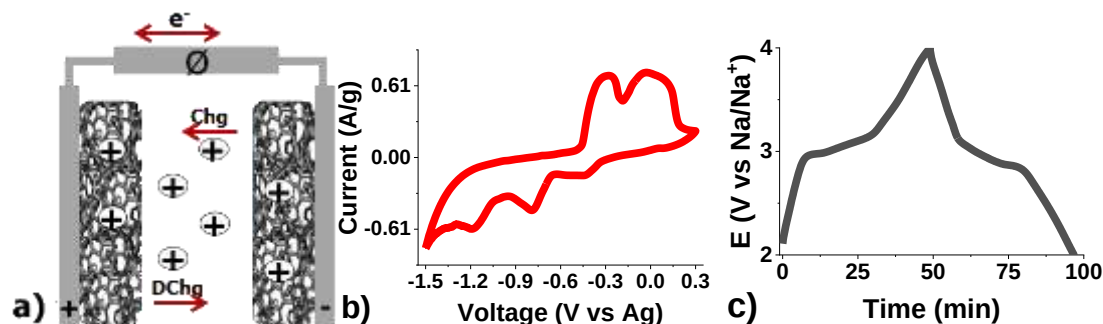


**Figure 1.5 :** a) Schematic diagram of the working mechanism of secondary battery; b) Cyclic voltammogram of SnMo CNF in 3-electrodes electrochemical system with aqueous electrolyte and c) Charge-discharge profile of Prussian Blue electrode in half-cell Na-ion battery.

Contrary to supercapacitors, batteries' electrodes do not store the same amount of energy through their whole voltage window (Figure 1.5-b) [16]. This is due to their faradaic charge storage mechanism which involves redox reactions that occur only at certain voltage value. This behavior is also reflected on their charge-discharge profiles, where the curves have a plateau region that correspond to the voltage at which redox reaction occur (Figure 1.5-c). Thus, electrochemical capability to store charges is defined as capacity and measured in mAh. The performances of the batteries depends on the chemistry involved [21]. Figure 1.6 shows theoretical and practical gravimetric energy values of several different battery chemistries.

Rechargeable lithium ion batteries (LIB), even though commercial, are still subject to research in order to improve their energy density, stability, safety issues and make it more environmentally friendly [23]. Lithium oxygen (Li/O) and lithium sulfur (Li/S) batteries are next most widely investigated chemistries, due to their high theoretical energies [24,25]. Both technologies are still under investigation since both suffer from side reactions during cycling which decreases their energy content and cycle life. In the case of Li/O system, it also suffers from entry of oxygen contaminated with water or carbon dioxide during cycling which additionally prolongs its commercialization [22]. After lithium, sodium has been reported as most advantageous electrochemical equivalent and standard potential and is in its relatively early stage of investigation [26]. Additionally, both Li- and Na-ion

technologies have similar working principle and production methodology, thus, in recent years, they are in the research agenda of many scientist.

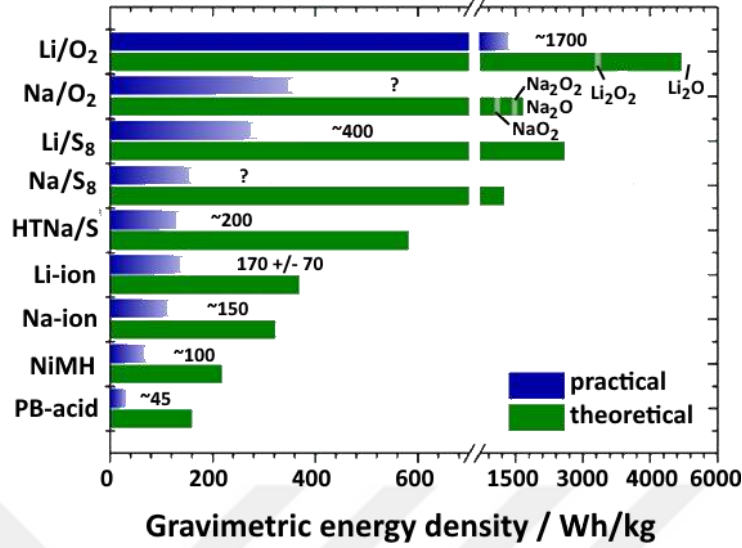


**Figure 1.6 :** Theoretical and practical gravimetric energy densities of different battery chemistries [22].

Commercial LiB, as most widely used batteries nowadays, can reach specific energy up to 170 Wh/kg, while their specific power ranges between 1 and 6.5 kW/kg [19]. The inferior power values, compared to those of supercapacitors, are due to the slow redox mechanism of the batteries. The diffusion of the ions into the electrodes and the redox reactions that take place require more time than the charge absorption on the electrode surface in supercapacitors. Moreover, these redox reactions cause electrode degradation as a result of the volume expansion of the material, which decreases battery performances and its life time. Thus, the main research focus is in development of high capacity electrode structures with mechanical stability over prolonged cycling.

The choice of electrode and electrolyte materials for batteries depends on the chemistry involved and is different for anode and cathode. Generally, carbonaceous materials are usually used on the anode side in LiB, including graphite and hard carbons [27]. However, due to graphite's limited capacity, other more electrochemically active materials have been widely investigated either for Li- or Na-ion batteries [21,27]. On the cathode side, more open and highly conductive structures that allow reversible and stable insertion of ions are needed [28]. Thus, transition metal oxides, phosphates or chalcogenides with either layered, spinel, olivine or chevrel phase structures are the choice for LiB and NaB [21,28]. The

selection of electrolyte salts to be used as ion source in batteries is accompanied with organic solvents or polymers which makes the production of all solid-state batteries possible [29,30].

### **1.2.2.3 Hybrid energy storage devices**

Despite the recent advancement in the electrochemical energy storage technology, today's devices offer high energy (batteries) or high power (supercapacitors) and there is still a demand for higher energy and higher power delivered from one device. In order to achieve synergism of their properties, hybridization of different rechargeable energy storage systems has been proposed. The approaches for such hybrids can be characterized as external or internal depending on whether devices or their components are put together and each system can further be divided into serial or parallel, depending on the way their parts are connected [31]. For external hybridization, parallel systems made of one supercapacitor and one battery are more widely investigated since the adjustment of the voltage window of two devices is easier than the synchronization of their capacities. In the case of internal hybridization, electrodes and/or electrode materials are combined, in either serial or parallel fashion. Serial internal hybrids are usually made of activated carbon on one side and battery-like electrode made of wide range of active materials, on the other side [31–33]. Parallel internal hybrids use composite materials made of capacitive and battery-like materials as both, positive and negative electrode. Figure 1.7 shows schematic representation of the possible approaches in which different materials and electrodes can be combined to make a hybrid energy storage device.

As discussed above, supercapacitors do not meet the need for energy, while batteries the need for power. The energy of a supercapacitor can be improved by incorporating electrode materials that will not accept ions only superficially. On the other hand, high capacity battery can be achieved by using alloying materials. However, they suffer from high volume expansion during their reaction with ions [35]. This volume change can be partially suppressed by decreasing the size of the particles and by developing structures with increased surface area that will buffer the volume change of the active material. Thus, hybrid electrodes that combine the reactivity of battery-type material and the porosity of supercapacitor-like material are assumed to cover

their shortage. Such composite electrodes will be able to provide optimized energy and power, and prolonged cycle life of a given device.

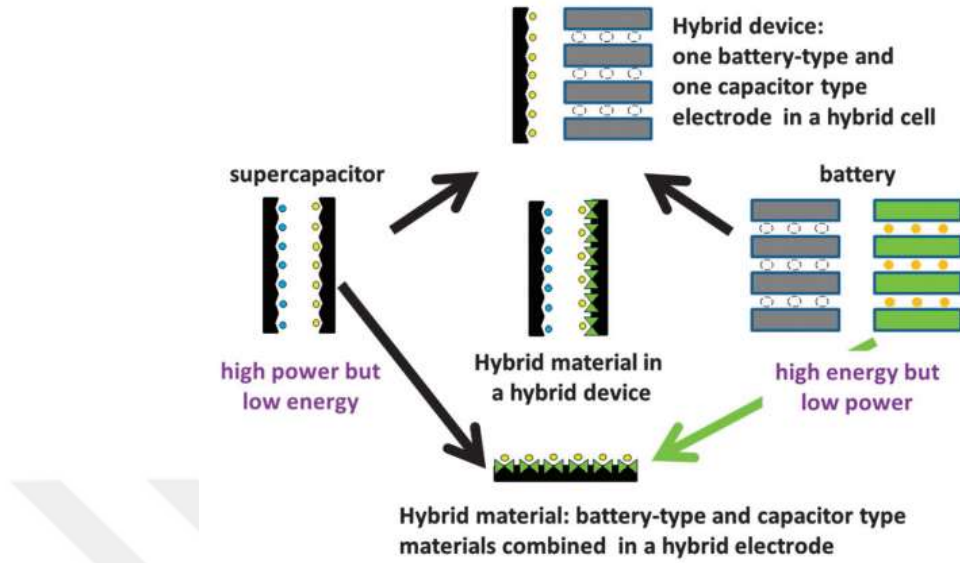


**Figure 1.7 :** Schematic representations of possible combinations between supercapacitor and battery electrodes and materials [34]

With the increased number of academic publications, and in order to describe and distinguish these devices, a new term, “supercapattery” has been proposed recently, [32]. Recent academic works on such hybrids, report specific energies up to 230 Wh/kg and about 55 kW/kg specific power, with more than 1000 cycles lifetime.

### 1.2.3 Materials and structures for energy storage

#### 1.2.3.1 Materials

Commercial energy storage devices use intercalation materials for their electrodes, ex. activated carbon for supercapacitors while, graphite or hard carbons and intercalation metal oxides or phosphates are the choice for LiB anode and cathode, respectively. However, for higher energy storage performances incorporation of active materials able to increase energy and power densities, and keep them stable is necessary. Thus, in the last decades many active materials (pseudocapacitive, alloy and conversion type) have been investigated. The choice of active material for a certain type of chemistry follows the trend in theoretical investigations for material types and structures suitable to that chemistry.

The reason behind the usage of intercalation materials in LiB is that they provide fast ion transport and relatively low volume expansion, which ensures high cycling

stability [36]. On the anode side, graphite with its layered structure additionally contributes with its electrical conductivity and electrochemical stability. Other than graphite, soft and hard non-graphitized carbonaceous materials are also widely investigated and used. Their electrical conductivity also makes them suitable for formation of composite structures with active materials, which usually have very low conductivity. Despite the low conductivity, active faradaic materials suffer from high volume change when alloying/de-alloying with Li- during charge/discharge processes. This volume change disturbs the mechanical and electronic integrity of the electrode as a result of the lost contact between the active material and the conductive additives that form the electrode slurry. Covering the active particle with carbon is one approach to buffer and suppress the volume expansion of the active material, and to improve the cycling stability of the electrode [8,36].

In the case of Li/O and Li/S battery systems, metal Li is used as anode and porous O<sub>2</sub> and S<sub>8</sub> holders as cathodes. Here, the cathodes, mainly carbon based, enable reduction of oxygen and sulfur and accommodates their products (Li<sub>2</sub>O, Li<sub>2</sub>S) during discharging [22]. For Li/S chemistries sulfur or sulfide cathodes coated with carbon, metal oxides or conductive polymers have been proposed as an alternative to suppress polysulfide dissolution and the formation of electrochemically inactive layer on the lithium anode (shuttle effect) during cycling which shorten the cycle life of the battery [37]. While Li/O system uses carbonaceous cathodes with embedded metal or metal oxides catalysts which allow oxygen to enter into the system and to reduce it when discharging [38].

Due to the similar working principle, production methodology, abundance and lower cost prime materials, Na-ion technology is considered as potential replacement for Li-ion batteries. Besides, after lithium, sodium has the most advantageous electrochemical equivalent and standard potential [26]. Therefore, the potential structures and materials for positive and negative electrodes for Na-ion batteries are analogues of those used in Li-ion battery [26]. However, it should be noted that Na cation shows different electrochemical behavior when intercalating into the cathode, hence materials with open and layered structures are more promising cathode materials due to the larger diameter of Na-ion. Similarly, more open anode materials are also needed, despite similar behavior of Na<sup>+</sup> intercalation into the anode, compared to Li<sup>+</sup>. Thus, porous carbons alongside low voltage metal-oxides or alloy

materials are more suitable here [39]. Table 1.1 lists the active materials and the theoretical values of most promising anode materials for Li and Na-ion batteries.

**Table 1.1 :** Active materials and the theoretical values of most promising anode materials for Li and Na-ion batteries.

| Active Material                          | Chemistry | Theoretical Specific Capacity<br>(mAh/g) |
|------------------------------------------|-----------|------------------------------------------|
| Si                                       | LiB / NaB | 4212 / 954                               |
| P                                        | LiB / NaB | 2596 / 2596                              |
| Ge                                       | LiB       | 1568                                     |
| MnO <sub>2</sub>                         | LiB       | 1230                                     |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> | LiB       | 1007                                     |
| Sn                                       | LiB / NaB | 990 / 847                                |
| Fe <sub>3</sub> O <sub>4</sub>           | LiB       | 900                                      |
| Co <sub>3</sub> O <sub>4</sub>           | LiB       | 890                                      |
| SnO <sub>2</sub>                         | LiB       | 790                                      |
| MoS <sub>2</sub>                         | LiB       | 670                                      |
| Pb                                       | LiB / NaB | 550 / 484                                |
| Graphite                                 | LiB       | 372                                      |

In the case of LiB, Si is the most widely investigated active material due to its highest theoretical value. However, its practical integration into commercial anodes is not yet achieved due to its large volume expansion (over 400%) during cycling which induces mechanical disintegration of the electrode and decrease of the contact between the particles and the current collector [27]. These effects further provoke fast decay in capacity and shorter cycle life of the cell. Optimization of Si nanoparticle size and structure, and synthesis of Si/C (including hard carbons, porous carbons, graphene, CNTs) or Si/SiO<sub>2</sub> composites have been proposed as a possible solution to these problems [40]. Tin is another metal widely investigated as anode active material for both Li- and Na-ion batteries. Its volume expansion in LiB is even larger than that of Si, and similar trend follows in NaB as well [36,39]. SnO<sub>2</sub> has been an alternative for LiB, since the difference in their theoretical capacities is not large [41,42], while its alloys with Sb, Ni and Cu have been proposed for NaB [39].

Transition metal oxides are conversion type electrodes able to store Li-ions without forming metal-lithium alloy, and thus lower volume expansion [27]. They are another group of active materials that could be used as anodes with improved cycling stability in LiB. TiO<sub>2</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> are among the most widely investigated from this group. Layered metal dichalcogenides, with MoS<sub>2</sub> as mostly used are type of materials that allow facile and reversible ion intercalation compared

to the previous two types [27]. Phosphorus and phosphides are another conversion type active materials, with high theoretical capacity values for both, Li- and Na-ion systems [36,39]. They belong to the group of conversion electrodes and show high theoretical capacity for both chemistries. However, the hazardous nature of phosphorus prevents their wider investigation.

In the case of supercapacitors and/or hybrid devices, pseudo capacitive materials such as,  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{SnO}$ ,  $\text{Fe}_2\text{O}_3$  offer high capacitance [43]. However, their choice depends on the electrolyte to be used [31]. Thus,  $\text{MnO}_2$  has been used for neutral aqueous electrolytes, Ni-oxides and hydroxides, vanadium and cobalt oxides for basic aqueous electrolytes, while Ti-oxides for Li-based organic electrolytes. Among them,  $\text{MnO}_2$  is the most widely investigated due to its availability, low cost and its theoretical capacitance value.

Through, the active materials provide high capacities, their large volume changes during electrochemical reactions and their low electrical conductivity makes them unsuitable to be used alone within electrode structure. Thus, they are usually combined with carbonaceous materials and/or conductive polymers, which improve the conductivity and serve as buffers for their volume expansion. On the other hand, the cycling stability of graphite and hard carbons makes them perfect materials for efficient energy storage devices. Therefore, they are already used in commercial energy storage, despite their limited capacity. Carbon electrodes are obtained by pyrolysis of various organic polymers either synthetic or natural [44]. Among them petroleum based polymers are most widely used because can be easily converted into carbon with high yield. That process includes carbonization in inert atmosphere with or without previous stabilization of their structure in air atmosphere. Phenolic resins and poly acrylonitrile (PAN) are the most widely used polymers. Other than those, polyimides (PI), polyvinylidene fluoride (PVDF), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) as synthetic, lignin and different kind of cellulose as natural biopolymers have been proposed as an alternative carbon precursors due to their lower cost or environmentally friendly character [45]. However, their long stabilization and carbonization processes have still to be investigated and optimized [46–48].

Among these polymers, lignin is the most promising precursor to replace PAN, especially for carbon fiber production, due to its high carbon content. Moreover, it is

an abundant, non-toxic, biocompatible, and low-cost polymer. It can be obtained from a variety of biomasses by solvent extraction as the most common method or as a byproduct in several industries [49,50]. Lignin can be used as fuel additive, emulsifier or dispersant in agriculture, as binder or reinforcement in different composite structures, or as antioxidant for polymers [51]. Additionally, due to its highly functionalized macromolecules it can be used as starting material for renewable polymers, such as polyesters, polyurethanes or polyanilines. Its versatility allows its application in energy storage devices either in carbonaceous or polymeric form [52–54].

Graphene and carbon nanotubes (CNT) are type of nanomaterials in which C-atoms are arranged in a regular hexagonal pattern forming a sheet or a tube, respectively. Their application in energy storage devices is due to their high conductivity, high surface area, thermal and chemical stability [20,55]. Incorporated into the electrode structure they can act as conductors in free-standing electrodes in which current collectors can be avoided. Due to their atomic-layered thickness and flexibility, they can be used as supporting materials in electrodes for transparent and flexible energy storage devices [56]. They can be functionalized and/or combined with a variety of organic and inorganic active materials into different structures forming electrodes for high performance batteries or supercapacitors [33,57]. Moreover, their interaction with active materials allows formation of binder-less free-standing electrodes that can be used without additional current collectors [58]. Despite these characteristics, it is still hard to get the maximum performance, principally due to the stacking of graphene layers and inaccessibility of the inner surface of CNTs are mayor, and also due to their high-cost production. Recently, cellulose fibrils have been proposed as an alternative way to produce low-cost nanocarbons [59]. However, their low carbon yield and conductivity should be improved in order to make them competitive and effective as CNT.

Other than inorganic materials, conductive polymers are other type of materials that can store charge via redox reactions. Among them PANi (polyaniline), PPy (poly pyrrole), PEDOT (Poly(3,4-ethylenedioxythiophene)), poly thiophenes are among the most widely investigated as electrode materials for energy storage [31,33]. Their average elasticity make them suitable for flexible devices [60]. Due to their ion exchange capability, they are suitable for hybrid devices when combined with

graphene and/or CNTs. Depending on the polymer used these electrodes made of redox active polymers containing CNTs may reach capacitance of about 700F/g [33]. Inorganic active materials in combination with conductive polymers not only improve the capacity, but also the cycling stability of a battery [61]. Modified conductive polymers with enhanced ductility and wettability can serve as binders in battery's electrode structures containing active materials with high volume expansion [62,63]. In this case, they buffer volume expansion of the active material and maintain their adhesion to the current collector. The improved mechanical and cycle stability of the electrode enhances their lifetime. Due to their low ionic conductivity, they should partially cover active particles or form porous structure in order to allow ion diffusion to the active side even at high c-rates [64]. The disadvantages of these materials are their rigidity, insolubility, and high sensitivity to air and moisture, which requires specific condition for their processing.

### **1.2.3.2 Structures**

Today's, energy storage devices use microstructures as main material of their individual components. However, the need to boost the performances of the devices put the focus on nanostructures, due to their high reactivity and strength. The application of nanomaterials in a wide range of areas increases progressively. It is expected that global nanotechnology market increases from 7.24 billion US\$ in 2019 to 24.56 billion US\$ in 2026 [65]. Their application in energy storage systems is not far behind. Global market analysis show that the market size of nanotechnology in only battery systems will grow for 17.35% in the period from 2018 to 2022 [66].

Nanostructures, either in particle- or fiber-like form can be produced by template synthesis [7,20]. This method allows formation of nanomaterials from a wide range of organic and inorganic materials in a variety of different forms with controlled morphology, size and alignment [67,68]. Different structures can be molded by using hard templates, which are membrane matrices with nano-scale pores, usually made of polycarbonate and alumina are used as templates. Polymeric solutions or melts can be poured over the membrane and let penetrate into the pores. Self-driven by capillary action of the polymer, pressure-driven action by vacuum or electrostatic forces can be used for deposition of the polymer into the template cavities. After deposition, the template is dissolved or the nanostructures are polishing them with

scalpel. Despite of the variety of shapes and sizes that can be achieved, complete removal of the template, without damaging the structure of the nanomaterial and the preparation of single-use templates are major drawbacks of this method. Another way to orient polymeric and/or non-polymeric molecules into ordered structures with specific dimensions and shape is by using specific molecular structures (such as liquid crystals and surfactants) or inorganic structures with certain shape [69], [70], [71]. Liquid crystal (LC) assisted nanostructures vary in morphology depending on the LC mesophase under certain concentration or temperature [72]. While the addition of surfactants promotes the fibril-like structures over aggregated polymeric particles [73]. On the other hand, inorganic structures serve as foundation for formation of coated or multilayered structures [74–76]. Further modification of the nanostructure architecture can be achieved by altering the amount and type of surfactant and oxidizing agent. Surfactants also help organizing inorganic molecules into fiber structure which can further be covered with carbon layer by chemical vapor deposition (CVD) [77].

Nanofibrous or 1D materials are one of the most promising types of electrode structures for energy storage. Nanotubes, nanorods, nanowires and nanofibers belong to this group. Among them, nanofibers attract attention due to the possibility for large scale industrial production [78]. Nanofiber electrodes either enable shorter ion diffusion lengths, or provide larger surface area [79], and can improve the electrical conductivity of the electrode (as in the case of carbon nanofibers). Further advantages of these structures is the possibility to add different active materials, or to design a variety of different structures (smooth, porous, hollow, multilayer or core-shell) and their usage as free standing electrodes or as membranes that separate the electrodes.

Nanofiber mats produced via these methods can be easily converted into carbon nanofibers (CNF). Neat CNF, doped or coated with pseudocapacitive or redox materials can be used as electrodes in either battery or supercapacitor systems [75,80,81]. Spinning systems with co-axial nozzle enable various polymer solutions to be simultaneous spun, which leads to formation of porous, hollow, core-shell and multi-layered nanofibrous structures can be achieved [82–85]. Moreover, nanofibrous mats can also serve as templates for organic, inorganic, porous or composite carbon nanofiber formation. In-situ deposition of other polymer over the

surface of CNF membrane in presence of oxidizing agent can be used to produce composite nanofibers [86]. Removing the organic part by annealing the electrospun polymeric fiber containing inorganic salts is another alternative used to form doped CNF [87], [88]. Polymer nanofibers containing inorganic particles can be converted into porous carbon nanofibers after leaching process which removes the inorganic part after carbonization [89]. Nanofiber mats can also serve as template for production of hollow conductive polymer nanofibers for high-performance supercapacitors [90].

Aerogels or nanofoams are 3D interconnected materials that exhibit high surface area and high porosity [91]. For energy storage applications, such structures are carbon-based and are usually used as supercapacitor electrodes [92]. Despite the porosity, the use of carbon aerogels (CAs) for energy storage applications is due to their conductivity, flexibility and moreover, because of their scalable production and the possibility for further modifications. CAs may be obtained by phase inversion of organogels and their subsequent carbonization. The inversion of phases may be done by freeze-drying or by supercritical CO<sub>2</sub> solvent exchange [93,94], while the precursors can be either synthetic or biopolymers [91,94]. Modification of aerogels by using different polymer precursors, addition of electrochemically active substances or modifying the production method allows production of aerogel structures with even more enhanced porosity, flexibility and conductivity. For example, physical or chemical activation of CAs can also take place, in order to obtain structures with improved surface area [95]. Addition of nanomaterials such as carbon nanotubes or graphene leads to formation of highly conductive CAs [96], while functionalization of CAs' surface improves their electrochemical properties. Such CAs can be prepared by in-situ coating, hydrothermal process or electrodeposition of the active material [97–99]. Template synthesis using cotton fibers or catalytic nanowires is another method to produce CAs [100,101]. Ultra-flexible aerogels can be produced from conductive polymers by hydrothermal methods or electro-polymerization [102,103]. Their flexibility depends on the crosslinking density of the polymers used. These aerogels usually contain graphene or CNTs but also can involve cellulose nanocrystals, or pseudocapacitive materials [104–107]. Recent studies on aerogels are focused on graphene or CNT based aerogels due to their conductivity and chemical stability, which makes them suitable

as current collectors. They may be obtained by sol-gel, hydrothermal or self-assembly synthesis [108–110] and also allow combinations with wide range of inorganic or organic active materials [105,111–113].

Surface engineering approaches can enable formation of active material doped carbonaceous electrodes or coating the active particles with carbon (or other material) via ALD (atomic layer deposition) or CVD or combination of both technics. Recent studies report that coating architecture, rather than the chemical composition is the feasible approach to keep the mechanical properties of the electrodes [114]. In this regards, bulk coating of the entire electrode, core-shell and yolk-shell structures have been reported as an alternative to suppress the volume expansion of the active material [114].

### **1.3 Hypothesis**

Development of structures that can reversibly accommodate large number of ions over prolonged cycling is of crucial importance for the progress in the research of energy storage devices and their commercialization. The development of new designs, production methodologies and materials would accelerate realization of that goal. Thus, the aim of the thesis is the development of novel fibrous structures as electrodes for energy storage devices. It is expected that such fibrous structures:

- 1) could be obtained from natural and environmentally friendly materials;
- 2) could be tailored so that their morphology will enable their application as electrodes for either battery, supercapacitor or/and hybrid energy storage devices;
- 3) could be flexible and can be applied without binders which will make possible the electrodes applied to be thick without compromising their performances;
- 4) could be produced via industrially feasible production methods.



## 2. METHODS AND EQUIPMENT

This chapter summarizes the applied methods and equipment that were used in this thesis. The first part of the chapter provides brief introduction into the equipment used for production of the materials developed in this thesis and the electrochemical configurations used to test their properties. As a second part, this chapter summarizes and briefly describes the principles of the methods used for characterization and analysis of the materials and cells discussed in this thesis.

### 2.1 Nanofiber Production Methods and Equipment

Nanofibrous materials developed in this thesis were produced via two spinning techniques:

**Electrospinning:** used only for the production of lignin-based porous carbon nanofibers. The production was conducted on a lab scale electrospinning device (Nanospinner24, Inovenso Inc). For the purpose of the thesis, bottom-up approach was used. The device was equipped with one nozzle, rotating collector with horizontal movement, power supply (up to 30 kV) and syringe pump (feeding rate up to 100 ml/h).

**Solution Blowing:** used for all other nanofibrous structures developed in this thesis. For the purpose of the thesis, lab-scale top-bottom set up solution blowing system (Aerospinner L1.0, Areka Advanced Ltd.) was used. The system consisted of concentric nozzle held at a given distance (up to 80 cm) from a fixed cylindrical collector, so that the fibers produced get collected inside the cylinder. On one end (opposite to the nozzle tip) the nozzle was connected to a syringe pump that delivered the polymer solution, and on the lateral side it was connected to compressed air reservoir. Whole system was placed into a closed cabin with exhaust system.

Detailed description of the material and process parameters used is given in each chapter containing experimental study.

## 2.2 Methods and Equipment for Carbon Structures

The production of carbon structures realized in several steps, depending on the precursor used. Generally, first step is stabilization of the precursor under specific temperature and atmosphere, followed by carbonization in inert atmosphere at high temperatures. Optimization of stabilization and carbonization parameters, such as temperature, heating rate and dwelling time were conducted in preliminary study in order to assure formation of desired carbon structures. Carbonization step was conducted on tubular carbonization furnace (Carbolite TZF 18/-/300) with multi step program set-up. It can operate at temperatures up to 1800 °C work under controllable atmosphere.

Detailed description of the material and process parameters used is given in each chapter containing experimental study.

## 2.3 Electrochemical Cell Assembly

The electrochemical performances of the electrodes developed in this thesis were analyzed in two electrochemical systems:

**Three-electrodes electrochemical system:** was used for investigating the properties of individual electrodes in aqueous electrolytes. The set-up consisted of electrochemical glass cell with three openings, one for each electrode. The electrodes developed in this thesis were used as working electrodes, silver wire was used as pseudo-reference electrode, and platinum plate as counter electrode. At each measurement, the cell was firstly filled with electrolyte, then each electrode was positioned in one of the openings of the cell and connected to the corresponding clips from the instrument on which they were tested.

**Two-electrodes electrochemical system:** was used for testing battery and supercapacitor performances. In battery systems, the electrodes developed in this thesis were working electrodes used against Li- and/or Na-metal, which acted as both, reference and counter electrode in the system. Full symmetrical or asymmetrical supercapacitor cells were assembled using the electrodes developed in this thesis, on the positive and negative side. In both cases, the electrodes were separated with glass-fiber membrane. After positioning three elements into the coin cell (CR2032) cases, the cells were filled with electrolyte and closed with hydraulic

crimper (Gelon Group) under pressure. All battery cells were assembled in a glovebox under controlled inert atmosphere.

Detailed description of the electrode preparation process, the materials and electrodes used is given in each chapter containing experimental study.

## **2.4 Characterization Methods**

### **2.4.1 Morphology and structure**

#### **2.4.1.1 Scanning electron microscopy (SEM)**

Scanning electron microscopy is used to investigate the morphology of the samples throughout all production steps. For that purpose, the sample - covered with conductive layer - is firstly put into device's vacuum chamber. Then the instrument uses a beam of electrons that target the sample [115]. Once the electrodes “touch” the sample, signals in form of secondary electrons and backscattered electrons are emitted to the detector and converted into magnified images. When the signals emitted to the detector are x-rays, they are used to provide information about the elemental composition of the material under observation. Such, technique is called energy dispersive x-ray spectroscopy (EDX).

SEM was used to visually identify the morphology and to determine the size of the structures developed in this thesis. The samples obtained at different process stages were analyzed from the SEM images obtained through ImageJ image processing software. EDX analysis, on the other hand was used to investigate the elemental content of new (as-obtained) samples, as well as for the post-mortem analysis of electrodes.

#### **2.4.1.2 Fourier transform infrared spectroscopy (FTIR)**

FTIR analysis is used to detect the different hetero-nuclear functional groups and polar bonds present in the samples. This is enabled with the infrared radiation sent from the instrument toward the sample [116]. Depending on the chemical structure of the sample, the absorbed infrared radiation gets converted into energy with a specific intensity and is presented as a spectrum in a given wavelength range. Any change of the characteristic patterns, the intensity of the absorption bands or their position in the spectrum indicates change in the chemical structure of the materials under

observation. Therefore, this technique is very convenient to follow the structural changes of the samples produced throughout all their preparation steps.

In this thesis, FTIR analysis was used to observe chemical structure change of the samples on at different stages of the production process, as well to determine the differences between different samples.

#### **2.4.1.3 Raman spectroscopy**

Raman spectroscopy is a spectroscopic technique that provides information about the homonuclear molecular bonds. The principle of Raman analysis lays in the laser light scattered at wavelengths different from that of the laser source, known as Raman scatter [117]. Since, each molecular bond has its own vibration energy, the chemical structure of the sample under observation determines the wavelengths at which the light will scatter. Similarly as in FTIR analysis, here too, the position of the scattered light and its intensity indicates structural changes.

Raman spectroscopy is widely used for characterization of carbonaceous structures, because of their homonuclear (C=C, C-C) bonds. Typical carbon structure is characterized with two main peaks. The first one (G) at wavelength of  $\sim 1580\text{ cm}^{-1}$  indicating ideal graphitic structure with  $E_{2g}$  symmetry, and the other one (D) at  $\sim 1350\text{ cm}^{-1}$  characteristic for disordered graphitic structure. The integrated area below these two peaks gives an inside into the degree of order (or disorder) in the carbonaceous structure under analysis [118], [119]. Additionally, appropriate processing of the Raman curves and its deconvolution can provide more detailed information about the chemical structure and crystallinity of the material.

Therefore, Raman spectroscopy was used to analyze the structural changes of the carbonized samples developed in this thesis. Detailed description of the methodology used for detailed Raman analysis is given in the chapters containing experimental study.

#### **2.4.1.4 X-ray diffraction (XRD)**

X-ray diffraction is a method used to identify the crystal structures of inorganics, polymers, and other materials. The principle behind XRD analysis lays in the diffraction of x-rays sent towards the sample, when Bragg's Law is satisfied [120]. This happens when the diffracted x-rays leave the crystal at the same angle the sent

(incident) x-rays at a specific angle ‘touched’ it. The wavelength ( $\lambda$ ) of the incident x-rays used during the analysis and the angle of incidence ( $\theta$ ) at which the sample is scanned provide information about the crystal lattice planar spacing ( $d$ ) through Bragg’s Law equation  $n \cdot \lambda = 2d \cdot \sin\theta$  (where  $n$  is the order of reflection) [121]. Once inter planar lattice spacing is obtained the material under analysis can be easily identified. Furthermore, structural changes in materials of the same type of material can also be deduced with an appropriate curve processing technique. The data obtained from such processing can be used to calculate the size of the crystal ( $L$ ) can also be calculated using Scherrer’s equation  $k \cdot \lambda = L \cdot \beta \cdot \sin\theta$  (where  $k$  is fitting pre-factor,  $\beta$  is full width at half maximum of a given peak) [122].

Determination of crystalline phases and unit cell dimensions of carbonized samples was conducted through XRD analysis. Detailed description of the parameters and methodology used for detailed XRD analysis is given in the chapters containing experimental study.

#### 2.4.1.5 Brunauer-Emmett-Teller (BET) surface area analysis

BET surface area analysis is a technique used to investigate the porosity of the materials. The analysis works on the principle of BET theory used to measure the “physical adsorption of gas molecules on a solid surface” [123]. As the gas molecules get adsorbed on the solid surface they start to interact between themselves forming layers. Each of those gas molecule layers has its own enthalpy of adsorption ( $E$ ), which equals the enthalpy of vaporization as the number of layers increases. The difference in the enthalpy values between the first ( $E_1$ ) and the higher layers ( $E_{n+1}$ ) gives the BET constant ( $c$ ) used to calculate the quantity of the adsorbed gas ( $v$  [ml]) through BET equation  $\frac{1}{v \left[ \frac{p_0}{p} - 1 \right]} = \frac{p_0}{p} \cdot \frac{c-1}{c \cdot v_m} + \frac{1}{c \cdot v_m}$ , where  $p$  [Pa] and  $p_0$  [Pa] are the partial and the saturated vapor pressure of adsorbate gas at temperature of 77 K, respectively;  $v_m$  [ml] is the volume of gas adsorbed in one layer on the surface of the solid sample. BET constant is calculated as  $c = e^{\left( \frac{E_1 - E_{n+1}}{R \cdot T} \right)}$ .

The data obtained from the measurements is generally depict as gas quantity ( $Q$ ) vs  $p_0/p$  graph which represents an isotherm of the gas adsorbed and desorbed at each  $p_0/p$  value. Based on the shape of the isotherms, all porous structures can be classified into six main types, namely microporous solids with small external surface

(type I), nonporous or macroporous structures (type II and III), mesoporous solid surfaces (type IV), microporous and mesoporous solids (type V) and highly uniform nonporous surfaces (type VI) [124]. Furthermore, all the information obtained from BET analysis can be used to calculate the density of the fluid adsorbed on the surface and in all pores of the solid material. Such method, called Density Functional Theory (DFT), can provide more detailed analysis of the adsorption phenomena and an estimation of the size of the pores present into the porous structure [123].

In this thesis, BET analysis was conducted to determine the specific surface area of the developed carbonaceous materials, as well as their pore size and distribution. Detailed description of the parameters used for the analysis is given in each chapter containing experimental study.

## **2.4.2 Electrochemical characterization**

### **2.4.2.1 Cyclic voltammetry (CV)**

Cyclic voltammetry is a versatile electrochemical technique used for characterization and synthesis of organic and inorganic materials. Its principle is based on Nernst equation  $U = U^0 + \frac{RT}{nF} \cdot \ln \frac{a_{OX}}{a_{RED}}$  which correlates the electrochemical potential of the cell ( $U$ ), the standard half-cell potential ( $U^0$ ) and the chemical oxidation ( $a_{OX}$ ) and reduction ( $a_{RED}$ ) activity of the material in an equilibrated system. So, during the measurement, it detects the current generated in the electrochemical cell as a result of the change of the potential over time [125]. CV is one of the techniques used to determine the electrochemical properties of a material in solution or absorbed on the working electrode. It is suitable to identify whether the reactions are initiated as a result of electrode transfer reactions or by reduction-oxidation processes.

CV is usually applied in electrochemical systems with three electrodes. In that case, CV measurement provides information about the electrochemical properties of the working electrode relative to the reference electrode, while the third (counter or auxiliary) electrode in system is used to close the current circuit in the cell. In some cases, as in half-cell batteries when the electrochemical properties of either anode or cathode material has to be investigated in closed inert cell, the reference electrode can also act as a counter electrode. In energy storage systems, CV is generally used to determine the electrochemical behavior of the material; to investigate the behavior

of the electrode/electrolyte at high and small scanning rates and its stability over a number of cycling steps; to detect the redox reactions between the electrode material and the electrolyte; to investigate the potential limits where the electrode can function without evolution of hydrogen and/or oxygen gases. Despite the current values obtained from the measurements, the shape of the CV curve can also be used to describe the electrochemical behavior of the material. For example, closed rectangular curve is characteristic for capacitive electrodes, quasi-rectangular for pseudocapacitive, while ‘duck’ like shape indicates redox processes, and thus represents a battery-like electrode.

In this thesis, CV was used to determine the electrochemical properties of the electrode materials developed, their maximum potential limits in different electrolytes and stability, as well as to estimate their capacity. Detailed description of the parameters used for the analysis and the formulas used to obtain the quantitative results are given in each chapter containing experimental study.

#### **2.4.2.2 Electrochemical impedance spectroscopy (EIS)**

Electrochemical impedance spectroscopy is a method that investigates the response of an electrochemical system as a result of perturbation frequency applied. Depending on the type of perturbation applied, it can be galvanostatic or potentiostatic. Between both of them, the later one is most widely used for lab-test of small electrochemical cells, where the behavior of an individual material is a point of interest. Potentiostatic EIS measures the current of the electrochemical cell when alternating current (AC) potential is applied, and uses Ohm’s law to determine the impedance ( $Z$ ) of the cell [126]. Since, the voltage applied over time ( $U_t$  [V]) and the response current ( $I_t$  [A]) are oscillating they can be represented as sinusoidal functions and the impedance can be calculated with the formula  $= \frac{U_t}{I_t} = \frac{U_0 \cdot \sin(\omega t)}{I_0 \cdot \sin(\omega t + \phi)}$ , where  $U_0$  [V] and  $I_0$  [A] are the corresponding potential and current amplitudes,  $\omega$  is the radial frequency and  $\phi$  is the phase shift.

For the sake of easier graphical representation, the impedance of the system can be described as a complex function ( $Z = Z' + Z''$ ) of real ( $Z'$ ) and imaginary ( $Z''$ ) parts and depict as a Nyquist plot ( $Z''$  vs  $Z'$ ). Nyquist plot is an Argand diagram on which curve with a specific connected semi-circular and linear shapes is drawn, representing each of the elements in the cell. To gather further information about the

individual element, the cell is represented as an electrical circuit. For example, in a supercapacitor cell, the first intersection of the plot on the real axis registered at high frequencies represents the first element of the circuit that corresponds to the resistance of the electrolyte ( $R_s$ ) [127]. The following semicircle in the high-to-mid frequencies represents the interfacial charge transfer resistance ( $R_{ct}$ ) of the electrode. The tail which describes the ion diffusion into the electrode and is represented by the Warburg element ( $W$ ) is drawn in the low-frequencies region. For detailed analysis, Bode plots ( $Z'$  or  $Z''$  vs frequency) can help connecting each impedance value from the Nyquist plot to the frequency it is measured [128].

EIS, in this thesis, was mostly used as a method to investigate the change of the internal resistance and ion diffusion in electrochemical cells before and after cycling. Detailed description of the parameters used for the analysis and the formulas used to obtain the quantitative results are given in each chapter containing experimental study.

#### **2.4.2.3 Galvanostatic charge-discharge (GCD)**

Charge-discharge tests of electrochemical cells are the most important techniques used to determine their practical performances. Despite the wide range of methods used to control the charge-discharge process, galvanostatic charge-discharge is the most widely when the performances of an individual material is a point of interest. GCD measurements are technique used to quantify the charges that the cell can deliver at given constant current over a determined voltage range [129]. Unlike CV and EIS, GCD measures the amount charges that pass through the cell when constant current ( $CC$ ) is applied to it. Since the current applied can be positive and negative, the cell can be charged and discharged, which makes a cycle. Repetitive charge-discharge cycles allows to make an estimation of the life of the cell, while the change of the current applied is used to determine its rate capability. In the latter case, there is a general trend of inversely proportional relation between  $CC$  and the capacity calculated and also the speed at which one cycle to be completed. Therefore, the current applied is generally named as a C-rate. A C-rate of 1 C is defined as the current needed the cell to complete half cycle in one hour.

GCD is the most widely used technique that determine the overall practical values and performances of all two- and three-electrodes electrochemical cells – batteries,

supercapacitors, electric double layer capacitors, hybrid devices. The results from the measurements are usually depict as ‘Capacity vs Cycle’ and ‘Voltage vs Time’ graphs. The later ones are called charge-discharge profiles, and provide an insight into the electrochemical behavior of the cell [130]. In this regard, specific triangular shape of the curves in the charge-discharge profiles indicates supercapacitor cell, while curves with long plateau at certain voltage indicate redox reactions, and thus a battery cells.

In this thesis, GCD was used to estimate the capacity, energy and power values, the rate capability and cycle life of all two-electrodes electrochemical cells assembled. Detailed description of the parameters used for the analysis and the formulas used to obtain the quantitative results are given in each chapter containing experimental study.



### **3. DEVELOPING AND CHARACTERIZATION OF LIGNIN-BASED FIBROUS NANOCARBON ELECTRODES FOR ENERGY STORAGE DEVICES<sup>1</sup>**

#### **3.1 Introduction**

Among the different energy storage devices, batteries provide the highest energy density, which makes them applicable for high energy storage demands. Nowadays, lithium ion batteries (LIB) are leading electrochemical devices used in a wide range of applications. As a constituent element of a battery, the anode is the crucial component for battery's storage capacity and rate capability. Graphite and hard carbons are commercially used in today's LIBs. However, their limited capacity and rate capability limit battery's energy and power densities.

The growing demand for green energy opened doors for development and research for a large number of new technologies. Na-ion batteries are the most promising to replace already commercialized Li-ion batteries. After lithium, sodium has the most advantageous electrochemical equivalent and standard potential [131]. Additionally, both technologies have similar working principle and production methodology. Besides that, Na-ion has the advantage of abundance and lower cost prime materials. Literature reports on positive and negative electrodes for Na-ion batteries are analogues of those used in Li-ion battery due to the similar behavior of ion intercalation into the anode. However, graphite is not suitable material for Na-ion technology due to the larger ion diameter of Na. Thus, not graphite but hard porous carbons are more suitable here together with low voltage metal-oxides or alloy materials [132].

Anodes with zero-, 1D-, 2D- and 3D nanostructures made of different materials have been proposed [133]. Among them 1D carbon nanofibers (CNF) due to their higher surface area can provide shorter lithium ion diffusion lengths and enhanced electron

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<sup>1</sup> This chapter is based on the article "Developing and Characterization of Lignin-Based Fibrous Nanocarbon Electrodes for Energy Storage Devices" published in *Composites Part B: Engineering*, , 158, 2019, 239-248. DOI: 10.1016/j.compositesb.2018.09.072

transport [79]. The possibility for adding different active materials into their structure and their usage as free standing electrodes are other advantages of CNFs. Another approach to facilitate ion diffusion and lithiation capability is to improve specific porosity of the material. Surface area increment of carbonaceous material can be achieved by several methods, generally classified as chemical or physical methods. Chemical activation is done by adding activating substances into the precursors [134], [135] or mixing them with already carbonized material [134]. On the other hand, pre-carbonized material can be physically activated at high temperatures under specific atmosphere conditions (steam, CO<sub>2</sub>) [136, 137]. The increase of the surface area, pore size and distribution can be controlled by the amount of activating substance added and/or the temperature and time applied for activation [138].

Lignin is an abundant, low-cost polymer obtained from a variety of biomasses by solvent extraction as the most common method [49, 50]. As a byproduct of paper industry it can be used as fuel additive, emulsifier or dispersant in agriculture, as binder or reinforcement in different composite structures or as antioxidant for polymers [139]. Due to its highly functionalized macromolecules it can be used as starting material for renewable polymers, such as polyesters, polyurethanes or polyanilines. In addition, its high carbon content allows its usage as precursor polymer for carbon fiber production. As a non-toxic and biocompatible polymer, it is a promising precursor to replace PAN (polyacrylonitrile) in carbon fiber and nanofiber production. However, its low molecular weight is an obstacle for its conversion into fibers. Thus, it is usually blended with high molecular weight polymers, such as poly (vinyl alcohol) (PVA), polyethylene oxide (PEO), poly acrylonitrile, polyethylene glycol, polypropylene, etc. [140-143] In regards to energy storage devices, lignin has been used as carbon precursor for carbonaceous electrodes [144] or as a binder [145]. Lignin-based carbonaceous materials as anodes for Li-ion batteries have been reported in the form of fibers obtained either by melt blowing [146] or electrospinning of lignin/PEO [147] or lignin/PAN [148] mixtures, or as carbon source for doped or porous carbon spheres [149, 150].

Here, we report the effect of activation process and the electrochemical properties of lignin-based submicron carbon fibers obtained by electrospinning of lignin/PVA solution. CNF mats were activated by two approaches: by adding activating agent in-situ into the polymer solution and/or by mixing it with pre-carbonized fibers.

Activated carbon fibers were used as free-standing anodes in a half cell lithium (LIB) and sodium ion batteries (SIB). Electrochemical behavior of the electrode was analyzed by cyclic voltammetry, while its rate capability and cycling stability were analyzed by galvanostatic cycling tests. The results showed that mesoporous submicron lignin-based carbon fibers can improve the capacity of the device and keep it stable over prolonged cycling.

## **3.2 Experimental**

### **3.2.1 Materials and preparation**

Water soluble alkali lignin (Sigma Aldrich), PVA (40-88, Poval) and distilled water were used for polymer solutions. Iodine (Merck Millipore) was used for stabilization of the electrospun nanofibers and potassium hydroxide (KOH, Sigma Aldrich) was used for activation. All of them were used as received.

Lignin and PVA were separately dissolved in water, forming 15 wt% solutions and then mixed in ratio 1:1. In another trial, 5 wt% KOH (based on total polymer concentration) was added into lignin solution before mixing it with PVA. As prepared solutions were electrospun on lab-electrospinning device with rotating collector under a potential of 22 kV, with 20 cm working distance and 1ml/h feeding rate. Nanofiber mats obtained after 6h electrospinning were stabilized under iodine vapor at 100 °C for 12 h, and then carbonized at 600 °C for 1h in argon atmosphere (heating rate of 1 °C/min up to 300 °C and 2 °C/min up to 600 °C). This carbonization was also the activation step for the nanofibers containing KOH within the solution, denoted as “KOH/CNF” in the text. CNF obtained from the neat lignin/PVA solution were further treated with KOH (with CNF:KOH mass ratio of 1:5) and activated at 600 °C for 1h in argon atmosphere. This sample is denoted as “a-CNF” in the text. The activation process for both samples treated with KOH was completed by immersing the CNF in 1M HCl and water, followed by drying at 100 °C for 1 h.

### **3.2.2 Characterization methods**

The morphology and structural changes of the samples were characterized by Scanning Electron Microscope (SEM), Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Spectrometer) and Raman Spectroscopy (Renishaw, 532 nm). Average fiber diameter was measured from five different SEM images of each

sample, by measuring a total of 100 fiber diameters. The porosity of the CNF was analyzed by multipoint BET analysis (Quantachrome Nova) in nitrogen atmosphere, at 77 K using slit pore NLDFT equilibrium model, after degassing the samples at 100°C during 2h.

Coin CR2032 batteries were prepared using the three types of CNF mats as free-standing anodes with average thickness of 30  $\mu\text{m}$ . They were cut into circular-shaped plates with diameter of 1.3 cm, forming electrodes with average mass loading of 2.5  $\text{mg}/\text{cm}^2$ . No additional binders or current collectors were used. Lithium and sodium metal were used as counter electrode, while glass fiber membrane was used as separator (Whatman, GF/B). The electrolyte for Li-ion cell was prepared using 1M  $\text{LiPF}_6$  in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 v/v), while the one for Na-ion cell consisted of 1M  $\text{NaClO}_4$  in ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:1 v/v) and 5 wt% fluoroethylene carbonate (FEC) (all of them purchased from Sigma Aldrich). The anodes were characterized by cyclic voltammetry (CV) at a scanning rate of 0.5 mV/s, electrochemical impedance spectroscopy (EIS) at open circuit potential, at frequency range from 0.1 Hz to 100 kHz and an AC amplitude of 5mV on Gamry potentiostat/galvanostat/ZRA and galvanostatic cycling tests on a Battery Analyzer (MTI Corporation) in the voltage range between 0.01-2.5 V at different current rates.

### **3.3 Results and Discussion**

#### **3.3.1 Morphology and structure**

The morphology of nanofibers characterized by SEM is shown in Figure 3.1. Fibers with diameter of 875 nm were obtained after carbonization of lignin/PVA nanofibers, which was an increase of about 300 nm compared to the diameter of the fibers before carbonization. The addition of KOH into lignin/PVA mixture gave fibers with average diameter of 773 nm, which decreased to 514 nm after carbonization. Despite the difference in diameter, the structure of the carbon nanofiber clothes obtained from the solutions with and without KOH was different. As shown in Figure 3.1b, carbon nanofibers from the non-KOH solution exhibit fusion on the intersection points of adjacent fiber. This phenomenon has been noticed in previous studies and is attributed to the polymer relaxation during carbonization and depends on the type of lignin constituents [151]. Moreover, neat CNF mats show a rough dotted surface,

while KOH/CNF exhibits a smooth surface. The dotted surface may be attributed to phase separation of the polyene and aromatic carbonaceous structures, as a result of the structural difference of both polymers and their weak interconnection. The formation of polyene segments is favored with the iodination of PVA [152]. Their presence within the carbonized samples can be attributed to their incomplete conversion into cyclic carbonaceous structure due to the relatively low carbonization temperature used. This phenomenon does not occur in presence of KOH which could be a result of the improved interaction between both polymers and thus fusion between adjacent fibers is suppressed during carbonization, as explained later with the FTIR analysis. It should be mentioned that with the increasing amount of KOH (larger than 5 wt% on total polymer concentration) the solution became non-spinnable due to its high viscosity, hence other KOH containing solutions were not spun.

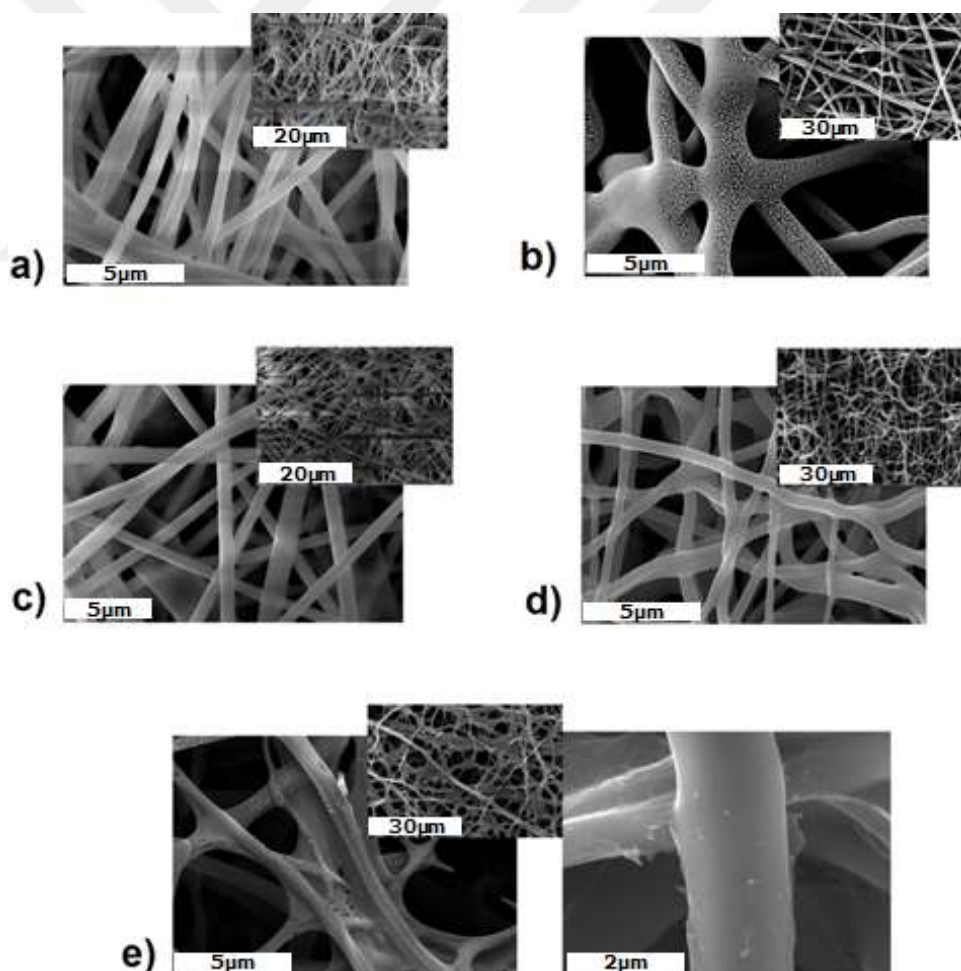


**Figure 3.1 :** SEM images a) lignin/PVA nanofibers, b) CNF, c) lignin/PVA/KOH nanofibers d) KOH/CNF and e) a-CNF at different magnifications.

As a reference sample, neat carbon nanofibers were treated with KOH and thermally activated. Such activated CNF exhibited more remarkable fusion resulting with fibrous sponge-like structure with pores that were not observed on the other two samples, Figure 3.1e. The change of the fibrous morphology of the sample into spongy-like structure is due to the large increase of the inter-plane space in the carbonaceous structure during the activation with KOH. As discussed in previous studies, activation of CNF under sever conditions causes rearrangements and may provoke collapse of the fibrous structure [153]. In our case, the activation at 600 °C resulted in formation of fibrous spongy-like structure with exfoliated C-planes on the fiber's surface (Figure 3.1e), which contribute to the enhanced porosity of a-CNF.

In order to investigate the effect of KOH and iodine presence on the chemical structure of the fibers, FTIR analysis was performed. Figure 3.2 shows the FTIR spectrum of the fibers with and without KOH before and after iodination. The curves for Lignin/PVA nanofibers with (Figure 3.2c) and without (Figure 3.2a) KOH show clear difference in the presence of carbonyl C=O groups. Neat lignin/PVA exhibits strong peak for aliphatic ( $1718\text{ cm}^{-1}$ ) C=O groups, while KOH containing fibers show lower intensity. Nonetheless, the intensity of aryl ( $1645\text{ cm}^{-1}$ ) carbonyl groups is the same for both samples. Lignin has a hindered chemical structure due to its multi-functionality, thus it requires modifications before processing [139]. In our case, KOH acts as a catalyst which propagates cross-linking between lignin and PVA, most probably through condensation reactions. Thus, in addition to the reduction of carbonyl groups, the intensities of hydroxyl C-O ( $1040\text{-}1096\text{ cm}^{-1}$ ), aromatic C-O ( $1246\text{ cm}^{-1}$ ), OH stretching ( $3338\text{ cm}^{-1}$ ) and CH side groups ( $2925\text{ cm}^{-1}$ ) are also lower for the sample containing KOH. As a result of the improved interaction between both polymers, non-C elements/groups were easily eliminated from the structure, which is promoted in the next steps of stabilization and carbonization. This improved interaction also suppresses the relaxation of the polymer and favors the formation of graphitic clusters during carbonization which results in non-fused fibers with smooth surface. Moreover, this may also explain the increased viscosity of the solutions with more than 5 wt% KOH, since larger amounts of KOH will propagate higher degree of cross-linking which makes the spinning process difficult or impossible.

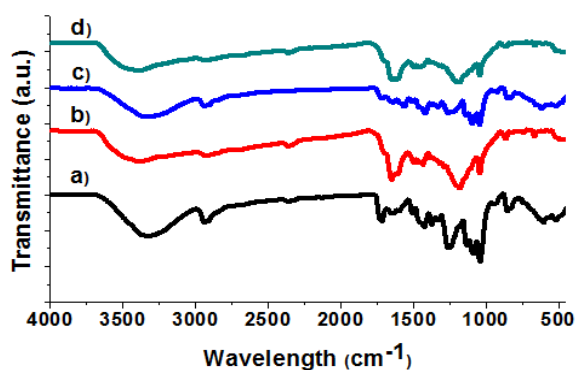


**Figure 3.2 :** FTIR spectrum of Lignin/PVA nanofiber a) before and b) after iodination and Lignin/PVA/KOH nanofiber c) before and d) after iodination.

The effect of iodine can be identified from Figure 3.2 by comparing the curves of the samples before (a) and c)) and after iodination (b and d). For both samples, with and without KOH, there is a decrease in the intensity of the broad peak between 3000 and 3600  $\text{cm}^{-1}$  indicating elimination of hydroxyl groups. However, iodination promotes partial elimination of these groups and leaves the structure with only phenolic OH-groups after iodination, which is demonstrated with the shift of peak from 3338  $\text{cm}^{-1}$  (characteristic for aliphatic OH) to 3395  $\text{cm}^{-1}$  (characteristic for phenolic OH). Iodine also selectively removes C=O and C-O groups, favoring the presence of aromatic C=O (1645  $\text{cm}^{-1}$ ), methoxy (1180  $\text{cm}^{-1}$ ) and primary hydroxyl C-O (1040  $\text{cm}^{-1}$ ) groups over aliphatic C=O (1718  $\text{cm}^{-1}$ ), aromatic and secondary hydroxyl C-O (at 1246 and 1096  $\text{cm}^{-1}$ , respectively) groups after complete iodination. This selectivity of iodine is due to its affinity for dehydration [152], which is higher for the aliphatic chains of PVA than the lignin molecules with hindered functional groups. Therefore, increased intensity of the aromatic C=O (1645  $\text{cm}^{-1}$ ) and methoxy (1180  $\text{cm}^{-1}$ ) groups and a single peak of primary hydroxyl C-O (1040  $\text{cm}^{-1}$ ) groups can be still observed after iodination. The density of methylene side groups (2925  $\text{cm}^{-1}$ ) and CH-deformation (1370 and 1430  $\text{cm}^{-1}$ ) is also reduced after iodination.

Raman spectroscopy (Figure 3.3) of the electrospun CNFs indicates disordered carbonaceous materials. The characteristic G and D-peaks were registered at about 1590  $\text{cm}^{-1}$  and 1365  $\text{cm}^{-1}$ , respectively. KOH used for activation promotes formation of more disordered amorphous  $\text{sp}^2$  carbon clusters [154]. Thus, larger disorder and larger number of defects are possible within the graphitic layers when KOH is used for activation of already carbonized nanofibers. It is also reflected on the increased ID/IG ratio in comparison to the CNF before activation. On the other hand, the

addition of KOH in-situ enhances the order of carbon clusters. As discussed above, the improved interaction between both polymers in presence of KOH enables easier elimination of non-C atoms and further formation of graphitic-like clusters during carbonization. The low intensity peaks at about 1070 and 850  $\text{cm}^{-1}$  can be attributed to polyene structures developed from PVA chains [155]. These peaks are more intense on the CNF sample and can explain the phase separation observed on the SEM images. EDAX analysis performed to determine the content of C and non-C atoms, confirmed that the addition of KOH improves the elimination of non-C atoms within the structure. However, it also showed a high content of oxygen within the structure which explains the large ( $>2$ )  $I_D/I_G$  ratio for the three samples, compared to previous studies [147]. The significant amount of oxygen within the structure can be attributed to the low carbonization temperature applied. The process parameters, such as carbonization temperature or time, can be subject of further optimization in order to increase the carbon content within the carbonized structure [146], [156].

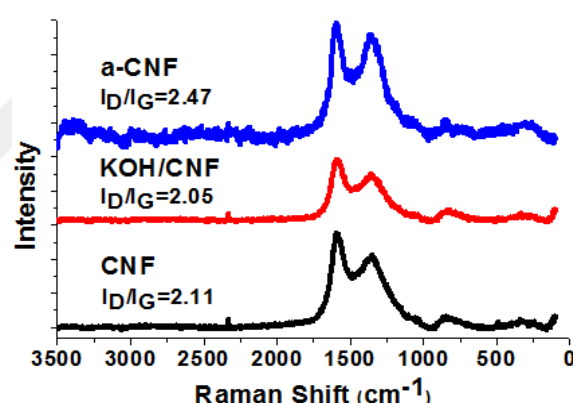


**Figure 3.3 :** Raman Spectroscopy of neat CNF, KOH/CNF and a-CNF.

Brunauer–Emmett–Teller (BET) analysis was conducted in order to investigate the change in porosity of the CNF treated with KOH. Table 3.1 shows the values of total, meso- and microporous specific surface area (denoted as  $SSA_{total}$ ,  $SSA_{meso}$ ,  $SSA_{micro}$ ), total pore volume ( $V_{total}$ ), the DFT cumulative pore volume for meso- and micropores (denoted as  $V_{meso}$ ,  $V_{micro}$ ), and average pore size ( $R_{AV}$ ) deduced from the BET analysis. Graphical presentation of pore size distribution and cumulative surface area (DFT) is given in Figure 3.4. The results indicate formation of porous structure when CNF mats are treated with KOH. SSA from multi point BET analysis is doubled for KOH/CNF (93.09  $\text{m}^2/\text{g}$ ) and significantly larger for a-CNF (1049  $\text{m}^2/\text{g}$ ), when compared to neat CNF mats (44.42  $\text{m}^2/\text{g}$ ). Moreover, KOH also influenced

pore sizes and its distribution. The porosity of the neat CNF mat is due to the presence of meso- and macropores, being the former 68% of the total pore volume. Significant change in pore size distribution was observed for a-CNF as a consequence of the development of microporous structure, which is 76% of the total pore volume. The increased microporosity is a result of the interaction of CNF with KOH at elevated temperatures, which leads to formation of gas molecules (such as CO, H<sub>2</sub>) that abandon the structure leaving vacancies within the fiber [157]. On the other hand, the addition of KOH in-situ changed the SSA of the CNF mat as a consequence of the increased mesoporous structure. Nearly 93% of the porous structure of KOH/CNF is mesoporous, which could be result of the decreased average fiber diameter and the absence of fusion of the carbonized fibers. No additional development of microporous structure was observed for this sample. The weak effect of in situ embedded KOH on the formation of microporous structure of lignin-based fibers opposes the already reported results in literature [138]. However, in our case this may be attributed to the interaction of KOH with both polymers in the solution, as discussed before, and a possible reaction between KOH and iodine during stabilization.

**Table 3.1 :** Structural parameters of activated and neat CNFs

|         | SSA <sub>total</sub><br>[m <sup>2</sup> /g] | V <sub>total</sub><br>[cm <sup>3</sup> /g] | V <sub>meso</sub><br>[cm <sup>3</sup> /g] | V <sub>micro</sub><br>[cm <sup>3</sup> /g] | R <sub>AV</sub> [nm] |
|---------|---------------------------------------------|--------------------------------------------|-------------------------------------------|--------------------------------------------|----------------------|
| CNF     | 44,42                                       | 0,0939                                     | 0,0642                                    | 0.0012                                     | 4,2270               |
| KOH/CNF | 93,09                                       | 0,1099                                     | 0,1026                                    | 0.0011                                     | 2,3610               |
| a-CNF   | 1049,00                                     | 0,4953                                     | 0,0464                                    | 0.3759                                     | 0,9442               |

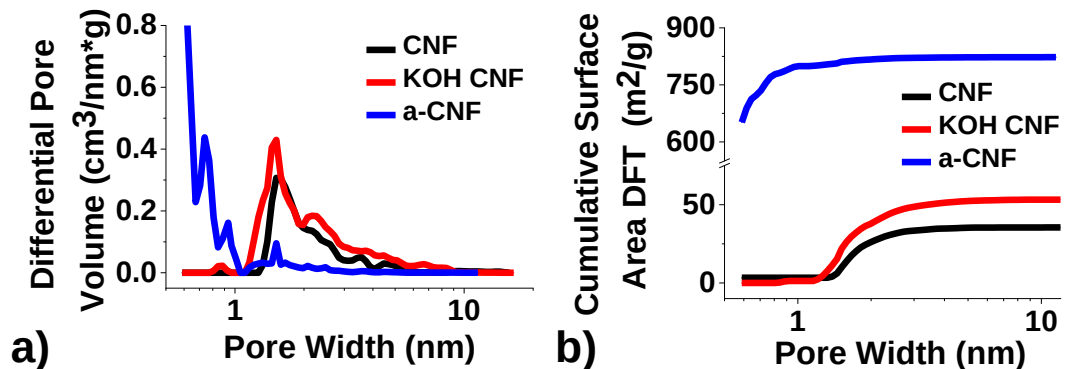


**Figure 3.4 :** a) Pore size distribution, and b) cumulative surface area (DFT) vs pore width graphs.

### 3.3.2 Energy storage performances

#### 3.3.2.1 Lithium ion battery performances

Charge-discharge curves obtained from galvanostatic tests conducted on half cells containing one of the three samples as a free standing anode are shown in Figure 3.5a-c. The three anodes exhibited a clear discharge inflection point during the first cycle, which is an indicator of solid electrolyte interface and irreversible Li-ion insertion into the CNFs. This point was observed at 0.5 V for the neat CNF, while it was moved to higher potentials at about 0.8 V and 0.75 V for KOH/CNF and a-CNF. They correspond to the reduction site of CV curves shown in Figure 3.5d. A broad strong peak, characterizing Li-ion de-intercalation was registered on the oxidation site of the curve for the neat CNF, which is in accordance with previous study on fused lignin-based carbon fibers [147]. For the other two samples, Li-extraction was recorded with much broader and weaker peaks, plus wider current range at higher voltages, which confirms the structural changes between the neat CNF and those treated with KOH.

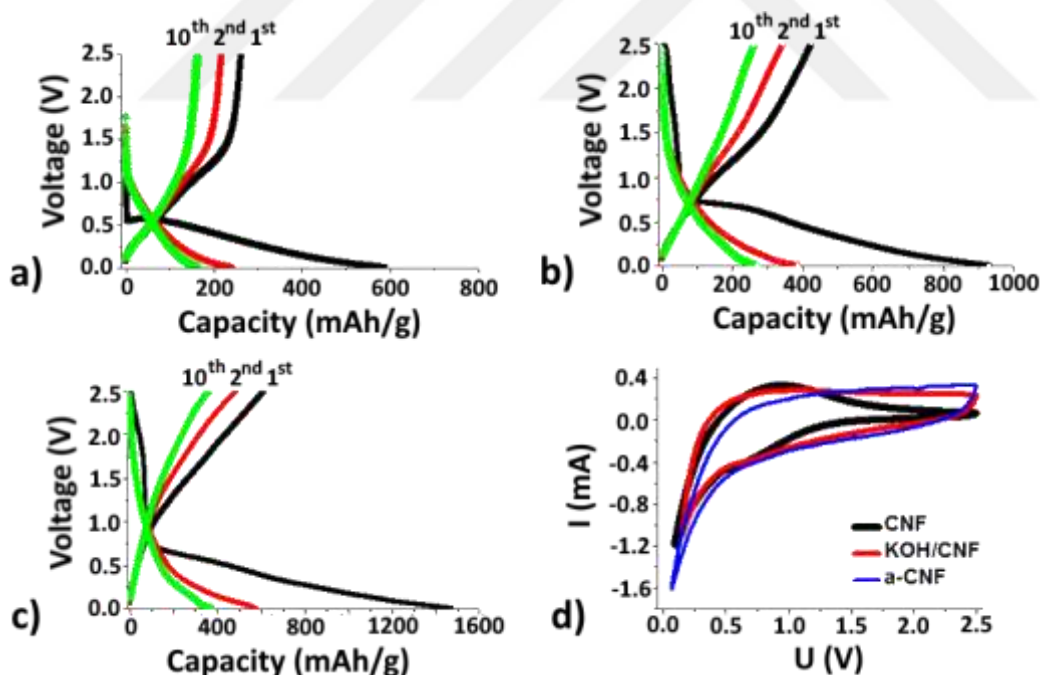


**Figure 3.5 :** Charge/Discharge curves of 1<sup>st</sup>, 2<sup>nd</sup> and 10<sup>th</sup> cycle at 50mA/g for a) CNF, b) KOH/CNF and c) a-CNF anodes in Li-ion half-cell and their d) cyclic voltammograms from the first cycle.

Electrochemical impedance spectroscopy was performed before cycling and after 3 charge/discharge cycles (Figure 3.6). In the high and medium frequency region, each

of the samples showed two semicircles which correspond to resistance of the SEI and the charge transfer resistance [158]. A typical inclined line at an angle of  $45^\circ$  which is a characteristic for Li-ion diffusion into the anode was recorded in the low frequencies region. Nyquist plots of fitted curves given in Figure 3.6, show lowest diameters of the semicircles for a-CNF, followed by KOH/CNF and neat CNF. LIB cells, before charging, show almost the same resistance ( $R_s$ ) arising from electrode material, electrolyte and contact interface for both KOH treated samples ( $17.7\ \Omega$  and  $13.6\ \Omega$  for KOH/CNF and a-CNF, respectively). However, their charge transfer resistance ( $R_{CT}$ ) differs significantly, being lower for a-CNF ( $625\ \Omega$  and  $327\ \Omega$ ). After three cycles,  $R_s$  does not change significantly, while  $R_{CT}$  doubles its value for these two samples. This indicates formation of SEI on the surface of the anode. Despite that, a-CNF exhibits lower  $R_{CT}$ , among the three samples, which indicate that larger amount of Li-ions can be inserted into the anode and thus a-CNF exhibits high capacity during the first cycles.

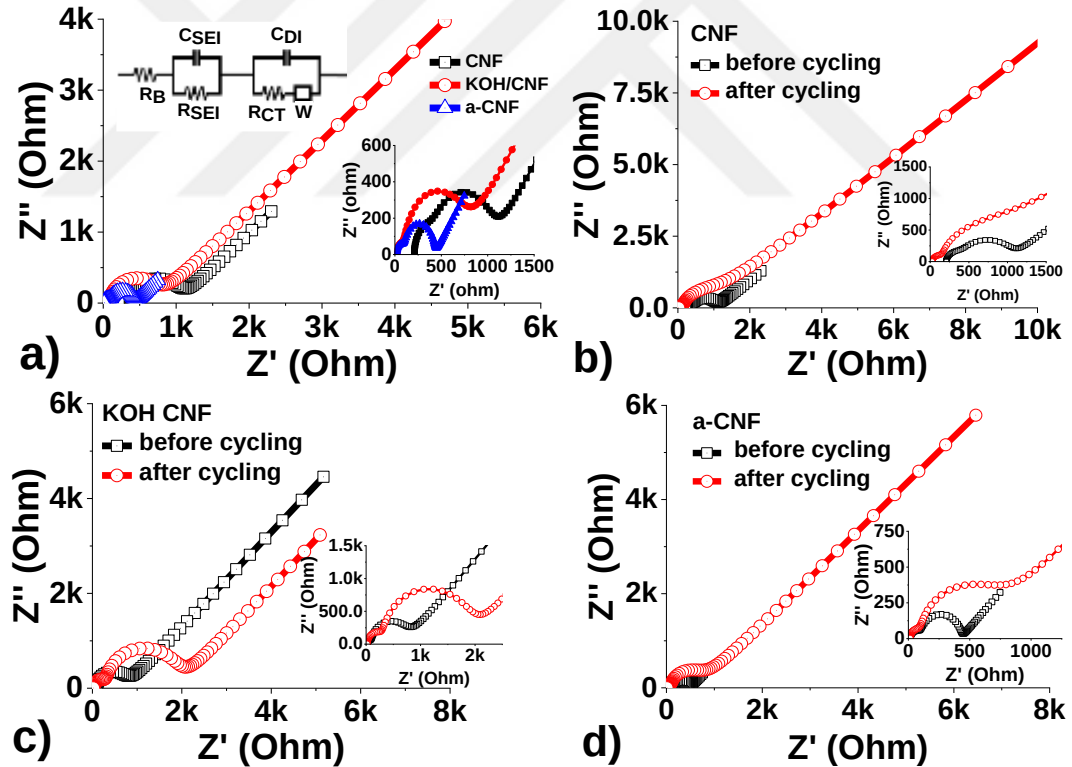


**Figure 3.6 :** Fitted Nyquist plots of a) CNF, KOH/CNF and a-CNF anodes in Li-ion half-cell before cycling (the equivalent circuit in inset), and b) - d) after three charge/discharge cycles.

Rate performances of the batteries are shown in Figure 3.7. Batteries were tested at current densities of 50, 100, 300 and 1000 mA/g, 10 cycles for each and then again at a current density of 50 mA/g. Initial discharge capacities of 586, 930 and 1471

mAh/g were recorded for the neat CNF, KOH/CNF and a-CNF anodes, respectively, while their initial Coulombic efficiencies (CE) were 44.6%, 45.7% and 41.7%. The low initial CE and the capacity fade during the first few cycles are consequence of the formation of solid electrolyte interface and high amount of oxygen left within the structure after carbonization, which consume Li-ion irreversibly. As discussed above, carbonization at higher temperatures or extended carbonization time may solve this issue. When tested at current density of 100 mA/g the discharge capacity dropped for all the samples and was the highest for the a-CNF (260 mAh/g).

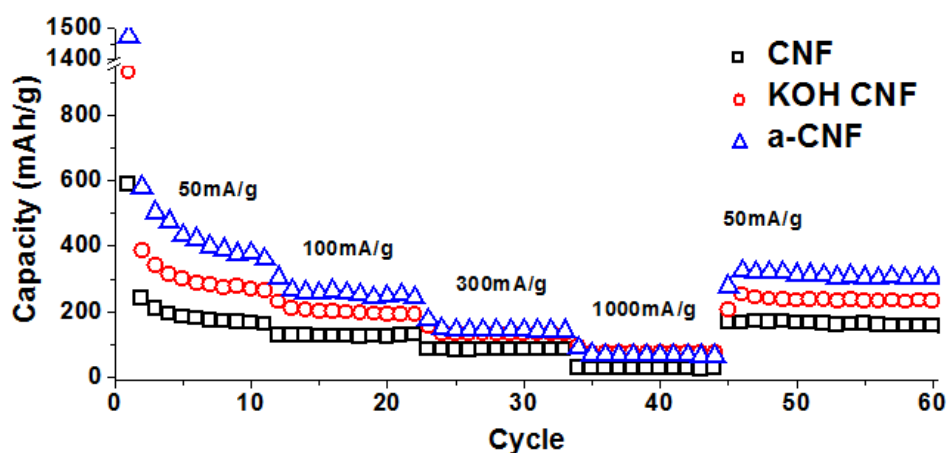


**Figure 3.7 :** Rate performances of neat CNF, KOH/CNF and a-CNF anodes in Li-ion half-cell.

When tested at current densities of 300 and 1000 mA/g the capacity for both samples treated with KOH was almost the same (145 and 135 mAh/g at 300 mA/g and 65 and 75 mAh/g at 1000 mA/g for a-CNF and KOH/CNF respectively), and doubled the neat CNF battery (82 and 23 mAh/g at 300 and 1000 mA/g respectively). Previous reports on free-standing neat lignin based carbon fibers show similar capacities at these current densities, but higher capacities for lower charge densities [147],[146]. However, it should be noted that the fibers reported here, were carbonized at a lower temperature which leads to highly disordered structure and high content of oxygen, hence reversible capacities lower than 370mAh/g were observed at lower charge densities.

Prolonged cycling of up to 1000 cycles were performed in order to investigate the cycling stability of the anodes. Cycle life of the batteries shown in Figure 3.8 shows capacity fading during the first 10 cycles after which it stabilizes. KOH/CNF and a-CNF batteries exhibited capacities of 215 and 272 mAh/g after 100 cycles at 50

mA/g, respectively. Further cycling at 300mA/g after another 900 cycles showed capacity of about 110 mAh/g and stable cycling with capacity fade of 16% for KOH/CNF battery. On the other hand, a-CNF battery showed capacity of 68 mAh/g, or more than 50% capacity fade and low CE constancy. This might be attributed to the decreased specific surface area of the anode after cycling.

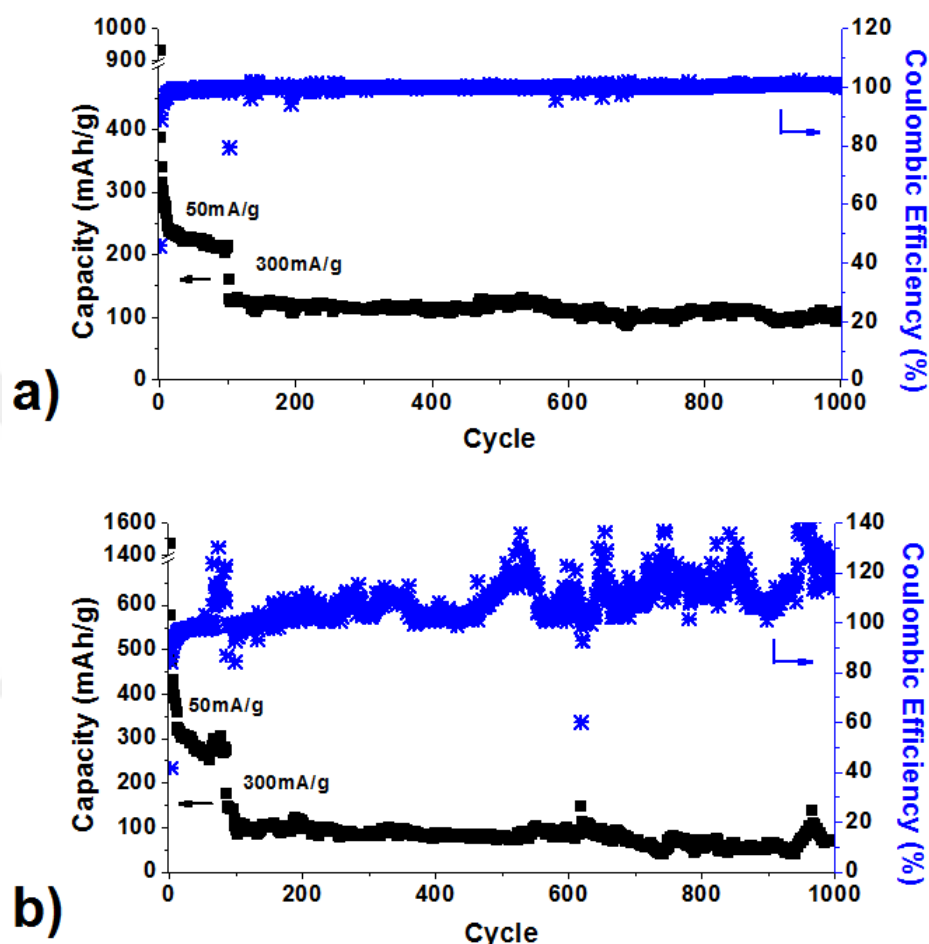


**Figure 3.8 :** Cycling performances of a) KOH/CNF and b) a-CNF anodes at 50 and 300 mA/g in Li-ion half-cell.

Post cycling SEM images (Figure 3.9) of the anodes revealed smooth surface of the a-CNF anode, indicating surface film growth, which covers the pores previously available. This further prevents reversible intercalation and de-intercalation of Li-ion, which results in irregular CE and capacity fade, as exhibited during the galvanostatic charge-discharge tests. On the other hand, KOH/CNF anode maintains its structural integrity after 1000 charge-discharge cycles. These results indicate that despite the low SSA, its mesoporosity enables KOH/CNF to exhibit high cycling stability.

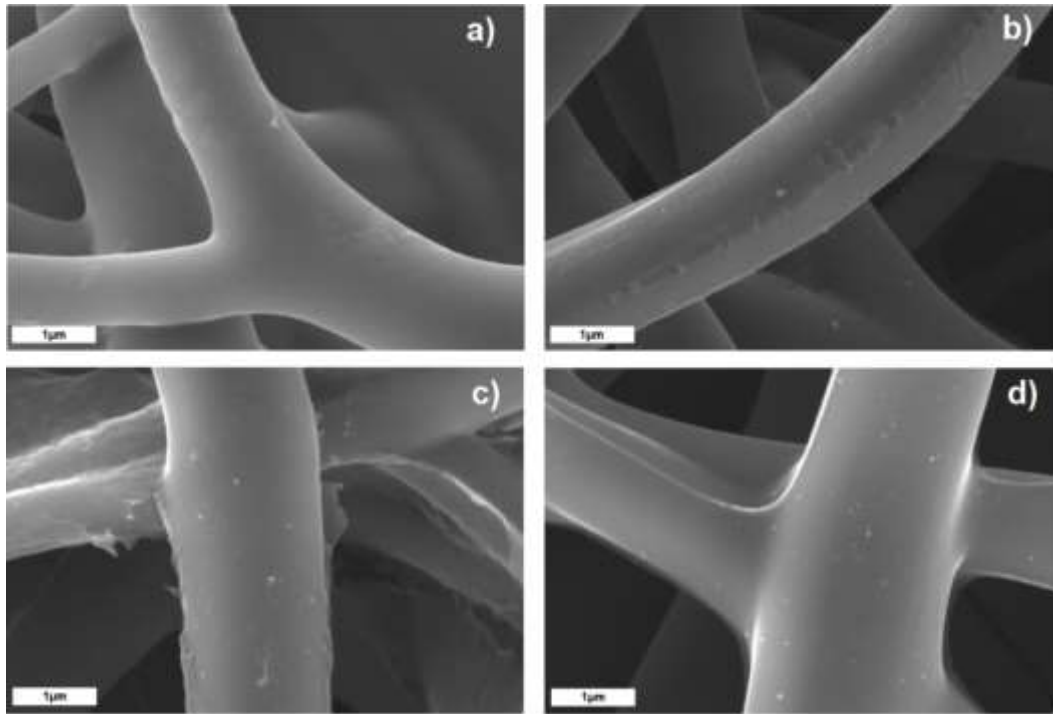


**Figure 3.9 :** SEM images of a) - b) KOH/CNF and c) – d) a-CNF anodes before (a, c) and after (b, d) cycling in Li-ion half-cell (scale bar 1 $\mu$ m).

### 3.3.2.2 Sodium ion battery performances

Charge-discharge curves obtained from galvanostatic tests conducted on SIB half cells are shown in Figure 3.10. The CNF and KOH/CNF anodes exhibited a clear discharge inflection point during the first cycle, which is an indicator of solid electrolyte interface and irreversible Na-ion insertion into the CNFs. This point was observed at 1.15 V for the neat CNF, while it was moved to lower potentials at about 0.75 V for KOH/CNF. The following cycles follow the same mechanism indicating stability of the SEI layer. On the other hand, a-CNF exhibited two inflection points during the first cycle, one at 1.75 V and the second one at 0.5 V indicating insertion of Na-ions into the anode via two mechanisms as a result of the highly porous structure, which allows high discharge capacity of 1039 mAh/g during the first cycle. However, this capacity is not retained for the following cycles, indicating highly irreversible Na-ion absorption due to formation of thick SEI layer.

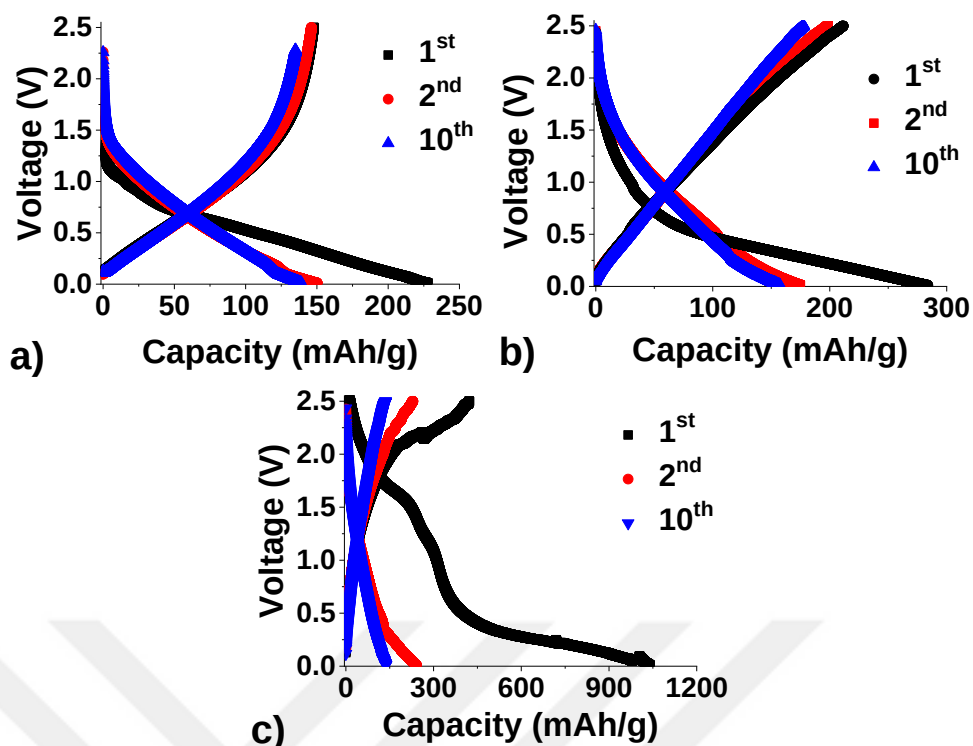


**Figure 3.10** : Charge/Discharge curves of 1<sup>st</sup>, 2<sup>nd</sup> and 10<sup>th</sup> cycle at current density of 10 mA/g for a) CNF, b) KOH/CNF, c) a-CNF anodes in Na-ion half-cell.

Figure 3.11 shows the rate performances of the electrodes tested in SIB half cells. Batteries were tested at current densities of 10, 50, 300, 500 and 1000 mA/g, 10 cycles for each and then again at a current density of 50 mA/g. Initial discharge capacities of 283, 227 and 1039 mAh/g were recorded for the neat CNF, KOH/CNF and a-CNF anodes, respectively, while their initial Coulombic efficiencies were 74%, 65% and 40%. When tested at current density of 50 mA/g the discharge capacity dropped for all the samples and was highest for the KOH/CNF anode (137 mAh/g). When tested at current densities of 300 and 500 mA/g, the capacities of CNF and a-CNF anodes were almost the same (50 and 40 mAh/g at 300 mA/g and 15 and 22 mAh/g at 500 mA/g for CNF and a-CNF, respectively). These values are much lower than those of KOH/CNF anodes (87 and 60 mAh/g at 300 and 500 mA/g respectively).

Cycling performances of the anodes were tested by cycling them up to 150 cycles at current density of 50 mA/g (Figure 3.12). CNF, KOH/CNF and a-CNF anodes exhibited initial capacities of 133, 105 and 77 mAh/g at current density of 50 mA/g. Further cycling at the same current density resulted in stable capacity only for KOH/CNF anode, which after 350 cycles showed capacity of 122 mAh/g.

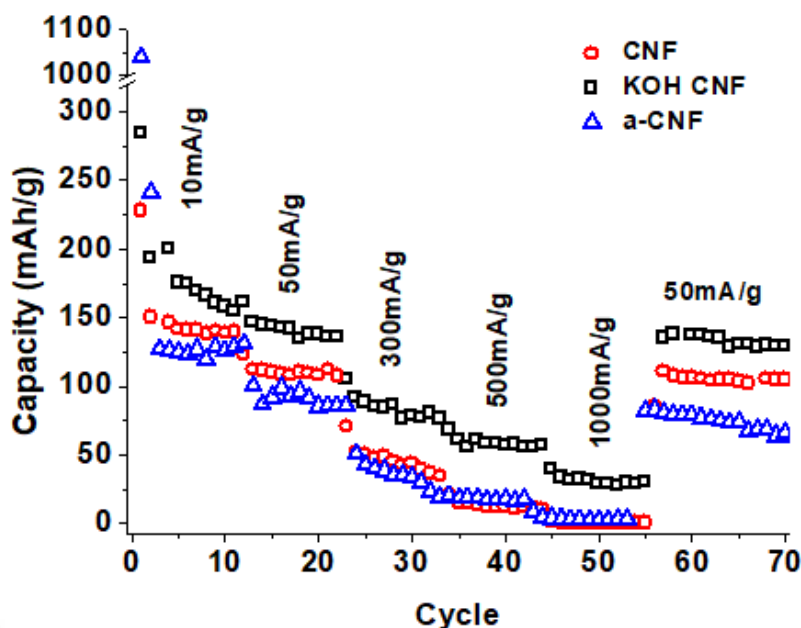


**Figure 3.11** : Rate performances of neat CNF, KOH/CNF and a-CNF anodes in Na-ion half-cell.

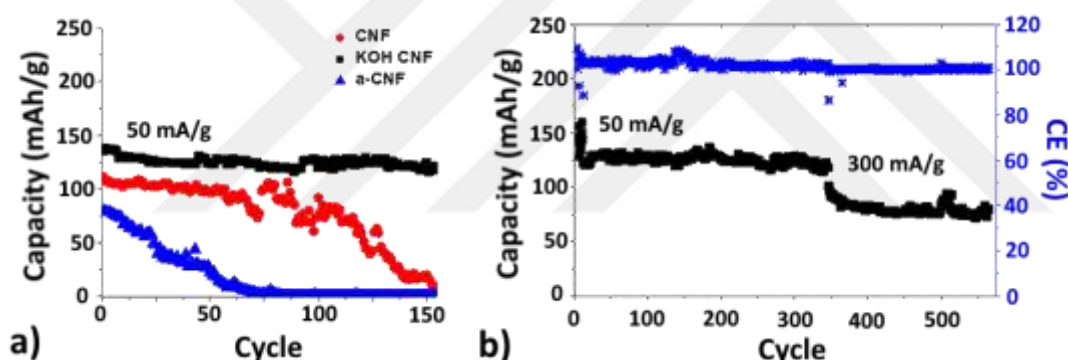


**Figure 3.12** : Cycling performances of a) CNF, KOH CNF and a-CNF anodes at 50 mA/g and b) KOH/CNF anode at 50 and 300 mA/g in Na-ion half-cell.

As can be observed on Figure 3.13, SEM images of the three anodes taken after cycling show fibers with three different surfaces. CNF anode exhibits rough surface covered with grains formed over a multiple SEI layers that prevent Na-ion insertion and results in total capacity fade. On the other hand, on the KOH/CNF anode can be observed small, separated grains that does not fully cover the fiber surface which allow reversible Na-ion de/intercalation into the anode structure. While the a-CNF exhibits smooth surface with multiple SEI layers (red arrows on Figure 3.13c) that significantly reduces the SSA of the anode and does not allow insertion and deinsertion of Na-ions and results in total capacity fade after only 50 cycles. The formation of thick SEI layer and grain-like structure, as a result of the decomposition of the electrolyte during cycling.

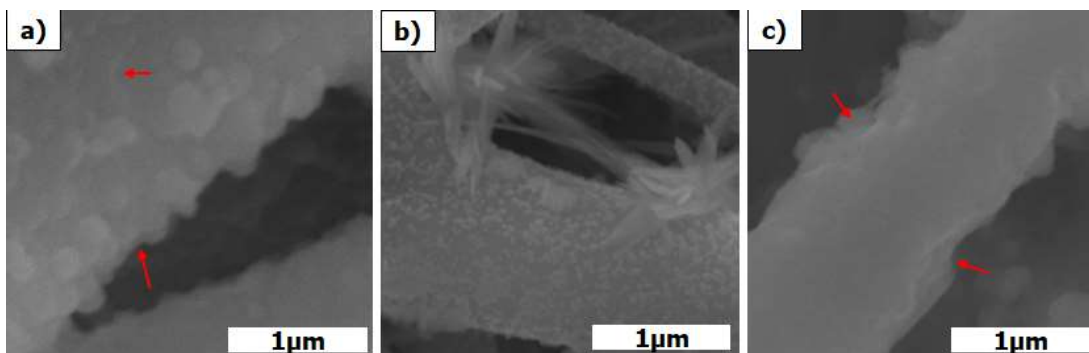


**Figure 3.13** : SEM images of a) CNF, b) KOH/CNF, c) a-CNF anodes after cycling in Na-ion half-cell.

In conclusion, this study shows a feasible route to produce carbon fibers from natural resources with controllable porous structure and anode stability. Despite of these characteristics, the drawbacks of these electrodes, such as low gravimetric capacity at low charge densities and low areal and volumetric capacities can be further improved [146–148,159]. Possible ways to improve the electrochemical performances would be by increasing carbonization temperature in order to increase the initial CE, or by optimization of the electrode thickness which affects battery's volumetric and areal capacities [160] and will be part of further research.

### 3.4 Conclusion

Lignin/PVA polymer solutions with and without KOH were electrospun into nanofibers, stabilized under iodine vapor and carbonized. As a third sample, the carbon submicron fibers obtained from the neat solutions were activated with KOH. As-obtained-CNFs exhibited different porosity and specific surface area values, being the a-CNF with microscopic structure and largest surface area of 1049 m<sup>2</sup>/g. Interestingly KOH/CNF mats had a mesoporous structure and surface area of 93 m<sup>2</sup>/g. Galvanostatic tests performed on Li- and Na-ion half-cells showed increased and stable capacity over prolonged cycling for the in-situ activated CNF mats, used as free standing anodes. Even though KOH/CNF anode obtained in a feasible one carbonization/activation step, exhibited lower capacity than a-CNF, it showed better rate capability, higher stability and low capacity fade for both LIB and SIB technology. The findings acquired from this research revealed that lignin as a renewable bio-source could be used to develop novel and high performance green energy storage devices.



## **4. BIO-WASTE CARBON PARTICLES: PREPARATION METHOD AND ENERGY STORAGE APPLICATION<sup>2</sup>**

### **4.1 Introduction**

The need for energy storage devices that can store the surplus energy generated by renewable sources (solar, wind and biomass) and used on demand follows the trend to reduce the dependence on fossil fuels and the greenhouse gas emission [161]. Even though the application of batteries and supercapacitors as energy storage systems is not new, the need for large scale energy storage over prolonged period of time requires new systems. The development of new designs, production methodologies and materials would accelerate the realization of that goal.

Carbon structures with high surface area store energy via non-faradaic mechanism which enables fast storage and release of energy, leading to high power densities [162]. Their application in energy storage technologies is not new, however there is still room for new developments, especially in the area of finding suitable production methodologies to convert biomass into carbon [163], [164]. The abundance of bio-waste attracts attention in society, while its organic origin attracts the attention of scientists, because it can be converted into energy via either thermochemical, biochemical or chemical processes [165]. Besides the low cost, the presence of cellulose, hemicelluloses, lignin, pectin, etc. in different agricultural crops and residues, aquatic crops, forest residues and animal wastes makes them excellent carbon precursors [163], [166], [167]. Controlled thermochemical processes can easily convert any of the biomass into carbon with specific morphology [166]. The general method used for this conversion consists of pretreatment, carbonization and activation. Before the carbonization, the biomass is usually chemically treated in order to remove undesired components or to add new elements, and to facilitate the

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<sup>2</sup> This chapter is based on the oral presentation entitled “Bio-waste active carbon for energy storage” presented on the 14th Nanoscience & Nanotechnology Conference, NanoTR-14, 22-25 September 2018, Cesme, Izmir, Turkey.

cyclization of adjacent hydrocarbon chains and thus to improve the quality and the yield of the final carbonaceous product [168], [169], [170]. Moreover, this step can also be used to shape and control the structure of the final product, and it can also be used as an activation step [170]. When the pretreatment does not satisfy the requirements for high surface area of the carbon obtained, it is activated either chemically [171] or physically [172], [173], [174] after the carbonization of the biomass.

Among the different agricultural bio-wastes, rice husk [169], date palm petioles [173], corn stalks [175], orange peel [170], coffee residues [176], and many others [163], [166], [168], [169], [170] have been investigated as carbon precursors. Peanut shells are also in the list due to their high cellulose and lignin content [177], [178] plus their fibrous-like structure [179]. Peanuts are edible seeds of a legume crop that have been used since 3500 years ago [180]. They were firstly discovered as food by Peruvian and Brazilian, but today they are eaten all over the world in a wide variety of combinations. In 2016, almost 44 million tones peanuts were produced, mainly in China (37.8 %), India (15.6), then Nigeria (6.9 %), USA (5.9 %), etc., while their average price is 2.4 US\$/kg [181]. From them, 20-30 % are peanut shells which end up as bio-waste [178] and can be easily be converted into carbonaceous material that can be used for both supercapacitor and battery electrodes [171], [182].

This chapter reports production of bio-waste active carbon particles and investigate its electrochemical properties. For that purpose, peanut shells, used as carbon source, were firstly chemically activated and then carbonized in order to produce active carbon particles. Such particles were further used to make an electrode. The electrochemical performances of the electrodes were tested in a 3-electrode system, by cyclic voltammetry in order to determine their operating voltage range and capacitance. Additionally 2-electrode supercapacitor cells were also produced and their energy storage properties were also tested.

## **4.2 Experimental**

### **4.2.1 Materials and methods**

Carbon particles were prepared using peanut-shells as carbon precursor. Grinded peanut-shells was mixed with activating agent zinc chloride ( $\text{ZnCl}_2$ , >98%, Merck)

and distilled water. The mixture was kept at room temperature for 4h and then was dried at 100 °C for 24h. Dred mixtures were carbonized at 900 °C for 1h (heating rate 5 °C/min) in inert atmosphere. The as carbonized powders were firstly washed with 1M HCl solution in order to remove residual Zn ions and then distilled water until their neutralization. The neutralized carbon powders were further dried at 110 °C and then used as active material and is denoted as Cp in the text below. In order to decrease the particle size and to achieve a more uniform particle size, the particles obtained were ball milled for 24 hours at 400 rpm.

#### 4.2.2 Characterization

The morphology of the particles was characterized by Scanning Electron Microscope (SEM, Vega3 Tescan). Average particle size was measured from five SEM images by making a total of 100 areal and 200 dimensional (width-length) measurements using ImageJ image processing program.

Structural changes of the particles were analyzed through Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Spectrometer), Raman spectroscopy (Thermo Scientific DXR instrument under 532 nm laser excitation) and X-ray diffraction analysis (XRD, Bruker D2 PHASER). Raman and XRD curves were deconvoluted until converged fit, using Origin software. Raman curve was fitted to five Voigt and the integrated area ( $A$ ) under the fitted curves was used to calculate the degree of disorder ( $R$ ) and the in-plane crystal size ( $L_a$ ) with the formulas:  $R = \frac{A_{D1}}{A_G}$  and  $L_a = \frac{4.4 \cdot A_G}{A_{D1}}$  [183], [184].

XRD curve was fitted to three Gaussian curves, which were used to calculate the interlayer spacing ( $d$ ) and crystallite size ( $L$ ) according to Bragg's  $d = \frac{\lambda}{2 \cdot \sin \theta}$  and Scherrer's  $L = \frac{k \cdot \lambda}{\beta \cdot \sin \theta}$  equations [185]; where,  $\lambda$  (1.54184 Å) is x-ray wavelength,  $\theta$  is the scattering angle in radians,  $\beta$  is full width at half maximum,  $k$  is a fitting pre-factor ( $k=0.94$ ) [186].

The porosity of the carbon particles obtained was investigated by BET analysis (Quantachrome Nova) in nitrogen atmosphere, at 77 K using slit pore NLDFT equilibrium model, after degassing the samples at 200°C during 2h.

### 4.2.3 Electrode preparation and characterization

Battery grade polyvinylidene fluoride (PVDF) Kynar LBG (copolymer) was used as binder, N-Methyl-2-pyrrolidone (NMP, ACS Reagent, Merck) as solvent, while the carbonized peanut-shell based particles were used as active material for preparation of a typical slurry-based film electrodes. The slurry was prepared using Cp:PVDF in ratio 9:1 (unless otherwise specified). After rigorous stirring at 60 °C for 2h, the slurry was casted on stainless steel foil (SS 304, 0.05 mm thick) and dried over night at 80 °C. Dried films were cut into squares with dimensions 1x1 cm and then used as electrodes.

All the samples were characterized in a 3-electrodes electrochemical systems by using them as working electrodes in a 3-electrodes system, with Ag-wire and Pt-plate as pseudoreference and counter electrodes, respectively. Symmetric supercapacitor cell with two identical Cp-based electrodes was also assembled in order to investigate the behavior of the electrode in a real cell. Aqueous 6M KOH solution was used as electrolyte for the electrochemical tests. The performances of the electrode and cell were determined by cyclic voltammetry on Gamry potentiostat/galvanostat/ZRA device. Discharge capacitance ( $C_D$ , F/g) was calculated from the cyclic voltammograms, using the following formula:  $C_D = \frac{\frac{1}{2} \int i(E) dE}{v \cdot \Delta V \cdot m}$  where,  $\int i(E) dE$  voltammetric charge obtained by integrating the area of the positive and negative sweep,  $v$  is the scan rate in V/sec,  $\Delta V$  is the working voltage window in V,  $m$  is the total mass of the electrode in g,  $t_D$  is the discharge time in hours. Specific energy and power were calculated with the formulas:  $E = \frac{C_D \cdot \Delta V^2}{2 \cdot m}$  and  $P = \frac{E_D}{t_D}$ .

## 4.3 Results and Discussion

### 4.3.1 Morphology and structure

Microscopic analysis was conducted in order to determine the morphology of the particles. SEM images of the carbonized bio-waste before (Figure 4.1-a) and after (Figure 4.1-b) ball milling are given in Figure 4.1. The images show that particles with irregular shape and large size were obtained after carbonization. From the images taken at low magnifications, we can conclude that there are bigger and smaller particles, indicating high particle size distribution in the batch. However,

after ball milling the size of the particles became significantly lower in size and more uniform in shape. Particle size measurements from SEM images was estimated to drop from 20.98 ( $\pm 11.3$ )  $\mu\text{m}$  before to 0.587 ( $\pm 0.328$ )  $\mu\text{m}$  after ball milling.

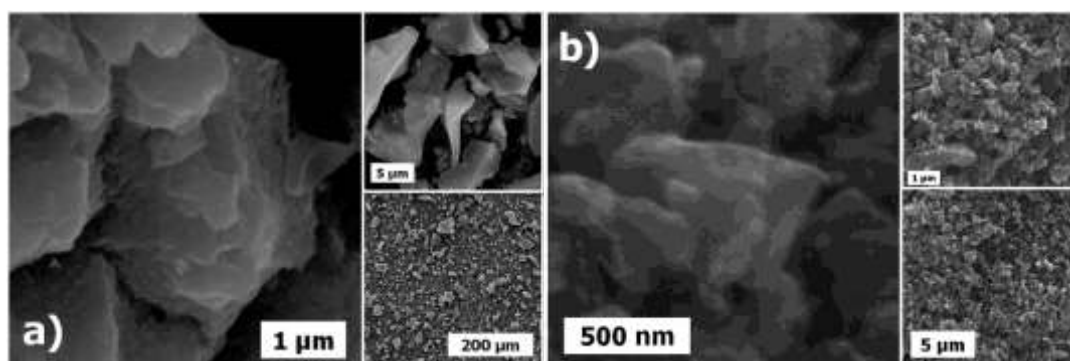


**Figure 4.1** : Carbonized peanut-shell particles a) before and b) after ball milling.

FTIR analysis was conducted to investigate the structural differences of the carbon precursors before and after carbonization (Figure 4.2-a). The analysis showed presence of C=O of aliphatic esters ( $1742\text{ cm}^{-1}$ ) and even more pronounced keto C=O ( $1615\text{ cm}^{-1}$ ) for peanut shells [187]. Moreover, peanut shell also contain of O-H groups ( $\sim 3330\text{ cm}^{-1}$ ), asymmetric and symmetric alkyl C-H vibrations ( $2850\text{--}3010$  and  $1300\text{--}1400\text{ cm}^{-1}$ ) [187], [188], and C-O, C-O-C, C-N and P-O vibrations from polysaccharides ( $900\text{--}1300\text{ cm}^{-1}$ ) [187], [188], [189]. The particles obtained after carbonization exhibit aromatic C=C ( $1545\text{--}1550\text{ cm}^{-1}$ ), C-O vibrations ( $1135\text{--}1210\text{ cm}^{-1}$ ), and they also maintain the aliphatic C=O ( $1740\text{ cm}^{-1}$ ) vibrations. The presence of C-O and C-H vibrations in the carbonized samples indicate disordered carbonaceous structure.

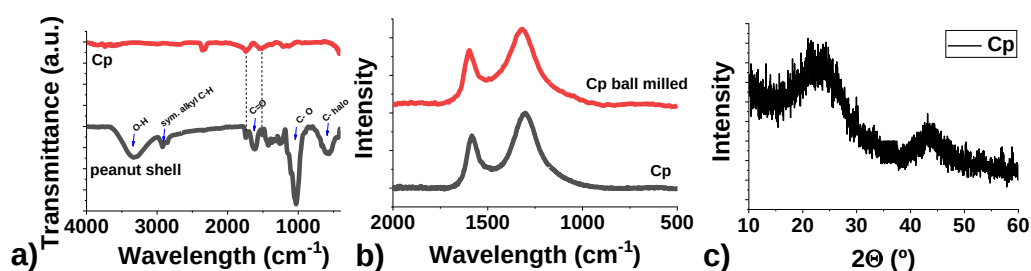


**Figure 4.2** : a) FTIR of neat and carbonized peanut shell; b) Raman and c) XRD spectra of carbonized peanut-shell.

Raman curve (Figure 4.2-b, black line) of the carbonized particles show the characteristic G and D peaks at  $1544$  and  $1302\text{ cm}^{-1}$ , respectively. Deconvolution of the curve emphasized five regions with peaks indicating ideal graphitic structure with  $E_{2g}$  symmetry (peak G, at  $1544\text{ cm}^{-1}$ ), disordered graphitic structure with  $A_{1g}$

symmetry ( $D_1$ ,  $1302\text{ cm}^{-1}$ ), graphite crystals with individual graphene layers at their surface ( $D_2$ ,  $1585\text{ cm}^{-1}$ ), amorphous carbon fractions containing organic functional groups ( $D_3$ ,  $1378\text{ cm}^{-1}$ ) and polyene-like structures ( $D_4$ ,  $1215\text{ cm}^{-1}$ ) [183], [184], [190], [191]. The degree of disorder of the particles ( $R=3.54$ ) indicates dominance of disorder which contains graphitic domains with length of  $1.243\text{ nm}$ .

XRD spectra (Figure 4.2-c) showed the typical carbon  $2\theta$  peak at  $23.46^\circ$  and a peak at  $2\theta\ 43.64^\circ$  characteristic for turbostratic graphitic structure [171]. Deconvoluted curve revealed that the particles contain graphitic domains with an average of 3 graphene layers on distance of  $3.792\text{ \AA}$ . The inter-layer distance much larger than graphite ( $3.335\text{ \AA}$  [192]) and coal based carbon particles ( $\sim 3.5\text{ \AA}$  [193]), but smaller than peanut shell carbon particles reported in literature ( $3.78\div 4.13\text{ \AA}$  [171]). Both, Raman and XRD, analysis emphasize small graphite domains and 63.5 % of amorphous carbon, which indicates disordered carbonaceous structure. This disorder, together with the large inter-layer distance in the graphitic domains can contribute to the electrochemical properties.

The porosity of the bio-waste carbon was investigated by Brunauer-Emmette-Teller (BET) analysis. Nitrogen adsorption/desorption isotherms (Figure 4.3-a, black line) show hysteresis loops of type H4, indicating micro-mesoporous structure of the particles [194]. The chemical activation with  $\text{ZnCl}_2$  resulted in formation of micro and mesopores due to its ability to decompose into zinc and chlorine at high temperatures, and later (after washing with  $\text{HCl}$ ) leaves pores into the carbonaceous structure [195], [196]. Despite,  $\text{ZnCl}_2$  also acts as a dehydrating agent of the precursor eliminating the amount of  $\text{OH}$  and  $\text{H}_2$  groups from their structure and thus increasing the yield of the carbonized product [196]. Specific surface area (SSA) of  $1167\text{ m}^2/\text{g}$  was obtained from Multipoint BET analysis for the as-obtained peanut-based carbons. In previous studies, higher surface areas were reported, however the differences in the peanut types as well as the preparation methods should be taken into account for such comparisons [197], [176]. On the other side, Density Functional Theory (DFT) is suitable method for determination of pore size distribution [198]. As can be seen on Figure 4.3-b most of the pores are micro size, which corresponds to 72,5 % of the total pore volume (Table 4.1).

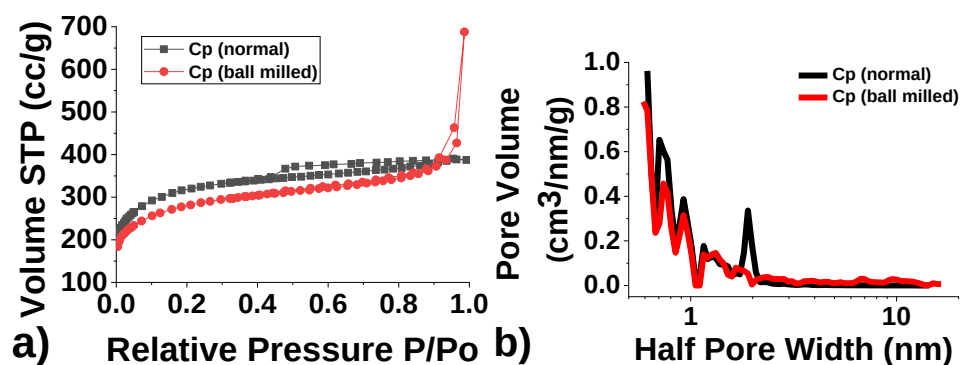


**Figure 4.3 :** a) BET isotherm and b) DFT pore size distribution of peanut-based carbon particles before and after ball milling.

In order to investigate the effect of ball milling on the carbonaceous structure, ball milled particles were also analyzed by Raman and BET ((Figure 4.2-b and Figure 4.3-a and -b, red line). It was noticed that the degree of disorder increases slightly after ball milling, however that degree of amorphous fractions containing functional groups increases significantly, which can be result of oxidation reactions during the ball milling process in aqueous media for such a long period of 24 hours. Moreover, the total surface area of the particles also decreased as a result of the increased mesoporous structure (from 27.5 % before to 48.1 % after ball milling, Table 4.1). The increased amount of mesopores can facilitate the ion diffusion and thus improve the electrochemical performances of the electrode [17].

**Table 4.1 :** Structural characteristics of carbonized particles obtained from Raman, XRD and BET analysis. [SSA: Specific Surface Area; SA: Surface Area; V: Volume]

|                                                 | Cp normal | Cp ball milled |
|-------------------------------------------------|-----------|----------------|
| <b>R</b>                                        | 3.541     | 3.902          |
| <b>R<sub>3</sub></b>                            | 1.148     | 3.256          |
| <b>X<sub>G</sub></b>                            | 0.22      | 0.204          |
| <b>L<sub>a</sub> [nm]</b>                       | 1.243     | 1.128          |
| <b>LC(002) [nm]</b>                             | /         | 1.003          |
| <b>D(002) [nm]</b>                              | /         | 0.3792         |
| <b>X<sub>A</sub> [%]</b>                        | /         | 63.5           |
| <b>BET SSA [m<sup>2</sup>/g]</b>                | 1167      | 1025           |
| <b>DFT Total Pore Volume [cm<sup>3</sup>/g]</b> | 0.5431    | 0.6560         |
| <b>meso V [%]</b>                               | 27.5      | 48.1           |
| <b>micro V [%]</b>                              | 72.5      | 51.9           |

### 4.3.2 Electrochemical Performances

The electrochemical performances of the Cp-electrodes were firstly tested in a 3-electrodes cell configuration. The purpose of such test was to determine the widest operating voltage window of the electrodes in aqueous electrolytes, as well as to determine their capacitance and rate capability. The operating voltage window was determined by cycling them at different voltage ranges at scan rate of 10 mV/s. Once the optimal potential window was determined, cycling voltammograms were also performed at different scanning rates in order to determine the rate capability and capacitance values of the electrodes. The tests were realized at scan rates from 2 to 100 mV/s.

Figure 4.4-a and -b show the cyclic voltammograms used to open the potential on the positive and negative voltages, respectively. The potential limits were determined from the curves, as potential at which the current starts to increase (or decrease) exponentially. When opening the positive voltage window from 0.1 up to 0.6 V vs Ag, sudden current leap was noticed at cut-off voltage of 0.5 V, meaning oxygen starts to evolve from this voltage onwards. Therefore, the positive limit was set at 0.4 V. On the negative side, there was gradual widening of the curve at each potential cut-off up to -1.1 V vs Ag indicating hydrogen absorption into the pores of the Cp particles [199]. With further increment of the negative cut-off voltage up to 1.5 V vs Ag, the electrode is still able to absorb hydrogen. Such hydrogen absorption increases exponentially and will cause irreversible charge transfer on long cycling periods [199]. Therefore, -1.1 V vs Ag was taken as negative voltage limit. This gives an operating voltage window ( $\Delta V$ ) of 1.5 V. However, taking into account the practical utilization of the electrode in terms of reversible charge transfer and high coulombic efficiency [199], the overall potential limits were narrowed in the range between 0.3 to -1 V vs Ag, which corresponds to  $\Delta V$  of 1.3 V vs Ag.

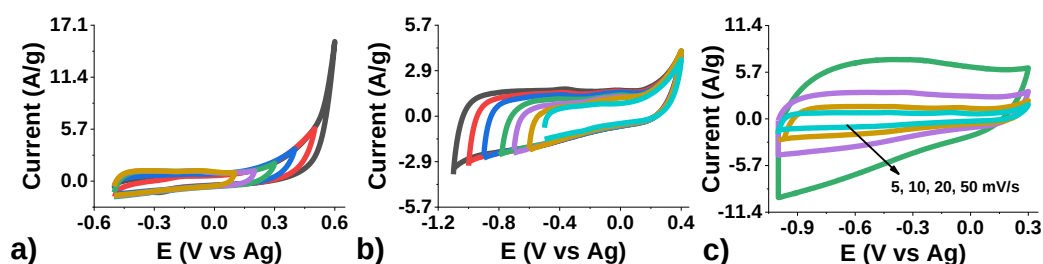


**Figure 4.4 :** Cyclic voltammograms of peanut-based carbon particles.

Once the optimal voltage window was determined, the electrodes were tested at different scan rates from 2 to 1000 mV/s. The calculated capacitance values Figure 4.5-a) were 67.6 F/g at scan rate of 2 mV/s and drops to 27.6 F/g at a rate of 1000 mV/s. Moreover, the electrodes show almost rectangular CV curves without redox-peaks which indicates a pseudocapacitive behavior. On the other side, electrode made with ball milled Cp particles showed increased capacitance (33.1 F/g at 1000 mV/s to 94.8 F/g at 2 mV/s). This may be attributed to the increased mesoporous fraction of the ball milled particles, which does not trap the ions, but let them move easy within the electrode [17]. Furthermore, small particles improve particle-to-particle contact which easy the electron transfer during cycling, and also contribute to an improved adhesion of the electrode film to the stainless steel foil that serves as a current collector.

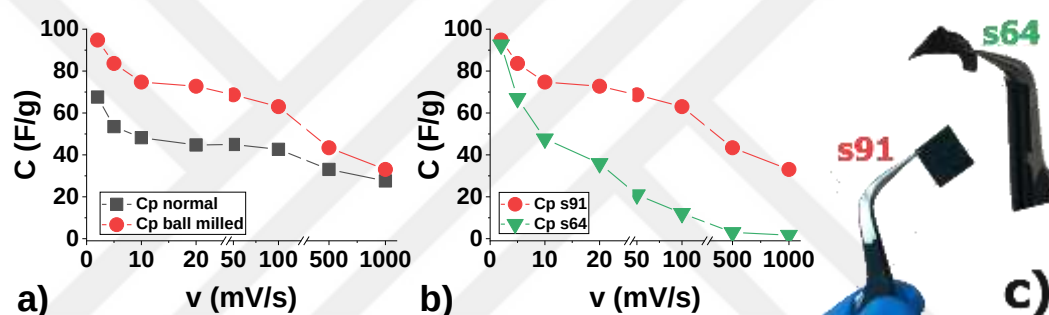


**Figure 4.5 :** Capacitance of a) electrodes with normal and ball milled Cp particles and b) electrodes with different binder content; c) Real image of electrodes with different carbon-to-binder ratio.

As mentioned earlier, the aim of this study – development of bio-waste carbon particles – is their implementation in fibrous electrodes. It is known that the rheology of a spinning solution is of outmost importance for fiber formation [200]. Therefore, this study was extended by investigating the electrochemical properties of film electrode containing ball milled Cp particles and larger amount of binder. The film electrode tested was made from a solution with Cp:binder ratio of 6:4 (denoted s64 in Figure 4.5-b). It is worth mentioning that the electrode was flexible and self-standing without current collector. The capacitance calculated from the CV curves (Figure 4.5-b) were comparable to those of regular s91 film electrodes. However, its capacity starts to decrease significantly after 20 mV/s, most probably as a result of the increased amount of binder which increases the bulk electrical conductivity of the electrode. Nevertheless, it is expected that fibrous electrode will show improved rate

capability due to its high surface-to-volume area and voids that would allow complete ion access through the whole electrode thickness.

In order to investigate the electrochemical behavior of the Cp-electrode in a real cell, symmetric cell was also assembled. Cyclic voltammograms (Figure 4.6-a) of the cell at different scan rates (from 5 to 100 mV/s) confirmed its capacitive behavior. The capacitance values (Figure 4.6-b) calculated from the CV curves were in the range from 6.6 F/g (at 100 mV/s) to 68.6 F/g (at 5 mV/s). This corresponds to gravimetric energy up to 16 Wh/kg and maximum power of 3.5 kW/kg, which is comparable to supercapacitors with bio-waste based carbon electrodes reported in literature (Table 4.2).

**Table 4.2 :** Characteristics and performances of symmetric supercapacitors with bio-waste-based carbon electrodes.

| Electrode<br>(C-precursor)           | Electrolyte                                | $\Delta V$ | F/g<br>(C-rate)  | E<br>(Wh/kg) | P<br>(kW/kg) | Ref       |
|--------------------------------------|--------------------------------------------|------------|------------------|--------------|--------------|-----------|
| AC (tobacco leaves)                  | 1M Li <sub>2</sub> SO <sub>4</sub>         | 0.8        | 165<br>(0.2 A/g) | /            | /            | [201]     |
| AC (tobacco waste)                   | 6M KOH                                     | 0.8        | 110<br>(1 A/g)   | /            | /            | [202]     |
| AC (rice husk)                       | 6M KOH                                     | 1          | 95<br>(5 mV/s)   | /            | /            | [203]     |
| AC (waste H <sub>2</sub> O purifier) | 1M H <sub>2</sub> SO <sub>4</sub>          | 1          | 125<br>(1 A/g)   | 10÷15        | 20÷0.1       | [204]     |
| AC (kapok shell)                     | 6M KOH                                     | 1          | 169<br>(1 A/g)   | 12.5         | 1.9          | [205]     |
| AC (palm leaves)                     | 1M H <sub>2</sub> SO <sub>4</sub>          | 1.2        | 45<br>(2 A/g)    | 3÷9          | 4÷37         | [206]     |
| AC (lignocellulose)                  | PVA/KOH gel                                | 1          | 45<br>(50 mV/s)  | 5            | 0.5÷4        | [207]     |
| AC (coconut shell)                   | 1M<br>Et <sub>4</sub> NBF <sub>4</sub> /AN | 2.5        | 162<br>(1 A/g)   | 20÷35        | 3.9÷0.4      | [208]     |
| AC (peanut shell)                    | 6M KOH                                     | 1.3        | 68.6<br>(5 mV/s) | 1÷16         | 0.5÷3.5      | This work |

Ragone plot (Figure 4.6-c) shows that the specific power of the Cp symmetric cell exceeds that of commercial Li-ion batteries, while its energy is in the range of commercial supercapacitors. It should be mentioned that the specific energy and power were calculated from the CV curves and corrected with a factor of 1/3 [31], in order to make them comparable to those of commercial energy storage devices (ESD).

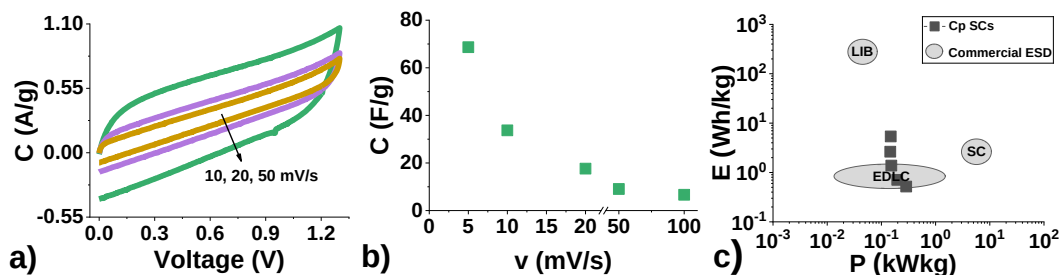


**Figure 4.6 :** a) Cyclic voltammograms, b) capacitance and c) Ragone plot of Cp-based supercapacitors in aqueous electrolyte.

#### 4.4 Conclusion

Biomass is an abundant, renewable and sustainable source of heat and electricity. Besides, it can also be used to produce sustainable materials that can later be used for different applications. There is a huge number of agricultural biomass that can be easily converted into active carbon suitable for energy storage. With their fibrous structure and cellulose content, peanut shells pretreated with  $\text{ZnCl}_2$  can give microporous carbon particles with surface area of  $1162 \text{ m}^2/\text{g}$ . This study, also investigated the effect of ball milling on the size and structure of the peanut-shell carbon particles. BET analysis showed that ball milling of such activated carbon can reduce particle size and also promote mesoporous structure, without reducing the overall specific surface area. Ball milling in aqueous media also slightly increased the degree of disordered carbonaceous structure. Electrodes made with peanut-shell carbon particles as main active material, showed stable capacitive behavior in the voltage range from -1 to 0.3 V vs Ag and capacitance up to  $67.6 \text{ F/g}$  (at  $2 \text{ mV/s}$ ). The capacitance of the electrodes increased up to  $94.8 \text{ F/g}$  when ball milled mesoporous particles were used. Symmetric supercapacitor cells with two Cp-based electrodes exhibited gravimetric energy comparable to that of commercial supercapacitors.



## **5. SOLUTION BLOWN POLYMER/BIOWASTE DERIVED CARBON PARTICLES NANOFIBERS: AN OPTIMIZATION STUDY AND ENERGY STORAGE APPLICATIONS<sup>3</sup>**

### **5.1 Introduction**

Energy storage systems allow energy to be stored and used when needed. The demand for rechargeable energy storage devices increases constantly in different areas. Nowadays, batteries and supercapacitors are energy storage devices widely used in areas such as consumer electronics, transportation, industry and storage of energy from renewable sources [209]. However, the low power values of batteries on one, and the low energy values of supercapacitors on the other side, forces their combination into one hybrid energy storage systems in order to meet the need for balanced power-energy demand for long-lasting large applications.

As energy storage devices, supercapacitors have faradaic charge-storage mechanism where the charges pass across the double layer of a capacitive or pseudocapacitive electrode [16]. Regarding the active materials used in supercapacitors, a variety of carbon-based materials are widely investigated due to their hierarchical structure, high surface area, high electrical conductivity and thermal stability, high chemical stability in basic and acidic aqueous as well as organic electrolytes and ionic liquids [210], [211], [212]. Among the carbon materials used in supercapacitors, activated carbon is the most widely used for commercial supercapacitors due to its low cost and high surface area [213]. Moreover, activated carbon can be easily obtained from a variety of bio-wastes [214], [176], [208], [215]. The possibility to functionalize and/or combine it with other electrochemically active materials makes it even more attractive [216], [217], [213], [218].

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<sup>3</sup> This chapter is based on the article “Solution Blown Polymer/Biowaste Derived Carbon Particles Nanofibers: An Optimization Study and Energy Storage Applications” published in Journal of Energy Storage, 26, 2019, 100962. DOI: 10.1016/j.est.2019.100962

Fibrous structures, such as nanotubes, nanorods, nanowires and nanofibers can find application in many areas, due to their unique properties. Among them, nanofibers attract attention due to the possibility for large scale industrial production [219]. Despite, nanofiber electrodes enable shorter ion diffusion lengths and improved surface area [79]. Their application in energy storage technologies is not new. However, there is still room for development of new designs, production methodologies and materials in order to achieve their industrial application. In the case of carbon nanofibers (CNF) when used as electrodes, the electrical conductivity of the electrode can be achieved without the addition of current collector. The possibility to add different active materials, or to design a variety of different structures (smooth, porous, hollow, multilayer or core-shell) and their use as free-standing electrodes or as membranes that separate the electrodes are the advantages of these structures.

Though, nanofibers are not new concept for electrodes for energy storage devices, most of the articles published emphasize the use of carbon [220], [221], [222], [223], [224], and/or conductive polymers [225], [226] as main materials. There have been many papers emphasizing the use of neat, porous, doped or coated carbon nanofibers obtained from various polymers such as, polyacrylonitrile, polybenzimidazol, polyvinylpyrrolidone, poly(vinyl alcohol), polyimide, phenolic resins, cellulose, silk cocoon, lignin etc. as carbon precursor [221], [227], [222], [228], [229], [230], [231]. Depending on the flexibility of such fibrous structures, they can be applied as free-standing electrodes or casted on current collector. Graphene and CNT free-standing aerogels [223], [232] or CNT-based yarns decorated with electrochemically active materials [224], [233] are another carbon-based materials used as electrodes for supercapacitors. However, the development of polymeric fibrous electrodes into which electrochemically active materials are embedded is another interesting approach towards high performance electrodes for energy applications [234], [235]. In these structures, the polymer will bind the particles into a fibrous structure that will provide a pathway for electrons and ions during charge/discharge, and will maintain the electrode structural integrity during cycling. The increased porosity of the fibrous structure will allow easier ion diffusion within the electrode structure and thus enhanced electrode/electrolyte interface. The voids between the fibers within the electrode structure allows enough space to accommodate the volume expansion of

the active materials, while the 1D structure of the fibers fixes the position of the active material preventing their aggregation during cycling. The polymer character of the fiber membranes provide flexibility to the electrodes. Their flexibility and free-standing character opens a possibility these electrodes to be also used in flexible energy storage devices. To the best of our knowledge, there are only few published articles, that deal with such fibrous structures as ready-to-use electrodes [235], [236], [237], [238], [239]. All of them were published in the last five years by *Pintauro* and co-workers, and used electrospinning as fiber production method and Li-ion as an application area. According to these studies, the polymer-particle (carbon, Si, TiO<sub>2</sub> and LiCoO<sub>2</sub>) composite fibers produced exhibit high areal capacities and specific energy density not only when applied in half LIB cells, but also as a full LIB cell [239].

Nanofibers can be obtained by different methods, among them electrospinning is the most commonly used among researchers due to its simple set-up and low cost for small lab scale samples [240]. However, this nanofiber production technique is known by its low production rate, safety concerns and the extremely high voltage demand for a large scale production [241], [200]. In this regard, few other non-electro approaches, have been reported as an alternative and industrially feasible methods [200], [242]. Solution blowing is one of the techniques that does not use electric forces for fiber formation. The novelty and versatility of this technique make it promising for various application such as filtration, biomedical, energy storage, etc. In solution blowing technique, compressed air is used for the fiber formation from diverse polymer solutions [200]. The parameters to be controlled in these production technique may be divided as material (polymer concentration, viscosity of the solution, molecular weight of the polymer, surface tension and vapor pressure), process (air pressure, nozzle-collector distance and solution feeding rate), system (nozzle diameter and its geometry) and ambient (temperature, humidity and atmospheric pressure) parameters. By controlling all these parameters, which affect the polymer rheology, fibers with a large range of diameters can be produced. The nozzle (Figure 5.1-a) consist of two concentric flow channels for compressed air flow (outer) and polymer solution flow (inner). When the compressed air meets the polymer solution at the tip of nozzle it forwards the polymer jet to the collector. The drag of the air on the surface of the polymer causes elongation of the polymer jet.

During this step, the solvent evaporates forming a fiber which gets collected on the surface of the collector [243].

In addition, the production rate used in this method (5-30 mL h<sup>-1</sup> per nozzle) is approximately 5 times higher than the production rates reported for electrospinning technique (0,5-2 mL/h per nozzle), which makes it suitable for the large-scale nanofiber production [200]. For comparison, small industrial nozzle-less electrospinning line operates with production rates of up to 40 ml/h in batch mode [10]. On the other hand, pilot version of 8-nozzles solution blowing line (tested in TEMAG Labs) operates at rates up to 100 ml h<sup>-1</sup> which means with solution blowing system, production rate can be increased for at least 2.5 times. This is still higher when compared with multi-nozzle electrospinning systems reported in literature [241], [244], [245].

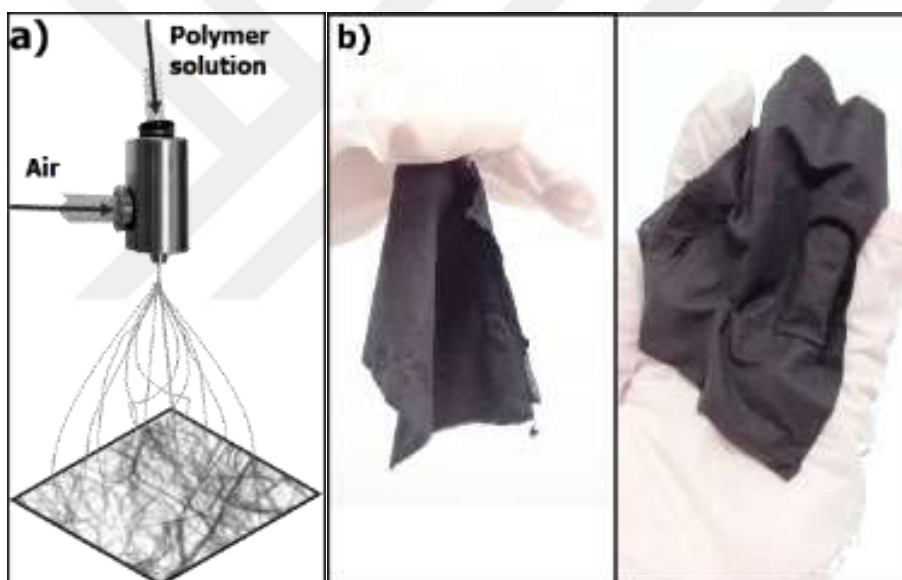


**Figure 5.1 :** a) Schematic representation of solution blowing system and b) real images of solution blown polymer/carbon fibrous mats.

In this study we report production of polymer/carbon fibrous materials and their application as electrodes for energy storage devices. The study explains the design and optimization of the production of such fibrous materials via solution blowing method that allows their immediate usage as electrodes. In the second part of the study, the produced fibrous materials are used as electrodes in a symmetrical supercapacitor cell with aqueous and organic electrolytes.

## 5.2 Experimental

### 5.2.1 Materials

For the production of fibrous electrodes, battery grade polyvinylidene fluoride (PVDF, Kynar LBG) was used as main fiber formation material. N, N-Dimethylformamide (DMF, ACS Reagent, Merck) and acetone (ACS Reagent, Merck) were used as solvents. Carbon nanoparticles (Cs np, 50 nm average particle size, surface area  $110 \text{ m}^2 \text{ g}^{-1}$ , SAT NANO, China) were used as conductive material. Bio-waste carbon was obtained by carbonization of peanut shell-waste following pre-carbonization treatments usually used for preparation of carbon from bio-mass, reported elsewhere [176]. Briefly, grinded peanut shells were mixed with Zinc chloride ( $\text{ZnCl}_2$ , >98%, Merck) in ratio 1:1, distilled water was added and the mixture kept for 4h at room temperature and then dried at  $110^\circ\text{C}$  for 15h. Dried mixture was carbonized at  $900^\circ\text{C}$  for 1h ( $3^\circ\text{C min}^{-1}$  heating rate), then washed with 1M HCl and water. Neutralized and dried carbon particles were ball milled for 24h at 400 rpm (2:1 ball-to-carbon volume ratio) in order to obtain small and uniform submicron-sized particles with surface area of  $1025 \text{ m}^2 \text{ g}^{-1}$  (determined by BET analysis).

### 5.2.2 Methods

#### 5.2.2.1 Optimization study

Spinning solutions were prepared by dissolving PVDF into mixture of DMF and acetone. Commercial carbon (Cs) nanoparticles were firstly dispersed into a portion of DMF:acetone mixture in a sonication bath for 1 hour and then added into the dissolved PVDF solution. The ratios between all materials for each solution are given in Table 5.1. The fibrous electrodes were spun in a lab-scale solution blowing device (by Areka Advanced Ltd.), using the following spinning parameters:  $7 \text{ ml h}^{-1}$  flow rate, 3 bar air pressure, and 45 cm nozzle-to-collector distance. All spun samples were collected over a polyethylene mesh.

#### 5.2.2.2 Characterization

The morphology and structural changes of the samples were characterized by Scanning Electron Microscope (SEM, Vega3 Tescan) and Fourier transform infrared

spectroscopy (FTIR, Bruker, Vertex 70 Spectrometer). Average fiber diameter was measured from five SEM images (magnification 20000) taken at different points of each sample, by making a total of 100 fiber diameter measurements. The number of defects was also determined from SEM images, as explained in the paper by *Krifa et. al* [246]. Five SEM images (magnification 1000X) taken at five different locations from each sample were used for this analysis. Each image was divided into a grid with squares of  $400\text{ }\mu\text{m}^2$  and the number of defects/beads on each square was recorded. The total number of defects per unit area was calculated as an average value. Fiber-to-void ratio was calculated as ratio between the density of the fibrous mat and the density of a thin film made from the same polymer solution, as reported by *E.C. Self et. al* [235]. The real volume of the fibrous mat was calculated by multiplying the actual volume with the percent of the pixels representing white (fiber) areas of five SEM images from each sample converted in binary mode.

### 5.2.3 Electrochemical set-up and characterization

The fibrous materials produced and hot-pressed were cut into circular free standing electrodes with diameter of 10 mm. Electrochemical properties of the fibrous electrodes were tested in a symmetric supercapacitor cells (CR2032) using the same type of fibrous material with balanced mass ratio of positive and negative electrodes and without a current collector. Glass fiber membrane was used as separator (Whatman, GF/A). Two types of supercapacitor cells were prepared, one with aqueous 6M KOH solution as inorganic, and one with TEATFB (Tetraethylammonium tetrafluoroborate) in acetonitrile as an organic electrolyte. Cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic cycling tests were used to determine the electrochemical properties of the fibrous electrodes. Rate capability and cycling performances of the cells were tested at voltage range between 0 and 1.3 V for aqueous and between 0 and 2.3 V for organic cells on MTI battery analyzer and a Potentiostat/Galvanostat (Gamry Instruments). Cycling voltammetry was performed at a scan rate of 10 mV/s on Potentiostat/Galvanostat (Gamry Instruments). Potentiostatic electrochemical impedance was performed at frequency range from 10 mHz to 1 MHz and an AC amplitude of 5 mV. Capacitance (C), energy (E) and power (P) values were calculated with the formulas given below [247],[248]:

$$C = \frac{I \cdot dt}{dU} \cdot \frac{1}{m_t} \quad E = \frac{I \cdot \int_{U_{min}}^{U_{max}} U dt}{m_t} \quad P = \frac{3600 \cdot E}{t}$$

where:  $I$  [A] is the applied discharge current;  $t$  [sec] is discharge time;  $U_{min}$  and  $U_{max}$  [V] are the lowest and the highest voltages corrected from the ohmic drop;  $m_t$  [g] is the mass of both electrodes in the cell, including the mass of polymer binder and carbon particles.

Ionic conductivity ( $\sigma$ ) was calculated with the formula  $\sigma = \frac{h [\text{cm}]}{R_s [\Omega] \cdot A [\text{cm}^2]}$ , [249] where  $R_s$  is electrolyte resistance obtained from EIS,  $h$  is the thickness and  $A$  is the area of the electrode.

When three-electrode electrochemical system was used to test the properties of individual electrodes, the set-up consisted of the fibrous electrode sandwiched between two stainless steel plates (if not otherwise stated) as working electrode, Ag wire as pseudo-reference electrode and Pt-plate as counter electrode. All three were immersed into glass cell with aqueous 6M KOH as electrolyte.

Bulk resistance of hot pressed fibrous mats was determined by 4-probe resistivity measurement method on SourceMeter SMU Instrument (Model 2450) applying current and voltage limits of 10  $\mu$ A and 2.1 V, respectively. Thickness gauge (Mitutoyo 547-401) was used for measuring the thickness of the electrodes. The bulk resistivity ( $\rho$ ) of the film was calculated with the formula  $\rho = \sigma_s \cdot h$ , where  $\sigma_s$  is sheet resistance ( $\Omega$ ) and  $h$  is the thickness of fibrous mats (cm). Sheet resistance of the film was measured by using the formula  $\sigma_s = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot k = 4.532 \cdot R$ , where  $V$  is the measured voltage (V),  $I$  is the magnitude of the source current (A),  $k$  is a correction factor and  $R$  is the measured four-point probe resistivity ( $\Omega$ ).

## 5.3 Results and Discussion

### 5.3.1 Optimization study: Morphology and structure

Polymeric fibrous mats were produced on a lab-scale solution-blowing device. In order to find the most suitable solution for effective formation of uniform and defect-free submicron fibers nine solutions with different polymer concentrations, carbon content and co-solvent, were spun. The solution parameters for all nine solutions

prepared were determined using Taguchi array. All process parameters, together with the outputs obtained from the trials were given in Table 5.1.

**Table 5.1 :** Solution parameters used for optimization and the properties of the products and production process.

| Sample                                  | 1              | 2              | 3              | 4              | 5              | 6              | 7              | 8              | 9              |
|-----------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| <b>Polymer concentration</b>            | 6%             | 6%             | 6%             | 8%             | 8%             | 8%             | 10%            | 10%            | 10%            |
| <b>Carbon content</b>                   | 50%            | 60%            | 70%            | 50%            | 60%            | 70%            | 50%            | 60%            | 70%            |
| <b>Second solvent (acetone content)</b> | 10%            | 30%            | 50%            | 30%            | 50%            | 10%            | 50%            | 10%            | 30%            |
| <b>Average fiber diameter [nm] (SD)</b> | 91.3<br>(77)   | 85.1<br>(42)   | 123.5<br>(81)  | 279.3<br>(178) | 633.1<br>(288) | 361.1<br>(195) | 683.8<br>(224) | 442.5<br>(169) | 961.3<br>(327) |
| <b>Beads [au] (SD)</b>                  | 1.49<br>(0.86) | 1.57<br>(0.64) | 1.10<br>(0.27) | 0.45<br>(0.15) | 0.21<br>(0.07) | 0.41<br>(0.09) | 0.09<br>(0.06) | 0.13<br>(0.05) | 0.13<br>(0.05) |

SEM images in Figure 5.2, give an insight into the fiber morphology of each sample. Using them, alongside with those at lower magnification, shown in Appendix A, Figure A.1, it was possible to grade the quality of fiber formation process in terms of defects (beads and/or droplets) formation and fiber diameter. It can be observed that fiber uniformity and bead formation (observed from SEM images at lower magnification) are primarily dependent on polymer concentration. Large defects interconnected with very fine fibers with diameter in the range from 91 to 123 nm were observed for the samples made from the solutions with lowest polymer concentration. In this three samples, carbon particles were noticed only as scattered agglomerates connected with polymeric strings (Figure 5.2). Increasing the content of carbon particles also decreases bead formation since their presence influence the viscosity of the solution and hence the distribution of the particles within a single fiber improved. The remaining solutions with 8 and 10 wt% polymer concentration gave fibers with average diameter from 279 to 961 nm, following the general trend, the lower the polymer concentration the lower the fiber diameter. However, not only polymer concentration, but also second solvent influenced the average fiber diameter. General tendency of larger fiber diameter, for higher amounts of second solvent was observed which may be attributed to the faster evaporation of acetone

which shortens the time for attenuation of the polymer jet on its way from the nozzle to the collector. Though, the amount of carbon was also a factor determining the fiber diameter especially for the solutions with highest polymer concentration for which the solutions were almost paste-like. Nonetheless, in this case, higher polymer concentration also means more uniform particle distribution within the fiber. Taking into account the final application of the fibrous mats, uniform distribution of the particles within each individual fiber is crucial. Since the polymer that binds the particles has insignificant electrical conductivity, particle-particle contact throughout the whole fiber length is crucial to establish electrical conductivity needed for the transfer of the electrons during the galvanostatic charge-discharge process. Therefore, defect-less fibrous mats with well distributed carbon particles alongside each fiber, and not their diameter, is primary factor to be taken into account when deciding optimal solution parameters.

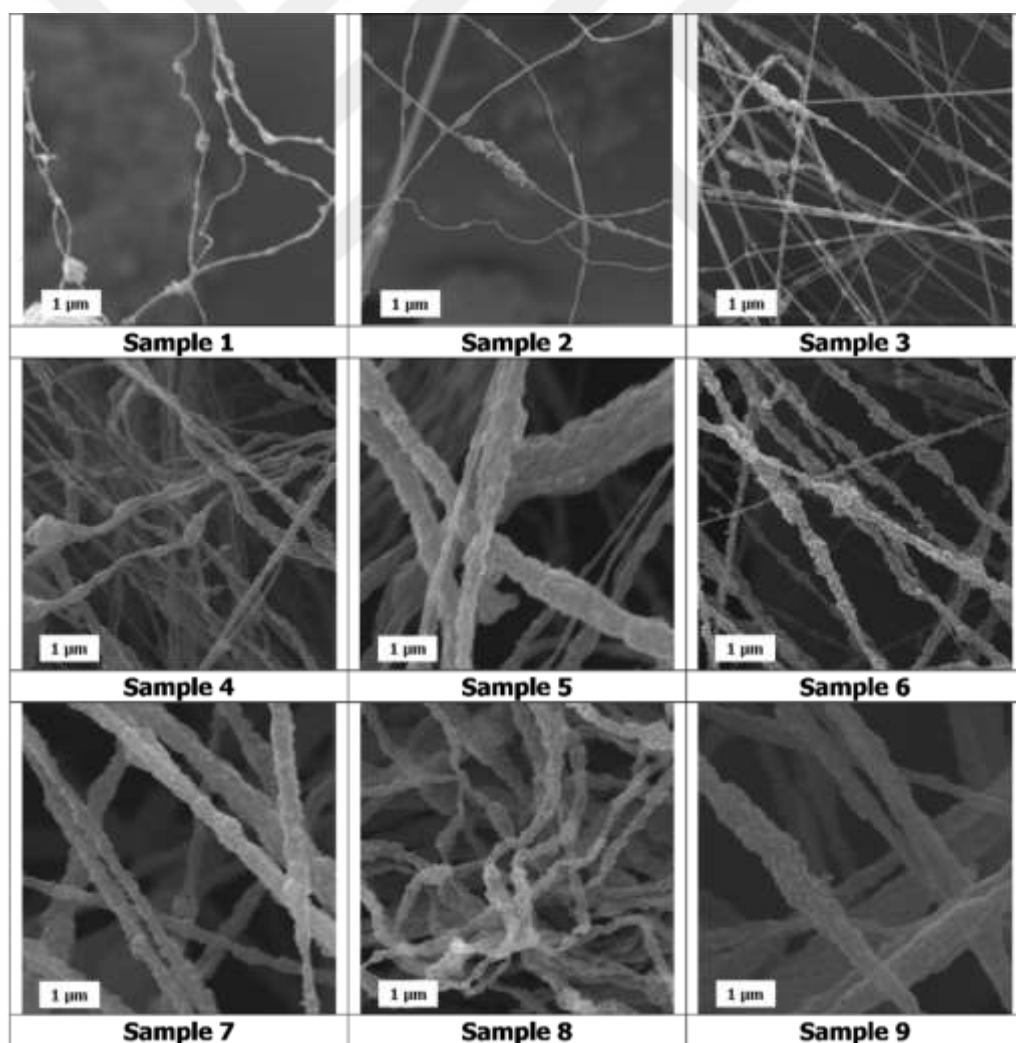


**Figure 5.2 :** SEM images of the fibers produced from the nine trial solutions (magnification 20000x).

In order to determine the best solution parameters Taguchi analysis was conducted taking the number of defects (beads) per unit area as a response data. The average number of defects are reported in Table 5.1. Signal-to-Noise (S/N) ratio of the Taguchi analysis was calculated in Minitab 16 Statistical Software, with ‘smaller is better’ option according to the formula  $S/N = -10 \cdot \log \left( \frac{1}{n} \sum_{i=1}^n Y_i^2 \right)$ , where  $Y_i$  is the value of average fiber diameter of the  $i^{\text{th}}$  experiment and  $n$  is the number of experiments [250]. Response table for S/N ratios are given in Table 5.2. The analysis ranks the three parameters (polymer concentration, carbon content and second solvent content) according to their influence on the results, based on the delta value following principle: the higher the delta value the higher the influence of that parameter. In this case, polymer concentration is the most influencing factor, followed by second solvent and carbon content. On the other hand, the means of S/N ratios for each parameter gives an insight into the optimum condition for each parameter based on their variances. It is based on the principle: the smaller the variances, the higher the mean value. Based on this analysis, fibers with defect-less structure can be obtained from a 10 wt% polymer solution with 60 wt% C content (based on polymer content) and 50 wt% second solvent. These solution parameters were taken as optimal and were used for all the samples prepared in the further studies reported here.

**Table 5.2 :** Response table for S/N ratios (Smaller is better).

| <b>Level</b> | <b>Polymer concentration</b> | <b>Carbon content</b> | <b>Second solvent</b> |
|--------------|------------------------------|-----------------------|-----------------------|
| <b>1</b>     | -2.747                       | 8.167                 | 7.298                 |
| <b>2</b>     | 9.380                        | 9.101                 | 6.981                 |
| <b>3</b>     | 18.882                       | 8.247                 | 11.236                |
| <b>Delta</b> | 21.629                       | 0.934                 | 4.256                 |
| <b>Rank</b>  | <b>1</b>                     | <b>3</b>              | <b>2</b>              |

After the optimization of the spinning parameters, electrode samples were produced to confirm that the chosen parameters would give the expected fibrous structure. The morphology of the fibers obtained were analyzed through SEM images (Appendix A, Figure A.2). Fibers with diameter of 476 ( $\pm 180$ ) nm were obtained. SEM images at larger magnifications (Appendix A, Figure A.2-c) show porous-like structure of the fibers which makes a polymer-carbon fibrous network within the fiber itself. This effect may be attributed to the large amount of carbon nanoparticles present in the

solution and to the air forces used for fiber formation, which instead of formation of stacked fibrils, splits the polymer/carbon jet out and prevent agglomeration of carbon nanoparticles in the core of the fiber.

To provide an insight into the compactness of the fibers within the fibrous mat produced with the optimal parameters, its fiber volume fraction was investigated. The as-spun fibrous mats (Appendix A, Figure A.3-a) contained loosely distributed fibers with a lot of voids between them and thus voluminous. The fiber-to-void ratio of the mat was estimated to be 27:73 via image processing analysis. In order to decrease the void fraction in the mat and thus to increase the contact between adjacent fibers which would lead to enhanced electrical conductivity of the fibrous mat, the mats were pressed under pressure of 4.5 MPa for 3 minutes. Additionally, different temperatures were used in order to achieve the highest possible fiber volume fraction without damaging the fiber morphology. For that purpose, the mats were pressed at room temperature and at 50 °C. The effect of the pressure and temperature applied on the fiber-to-void ratio in the fibrous mat is illustrated in Appendix A, Figure A.3-b) and c). The void fraction was reduced as the press temperature increased. This visual effect was also confirmed with the calculation of fiber-to-void ratio, and was estimated to be 40:60 and 66:34 for the mats pressed at room temperature and at 50 °C, respectively. It is worth mentioning that even when pressed at 50 °C, the morphology of the fibers, nor their average diameter did not change. Preliminary EIS analysis (Appendix A, Figure A3-d) performed in half-cells against Li-metal reference electrode with EtAN electrolyte, showed that hot-pressed (at 50 °C) PVDF/C nanofibrous electrodes have significantly lower resistivity values (549 vs 2100 ohms for Cp nf). The capacity values of the cell with hot-pressed electrode also showed improved capacity (20 mAh/g vs 8 mA/g for as-spun electrode). So, large gaps between adjacent fibers have negative impact on the conductivity of the electrode. On the other side, lower fiber-to-void ratio results in higher porosity of the electrode, which in turn improves the ion accessibility. However, it is reasonable to say that despite the decreased porosity after hot-press, the fibrous electrode still has (~ 35 %) voids that enable increased electrode-electrolyte interface, when compared to film-based electrode. This, plus the increased electrical conductivity contribute to an improvement of the overall electrochemical properties of the electrode, including its capacity. Similar effect was also noticed in a

previous study by *E.C. Self et. al* [235]. Therefore, hot-press at 50 °C, under 4.5 MPa pressure for 3 minutes was determined as optimal press parameters.

### 5.3.2 Electrodes and electrochemical performances

Following the optimized production and post-treatment parameters, polymer/carbon fibrous electrodes were produced using peanut-based (Cp) and commercial (Cs) carbon particles. Peanut-based carbon particles were chosen as main active material for supercapacitor electrodes due to their high capacitance and larger operating voltage window. Electrochemical performances of both types of carbon were determine via cyclic voltammograms in 3-electrode system with 6M KOH as electrolyte. For that purpose, typical inks containing Cp or Cs particles and PVDF were casted on stainless steel foils, dried and cut into electrodes with dimensions 1x1 cm<sup>2</sup>. CV-curves (Appendix A, Figure A4-b) of these electrodes, showed that Cs particles have insignificant capacitance (5.6 F/g at 10 mV/s), compared to biowaste carbon particles (48.2 F/g at 10 mV/s). Additionally, Cp electrodes showed stable CV-curves (without signs for hydrogen or oxygen evolution) at potential window of 1.3 V (voltage range from -1 to 0.3 V vs Ag), which was 0.4 V larger than that of Cs electrodes (-0.5 to 0.4 V vs Ag). This can be related to the differences in the porosity of both types of carbon. BET analysis (Chapter 4) of the particles revealed specific surface area of 1025 and 110 m<sup>2</sup> cm<sup>-1</sup> for peanut based and commercial carbon particles, respectively. Moreover, the analysis showed that 52 % of the total pore volume in Cp particles is microporous, while whole pore volume in Cs is mesoporous. FTIR analysis was also performed, in order to investigate the functionalities on the surface of the carbon particles used in this study. FTIR spectra (Appendix A, Figure A4-a) showed presence of C-C stretching (1200 cm<sup>-1</sup>); aromatic C=C (1530 cm<sup>-1</sup>), carboxylic C=O groups (1740-1775 cm<sup>-1</sup>) and phenolic OH groups or adsorbed H<sub>2</sub>O (3600-3850 cm<sup>-1</sup>) in both types of carbon particles [251], [252]. However, FTIR spectra of Cp particles also shoed presence of C-O stretching (1130 cm<sup>-1</sup>), which was not the case for Cs particles [252].

Two types of polymer/carbon fibrous electrodes were prepared, one containing only Cp (denoted as Cp nf) and another one containing a mixture of Cp and commercial Cs particles in ratio 3:1 (denoted as CpCs nf). They were obtained from two spinning solutions prepared using the same method as for the optimization study, except that

here only Cp or mixture of Cp/Cs nanoparticles were added. The as-spun nanofibrous mats were hot-pressed (using the optimized parameters in section 3.1) before being used as electrodes in order to increase the fiber-to-void ratio. The fiber-to-void ratio of these two types nanofiber was estimated as 65:35 for both Cp nf and CpCs nf. Since the fiber-to-void ratio is similar to that of PVDF/C nanofibrous electrodes from the optimization study, it is expected that they are porous enough to provide high ion accessibility and low resistivity.

The composite fibers obtained from both solutions have rough morphology and well distributed and well “packed” side-by-side particles, as shown in Figure 5.3-a) and b). The homogenous distribution of the particles was confirmed by EDAX mapping (given in Appendix A, Figure A5), which showed homogeneously distributed presence of F and O throughout the whole surface of each fiber. Average fiber diameter of CpCs nf was about 170 nm lower than that of Cp nf ( $531 \pm 184$  nm for CpCs nf and  $708 \pm 211$  nm for Cp nf) as a result of the smaller particle size of the commercial carbon and its lower surface area which makes the spinning solution less viscous.

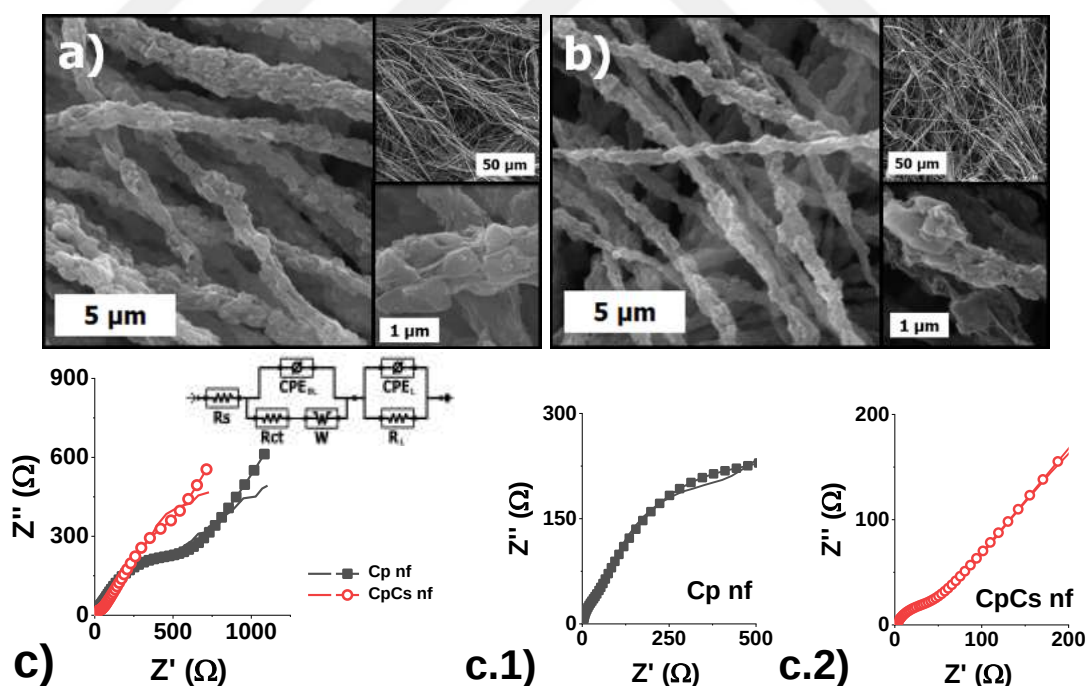


**Figure 5.3** : SEM images of polymeric fibers containing a) peanut-based Carbon particles and b) mixture of peanut-based and commercial C particles. c) Nyquist plots of EIS of Cp and CpCs nf electrodes in a 3-electrode electrochemical cell. In inset the equivalent circuit of modified Randle's model used to fit the experimental data. Smaller impedance range of the same Nyquist plots for c.1) Cp and c.2) CpCs nf electrodes.

Taking into account the final application of these fibrous mats and the importance of the electrical conductivity of the electrodes in an electrochemical cell, their electrical properties were investigated via electrochemical impedance spectroscopy and 4-probe measurements. Ionic conductivity was also calculated due to the larger amount of polymer present into this type of electrodes. The results obtained from the resistivity measurements of the electrodes using 4-probe method and EIS are given in Table 5.3 and Figure 5.3-c. Bulk resistance ( $R_b$ ) of the electrodes determined via Four-probe measurements showed almost seven times smaller values for CpCs than for Cp nf. Charge transfer resistance ( $R_{ct}$ ), obtained from the electrochemical impedance spectroscopy measurements conducted in a 3-electrode cell followed the same trend. This can be result to the presence of small sized Cs nano particles. As observed on the SEM images, Cs particles act as fillers, filling the gaps between the large Cp- particles within a single fiber and thus increasing the contact between them which results in decreased bulk resistance of the fibrous electrode. On the other hand, Cp showed smaller resistance towards electrolyte ( $R_s$ ) and also smaller ion diffusion resistance ( $R_d$ ) which can be attributed to the presence of larger amounts of carbonized peanut shell particles, which have residual carbonyl groups and higher surface area observed from FTIR and BET analysis of the particles (shown in Chapter 4). The higher  $R_s$  and  $R_d$ , which in turn result in lower ionic conductivity ( $\sigma$ ), is expected to reduce the ion accessibility into CpCs nf electrode and thus to decrease its capacitance. However, the reduced  $R_{ct}$  (and  $R_b$ ) of this fibrous electrode is expected to improve its cycling stability.

**Table 5.3 :** Resistance and ionic conductivity values obtained from EIS and (\*) bulk resistance obtained from 4-probe measurement.

|                | $R_s (\Omega \cdot \text{cm}^2)$ | $R_d (\Omega \cdot \text{cm}^2)$ | $R_{ct} (\Omega \cdot \text{cm}^2)$ | $\sigma (\text{S} \cdot \text{cm}^{-1})$ | $R_b^* (\Omega \cdot \text{cm})$ |
|----------------|----------------------------------|----------------------------------|-------------------------------------|------------------------------------------|----------------------------------|
| <b>Cp nf</b>   | 2.10                             | 46.20                            | 727.91                              | 0.0072                                   | 529.5                            |
| <b>CpCs nf</b> | 3.00                             | 67.70                            | 204.48                              | 0.0053                                   | 78.7                             |

### 5.3.2.1 Electrochemical performances in aqueous electrolyte

Electrochemical performances of the fibrous electrodes were investigated in a symmetric supercapacitor cells with aqueous electrolyte. The positive-to-negative mass ratio ( $m^+/m^-$ ) of the electrodes was determined by the ratio of the maximum negative ( $E^- = E_{\min} - E_{oc}$ ) and positive ( $E^+ = E_{\max} - E_{oc}$ ) of the electrode [247]. Even

though it is a common method used to balance the charges stored on each electrode in asymmetric (hybrid) cells [199], [253], mass balancing method can also be used to maximize the potential utilization of both electrodes [247], [254]. The minimum and maximum operating voltage range, as well as the open circuit potential, of the electrodes was determined from cyclic voltammetry tests performed on a Cp and CpCs nf electrodes in a 3-electrodes electrochemical system. The calculated positive-to-negative electrode mass ratio was 1.8 for Cp nf and 2 for CpCs nf. Supercapacitor cells were assembled with total electrode mass loading of approximately  $30 \text{ mg cm}^{-1}$ , unless otherwise specified.

Rate capability of the symmetrical cells was investigated by cycling them at current rates from  $0.1$  to  $10 \text{ A g}^{-1}$  (based on the mass of both electrodes in the cell). The results are shown in Figure 5.4-a. After 10 cycles at each current rate at cut-off voltage of  $1.3 \text{ V}$ , Cp nf symmetric cells delivered capacitance of  $18.7, 15.4, 11.8, 9.1$  and  $4.3 \text{ F g}^{-1}$  at rates of  $0.1; 0.5; 1; 2$  and  $5 \text{ A g}^{-1}$ , respectively. CpCs nf showed lower capacitance than Cp nf when tested at low current rates ( $14.5; 12.6; 10.9 \text{ F g}^{-1}$  at  $0.1; 0.5$  and  $1 \text{ A g}^{-1}$ ). However, its capacitance at higher currents was higher ( $9.2; 6.3$  and  $3.5 \text{ F g}^{-1}$  at  $2, 5$  and  $10 \text{ A g}^{-1}$ ). The higher capacitance of Cp nf can be attributed to the increased amount of “functionalized” Cp particles within a single fiber. On the other hand, the increased rate capability of CpCs nf at higher currents can be attributed to the higher electrical conductivity of this type of electrode. Charge-discharge profiles at different currents are shown in Appendix A, Figure A.6-a for Cp nf and Appendix A, Figure A.6-b for CpCs nf symmetric cell. In both cases, the curves show capacitive behavior at low currents. However, while CpCs nf keeps its symmetric charge-discharge curves at all current rates, Cp nf shows asymmetric curves and high overpotential at current rates above  $5 \text{ A g}^{-1}$  most probably as a result of the high internal resistivity of this electrode, as discussed above.

For comparison, supercapacitor cells were assembled using film-electrodes obtained by casting the spinning solution on a stainless still foil (denoted Cp film s64), as well as from a solution with binder-to-active material ratio of 2:8 (denoted Cp film s28). As shown of Figure 5.4-a capacitance values of film-electrodes are significantly lower than those of the fibrous electrodes. This can be attributed to the increased porosity of the fibrous electrode that allow easier penetration of the electrolyte throughout the whole thickness of the electrode which becomes more difficult into

the film-electrode, especially when the electrode is made from a paste containing larger amount of binder.

The possibility to implement of thick electrodes into energy storage devices is of great importance for their practical, since they can lower the production cost and the usage of multiple current collector layers [255]. Therefore, fibrous electrodes with different thickness up to 535  $\mu\text{m}$  were prepared and their performances were investigated. The capacitance of Cp and CpCs nf electrodes was investigated on cells assembled with electrodes with low (10//5  $\text{mg cm}^{-2}$ ), medium (20//10  $\text{mg cm}^{-2}$ ) and high (40//20  $\text{mg cm}^{-2}$ ) mass loading, keeping balanced positive-to-negative mass ratio. The thickness of the electrodes was 65; 155; 298 and 534 ( $\pm 7$ )  $\mu\text{m}$  for mass loadings of 5, 10, 20 and 40  $\text{mg cm}^{-2}$  respectively.

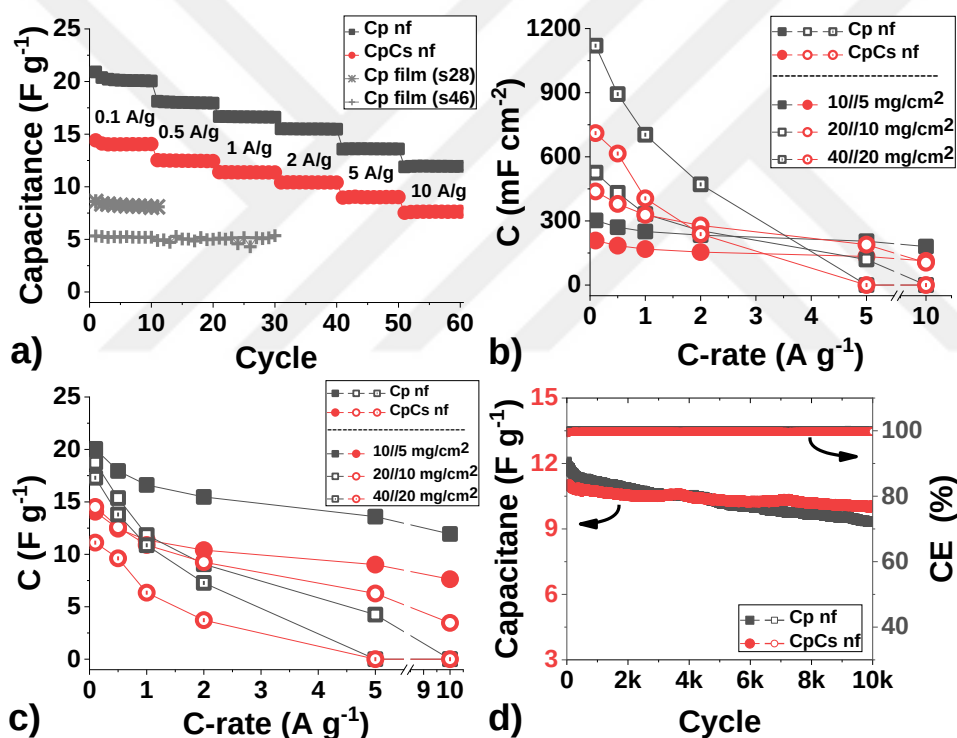


**Figure 5.4 :** a) Rate performances ( $\text{F g}^{-1}$ ) of symmetric supercapacitor cells with Cp and CpCs nanofibrous and film electrodes; b) Areal and c) Gravimetric capacitance of symmetric Cp nf and CpCs nf supercapacitor cells with different electrode mass loading in aqueous electrolyte. d) Cycling performances and Coulombic efficiency of symmetric Cp nf and CpCs nf supercapacitor cells in aqueous electrolyte. (Current: 1  $\text{A g}^{-1}$ ; voltage: 1.3 V; Electrode mass loading 20//10  $\text{mg cm}^{-2}$ )

Areal and gravimetric capacitance of the cells with different mass loading are shown in Figure 5.4-b) and c), respectively. The areal capacitance of the cells with medium electrode mass loading was in the range from 526 (at 0.1  $\text{A g}^{-1}$ ) to 119  $\text{mF cm}^{-2}$  (at 5  $\text{A g}^{-1}$ ) for Cp nf, while that of CpCs nf was lower (438  $\text{mF cm}^{-2}$ ) at currents up to 1

A g<sup>-1</sup>, but significantly higher (104 mg cm<sup>-2</sup>) at 10 A g<sup>-1</sup>. The areal capacitance increased significantly for the cells with high electrode mass loading, for currents up to 2 A g<sup>-1</sup>, reaching values of 1120 mF cm<sup>-2</sup> (at 0.1 A g<sup>-1</sup>) for Cp nf. On the other side, low mass loading electrodes exhibited higher areal capacitance at high currents due to their low thickness. Maximum volumetric capacitance (Appendix A, Figure A7-b) of 13.5 F cm<sup>-3</sup> (at 0.1 A g<sup>-1</sup>) was calculated for the cells with thickest Cp nf electrodes, and 11.8 F cm<sup>-3</sup> (at 0.1 A g<sup>-1</sup>) for the thinner ones.

Cycling performances of the cells were investigated by testing the symmetric cells at current rate of 1 A g<sup>-1</sup>. Aqueous cells were cycled up to 10000 cycles. The results (Figure 5.4-d) showed that CpCs nf has higher capacity retention 91 % versus 77.1 % of Cp nf after 10000 cycles. Aqueous Cp nf cell losses large (~6.5%) percent of its capacitance during the first 500 cycles, probably as a result of irreversible reactions between Cp and the electrolyte due to its functionalities. On the other hand, the presence of Cs prevents these reactions due to its redox inertness. The cycling stability of CpCs nf may also be attributed to lower Rct of this electrode (Table 5.3), as a result of the “filling” effect of Cs particles which maintain the electrical conductivity of the cell throughout whole cycling life. The initial coulombic efficiency of Cp nf cell was 99.4 %, while that of CpCs nf 99.2 %. It was increasing up to 100% and 99.7% for Cp and CpCs nf, respectively, during the first 50 cycles and remained stable throughout the whole cycling test.

Cycling voltammetry tests of the symmetric cells before and after cycling were performed in order to confirm that there is no presence of hydrogen and oxygen evolution reactions during cycling. The cycling voltammetry graphs are presented in Figure 5.5-a and -b. It can be seen that CpCs nf cell exhibit deviated CV-curved, when compared to Cp nf. This can be attributed to the lower ionic conductivity of CpCs nf electrode - discussed in section 5.3.2 - and can be the reason for the lower capacitance of this cell (Figure 5.4-a). This deviation from the quasi-rectangular shape, which might be attributed to inadequate electrical and/or ionic conductivity, was reduced at higher scan rates (Appendix A, Figure A.7-a) and is consistent with the capacitance values obtained from the rate capability tests, shown in Figure 5.4-c. However, cycling at cut-off voltage of 1.3 V does not cause electrolyte decomposition at the negative electrode, nor visible oxygen gas evolution on the positive electrode [253]. The shape of the CV curves does not change significantly

after cycling. There is only small shrinkage of the post-cycling CV curve (dashed line on Figure 5.5-a) for Cp nf cell, indicating its capacitance decay. The capacitance decay can be related to the ohmic drop (of about 0.4 V), noticed on the charge-discharge profile of Cp nf cell shown in Figure 5.5-c. The reason behind this will be discussed later.

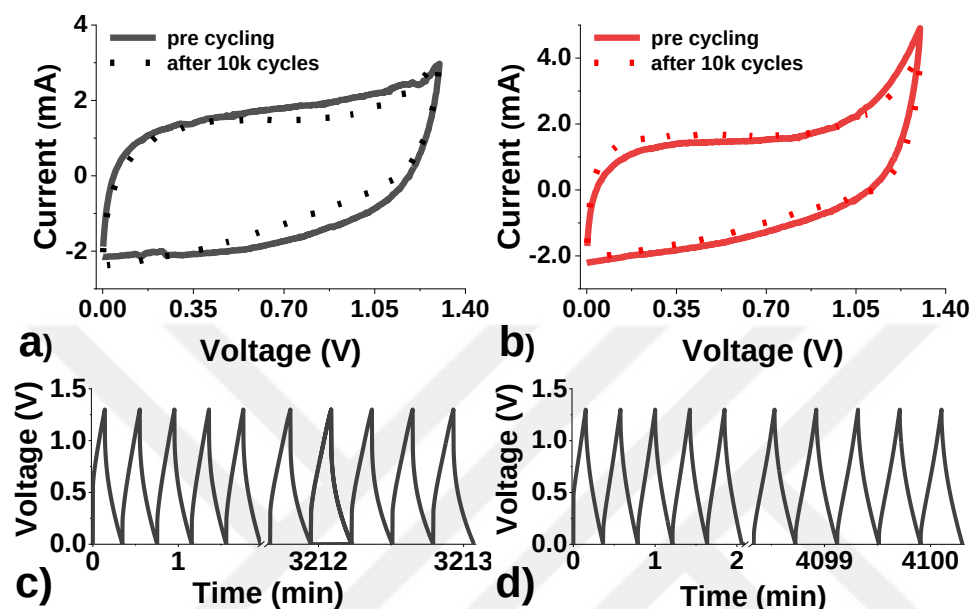


**Figure 5.5 :** Cyclic voltammetry curves of symmetric a) Cp nf and b) CpCs nf supercapacitors before and after 10000 cycles at  $1 \text{ A g}^{-1}$  in aqueous electrolyte. Galvanostatic charge-discharge profiles of the first and last 5 cycles of symmetric c) Cp nf and d) CpCs nf supercapacitors after 10000 cycles at  $1 \text{ A g}^{-1}$  in aqueous electrolyte. (Electrode mass loading 10//20  $\text{mg cm}^{-2}$ ; CV scan rate:  $10 \text{ mV s}^{-1}$ )

### 5.3.2.2 Electrochemical performances in organic electrolyte

Organic symmetric cells were assembled using only CpCs nf electrode in order to investigate the compatibility and performance of the electrodes with organic electrolytes. CpCs nf was chosen due to its higher electrical conductivity and good cycling stability in the aqueous cell. The total mass loading of the electrodes was about  $22 (\pm 0.2) \text{ mg cm}^{-2}$ , with positive-to-negative electrode mass ratio of 1.1. It was determined from a CV measurements of the electrode in a half-cell against Li-metal as counter and reference electrode. Rate capability of the cell was determined at current rates from  $0.1$  to  $10 \text{ A g}^{-1}$ , at cut-off voltage of  $2.3 \text{ V}$ . Organic CpCs nf cell delivered capacitance of  $9.95$ ;  $9.05$ ;  $8.59$ ;  $8.02$ ;  $7.19$  and  $6.3 \text{ F g}^{-1}$  at  $0.1$ ;  $0.5$ ;  $1$ ;  $2$ ;  $5$  and  $10 \text{ A g}^{-1}$ , respectively. It exhibited symmetric charge-discharge profiles (Figure 5.6-d). Similarly to the inorganic cells, the cycle life of the organic cell was tested at  $1 \text{ A g}^{-1}$  for 10000 cycles. Organic CpCs nf showed quite stable cycling behavior,

losing only 3.6 % of its capacitance after 10000 cycles (Figure 5.6-b). The cycling stability of the electrode was also confirmed with the CV (Figure 5.6-c) showing no evidence of HER and OER, nor ohmic drop on the charge-discharge profiles.

In terms of energy and power, aqueous cells can deliver maximum energy of 3.8 Wh kg<sup>-1</sup> (calculated for the total mass of both electrodes) and specific power of 8.5 kW kg<sup>-1</sup>, which is higher than the values obtained when film electrodes were used (1.7 Wh kg<sup>-1</sup> and 0.5 kW kg<sup>-1</sup>). On the other hand, the organic cell has higher specific energy of 7.5 Wh kg<sup>-1</sup>, on expense on the power which is limited up to 7 kW kg<sup>-1</sup>. These values can be calculated based on mass per volume (based on the principle provided in the paper by *M. Tebyetekerwa et. al*, [256] and with th purpose to make a more reasonable comparison between different types of electrodes published in literature) are equal to 0.09 Wh cm<sup>3</sup> kg<sup>-1</sup> and 0.03 kW cm<sup>3</sup> kg<sup>-1</sup>. Taking into account the operating voltage window, current rate applied and electrode mass loadings, all these values are comparable to the values of symmetric capacitor cells based on active carbon electrodes reported in literature which are in the interval from 3-12 Wh kg<sup>-1</sup> for energy and from 1.5-11 kW kg<sup>-1</sup> for power [247], [257], [258] [253], [199].

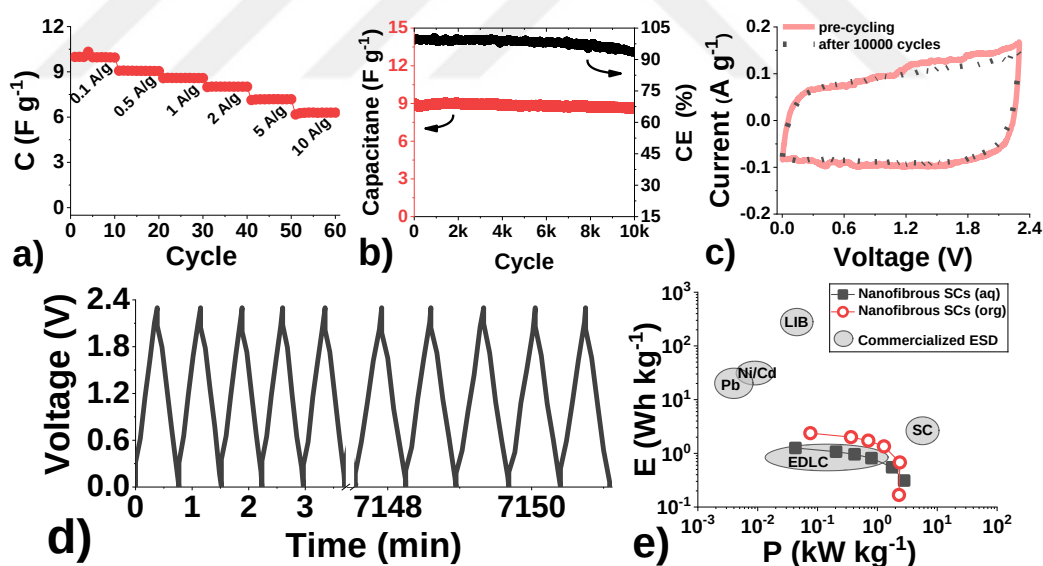


**Figure 5.6 :** a) Rate performances ( $F g^{-1}$ ); b) Cycling performances and Coulombic efficiency of symmetric CpCs nf supercapacitors in organic electrolyte; c) Cyclic voltammetry curves of symmetric CpCs nf supercapacitors before and after 10000 cycles in organic electrolyte at  $1 A g^{-1}$ ; d) Galvanostatic charge-discharge profiles of the first and last five cycles. (Voltage: 2.3 V; Electrode mass loading 11//10 mg cm<sup>-2</sup>). e) Ragone plot of symmetric nanofibrous supercapacitor cells in aqueous (solid symbols) and organic electrolyte (open symbols) along with various commercial energy storage devices.

Ragone plot showing energy versus power values of the cell reported in this study and commercial energy storage devices is shown in Figure 5.6-e. The values presented are based on a device mass, calculated with a packaging factor of 1/3 [259]. It can be concluded that the energy values obtained for the aqueous cells are comparable to those of commercial double layer capacitors, while that of the organic cell is in the range of commercial supercapacitors. On the other hand, power values for all of them, are in the range of the power values of commercial double layer capacitors. Despite the relatively low energy and power values, it has to be emphasized that they are achieved using aqueous based electrolyte which limits the maximum voltage of the cell due to hydrogen-oxygen evolution reactions at higher voltage. On the other hand, commercial SC operate with organic electrolytes at voltages from 2.5-3.3 V, which are higher than those used in this study. Taking into account the flexible nature of the polymer/carbon nanofibrous electrodes, their potential application in flexible, especially wearable energy storage devices should be considered. So, it is also reasonable to compare them with other flexible electrodes. In that regard, the supercapacitor cells developed in this study show comparable energy and power values to flexible asymmetric CNT-PP-C cloth//CNT-C cloth (3.9 Wh/kg and 10.9 kW/kg) [225], flexible symmetric N-Graphene-PAA-PANI-C cloth supercapacitor (5.8 Wh/kg and 1.1 kW/kg) [226], symmetric supercapacitor with mesoporous C spheres-GO electrodes (5.5 Wh/kg and 4.2 kW/kg) [260], or PVA-based C particles (1 Wh/kg and 2.6 kW/kg) [261]. However, to further improve the performances of these polymer/particle fibrous electrodes, other than carbon-based electrochemically active materials can be used.

### 5.3.2.3 Postmortem analysis

Post mortem analysis was conducted after testing the cells for 10000 cycles at 1 A g<sup>-1</sup>. SEM images of post-cycling positive and negative Cp nf and CpCs nf electrodes are shown in Figure 5.7. It can be observed that the electrodes retain the fibrous morphology after 10000 cycles in both aqueous and organic cells. In both cases with CpCs nf electrodes, no significant changes on the surface of the electrodes can be noticed, which was not the case with Cp nf where round pellets (white arrows on Figure 5.7-c and -d) could be seen. FTIR analysis was performed, to further investigate this effect.

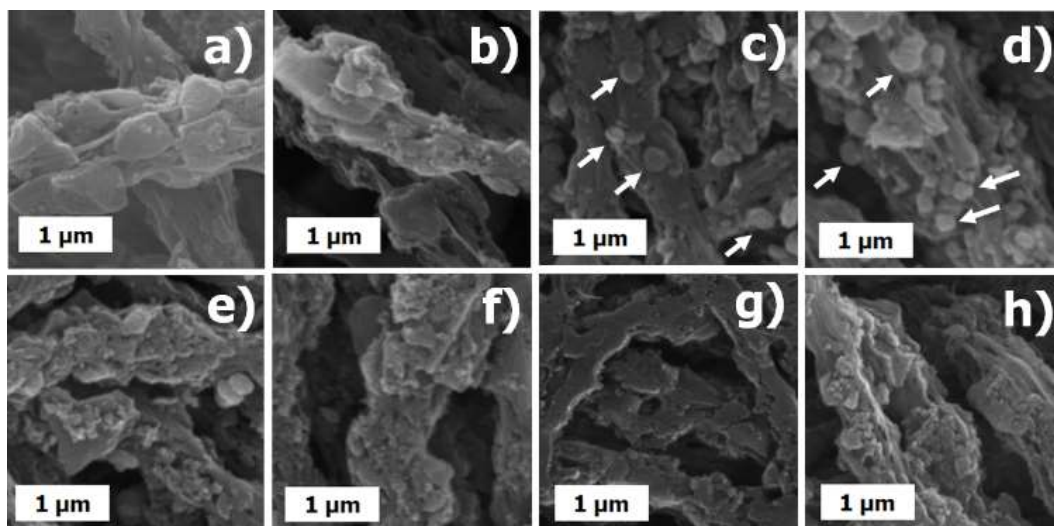


**Figure 5.7 :** SEM images of a) Cp and b) CpCs nf electrodes before cycling and c-h) after 10000 cycles at  $1\text{A g}^{-1}$ . [c-e) positive and d-f) negative Cp nf (c-d) and CpCs nf (e-f) electrodes in aqueous electrolyte; g) positive and h) negative CpCs nf electrode in organic electrolyte].

FTIR analysis of the fibrous electrodes was performed before and after cycling in order to investigate the structural changes during cycling. New fibrous electrodes are mainly characterized with a broad peak at  $1565\text{ cm}^{-1}$  signaling presence of conjugated C=C bonds from the carbon particles, and peaks typical for fluoropolymers, indicating presence of crystalline  $\alpha$ -phase ( $1390, 870, 795\text{ cm}^{-1}$ ) of PVDF, as well as its  $\beta$ - ( $1270, 1170, 470\text{ cm}^{-1}$ ) and  $\gamma$ -phases ( $830, 500\text{ cm}^{-1}$ ) [262]. Post-mortem FTIR analysis of the electrodes from the aqueous cells (Figure 5.8, curves 2, -3, -5, -6) shows decreased intensities of all PVDF peaks, with emphasis on the peaks ( $470, 500$ , and  $795\text{ cm}^{-1}$ ) indicating crystalline PVDF phases which almost disappear in Cp nf after cycling. The appearance of peaks at  $\sim 975$  and  $730\text{ cm}^{-1}$  characteristic for  $\text{CH}_2$  side groups and amorphous phases in PVDF [263] also indicates decrease of the crystalline structure of PVDF during cycling. This phenomena is especially visible for Cp nf electrodes. On the other hand, organic electrolyte does not affect the crystalline structure of PVDF significantly. For the electrodes cycled in organic electrolyte, the main differences with the new electrodes are the decrease of intensity of  $\beta$  and  $\gamma$ -phase crystals ( $470, 500$  and  $795\text{ cm}^{-1}$ ) [262]. In both, organic and inorganic cells, all the structural changes are more emphasized in Cp nf electrodes. Since there is no visible sign for oxygen/hydrogen evolution reactions (OER/HER) on the post-mortem cyclic voltammograms (Figure 5.5-a and -b) the reason for this can be decomposition of carbon surface functional groups which takes place continuously during cycling [264]. Previous studies show that such

decomposition reactions lead to evolution of CO and CO<sub>2</sub> gases within the cell [264]. In such case, it is believed that these side products further lead to formation of insoluble carbonate precipitates that may block the pores of the carbon particles and hence lower the capacitance of the cell. However, further analysis is required to confirm the formation of these gases into the cell. The formation of CO and CO<sub>2</sub> gases within the cell during decomposition reactions may further lead to formation of insoluble carbonate precipitates that may block the pores of the carbon particles and hence lower the capacitance of the cell. The presence of more functionalized peanut shell-based carbon particles in Cp nf explains why those structural changes are more accentuated. Similarly, the presence of lower amount of functionalized carbon surface in the organic CpCs nf cell reduces the possibility for decomposition of BF<sub>4</sub><sup>-</sup> and BF<sub>x</sub>O<sub>y</sub><sup>-</sup> anions [265], [266]. The decreased intensity of the peaks indicating crystalline PVDF phases on the positive electrode in this cell indicate these reactions are more emphasized on the positive electrode. However, the absence of new peaks and the almost identical CV- curves of new and cycled cells (Figure 5.6-c) indicate no significant reactions occur during cycling, hence the high cycling stability of these cell.

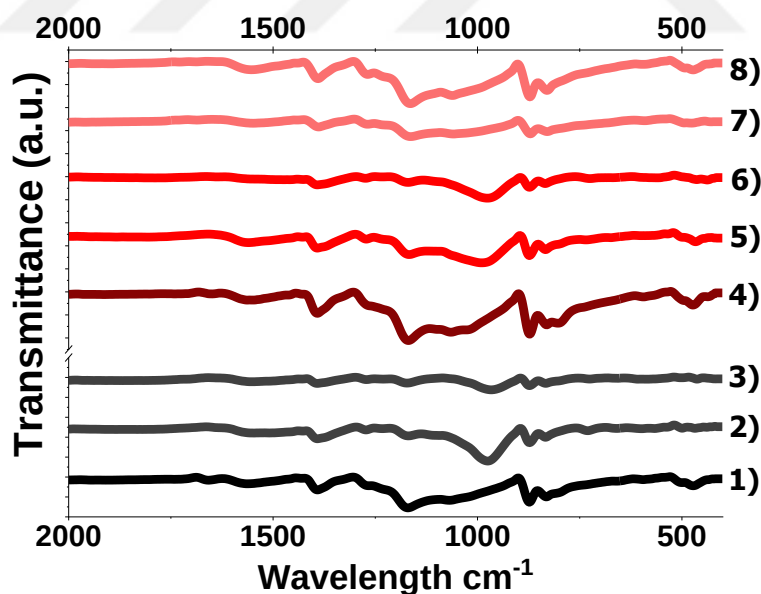


**Figure 5.8 :** FTIR analysis of positive and negative Cp nf and CpCs nf electrodes before and after cycling. 1) New Cp nf; 2) positive and 3) negative Cp nf after cycling in aqueous; 4) new CpCs nf; 5)-7) positive and 6)-8) negative CpCs nf after cycling in (5-6) aqueous and (7-8) organic electrolyte.

Electrochemical impedance spectroscopy was performed in order to investigate the behavior of the nanofibrous supercapacitor cells before and after 10000 cycles (at 1

A  $\text{g}^{-1}$  in a voltage range of 1.3 V for aqueous and 2.3 V for organic cells). Figure 5.9 shows Nyquist plots of aqueous and organic Cp and CpCs nf cells before and after cycling. The first resistance measured at high frequencies on the intercept of the curve with the real part of the impedance corresponds to the electrolyte resistance ( $R_e$ ), while the semicircle that follows can be interpreted as charge-transfer resistance ( $R_{ct}$ ) related to the porosity and surface functional groups of the electrode [258]. Both resistances together give the internal resistance of the device ( $R_i$ ). The vertical line at low frequencies represent capacitive behavior.

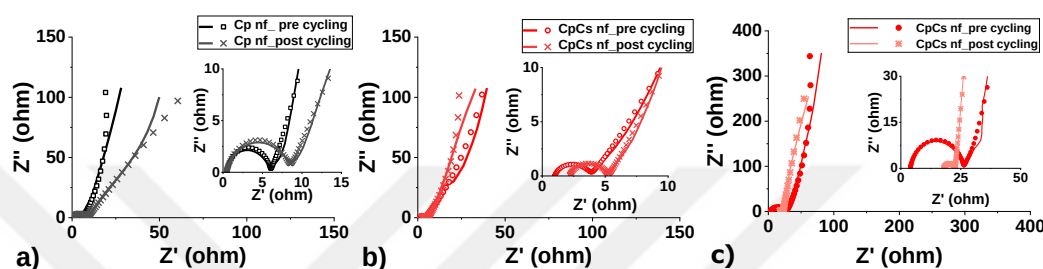


**Figure 5.9 :** Nyquist plots of symmetric a) Cp nf and b) CpCs nf supercapacitors after cycling at  $1 \text{ A g}^{-1}$  in aqueous electrolyte and c) CpCs nf in organic electrolyte (the circuit used to fit the data is same as in Figure 5.3-c; solid line: measured, symbols: fitted values).

Nyquist plots of aqueous Cp nf supercapacitor (Figure 5.9-a) shows increased charge transfer resistance of the electrodes after cycling which can be associated to the surface modification of the electrodes as discussed above. This results show increase of the internal resistance from  $2.3$  to  $3.2 \text{ } \Omega \cdot \text{cm}^2$  after 10000 cycles. On the other hand, the aqueous CpCs nf cell exhibits smaller internal resistance, which increases from  $1.4$  to  $2 \text{ } \Omega \cdot \text{cm}^2$  during cycling. Characteristic for CpCs nf cell is its higher electrolyte resistance ( $0.39$  and  $0.84$  vs  $0.19$  and  $0.17 \text{ } \Omega \cdot \text{cm}^2$  for Cp nf before and after cycling, respectively) which was also noticed during the EIS measurements in 3-electrode set-up (Figure 5.3-c). This can be attributed to the presence of larger amount of non-functionalized carbon particles (Cs) which reduce the wettability of the electrode. Similar behavior was also observed in the organic CpCs nf cell, with much more emphasized increment of  $R_e$  during cycling ( $1.52$  to  $6.9 \text{ } \Omega \cdot \text{cm}^2$ ). However, there was significantly reduced charge transfer resistance ( $8.57$  to  $1.82 \text{ } \Omega \cdot \text{cm}^2$ ) which kept the overall internal resistance of the electrode almost the same as in the new cell. It was discussed in section 5.3.2 that CpCs has much lower bulk resistance as of the presence of Cs particles, which behave as ‘fillers’ into the composite polymer/particle structure. On the other side, the lower amount of side

products noticed with the FTIR analysis (Figure 5.9-7 and -8) enable constant ion accessibility through whole electrode thickness during cycling. It is believed that the free pathway for ions, plus the higher electrical conductivity of CpCs nf electrode are the reason behind the improved charge transfer resistance of the cell during cycling.

## **5.4 Conclusion**

Polymeric nanofibers containing large amount of carbon particles were produced via solution blowing technique. Production parameters, such as polymer concentration, solvents, and carbon particle content were optimized in order to obtain defect-less fibers with the largest possible amount of carbon particles. The optimized parameters were further used to produce polymer/carbon fibrous electrodes, using bio-waste based carbon particles with high surface area.

Polymer/carbon fibrous materials with average fiber diameter below 500 nm were used as electrodes for aqueous and organic supercapacitor cells. Aqueous supercapacitor cells with high electrode mass loading showed areal capacitance up to  $1120 \text{ mF cm}^{-2}$ . Moreover, polymer/carbon fibrous electrodes with increased electrical conductivity showed high rate capability at high currents and high cycling stability losing only 9 % of its capacity after 10000 cycles. The cycling stability of the electrodes was even more emphasized in organic supercapacitor cells where the cell retained 96.4% of its capacitance. Both, aqueous and organic supercapacitor cells with polymer/carbon fibrous electrodes exhibit energy and power values comparable to those of commercial devices.

## **6. CARBON NANOFIBERS AS THICK ELECTRODES FOR AQUEOUS SUPERCAPACITORS<sup>4</sup>**

### **6.1 Introduction**

The demand for storing energy from renewable resources and using when needed requires energy storage devices that can deliver high energy and power. The limited performances of today's energy storage devices are result of the limited ability of their constituents to store high amount of energy and their relatively short lifetime. Supercapacitors, as electrochemical energy storage devices with fast charge storage mechanism give higher power and cycling stability than batteries and higher energy than conventional double-layer capacitors [16]. Despite their high specific power capabilities, higher energy densities are still a goal to be achieved.

High energy densities of energy storage devices can be achieved 1) by increasing the capacity/capacitance of the active material, 2) by increasing the operating voltage window, or 3) by increasing the mass loading of the electrodes [267], [268]. Regarding the first approach, wide variety inorganic and organic active materials with pseudocapacitive behavior or hybridized battery-capacitor materials and structures have been proposed [269], [162], [270]. The operating voltage window can be increased by either choosing an electrolyte electrochemically stable at high voltages (such as organic electrolytes, ionic liquids or highly concentrated aqueous electrolytes [271], [272], [273], [274]) or by assembling a hybrid device with one capacitive and one battery-like electrodes [275], [276], [277], [31]. While these two approaches have been widely covered in literature, there is very limited number of publications that cover the later approach – increasing electrode mass loading in either, supercapacitors [278], [279], [280], [281], [282] or batteries [283], [284]. The main reason behind this is the general electrode production method – casting a paste

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<sup>4</sup> This chapter is based on the article “Carbon Nanofibers as Thick Electrodes for Aqueous Supercapacitors” published in Journal of Energy Storage, 26, 2019, 100981. doi.org/10.1016/j.est.2019.100981

onto a conductive foil - which allows production of commercially efficient electrodes with mass loading of maximum  $10 \text{ mg/cm}^2$  corresponding to thicknesses up to  $150 \text{ }\mu\text{m}$  [285], [286], [287]. With this values, electrodes occupy one third part of the total mass of the energy storage device. Electrodes with lower active material mass loading are not of practical use for industrial scale energy storage devices, because in such cases the mass and volume of the passive elements of the device become much larger and the energy density of the device decreases significantly [288]. Meaning, the higher the mass loading/thickness of the electrode, the larger the amount of energy stored within the cell. Additionally reduced weight and volume of the passive elements will result in improved volumetric energy density of the device. On the other side, electrodes with higher mass loading (and thickness) lead to lower ion accessibility, higher ion transportation distances, and in many cases delamination of the electrode film from the current collector which leads to higher internal resistance and thus lower performances and short life of the device [289], [290], [278]. Most of the studies that explain the effect of electrode thickness and/or mass loading on supercapacitor performances produce graphene-based foams, hydrogels or 3D printed structures with mass loadings and thicknesses in the range of the commercial ones [279], [280], [281] or use commercially active carbon or coarse carbon particles to make conventional film electrodes with thicknesses up to  $800 \text{ }\mu\text{m}$  [278], [282]. To the best of our knowledge, there is no article showing the potential use of thick carbon nanofiber electrodes.

Generally, supercapacitors use active carbon and/or pseudocapacitive materials as electrodes and organic electrolytes that allow operating voltage of at least  $2.3 \text{ V}$  which favors the specific energy of these devices [17]. The reason behind the choice of active carbon, as most commonly used active material in commercial supercapacitors, is its high surface area which allows low ion diffusion distances and more efficient ion transportation pathway, plus its electrical conductivity. However, many novel structures that can improve the capacity of supercapacitors have been proposed in the last few decades [291]. Among them, nanofibrous carbon materials show advantages principally due to their stable 1D structure, high surface area to volume ratio and the possibility to modify them into composite structures with different active materials [292], [293], [294], [295], [296]. Carbon nanofibers (CNF) are generally obtained after carbonization of polyacrylonitrile nanofibers [297]. Even

though electrospinning is the mostly commonly used method to produce nanofibers, due to its easy set-up for lab-scale production, nanofibers can also be produced by several other techniques [298], [299]. Solution blowing, as non-electro spinning technique, uses compressed air as a force that attenuate the polymer jet and converts it into fiber [200]. It allows fast production of nanofibrous materials using high feeding rates (5-30 mL/h/nozzle) which is approximately five times higher than production rates used in electrospinning. Pilot version 8-nozzles solution blowing die (developed by Areka Advanced Ltd. and tested in TEMAG Labs) operates at rates up to 100 mL/h which in comparison to multi-nozzle electrospinning systems reported in literature [241], [244], [245] is high.

In this study we report production of CNF via solution blowing method and their application as flexible and free-standing electrodes for aqueous based supercapacitors. We investigate the electrochemical behavior of CNF electrodes with thicknesses up to 1.2 mm and the performances of symmetric supercapacitor cells with thick CNF electrodes.

## **6.2 Experimental**

### **6.2.1 Materials and methods**

Polyacrylonitrile (PAN, homopolymer, Mw 225 000) supplied by AKSA and N, N-Dimethylformamide (DMF, ACS Reagent, Merck) was used as polymer precursor and solvent, respectively. Polymer solution with 8 wt% PAN/DMF and viscosity of 504 mPa·s (measured on Rotational Viscometer, Fungilab, Alpha Series) was prepared as spinning solution. Lab-scale solution blowing device was used to produce the fibers, using the following spinning parameters: 10 ml/h flow rate, 2 bar air pressure, and 55 cm nozzle-to-collector distance. As spun fibers were stabilized under oxygen atmosphere at 250 °C for 2.5 h, and then carbonized at 900 °C for 1h in argon atmosphere (heating rate 3 °C/min). Prior to carbonization all samples were pressed with hydraulic press under pressure of 16 MPa in order to reduce the fiber-to-void ratio.

The mass loading of the samples was controlled by adjusting the spinning time and assuming a mass-yield of 50 wt% after carbonization (which was determined in internal studies). The size of the samples was controlled by holding the samples in a

relaxed form with ceramic rods on each side, during stabilization and carbonization processes, so that geometric (area)-yield of about 50 % could be achieved. The thickest PAN sample produced had a mass loading of 10 mg/cm<sup>2</sup> and thickness of about 500 μm. The thicker samples used in this study were produced by merging layers of stabilized PAN nanofibers. The mass loading and thickness of the carbonized samples was determined as an average value of at least 20 pieces CNF cut in circular shape with diameter of 10 mm. Thickness was measured with micrometer.

Fiber-to-void ratio was calculated as ratio between the density of the fibrous mat and the density of a thin carbonized film [160]. The real volume of the fibrous mat was calculated by multiplying the actual volume with the percent of the pixels representing white (fiber) areas of five SEM images from each sample converted in binary mode. The estimated fiber-to-void ratio of the carbonized samples was 45%.

### 6.2.2 Characterization

The morphology and structural changes of the samples were characterized by Scanning Electron Microscope (SEM, Vega3 Tescan). Average fiber diameter was measured from five SEM images (magnification 5000x) taken at different points of each sample, by making a total of 100 fiber diameter measurements. CNF structure was analyzed through Raman spectroscopy (Thermo Scientific DXR instrument under 532 nm laser excitation), X-ray diffraction analysis (XRD, Bruker D2 PHASER) and Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Spectrometer).

Deconvolution of XRD was performed by fitting the XRD curve was fitted to three Gaussian peaks using Origin software [300]. The 2 $\theta$  position and width at half maximum obtained from the fitted curves were used to calculate the interlayer spacing (d) and crystallite size (L) according to Bragg's and Scherrer's equations, as follows [301]:

$$d = \frac{\lambda}{2 \cdot \sin \theta} \quad L = \frac{k \cdot \lambda}{\beta \cdot \sin \theta}$$

where,  $\lambda$  (1.54184 Å) is x-ray wavelength,  $\theta$  is the scattering angle in radians,  $\beta$  is full width at half maximum,  $k$  is a fitting pre-factor ( $k=0.94$ ) [186].

Raman spectra was fitted to five curves with Voigt profile until converged fit, using Origin software [302], [303]. The integrated area ( $A$ ) under the curves was used to calculate the degree of disorder ( $R$ ) and the in-plane crystal size ( $La$ ) with the formulas:  $R = \frac{A_{D1}}{A_G}$  and  $La = \frac{4.4 \cdot A_G}{A_{D1}}$  [183], [184].

The porosity of the carbon particles obtained was investigated by BET analysis (Quantachrome Nova), at 77 K using slit pore NLDFT equilibrium model. Before the analysis the sample was degassed at 200°C during 2h.

### 6.2.3 Electrochemical set-up and characterization

The fibrous electrodes were prepared by cutting the CNF produced into circular free standing electrodes with diameter of 10 mm. Electrochemical properties of individual electrode were firstly tested in a 3-electrode set-up, where CNF were working electrodes, while Ag-wire and Pt were used as pseudo-reference and counter electrodes, respectively. Electrochemical properties of a device were tested by assembling symmetric supercapacitor cells (CR2032) using the CNF as positive and negative electrode. Symmetric supercapacitor cells were prepared with aqueous 6M KOH solution as electrolyte. Glass fiber membrane was used as separator (Whatman, GF/A). Before assembly, the separator was soaked into electrolyte solution for 12h (after which increased its weight for 14 times), and only for the thickest electrodes additional drops electrolyte was added into the cells. The cells were assembled with balanced mass ratio of positive and negative electrodes and without a current collector. Taking into account the thickness of the electrodes, in order to achieve same pressure within the cell, the cells with thickest electrodes were assembled without spacers and/or springs, while in the cells with thinnest electrodes multiple spacers were added. Cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic cycling tests were used to determine the electrochemical properties of the fibrous electrodes on Potentiostat/Galvanostat Gamry and MTI battery analyzer. Cycling voltammetry was performed at scan rates of 10 mV/s on Potentiostat/Galvanostat Gamry. Potentiostatic electrochemical impedance was performed at frequency range from 10 mHz to 1 MHz and an AC amplitude of 5 mV. Capacity ( $C$  in mAh/g or mAh/cm<sup>2</sup>), energy ( $E$  in Wh/kg or Wh/L) and power ( $P$  in kW/kg or kW/L) values were calculated with the formulas [247],[248]:

$$C = \frac{I \cdot dt}{dU} \cdot \frac{1}{X_t} \quad E_{electrodes} = \frac{I \cdot \int_{U_{min}}^{U_{max}} U dt}{X_t}$$

$$E_{Vdevice} = f \cdot E_{Velectrodes} \quad P_{device} = \frac{3600 \cdot E_{Vdevice}}{t}$$

where:  $I$  [A] is applied discharge current;  $t$  [sec] is discharge time;  $U_{min}$  and  $U_{max}$  [V] are the lowest and the highest voltage corrected from the ohmic drop;  $X_t$  is the area [cm<sup>2</sup>] or the mass [g] or the bulk volume [dm<sup>3</sup>] of both electrodes in the cell;  $f$  is the volume fraction of the two electrodes within the cell.

## 6.3 Results and Discussion

### 6.3.1 Morphology and structure

The morphology of the fibers was investigated via SEM imaging. SEM images of the as-spun, stabilized PAN nanofibers and also the carbonized ones are given in Figure 6.1. As-spun fiber exhibited rugged-like surface and average diameter of 570 (±180) nm. After stabilization, the surface of the fibers smoothened and their diameter decreased for almost 100 nm. Carbonized fibers showed smooth surface and diameter of 335 (±60) nm.

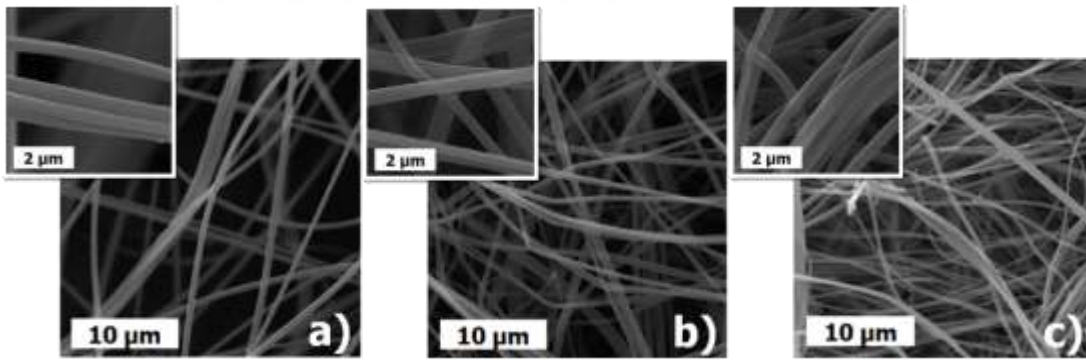


**Figure 6.1 :** SEM images of a) as-spun PAN nanofibers, b) stabilized PAN nanofibers and c) CNF.

In order to investigate the structure of the carbonized nanofibers Raman spectroscopy and XRD analysis were performed. In both cases, the curves were deconvoluted in order to get more detailed insight into the carbonized structure. From the XRD curve (Figure 6.2-a) two diffraction peaks at  $2\Theta$  angle of 24.5° and 43.7° were emphasized. The first peak is characteristic for (002) graphitic crystals, while the later one indicates presence of turbostratic graphite. The average crystallite thickness ( $L_c$ ) was calculated as 0.96 nm with 3.6 Å interplanar space ( $d_{002}$ ) between graphene layers.

Compared to other carbonized nanofibrous structures reported in literature [186], [301], [304], the large interplanar space and the small crystallite thickness indicate presence of few-layered crystals and thus a disordered carbonaceous structure.

Raman analysis of the carbonized sample was conducted in order to determine the degree of disorder of the CNF structure. For that purpose, Raman spectra was deconvoluted into five Voigt profiles (Figure 6.2-b) that emphasize the ideal graphitic structure with  $E_{2g}$  symmetry (peak G), disordered graphitic structure with  $A_{1g}$  symmetry ( $D_1$ ), graphite crystals with individual graphene layers at their surface ( $D_2$ ), amorphous carbon fractions containing organic functional groups ( $D_3$ ) and polyene-like structures ( $D_4$ ) [183], [184], [190], [303]. All five profiles were detected during the deconvolution, with peaks at  $1223.7\text{ cm}^{-1}$  (peak  $D_4$ );  $1333.0\text{ cm}^{-1}$  ( $D_1$ );  $1466.2\text{ cm}^{-1}$  ( $D_3$ );  $1567.8\text{ cm}^{-1}$  (G) and at  $1626.2\text{ cm}^{-1}$  (peak  $D_2$ ). The values of D/G ratio and the in-plane crystal size  $L_a$  were 5.16 and 0.85 nm, respectively. The high D/G ratio and the small crystalline size suggests highly disordered structure, which is consistent with the XRD results discussed earlier. Taking into account the relatively low stabilization ( $250\text{ }^{\circ}\text{C}$ ) and carbonization ( $900\text{ }^{\circ}\text{C}$ ) temperature, the disordered structure is an expected outcome [183].

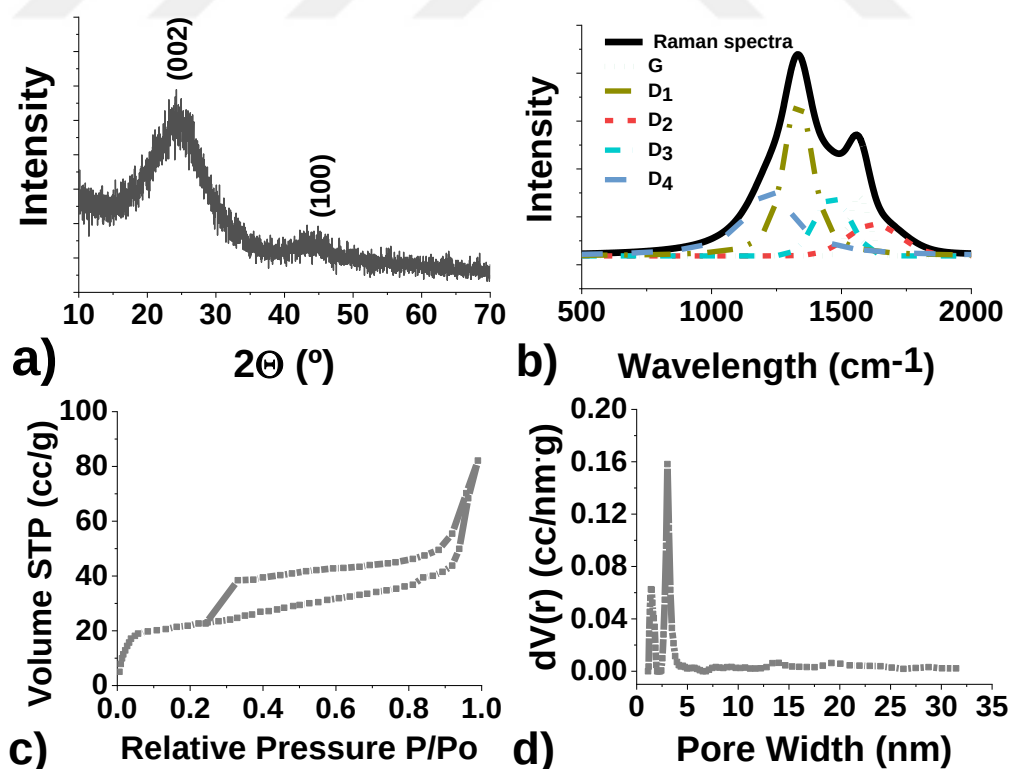


**Figure 6.2 :** a) XRD, b) Raman spectra, c) BET isotherm and d) DFT pore size distribution of CNF.

Multipoint Brunauer-Emmette-Teller (BET) analysis was performed to determine the porosity of the carbonized nanofibers. Nitrogen adsorption/desorption isotherm (Figure 6.2-c) show hysteresis loops of type H4, indicating presence of micro-mesoporous structure [198], [305]. The estimated BET surface area of CNF was 112.3 m<sup>2</sup>/g, with total pore volume of 0.1268 cm<sup>3</sup>/g and average pore size of 4.516 nm. According to the DFT pore distribution analysis (Figure 6.2-d) half of the porous structure belongs to mesoporous (53.4 % of all pore volume) and about 12 % to microporous structure. The remaining part (34.6 %) of the pore-volume are macropores that occupy 54 % of the total surface area of the CNF mat.

### 6.3.2 Electrochemical properties of single electrode

The overpotentials for O<sub>2</sub> and H<sub>2</sub> evolution at electrolytes with different pH values were investigated in order to determine the aqueous electrolyte at which CNF would have the widest operating potential window. Cyclic voltammetry was performed in a 3-electrode set up using the CNF sandwiched between two stainless steel foils as working electrode, silver wire and platinum plate as pseudo-reference and counter electrodes, respectively. The overpotentials were determined in electrolytes with the following pH values: pH1 (1M HCl), pH3 (2M KCl/HCl), pH6 (2M KCl), pH10 (2M KCl/KOH) and pH14 (6M KOH).

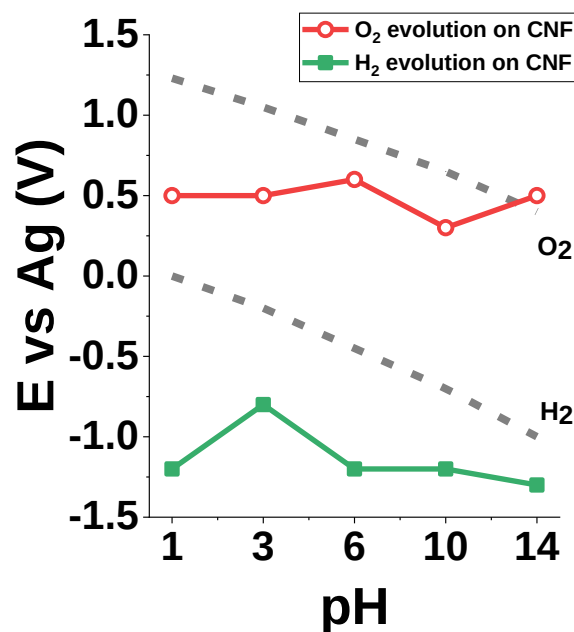


**Figure 6.3 :** Potential-pH diagram with the kinetical limits for (■) H<sub>2</sub> and (○) O<sub>2</sub> evolution on CNF and (dashed lines) the corresponding thermodynamic equilibrium potentials of O<sub>2</sub> and H<sub>2</sub> evolution from water decomposition.

The kinetical limits of  $O_2$  and  $H_2$  evolution on CNF in each electrolyte were the potentials at which fast current leap starts to appear on either the positive or the negative side on the CV curves [199]. Figure 6.3 shows the experimental values of the kinetical limits in each electrolyte. It can be observed that in all electrolytes, the potential limit of  $H_2$  evolution on CNF exceeds that of the thermodynamic equilibrium potential of  $H_2$  from water decomposition. On the other side, the limit for  $O_2$  evolution was overpassed only in the electrolyte with pH14. The potential difference, 1.8 V was almost the same for pH1, pH6 and pH14 indicating CNF is electrochemically stable at high potential windows in all three aqueous electrolytes.

Cyclic voltammetry (CV) curves of CNF in 6M KOH electrolyte used to determine its electrochemical stability are shown in Figure 6.4-a) and b). The maximum negative voltage window was determined from the voltammograms taken at different negative voltages up to -1.5 V vs Ag (Figure 6.4-a). When increasing the negative voltage limit, starting from -0.5 V vs Ag, gradual widening of the CV-curve is observed. Extending the negative potential cut-off allows CNF with their porous structure to reversibly absorb hydrogen [199], which in turn also increase their capacity. CV-curve with a tail, on the negative side, due to fast current leap indicating hydrogen evolution appeared when the CNF electrode was cycled at -1.5 V vs Ag as a negative limit. Up to this negative limit, the CV-curve showed only gradual increase of the maximum positive and negative current, which means CNF can operate at voltages up to at least -1.3 V vs Ag, without  $H_2$  evolution. When opening the positive voltage window (Figure 6.4-b), current leap appeared at 0.6 V vs Ag as maximum positive voltage and no current changes were noticed below that limit. Maximum negative voltage limit of -1.3 V vs Ag and maximum positive of 0.5 V vs Ag, give a maximum voltage window of 1.8 V, at which CNF can operate without HER (hydrogen evolution reaction) or OER (oxygen evolution reaction). However, for practical purposes in energy storage device, high coulombic efficiency and long cycle life are required [199]. In order to assure electrochemical stability and high coulombic efficiency during prolonged cycling the optimal voltage was limited in the range from -1 to 0.4 V vs Ag. The final total voltage window was confirmed with coulombic efficiency values of a symmetric CNF cell tested at cut-off voltages above 1.2 V. It was noticed that coulombic efficiency decreased from 98.2 % at 1.2 V and 1.4 V through 97.3 % (1.6 V), 96 % (1.7 V) to 93.7 % at 1.8 V. Cyclic

voltammograms of the CNF in the optimal voltage window at different scan rates are given in Figure 6.4-c). The quasi-rectangular shape and the absence of redox peaks indicate that CNF are pseudocapacitive electrodes [16]. The estimated capacity of the electrode was 256, 160 and 150 C/g at scan rates of 2, 10 and 20 mV/s, respectively.

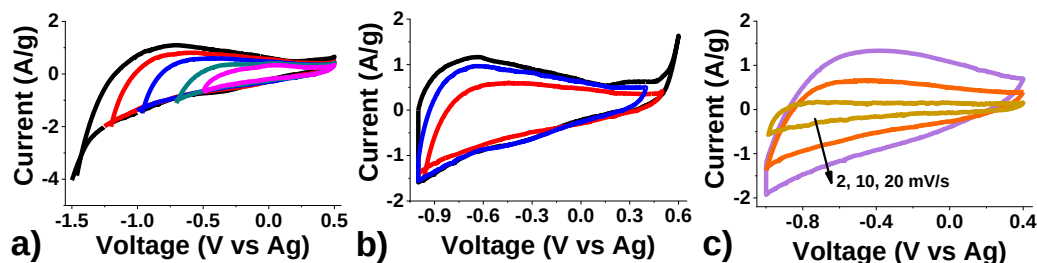


**Figure 6.4 :** Cyclic voltammograms of CNF in 6M KOH. a) Negative voltage opening and b) positive voltage opening at scan rate of 10 mV/s. c) Cyclic voltammograms at the optimal voltage window ( $-1 \div 0.4$  V vs Ag) at different scan rates.

The possibility to implement thick electrodes into energy storage devices is of great importance for their practical application, since they can lower the production cost and the use of multiple current collector layers [284], [283]. Therefore, fibrous electrodes with different thickness up to 1258  $\mu\text{m}$  were prepared and their performances were investigated.

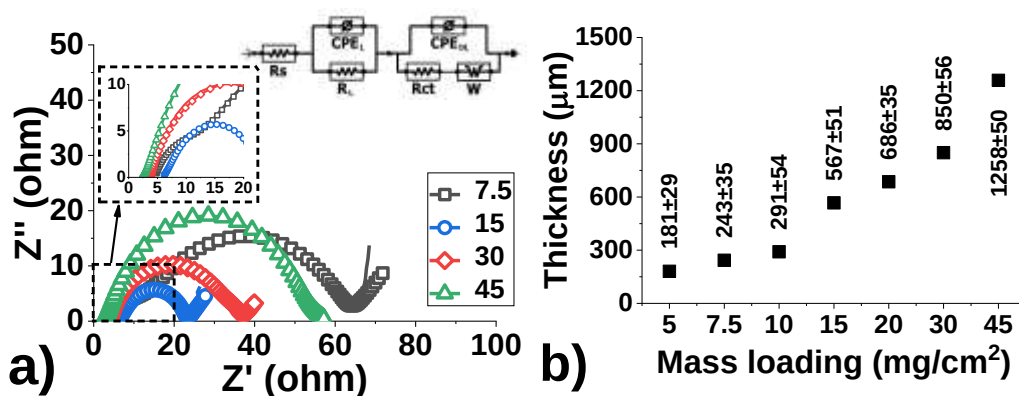


**Figure 6.5 :** a) Nyquist plots of CNF with different mass loadings (inset: modified Randles circuit used to fit the data; solid line: measured, symbols: fitted values) and b) thickness vs mass loading diagram.

Electrochemical impedance spectroscopy of CNF electrodes with different mass loadings of 7.5, 15, 30 and 45  $\text{mg/cm}^2$  (labeled 7.5, 15, 30 and 45, respectively) was conducted in order to investigate the electrical properties of CNF. The EIS was performed in a 3-electrodes system. Nyquist plots are shown in Figure 6.5-a), while the thickness-mass loading relation is given in Figure 6.5-b). The Nyquist plots were fitted with a circuit shown as inset in Figure 6.5-a). The first element of the circuit

that corresponds to the resistance of the electrolyte ( $R_s$ ) is shown as the first intersection of the plot on the real axis and is registered at high frequencies [306]. The semicircle in the high-to-mid frequencies represents the interfacial charge transfer resistance ( $R_{ct}$ ) of the electrode, while the tail in the low-frequencies region which describes the ion diffusion into the electrode is represented by the Warburg element ( $W$ ). The values of the calculated areal resistivity (Table 6.1) show an expected trend of charge transfer resistance increase as the electrode thickness increases. On the other hand, electrolyte resistance and ion diffusion resistance decreased with the increase of electrode thickness. As the thickness of the electrode increases, the number of fibers also increases. However, thicker electrode also brings larger portion of pores and voids within the electrode, which allows higher electrolyte uptake. This in turn, improves the electrode-electrolyte interface and results in increased ion diffusion ( $W_o$ ) and decreased electrolyte resistance ( $R_s$ ). On the other side, the larger amount of voids does not allow “smooth” transition of charges and thus negatively affects the charge transfer resistance ( $R_{ct}$ ).

**Table 6.1** : Resistance values obtained from EIS measurements of CNF electrodes with different thicknesses.

| Sample | $R_s$ ( $\Omega \cdot \text{cm}^2$ ) | $R_{ct}$ ( $\Omega \cdot \text{cm}^2$ ) | $W_o$ ( $\text{S} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2}$ ) |
|--------|--------------------------------------|-----------------------------------------|----------------------------------------------------------------|
| 7.5    | 7.09                                 | 12.40                                   | 0.214                                                          |
| 15     | 9.07                                 | 22.34                                   | 0.397                                                          |
| 30     | 5.81                                 | 46.19                                   | 0.568                                                          |
| 45     | 3.50                                 | 66.50                                   | 60.308                                                         |

### 6.3.3 Electrochemical performances of symmetric cell

Electrochemical performances of the fibrous electrodes were investigated in a symmetric supercapacitor cells with balanced positive-to-negative electrode mass in order to maximize the potential utilization of both electrodes [247], [307]. Positive-to-negative mass ratio ( $m^+/m^-$ ) of the electrodes was determined by the ratio of the maximum negative ( $E^- = E_{\min} - E_{oc}$ ) and positive ( $E^+ = E_{\max} - E_{oc}$ ) potential of the electrode [247]. The calculated positive-to-negative electrode mass ratio was 1.5. Supercapacitor cells were assembled with total electrode mass loading of 12.5; 25; 50 and 75  $\text{mg}/\text{cm}^2$  which corresponds to total electrode thickness of 424, 858, 1536 and 2108  $\mu\text{m}$ , respectively. The cells are denoted as 12.5 (for positive//negative mass

loading of 7.5//5 mg/cm<sup>2</sup>), 25 (for 15//10 mg/cm<sup>2</sup>), 50 (30//20 mg/cm<sup>2</sup>) and 75 (45//30 mg/cm<sup>2</sup>).

Rate capability of the symmetrical cells was investigated by cycling them at current rates from 0.1 to 10 A/g (based on the mass of both electrodes in the cell) and cut-off voltage from 0 to 1.4 V. Due to the pseudocapacitive nature of the CNF electrodes, all capacity values of the full cells are reported as mAh/g, taking into account the weight of both electrodes.

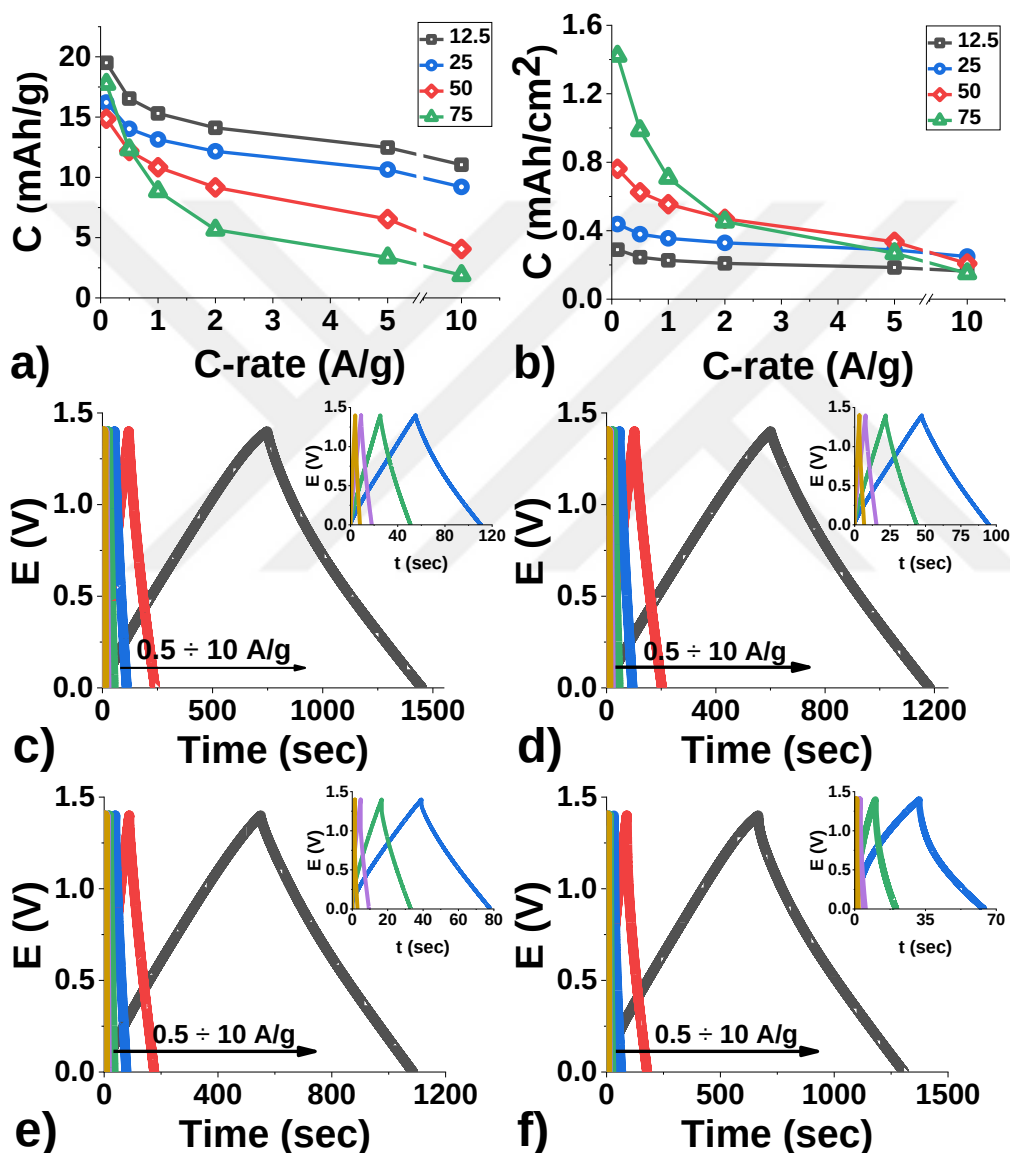


**Figure 6.6 :** a) Gravimetric and b) areal capacity of symmetric CNF supercapacitor cells with different electrode mass loading. c)-f) Galvanostatic charge-discharge profiles at different current rates of symmetric CNF supercapacitor cells with electrode mass loading of c) 12.5, d) 25, e) 50 and f) 75 mg/cm<sup>2</sup>.

Gravimetric and areal capacity values of the cells, obtained after 10 cycles at each current rate, are given in Figure 6.6–a) and b), respectively. Capacity values from 11

mAh/g to 19.5 mAh/g were registered for the cell with the lowest mass loading, which correspond to areal capacity in the range from 0.16 (at 10 A/g) to 0.29 mAh/cm<sup>2</sup> (at 0.1 A/g). Areal capacity increased up to 0.44 and 0.76 mAh/cm<sup>2</sup> for the cells with total mass loading of 25 and 50 mg/cm<sup>2</sup>, respectively. The cell with the highest mass loading and electrodes thickness delivered the highest areal capacity (0.45 - 1.42 mAh/cm<sup>2</sup>) at current rates up to 2 A/g. At higher currents, its capacity dropped, which was expected due to its extremely high thickness.

Charge/discharge profiles of the cells tested at different current rates are given in Figure 6.6 (c-f). All cells exhibit symmetrical profiles at charge and discharge at all current rates, except for cell 75 where deviation on the discharge curve could be noticed due to an ohmic voltage drop. It can be noticed that there is a discrepancy of cycling time when cycling at low c-rates Figure 6.6 (c-f). This can be attributed to the presence of functional groups on the CNF surface (reveled by FTIR analysis, shown in section 6.3.5), which at low currents contribute to faradaic reactions that increase the capacity of the cell [16]. As the c-rate increases, more dominant are the non-faradaic reactions at the interface of the porous electrode which leads to capacity decay. This can also be confirmed with the shape of the CV-curve (Figure 6.1-c), more precisely its widening as the scan rate increases.

Cycling performances of the cells were investigated by testing the cells at current rate of 2 A/g for 10000 cycles. The results (Figure 6.7-a) showed that the cell with mass loading up to 25 mg/cm<sup>2</sup> retain their capacity, almost without loses, which is not the case with the other two cells. The cell with mass loading of 50 mg/cm<sup>2</sup> retains 85% of its capacity, while the one with the highest mass loading loses half of its capacity. The capacity loss of the later cells may be attributed to low ion accessibility due to their high thickness. The coulombic efficiency (Figure 6.7-b) of the cells was 99.99, 99.92, 99.83 and 99.8 % for the 12.5, 25, 50 and 75 cells, respectively.

In terms of energy and power, aqueous cells can deliver specific energy from 6.3 to 11.5 Wh/kg (calculated for the total mass of both electrodes) and power in the range from 0.14 to 12.8 kW/kg for 12.5 and 25 cells. Specific energy values for the other two cells drop to 1 Wh/kg at the highest current rate corresponding to specific power of 7.5 kW/kg. These values are in the range of specific energy (1÷25 Wh/kg) and power (0.1÷10 kW/kg) values reported in literature for symmetric CNF-based

supercapacitors (summarized in Table 6.2). On the other side, volumetric energy and power of 12.5 cell range from 2.2 to 4 Wh/L and 0.04 to 4.5 kW/L (calculated for the total bulk volume of both electrodes), respectively. As the electrode thickness increases, maximum energy of the cell decreases slightly (3.8 Wh/L for 75 cell). Taking into account that the thicker the electrodes, the larger their volume into the cell, the volumetric energy of the whole device increase significantly. Moreover, thicker electrodes reduces the number of electrode layers and thus the use of multiple current collectors, which results in lower cell weight and its overall cost [288]. Volumetric energy and power of CNF-based supercapacitor cells, described in this study,, they are also comparable to supercapacitors with high mass loading/thick carbon-based electrodes reported in literature [278], [308], [309], [310]. Specific and volumetric energy and power values of supercapacitors with thick electrodes and/or high mass loading are summarized in Table 6.3.

**Table 6.2** : Characteristics and performances of symmetric CNF-based supercapacitors.

| Electrode<br>(positive //<br>negative) | Production<br>Method | Electrolyte                       | Mass<br>Loading                                          | $\Delta E$ (V) | Energy<br>(Wh/kg) | Power<br>(kW/kg) | Ref   |
|----------------------------------------|----------------------|-----------------------------------|----------------------------------------------------------|----------------|-------------------|------------------|-------|
| Fe-CNF                                 | electro-pinning      | 1M H <sub>2</sub> SO <sub>4</sub> | /                                                        | 1              | 1-10              | 0.1-10           | [295] |
| CNF                                    |                      | 2M KOH                            | /                                                        | 1.6            | 7.8-2             | 0.4-4            | [292] |
| MoN-CNF                                |                      | 1M H <sub>2</sub> SO <sub>4</sub> | /                                                        | 1.3            | 4.5               | 0.25             | [311] |
| B-CNF                                  |                      | 6M KOH                            | 4.6mg/cm <sup>2</sup>                                    | 1              | 20-23             | 0.5-10           | [312] |
| MnCoO-N-CNF                            |                      | 6M KOH                            | 3mg                                                      | 0.5            | 2-30              | 0.1-8            | [313] |
| MnO-B-CNF                              |                      | 6M KOH                            | 6.7-<br>13.5mg/cm <sup>2</sup><br>for both<br>electrodes | 1              | 20-25             | 0.5-10           | [314] |
| porous CNF                             |                      | 6M KOH                            | 2.7mg/cm <sup>2</sup>                                    | 1              | 5-7               | 0.1-10           | [315] |
| CNF                                    |                      | 6M KOH                            | 1.5mg/cm <sup>2</sup>                                    | 1              | 2-4.7             | 0.25-9           | [316] |

**Table 6.3** : Characteristics and performances of supercapacitors with high mass loading (thick) electrodes.

| Electrodes<br>(positive //<br>negative)                   | Electrolyte                               | Electrode<br>details                                                                      | $\Delta E$ (V) | Energy and<br>Power                                                                                                                   | Reference |
|-----------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------------|----------------|---------------------------------------------------------------------------------------------------------------------------------------|-----------|
| AC (sym)                                                  | 0.1-1M<br>Na <sub>2</sub> SO <sub>4</sub> | 50-300 $\mu$ m<br>thickness                                                               | 1              | 5.7-6.1 Wh/kg <sub>AC</sub>                                                                                                           | [278]     |
| NoCo <sub>2</sub> O <sub>4</sub> -<br>NSCS // NGN-<br>CNT | 6M KOH                                    | 540-1430<br>mg/cm <sup>3</sup> , 24-<br>72 $\mu$ m thickness<br>for positive<br>electrode | 1.6            | 30-50 Wh/kg;<br>0.5-10 kW/kg<br>20-30 Wh/L;<br>0.3-10 kW/L                                                                            | [317]     |
| Vo <sub>x</sub> -C cloth //<br>MnO <sub>x</sub> -C cloth  | 5M LiCl                                   | 33 mg/cm <sup>2</sup> for<br>two electrodes                                               | 2.2            | 1-10 Wh/L;<br>0.01-1 kW/L                                                                                                             | [308]     |
| Macroporous<br>C monoliths<br>(sym)                       | 2M H <sub>2</sub> SO <sub>4</sub>         | 1.1 mm<br>thickness                                                                       | 1.4            | 2.5-15 Wh/kg <sub>electr</sub> ;<br>0.07-1. 6 kW/kg <sub>electr</sub>                                                                 | [309]     |
| MnO <sub>2</sub> (sym)                                    | 1M Na <sub>2</sub> SO <sub>4</sub>        | 5-25<br>mg <sub>MnO2</sub> /cm <sup>2</sup>                                               | 1              | 24-27 Wh/kg (for<br>5mg/cm <sup>2</sup> ),<br>12-19 Wh/kg (for<br>25mg/cm <sup>2</sup> );<br>0.05-8 kW/kg                             | [318]     |
| AC cloth<br>(sym)                                         | 6M KOH                                    | 10 mg/cm <sup>2</sup> ; 150<br>$\mu$ m thickness                                          | 1              | 6.2 Wh/kg;<br>0.1-2 kW/kg<br>5 Wh/L                                                                                                   | [310]     |
| PEDOT/PSS-<br>MWCNT<br>(sym)                              | PVA/H <sub>3</sub> PO <sub>4</sub>        | 500 $\mu$ m<br>thickness                                                                  | 1.2            | 540 $\mu$ Wh/cm <sup>2</sup> ;<br>3.24mW/cm <sup>2</sup>                                                                              | [319]     |
| doped G<br>raphene<br>hydrogel<br>(sym)                   | EMIMBF <sub>4</sub> /<br>AN               | 150 $\mu$ m<br>thickness,<br>10mg <sub>G</sub> /cm <sup>2</sup>                           | 3.5            | 134 Wh/kg;<br>83 kW/kg;<br>89 Wh/L                                                                                                    | [279]     |
| Coars C<br>particles (sym)                                | TEMABF <sub>4</sub> /<br>AN               | 200-800 $\mu$ m<br>thickness                                                              | 2.7            | 19.5 Wh/kg (200 $\mu$ m<br>electrode),<br>18.2 Wh/kg (800 $\mu$ m<br>electrode);<br>24 Wh/L (200 $\mu$ m),<br>21.5 Wh/L (800 $\mu$ m) | [282]     |
| NHC-GO<br>hydrogel<br>(sym)                               | EMIMBF <sub>4</sub>                       | 0.32-11.2<br>mg <sub>NHC</sub> /cm <sup>2</sup> ; 2-<br>70 $\mu$ m<br>thickness           | 3.5            | 84 Wh/kg;<br>0.8 kW/kg (for 11.2<br>mg/cm <sup>2</sup> )<br>138 Wh/L;<br>1.4 kW/L (for 11.2<br>mg/cm <sup>2</sup> )                   | [280]     |

Figure 6.7-c represents Ragone plot with volumetric energy and power values of the cell reported in this study and commercial energy storage devices. The values presented are based on a device volume. It can be concluded that the energy and power values obtained for the CNF supercapacitors are comparable to those of commercial supercapacitors. It has to be emphasized that, commercial SC use organic electrolytes and operate at voltages starting from 2.5 V, while the values of the devices reported in this study are achieved using aqueous based electrolyte which limits the maximum voltage of the cell up to 1.4 V.

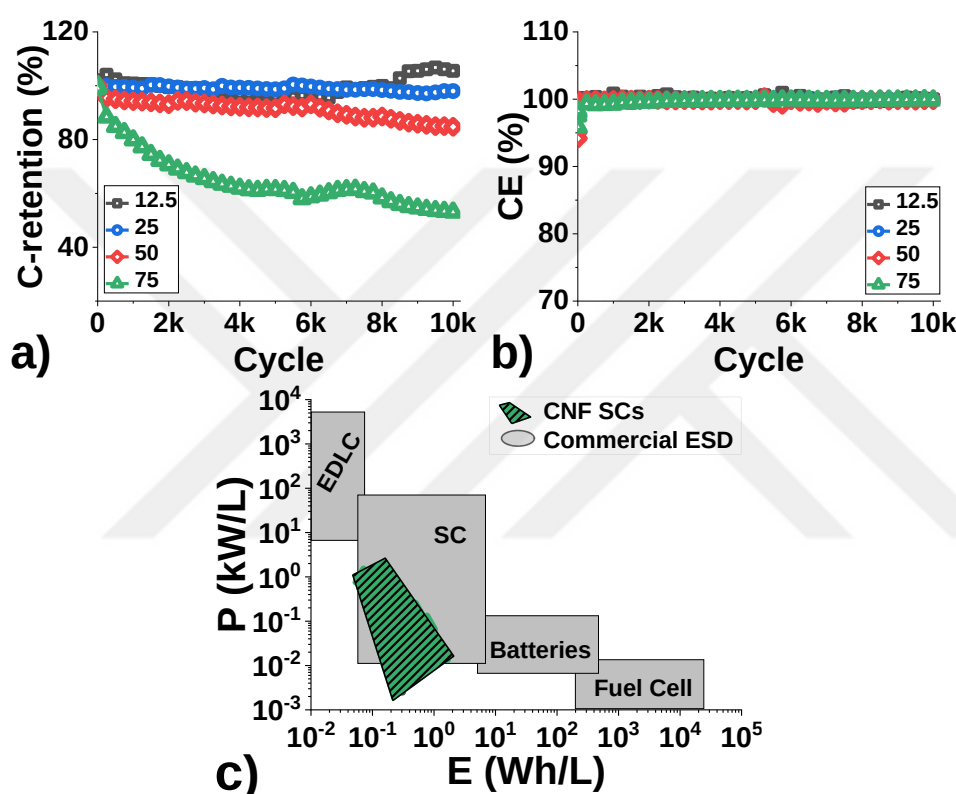


**Figure 6.7 :** a) Capacity retention and b) Coulombic efficiency of symmetric CNF supercapacitor cells with different mass loading (Current: 2 A/g; cut-off voltage: 1.4 V). c) Ragone plot of symmetric CNF supercapacitor cells along with various commercial energy storage devices.

### 6.3.3.1 Electrochemical impedance spectroscopy analysis

Electrochemical behavior of CNF SC cells before and after cycling was investigated by EIS analysis. Nyquist plots and the corresponding resistivity values obtained from the EIS measurements of the symmetric CNF cells before and after cycling are shown in Figure 6.8 and Table 6.4.

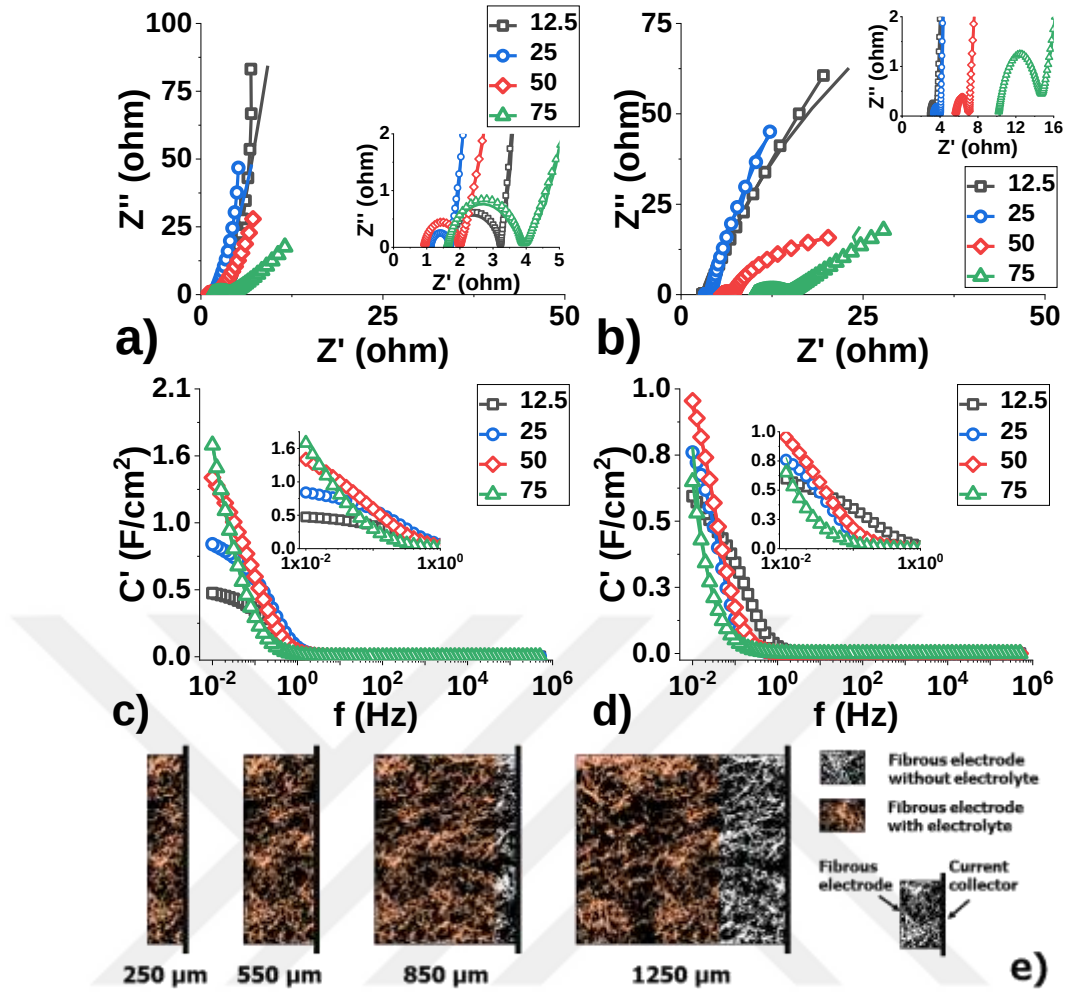


**Figure 6.8 :** a)–b) Nyquist and c)–d) Complex Bode plots of symmetric CNF supercapacitor cells with different mass loadings a)–c) before and b)–d) after 10000 cycles at 2 A/g. (The circuit used to fit the data is same as in Figure 6.5; solid line: measured, symbols: fitted values). e) Schematic representation of ion accessibility in electrodes with different thicknesses.

Except for the 75 cell, all other new cells exhibit almost-vertical line in the low frequency domain of the Nyquist plot (Figure 6.8-a), characteristic for capacitive behavior [320]. The cell with thickest electrodes shows more inclined line indicating non-capacitive behavior. New symmetric cells also showed increased charge transfer resistance ( $R_{ct}$ ) and lower ion diffusion resistance with the increase of the electrode thickness, which is consistent to the results obtained from the EIS of single electrodes. The high internal resistance ( $R_i = R_s + R_{ct}$ ) of the cell with the thinnest electrodes, may be attributed to the larger number of spacers added into the cell with the purpose to achieve the same internal pressure with the other cells. After cycling, revers resistivity vs thickness relation was observed. Charge transfer resistance doubled in all cells. More significant increase was noticed for the electrolyte

resistance which increased exponentially as the electrode thickness increased. On the other hand, Warburg resistance didn't change significantly for the cells with mass loading up to 25 mg/cm<sup>2</sup>, but it did increased six-fold for the 50 cell and in an order of magnitude for the cell with thickest electrodes. This effect can also be observed from their behavior (inclined lines) in the low frequency region of the Nyquist plot in Figure 6.8-b. This significant changes of ionic resistivity in the last two cells, explain their capacity loss during cycling.

**Table 6.4** : Impedance values obtained from EIS measurements before and after cycling of CNF SCs with different mass loading.

| Cell      | Rs ( $\Omega \cdot \text{cm}^2$ ) | Rct ( $\Omega \cdot \text{cm}^2$ ) | Wo ( $\text{S} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2}$ ) | $\tau$ (sec) |
|-----------|-----------------------------------|------------------------------------|-------------------------------------------------------------|--------------|
| 12.5_new  | 2.58                              | 2.38                               | 0.00593                                                     | 4.0          |
| 25_new    | 1.72                              | 0.9                                | 0.01213                                                     | 4.0          |
| 50_new    | 1.44                              | 1.62                               | 0.04535                                                     | 12.6         |
| 75_new    | 2.5                               | 3.45                               | 0.32562                                                     | >100         |
| 12.5_post | 4.52                              | 1.15                               | 0.00889                                                     | 6.3          |
| 25_post   | 5.01                              | 1.25                               | 0.01097                                                     | 25.1         |
| 50_post   | 8.66                              | 2.23                               | 0.00759                                                     | >100         |
| 75_post   | 15.6                              | 7.02                               | 0.00012                                                     | >100         |

Since the resistance (R) and capacity (C) are frequency dependent properties, the impedance of a cell ( $Z = R + \frac{1}{jC\omega}$ ) can also be used to estimate the capacity of the cell [128]. Similarly to the resistance, the capacity of the cell can be presented as real ( $C'(f) = \frac{-Z''(f)}{\omega|Z(f)|^2}$ ) and imaginary ( $C''(f) = \frac{-Z'(f)}{\omega|Z(f)|^2}$ ) capacity, where C' is indicator of the real capacity of the cell obtained at constant current, and C'' explains the energy loss due to irreversible processes [128]. Even though, Complex Bode plot C' vs f is usually used to evaluate the rate capability of the cell, it can also be used to explain the ion transport into the electrodes [320].

The capacitive behavior of 12.5 and 25 cells was confirmed with the C' vs frequency plot (Figure 6.8-c). The plateau of the curve at low frequencies indicates that the ions penetrated through the whole electrode thickness (ex. the electrodes during charging with thickness 250 and 550  $\mu\text{m}$  in Figure 6.8-e), so the maximum capacity can be reached. The 50 cell showed smaller plateau indicating that the ions did not reach to all pores through the whole electrodes thickness (ex. the electrode during charging with thickness 850  $\mu\text{m}$  in Figure 6.8-e). While for the cell with the thickest

electrodes,  $C'$  sharply increases as the frequency goes down, which can be explained as low ion adsorption through the whole thickness of the electrodes, as shown in the schematic in Figure 6.8-e for electrode during charging with thickness 1250  $\mu\text{m}$ . In correlation to the results obtained from the Nyquist plot, the proportional relation between the ion diffusivity and electrode thickness means thicker electrodes can adsorb large amount of ions. However, at extreme electrode thickness, at given frequency the ions adsorbed by these electrodes reach only a part of the electrode thickness and do not get the other side (closer to the current collector) of the electrode. Therefore,  $R_s$  increases in the new cell with the thickest electrodes. Post mortem  $C'$  vs frequency plot (Figure 6.8-d) shows reduced plateau length for 12.5 and 25 cells, and almost no plateau for 50 cell which implies lower ion adsorption after cycling, which results in higher  $R_s$ . The cell 75 shows even shorter frequency dependence (in the range between 0.01 to 0.1 Hz) of its capacity than before cycling (0.01 to 1 Hz), therefore its  $R_s$  increases even more after cycling. Since, the  $R_{ct}$  of all electrodes, regardless their thickness, increases by a factor of 2, the decrease of the capacity in the cells can be attributed to the lower ionic diffusivity within the electrode. The reason behind this will be discussed later.

The time constant ( $\tau = \frac{1}{f_{C''}}$ ) calculated from  $C''$  vs frequency plot (given in Appendix B, Figure B.2) which explains the relaxation time of a cell, showed values (4-12.6 sec for cells 12.5, 25 and 50) in the range of those reported in literature for active carbon based supercapacitors [128], [321], meaning that higher discharge powers can be achieved with these cells. On the other hand, for 75 cell no peak was observed on  $C''$  vs frequency graph, indicating a  $\tau$  value higher than 100 sec. This is consistent to the power values obtained from charge-discharge analysis.

### 6.3.3.2 Post-mortem analysis of CNF electrodes

In order to get closer insight into the behavior of the electrodes within the cells, cyclic voltammetry was conducted on each cell before and after cycling. From the voltammograms on Figure 6.9-a can be seen that symmetric CNF SCs exhibit nearly rectangular shape at the selected optimal voltage window of 1.4 V. It is interesting to note that as the thickness of the electrodes increases the shape of the voltammograms becomes more quasi-rectangular, which is in accordance to the behavior of thicker electrodes reported in literature [322]. Despite, the shape of the voltammograms of

all the cells remains almost the same, even after 10000 cycles at current of 2 A/g (Figure 6.9-b), with no signs for neither hydrogen nor oxygen gas evolution. However, the area of the curves for the cells with mass loading of 50 and 75 mg/cm<sup>2</sup> decreased which confirms their capacity loss during cycling. Galvanostatic charge-discharge profiles (Figure 6.9-c and d) of the cells also confirm the behavior of the cells. Constant ohmic drop of about 0.04 V was registered for the cells 12.5, 25 and 0.23 V for 50 cell. While for the cell with the thickest electrodes the ohmic voltage drop increased from 0.15 V at the first cycles to 0.46 V after 10000 cycles.

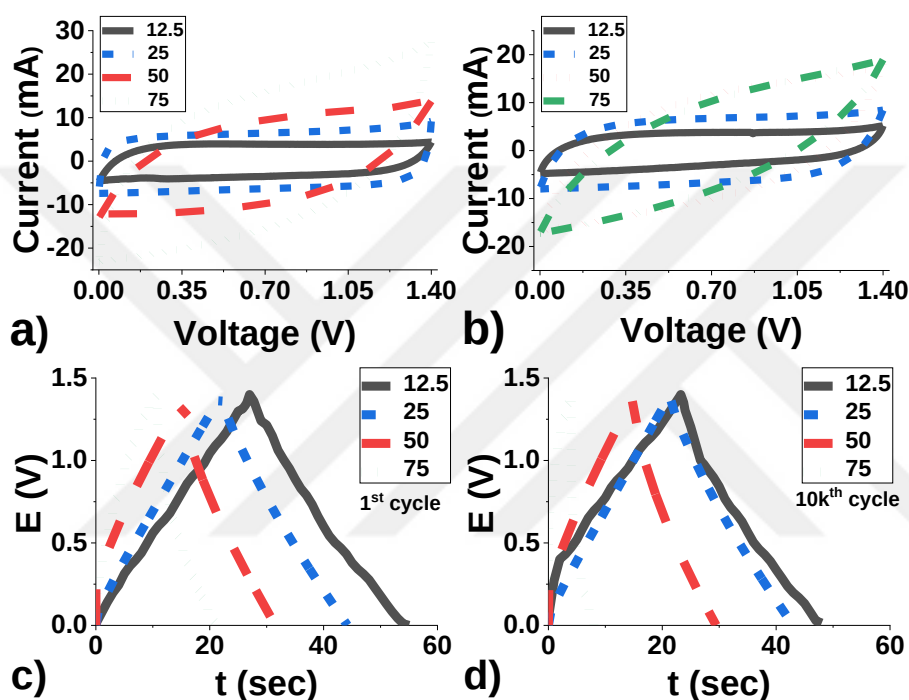


**Figure 6.9 :** a)-b) Cyclic voltammetry curves (scan rate: 20 mV/s) and c)-d) Galvanostatic charge-discharge profiles of symmetric CNF supercapacitor cells with different mass loadings (a-c) before and (b-d) after 10000 cycles at 2 A/g.

To further explain the reason behind the capacity loss and the increase of the resistivity, post mortem SEM, FTIR and Raman analysis were conducted on the electrodes, after testing the cells for 10000 cycles at 2 A/g. For that purpose, the cells were opened, the electrodes were separated, washed with distilled water and dried before the analysis.

SEM images of positive and negative electrodes after cycling are shown in Figure 6.10-b) and c). It can be seen that the electrodes kept their fibrous structure, however the diameter of the fibers increased to 485 nm. The images also reveal that the surface of the fibers became rough and coated-like, which results in fiber diameter increment. The pellet-like deposition on the surface of fibers can be attributed to

formation of CO and CO<sub>2</sub> gases within the cell as a result of decomposition reactions between the functional groups in the amorphous carbon fractions and the electrolyte [323]. This further lead to formation of carboxyl acid salts that block the pores of the CNF. Pallets with larger size, and even regions where fibers were joint together forming fiber-matrix-like structure were noticed on the electrodes with highest thickness (SEM images are given in Appendix B, Figure B.3). This fiber-matrix structure blocks not only the pores of CNF, but also the voids between the fibers which negatively affects the ion diffusivity. Therefore, the ion diffusion of the cells decreases after cycling. This effect is more emphasized as the thickness of the electrodes increases (Table 6.3) and explains the low cycling stability of the cells with thickest electrodes. Though, the amount of electrolyte in the cells with thick electrodes can also be taken as a reason behind their low cycling stability. As reported in few studies discussing the effect of electrolyte volume on the performances of pouch cell Li-ion battery [324], [325], there is an optimal ratio of electrolyte volume to total pore volume of electrodes and separators for stable cell performances. Namely, low electrolyte volume increases the impedance of the cell and contributes to higher capacity fade [324]. Taking into account that in this study, all cells were loaded with the same amount of electrolyte, it is possible that that amount is too less for the cells with thicker electrodes, especially for cell 75. However, further analysis, using more analytical approach, is required to obtain clearer and more detailed picture over this phenomenon.

FTIR spectra of new CNF and cycled positive and negative electrodes is shown in Figure 6.10-d. It can be seen that new CNF electrodes contains C=O (broad peak at ~1850 cm<sup>-1</sup>), alkynes and/or nitrile (broad peak starting at ~2080 cm<sup>-1</sup>) [326], [327]. All of them remain after cycling as well. The main structural change after cycling is emphasized with the new sharp peaks in the low IR range. Cycled CNF show three peaks in the region below 1000 cm<sup>-1</sup> (at 695, 826 and 960 cm<sup>-1</sup>) indicating aromatic C-H out-of-plane groups [327] which can be a result of H<sub>2</sub> chemisorption and storage that occurs at high voltages [323]. On the other hand, the peak at 1400 cm<sup>-1</sup> with a shoulder at 1360 cm<sup>-1</sup> and the peak at 1615 cm<sup>-1</sup> can be attributed to potassium carboxylic acid salts [328]. These salts are result of a reaction between the electrolyte and the carboxylic ions that form during the oxidation reactions on the surface of CNF at low voltages [323]. During long cycling, such organic carboxylic acid salt

form complex crystal-like structures [329], which get deposited on the surface on the CNF. The higher the mass loading of the electrodes, the larger the number of the nanofibers and the voids between them, accessible for formation of such crystals. This explains the formation of fiber-matrix structure noticed on SEM images and the increased ion diffusion resistivity of the thicker electrodes. Raman spectra (Figure 6.10-e) of cycled electrodes showed decreased disorder  $R$  structure (5.16 for new CNF; 2.20 for positive and 3.22 for negative cycled electrode) and increased crystal size  $L_a$  (0.85 for new CNF; 1.99 for positive and 1.36 for negative cycled electrode) which can be attributed to the crystal-like layer deposited on the surface of CNF and not due to a change of the carbon structure inside the CNF. However, further analysis is required to confirm this hypothesis.

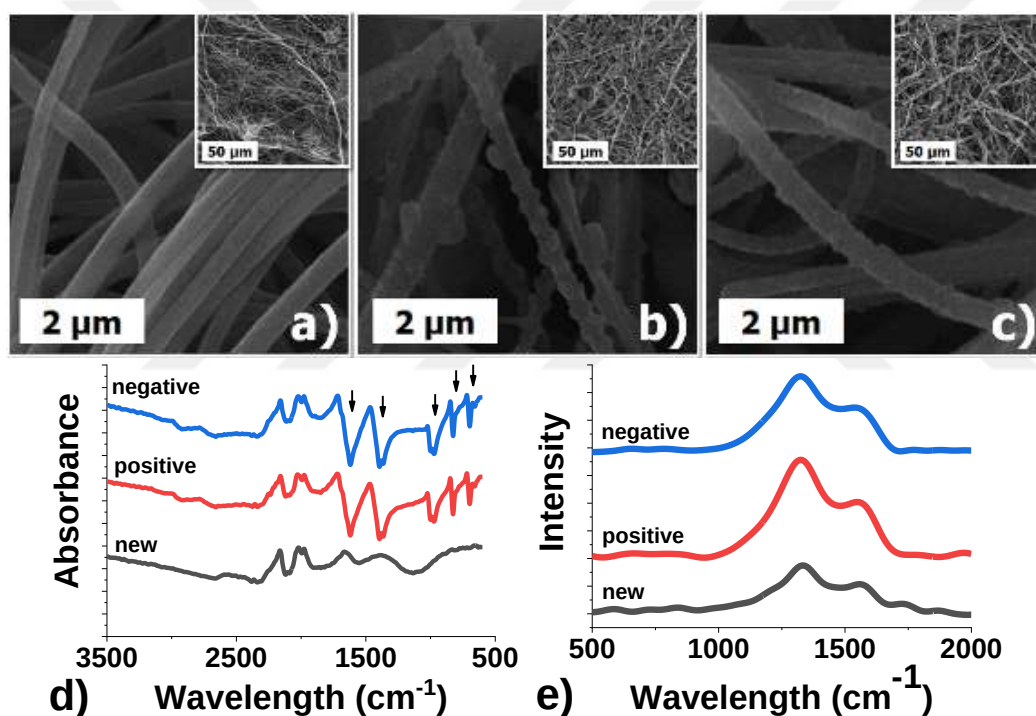


**Figure 6.10 :** SEM images of a) new CNF electrode, b) positive and c) negative cycled CNF electrode. d) FTIR and e) Raman spectra of CNF electrodes before and after 10000 cycles at 2 A/g.

CV curves of the cycled cells (Figure 6.9-a and b) did not show signs for OER or HER. The increase of  $R_{ct}$  after cycling did not show significant dependence on the electrode thickness. However, electrode thickness significantly influences the resistivity towards the electrolyte and the ionic diffusivity (Table 6.4). On the other hand, SEM and FTIR analysis of the cycled CNF electrodes (Figure 6.10) showed presence of crystal-like layer on the surface of the thin CNF, which increased forming fiber-matrix like structure with the increase of the thickness of the

electrodes. These findings confirm the hypothesis that the decreased capacity of the cells with thicker electrodes is a result of the reactions between the functional groups of CNF and the electrolyte. Taking into account that CNF can be used as supercapacitor electrodes in electrolytes with different pH, the behavior and stability of thick CNF in those electrolytes can be subject of further investigation. In order to improve the performances of the CNF based supercapacitor cells, doped and/or coated CNF with active materials that will increase the specific capacity and/or will prevent the formation of carboxylic acidic salts will be investigated in another study.

#### **6.4 Conclusion**

Increasing the thickness and mass loading of electrodes is of great importance towards the goal for energy storage devices with high energy density. Implementation of binder-free electrodes as a strategy to increase the thickness without increasing the charge transfer resistance of the electrodes shows promising results. However, limited types of materials can be used without binder. In that regard, the potential application of CNF as flexible and free-standing electrodes in symmetric supercapacitor cells were investigated.

Solution blowing method was shown to be a suitable spinning technique for production of thick polyacrylonitrile nanofibrous mats which can be easily converted into thick flexible CNF mats with thickness up to 1,2 mm. Smooth CNF with diameter of 335 nm, with turbostratic carbon structure and mostly mesoporous were produced. Such CNF can increase the thermodynamic potential limits for oxygen and hydrogen evolution in aqueous electrolytes with different pH, up to 1.8 V. When applied as electrodes in symmetric aqueous SCs, CNF mats with mass loading up to 25 mg/cm<sup>2</sup> show stable cycling behavior with no capacity loss after 10000 cycles at current rates of 2 A/g. These cells can also deliver energy and power densities in the range of those of commercial supercapacitors. CNF electrodes with mass loading of 50 mg/cm<sup>2</sup> lose 15 % of their capacity (under same cycling conditions) as a result of reactions between CNF and the electrolyte which form side products that block the voids between the fibers and thus decrease the ion diffusion within the electrodes. The wide range of possibilities to modify the CNF leave a room to suppress this negative effect and to further improve the performances of this thick binder-free electrodes.



## **7. DOPED CARBON NANOFIBERS AS ELECTRODES FOR SYMMETRIC AND ASYMMETRIC SUPERCAPACITORS**

### **7.1 Introduction**

Depending on the mechanism in which they store the electrical charges, supercapacitors may be ideal and non-ideal, as represented in Figure 7.1 [16]. Ideal supercapacitors or electrochemical double layer capacitors (ELDCs) store electrical charge through electrostatic mechanism as a consequence of reversible electrostatic accumulation of charges on the surface of the electrode [17]. On the other hand, non-ideal supercapacitor or supercapacitor with pseudocapacitive electrodes uses faradaic charge-storage mechanism where the charges pass across the double layer and the charge-storage is pseudocapacitive [16]. The pseudocapacitive behavior includes fast and reversible faradaic reactions and electrochemical conversion of the active material used. Due to its storage mechanisms, supercapacitors provide high power, but low energy. In terms of their constituent elements, supercapacitor generally use electrodes of the same type on both sides, positive and negative, and thus are called symmetric supercapacitors [247]. However, it is also possible to combine two different electrodes, in order to obtain a cell with a higher operating voltage and at the same time to improve its performances. Such cell is called internal hybrid or asymmetric supercapacitor cell. They might contain electrodes, made of a single main material (SME) but with different storage mechanism (one supercapacitor-like (CE) and one battery-like (BE) electrode) [330] or composite electrode made of battery and capacitor-like materials (CBE) [277], [331], [332]. In order to maximize the performances of such hybrid cell, both electrodes should be balanced by mass, so that the charge stored be the same on both sides [253].

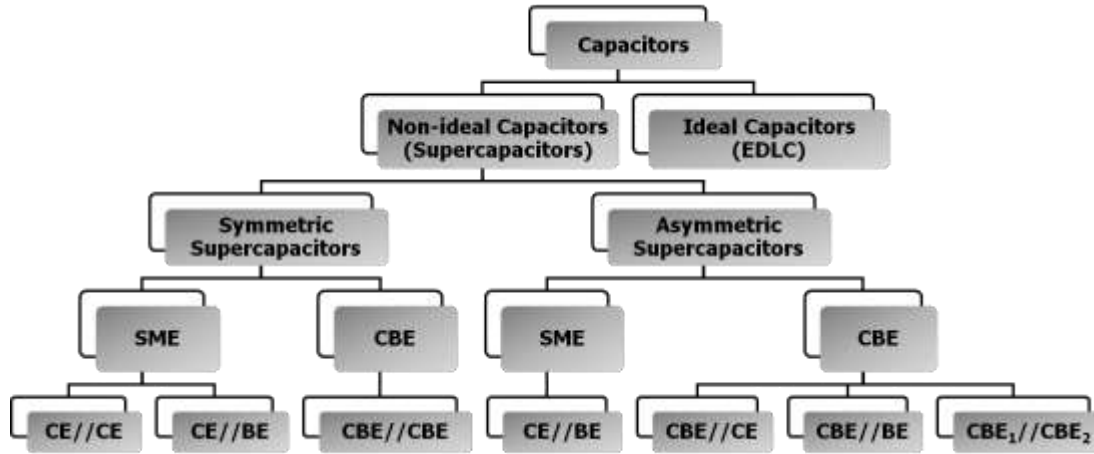


**Figure 7.1 :** Schematic representation of the types of supercapacitors based on the electrodes' type and combinations.

Regarding the electrode materials, supercapacitors use activated carbonaceous materials with well-defined high surface area, pore size and distribution such as, porous carbon nanostructures, templated carbons, carbon aerogels, carbon nanofibers, carbon nanotubes or graphene [17], [20]. While these carbonaceous structures give the non-faradaic character, pseudocapacitive behavior can be achieved by composite structures which despite carbon include conductive polymers, metal oxides or heterotopic dopants as active redox materials. Some of the active materials that have shown promising results due to their battery and/or pseudocapacitive character are tin (Sn) [333], [334], manganese (Mn) [335], [336], molybdenum disulphide/oxides ( $\text{MoS}_2/\text{MoO}_x$ ) [337], [338], or Prussian blue [339], [340]. Mn-based materials are among the most widely investigated as both battery and capacitive electrodes due to their capability not only for redox reactions but also for the ability of some  $\text{MnO}_x$  structures for fast faradaic reactions [336]. Sn based electrodes are well known for their redox reactions with either Li or Na ions [341], however their application as supercapacitor electrodes is barely investigated. Studies reporting the potential application of Sn-based electrodes in supercapacitor cells emphasize their porosity as a crucial factor for high performance [334]. On the other hand,  $\text{MoS}_2/\text{MoO}_x$  with its 2D structure is known for providing stable cycling of batteries and also supercapacitors [338]. While, Prussian blue analogues with their specific octahedral structure offer high capacitance and cycling stability [340]. Despite, all these active materials can be embedded into a wide range of electrode structures. Among them, nanofibers with their 1D structure enable shorter ion diffusion lengths and improved surface area [79]. In the case of carbon nanofibers

(CNF) can also improve the electrical conductivity of the electrode. CNF can also be doped or coated with wide range of pseudocapacitive or redox materials that improve the electrochemical performances of the devices [342], [343], [344]. Moreover, nanofibers can be obtained by methods, suitable for industrial production [200], [240].

The electrolyte, as an ion source in supercapacitors may be aqueous or organic solutions or ionic liquids as electrolytes [17], [271]. Among them, aqueous electrolytes have the advantage of being more cost effective, non-toxic, and easy to deal with, since they are not flammable and thus do not require special environment for handling. However, aqueous electrolytes have narrow potential interval that limits the electrochemical performances of the cell. In order to overcome this shortage active materials that can move the thermodynamic potential limits for oxygen and hydrogen evolution can be used as electrodes [199].

In that regard, this chapter explains the production of several doped CNF mats using precursor salt or nanoparticles as doping agents. The effect of doping agent used on the CNF structure is investigated. Furthermore, the electrochemical properties of such doped CNF electrodes in aqueous KOH electrolyte are analyzed. The behavior and performances of the electrodes in symmetric and asymmetric supercapacitor cell are also analyzed and discussed.

## **7.2 Experimental**

### **7.2.1 Materials and Methods**

Polyacrylonitrile (PAN, homopolymer, Mw 225 000) supplied by AKSA and N, N-Dimethylformamide (DMF, ACS Reagent, Merck) were used as polymer precursor and solvent, respectively. Tin (IV) chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 98%, Sigma Aldrich), Manganese (II) acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2$ , 98%, Sigma Aldrich), Tin nanoparticles (Sn, 50 nm, Sat Nano, China), Molybdenum disulfide nanoparticles ( $\text{MoS}_2$ , 200 nm, Sat Nano, China) and Prussian blue nanoparticles (PB, 250÷700 nm, Altris, Sweden) were used as doping materials.

All spinning solutions were prepared using 8 wt% polymer solution into which doping materials were added. The amount of doping material added for each different solution was calculated based on the weight of PAN polymer into the

solution, and is given in Table 7.1. Polymer solution with 8 wt% PAN was prepared by dissolving PAN into DMF at 60 °C for 5 h, then the corresponding amount of doping material was added into the dissolved solution and stirred at 30 °C for 12 h in order to achieve homogeneous solutions. All solutions were spun immediately. Lab-scale solution blowing device was used to produce the fibers, using the following spinning parameters: 10÷15 ml/h flow rate, 2÷2.5 bar air pressure, and 55 cm nozzle-to-collector distance. As spun fibers were stabilized under oxygen atmosphere at 250 °C for 2.5 h, and then carbonized at 900 °C for 1h in argon atmosphere (heating rate 3 °C/min). Prior to carbonization all samples were pressed with hydraulic press under pressure of 16 MPa in order to reduce the fiber-to-void ratio.

**Table 7.1 :** Amount of doping material into 8 wt% PAN solution.

| <b>Solution</b>        | <b>Doping material</b>                                                                 |
|------------------------|----------------------------------------------------------------------------------------|
| SnCl <sub>4</sub> /PAN | 5 wt% SnCl <sub>4</sub> ·5H <sub>2</sub> O                                             |
| MnAc/PAN               | 5 wt% Mn(CH <sub>3</sub> COO) <sub>2</sub>                                             |
| SnMo/PAN               | 20 wt% Sn and MoS <sub>2</sub> nanoparticles<br>(Sn:MoS <sub>2</sub> 1:1 weight ratio) |
| PB/PAN                 | 5 wt% Prussian blue nanoparticles                                                      |

## 7.2.2 Characterization

The morphology and structural changes of the samples were characterized by Scanning Electron Microscope (SEM, Vega3 Tescan). Average fiber diameter was measured from ten SEM images (magnification 5000x) taken at different points of each sample, by making a total of 100 fiber diameter measurements. The chemical structure of as-spun, stabilized and carbonized samples was analyzed through Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 70 Spectrometer), Raman spectroscopy (Thermo Scientific DXR instrument under 532 nm laser excitation) and X-ray diffraction analysis (XRD, Bruker D2 PHASER).

Deconvolution of XRD was performed by fitting the XRD curve was fitted to three Gaussian peaks using Origin software [352]. The  $2\theta$  position and width at half maximum obtained from the fitted curves were used to calculate the interlayer spacing ( $d$ ) and crystallite size ( $L$ ) according to Bragg's  $d = \frac{\lambda}{2 \cdot \sin \theta}$  and Scherrer's  $L = \frac{k \cdot \lambda}{\beta \cdot \sin \theta}$  equations [345] where,  $\lambda$  (1.54184 Å) is x-ray wavelength,  $\theta$  is the

scattering angle in radians,  $\beta$  is full width at half maximum,  $k$  is a fitting pre-factor ( $k=0.94$ ) [186].

Raman spectra was fitted to five curves with Voigt profile until converged fit, using Origin software [346], [303]. The integrated area ( $A$ ) under the curves was used to calculate the degree of disorder ( $R$ ), degree of amorphous carbon fractions ( $R_3$ ), percent of graphitic domains ( $X_G$ ) and the in-plane crystal size ( $La$ ) with the formulas:  $R = \frac{A_{D1}}{A_G}$ ,  $R_3 = \frac{A_{D3}}{A_G}$ ,  $X_G = \frac{1}{1+R}$  and  $La = \frac{4.4}{R}$  [183], [184], [347]; where:  $A_G$  is the area under the peak at  $\sim 1620 \text{ cm}^{-1}$ ,  $D_1$  is the area under the peak at  $\sim 1330 \text{ cm}^{-1}$ , and  $D_3$  is the area under the peak at  $\sim 1500 \text{ cm}^{-1}$ .

### 7.2.3 Electrochemical set-up and characterization

The fibrous electrodes were prepared by cutting the CNF produced into circular free standing electrodes with diameter of 10 mm. Electrochemical properties of individual electrode were firstly tested in a 3-electrode set-up, where CNF were working electrodes, while Ag and Pt were used as reference and counter electrodes, respectively. Electrochemical properties of a device were tested by assembling symmetric and asymmetric supercapacitor cells (CR2032). Supercapacitor cells were prepared with aqueous 6M KOH solution as electrolyte. Glass fiber membrane was used as separator (Whatman, GF/A). Before assembly, the separator was soaked into electrolyte solution for 12h. The cells were assembled with balanced mass ratio of positive and negative electrodes and without a current collector. Cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic cycling tests were used to determine the electrochemical properties of the fibrous electrodes on Potentiostat/Galvanostat Gamry and MTI battery analyzer. Cycling voltammetry was performed at scan rates of  $2 \div 100 \text{ mV/s}$  on Potentiostat/Galvanostat Gamry. Potentiostatic electrochemical impedance was performed at frequency range from 10 mHz to 1 MHz and an AC amplitude of 5 mV. Capacity ( $C$  in mAh/g or mAh/cm<sup>2</sup>) was calculated using the formula  $C = \frac{I \cdot dt}{dU} \cdot \frac{1}{X_t}$ ; where,  $I$  [A] is applied discharge current;  $dt$  [sec] is discharge time;  $dU$  [V] is the cell potential corrected from the ohmic drop;  $X_t$  is the area [cm<sup>2</sup>] or the mass [g] of both electrodes in the cell. Energy ( $E$  in Wh/kg<sub>electrode</sub> or Wh/L<sub>device</sub>) and power ( $P$  in kW/kg<sub>electrode</sub> or kW/L<sub>device</sub>) values were calculated using the data obtained from the EIS measurements of each cell, with the formulas [247], [248]:

$$E_{electrodes} = \frac{C \cdot U^2}{2 \cdot 3600 \cdot m_t}$$

$$P_{electrodes} = \frac{U^2}{4 \cdot Z \cdot m_t}$$

$$E_{Vdevice} = f \cdot E_{Velectrodes}$$

$$P_{device} = \frac{3600 \cdot E_{Vdevice}}{t}$$

where:  $C$  [F] is the capacity of the cell;  $U$  [V] is the cell potential corrected from the ohmic drop;  $Z$  [ohm] is the impedance of the cell;  $m_t$  is the mass [g] of both electrodes in the cell;  $f$  is the volume fraction of the two electrodes within the cell.

## 7.3 Results and Discussion

### 7.3.1 Morphology and structure

Fiber morphology and surface characteristics were analyzed through SEM images (Figure 7.2). Similarly, to neat PAN nanofibers, all as-spun doped PAN nanofibers also had rugged-like surface. However, after carbonization, only the surface of Sn CNF and SnMo CNF smoothened significantly, but not completely, which is unlike neat CNF. PB CNF showed rougher surface. It was even more emphasized on Mn CNF where voids-like surface was noticed. This can be attributed to decomposition of the acetate part (from Mn precursor) during carbonization, which can also contribute to an increment of the porosity of the fibers [348].

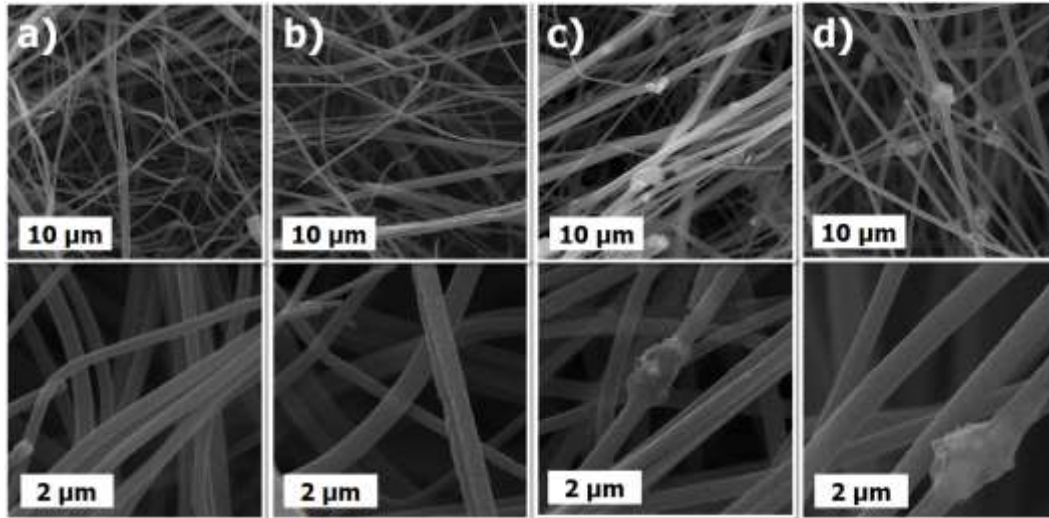


**Figure 7.2 :** SEM images of doped CNF: a) Sn CNF, b) Mn CNF, c) SnMo CNF and d) PB CNF.

In terms of fiber diameter, as-spun Sn and Mn based fibers showed slightly lower values to that of neat PAN,  $517 \pm 182$  and  $516 \pm 166$  nm, respectively (SEM images of all as-spun and stabilized samples are given in Appendix C (Figure C.1 and Figure C.2)). The lowest average fiber diameter was measured for as-spun SnMo ( $478 \pm 172$ )

and the thickest for as-spun PB ( $659 \pm 114$ ). After carbonization, the diameter of decreased to  $317 (\pm 59)$  nm,  $347 (\pm 73)$  nm,  $377 (\pm 87)$  nm and  $520 (\pm 105)$  nm for Sn, Mn, SnMo and PB, respectively. Sn, MoS<sub>2</sub> and PB particles protruding from the fibers are also spotted on the SEM images of SnMo CNF (Figure 7.2-c) and PB CNF (Figure 7.2-d).

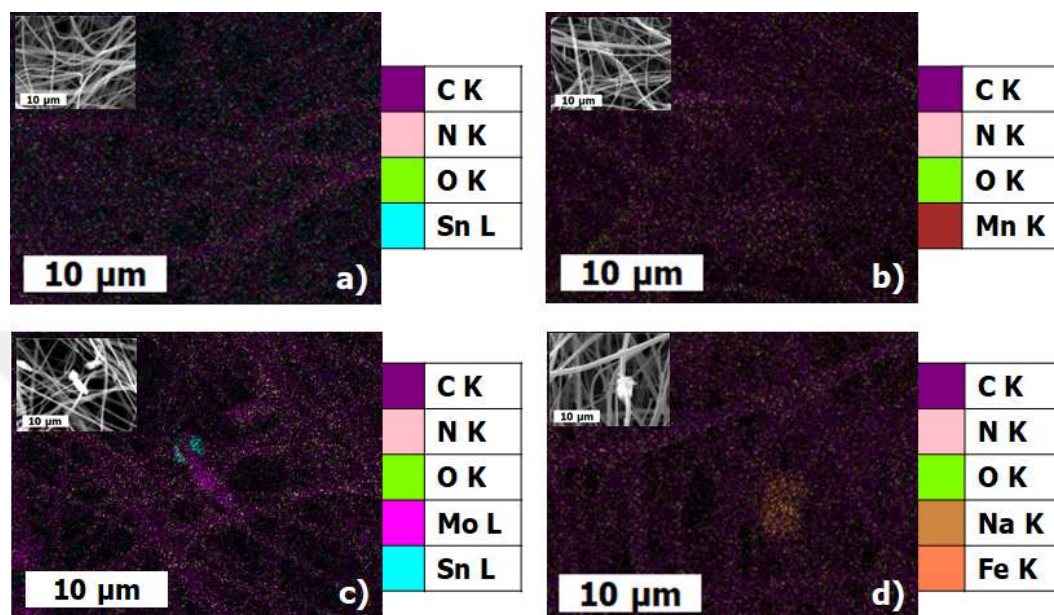


**Figure 7.3 :** EDAX mapping of a) Sn CNF, b) Mn CNF, c) SnMo CNF and d) PB CNF.

In order to confirm the presence of doping elements elemental analysis was performed. EDAX mapping images of all doped CNF are given in Figure 7.3. The weight percent of C decreased by almost 10 % for Sn, Mn and PB CNF, and by 30 % for SnMo CNF. In the case of Sn and Mn CNF, the decrease of C was due to addition of Sn (11 %) and Mn (12 %), respectively. Here, an increment of O level (from 4 % for neat to 6 % for Sn and Mn CNF) was also noticed which can be attributed to the presence of hydrated SnCl<sub>4</sub> and Mn-acetate in the precursor fiber, which promote oxidation reactions during stabilization and carbonization [349], [348]. No change in O level was noticed in PB CNF, but yes presence of Fe and Na, which are constituent elements of Prussian blue ( $\text{Na}_x\text{Fe}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ;  $x \approx 1$ ) nanoparticles. Similarly, for SnMo CNF, presence of Sn (8.5 %), Mo (12 %) and S (12.5 %) were noticed as a result of the addition of Sn and MoS<sub>2</sub> nanoparticles, without change of O nor N level. To better understand the effect of addition of doping agents/particles into the CNF structure FTIR, Raman and XRD analysis were performed.

FTIR spectra of as-spun nanofibers (Figure 7.4-a) showed typical nitrile ( $\text{-C}\equiv\text{N}$ ) peak at  $2244\text{ cm}^{-1}$  for all samples [327], [350], [351], [352]. Besides, there is also a peak at about  $2925\text{ cm}^{-1}$  with a shoulder at  $2860\text{ cm}^{-1}$  indicating C-H stretching and aldehyde CH groups [327], [350], which is more emphasized in the Mn PAN sample due to the presence of acetate from the Mn-precursor and explain the increase of oxygen amount into the carbonized structure. Presence of mixed C=C and C=N groups ( $1622\text{ cm}^{-1}$ ) and  $\delta\text{CH}_2$  bending ( $1450\text{ cm}^{-1}$ ) was registered in all samples [350], [351], [352], except for SnMo PAN sample where the presence of mixed C=C and C=N, together with amines was more emphasized by the board peak at  $1583\text{ cm}^{-1}$  [351]. On the hand, primer amines  $\text{-CH}_2\text{NH}$  in PAN, Sn PAN and Mn PAN were detected at  $1070\text{ cm}^{-1}$  and at  $1091\text{ cm}^{-1}$  for PB PAN [327]. PAN nanofibers with Sn components, either  $\text{SnCl}_4$  or Sn nanoparticles, showed presence of conjugated C=C bonds.

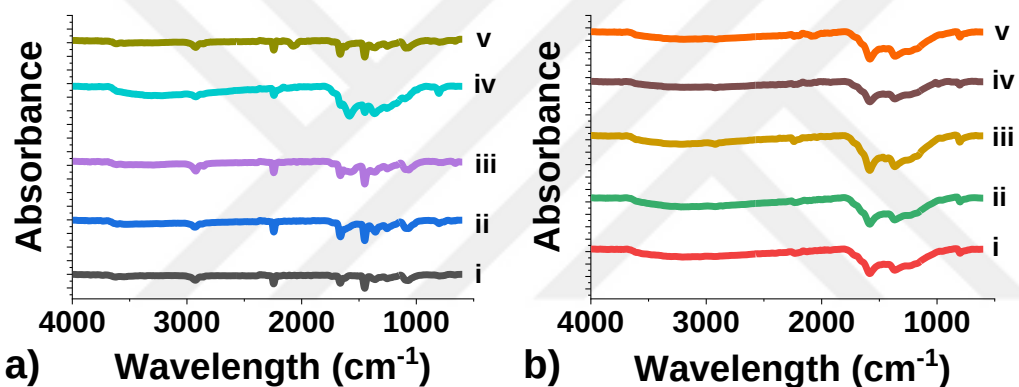


**Figure 7.4 :** FTIR spectra of a) as-spun and b) stabilized doped PAN nanofibers. [i. PAN , ii. Sn PAN, iii. Mn PAN, iv. SnMo PAN, v. PB PAN].

All stabilized PAN nanofibers (Figure 7.4-b) were mainly characterized with conjugated C=C ( $1583\text{ cm}^{-1}$ ) and  $\delta\text{CH}_2$  bending ( $1366\text{ cm}^{-1}$ ) in cyclized structure, as well as out-of-plane aromatic CH groups ( $802\text{ cm}^{-1}$ ) [350], [351], [352], [353]. Broad shoulder at  $1248\text{ cm}^{-1}$  indicating presence of mixed C-C and N-H groups was noticed for Sn, Mn and PB sPAN samples [351] which suggests they accelerate the cyclization process [354]. It was also noted in SnMo sPAN but with lower intensity. This effect of the different doping agents should further affect the structure of the carbonized fibers, and will be discuss later. Due to the limited minimum wavelength, the presence of Sn, Mn and Mo was not possible to be confirmed, however the ferricyanide ( $\text{Fe}(\text{CN})_6$ ) complex from Prussian blue particles was confirmed by the peak at  $2072\text{ cm}^{-1}$  before and at  $2089\text{ cm}^{-1}$  after stabilization [327].

Raman analysis (Figure 7.5-a) was used to investigate the structural order into the carbonized samples. Compared to neat CNF, doped samples showed higher degree of graphitic order (Table 7.2). Among them, PB CNF with R value of 1.37 and crystal length La of 3.2 nm has the most ordered carbonaceous structure and the lowest degree of organic functional groups and amorphous c-fractions ( $R_3 = 0.754$ ). It is followed by Sn CNF ( $R = 1.76$ ,  $La = 2.5$  nm and  $R_3 = 1.161$ ) and Mn CNF ( $R = 2.49$ ,  $La = 1.8$  nm,  $R_3 = 1.530$ ). The increased crystal size, compared to that of neat CNF ( $La = 0.85$  nm,  $R = 5.16$ ) indicates that the addition of  $SnCl_4$  and  $MnAc$ , as well as PB nanoparticles positively influence the cyclization of PAN chains during stabilization, as explained earlier with FTIR. On the other hand, SnMo CNF exhibited the most disordered carbonaceous structure with high degree of amorphous carbon fractions ( $R = 4.52$ ,  $La = 0.97$  nm,  $R_3 = 2.747$ ), meaning that Sn and  $MoS_2$  nanoparticles did not contributed to the organization of the structure during the stabilization process, neither they acted as nucleation centers during the carbonization step.

**Table 7.2 :** Raman and XRD values for doped CNF.

|          | <b>R</b> | <b>R<sub>3</sub></b> | <b>X<sub>G</sub></b> | <b>La</b> | <b>Lc<sub>002</sub> [nm]</b> | <b>d<sub>002</sub> [nm]</b> | <b>d<sub>100</sub> [nm]</b> |
|----------|----------|----------------------|----------------------|-----------|------------------------------|-----------------------------|-----------------------------|
| CNF      | 5.1632   | 1.793                | 0.1623               | 0.8522    | 0.9565                       | 0.3629                      | 0.2073                      |
| Sn CNF   | 1.7576   | 1.161                | 0.3626               | 2.5035    | 0.9809                       | 0.3549                      | 0.2024                      |
| Mn CNF   | 2.4864   | 1.530                | 0.2868               | 1.7696    | 0.9303                       | 0.3593                      | 0.2053                      |
| SnMo CNF | 4.5181   | 2.747                | 0.1812               | 0.9739    | /                            | /                           | /                           |
| PB CNF   | 1.3731   | 0.754                | 0.4214               | 3.2045    | 0.9838                       | 0.3619                      | 0.2055                      |

XRD analysis (Figure 7.5-b) of the samples gave typical carbon-curves for Sn, Mn and PB CNF, with  $2\Theta$  peak at about  $24.8^\circ$  with 002 plane, which explains the thickness of the graphitic domains [345]. The calculated domain thickness (Lc) was 0.981, 0.930 and 0.984 nm for Sn, Mn and PB CNF, respectively. While the distance ( $d_{002}$ ) between the graphene layers was 0.355, 0.359 and 0.362 nm. Another broad peak with low intensity at  $2\Theta$  above  $44.1^\circ$ , which characterizes turbostratic graphic structure, was also registered for these three samples. This indicates that doped CNF have structure with small few-layered graphitic domains, characteristic for disordered carbonaceous structure. On the other hand, on the curve of SnMo CNF, these carbon peaks were overlapped with Sn and  $MoS_2$  peaks, making the curve unsuitable for deconvolution. Despite the C/peak at  $2\Theta = 24.1^\circ$ , it showed peaks

indicating MoS<sub>2</sub> (14.7, 39.9 and 4.3 °), MoO<sub>x</sub> (26.5, 36.2 °) and Sn (30.8, 32.1, 45.1 and 64.6 °), which confirms the presence of Sn and Mo into the carbonized structure. The similar values for graphitic domain thickness with that of neat CNF indicates that doping agents - either salts or nanoparticles, does not affect the stacking of graphene layers during carbonization. However, Raman analysis shows that doping agent indeed affect the length of these graphitic domains and thus improve their order into the fibers.

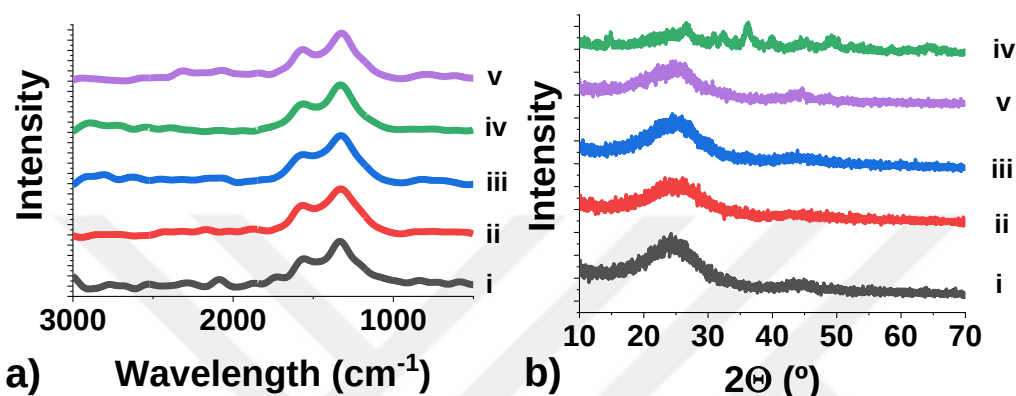


**Figure 7.5 :** a) Raman and b) XRD spectra of doped CNF. [i. PAN, ii. Sn PAN, iii. Mn PAN, iv. SnMo PAN, v. PB PAN].

### 7.3.2 Electrochemical properties of single doped CNF electrodes

Maximum operating voltage window of doped CNF was determined by cyclic voltammetry in 3-electrode set-up using the CNF sandwiched between two stainless steel foils as working electrode, silver wire as pseudo-reference and platinum plate as counter electrodes, respectively. Aqueous 6M KOH solution was used as electrolyte. The overpotentials for oxygen and hydrogen evolution were determined as potentials at which sudden current leap starts to appear on the cyclic voltammogram (CV), as explained in the Chapter 6. For that purpose, cyclic voltammograms were taken at different positive and negative cut-off potentials at scan rate of 10 mV/s. CV graphs showing positive and negative voltage-opening for each of the four doped CNF are given in Appendix C, Figure C.3. The optimal voltage window shrank slightly for Sn and Mn CNF (in the range between  $-0.8 \div 0.5$  V vs Ag,  $\Delta V=1.3$  V) than neat CNF ( $-1 \div 0.4$  V vs Ag,  $\Delta V=1.4$  V). It was more negative for SnMo CNF ( $-1.2 \div 0$  V vs Ag,  $\Delta V=1.2$  V) and slightly wider for PB CNF ( $-1 \div 0.5$  V vs Ag,  $\Delta V=1.5$  V). Figure 7.6 shows CV at optimal voltage window taken at different scan rates. The shape of the CV-curves was quasi-rectangular indicates pseudocapacitive behavior of doped CNF. The absence of redox peaks can be attributed to the dominance of the

pseudocapacitive carbon matrix within the CNF structure. An exception is PB CNF (Figure 7.6-d), whose CV curves did show low intensity peaks at low scan rates. The active material into the CNF structure act as catalyst to the evolution of carbonaceous structure, which later affects the potential limits for oxygen and hydrogen evolution, without being involved into redox reactions with the ions from the electrolyte.

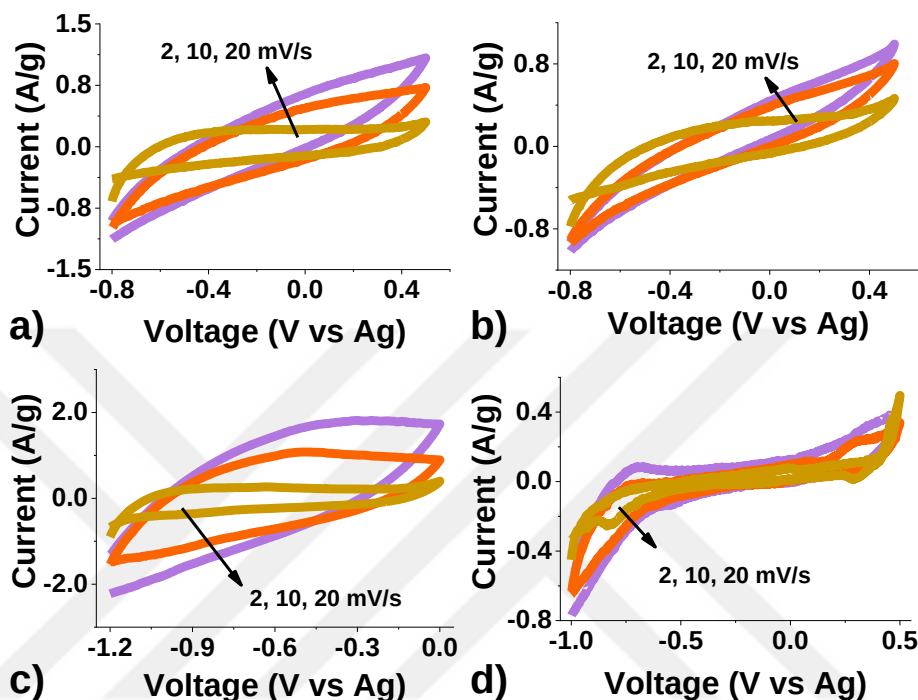


**Figure 7.6 :** Cyclic voltammograms at the optimal voltage window at different scan rates: a) Sn CNF (-0.8 ÷ 0.5 V vs Ag), b) Mn CNF (-0.8 ÷ 0.5 V vs Ag), c) SnMo CNF (-1.2 ÷ 0 V vs Ag) and d) PB CNF (-1 ÷ 0.5 V vs Ag).

The estimated capacity of each of the doped CNF electrodes at different scan rates is given in Table 7.3. In comparison to neat CNF, composite CNF containing Sn and Mn compounds and SnMo nanoparticles provide higher capacity at very low scan rates. However, as the scan rate increases their capacity drops, which is typical behavior for battery-like materials. Among the three, SnMo CNF shows higher capacity retention at high scan rates which can be attributed to its structural organization. As discussed earlier, SnMo CNF has the most alike disorganized carbonaceous structure to that of neat CNF, in terms of graphitic domain length ( $L_a$ ), percent of graphitic domains ( $X_G$ ) and degree of organization ( $R$ ), therefore its rate capability is comparable to that of neat CNF. On the other hand, Sn and Mn CNF, due to their highly ordered structure are more efficient at lower rates. While, PB CNF showed the lowest capacity. Despite the presence of Prussian blue particles, the

highest graphitic order (R), largest graphitic domain ( $L_a$ ) of the carbonaceous matrix does not favor the capacitive charge storage mechanism in aqueous electrolytes.

**Table 7.3 :** Capacity values of doped CNF at different scan rates, calculated from CV measurements.

|                  | CNF     | Sn CNF | Mn CNF | SnMo CNF | PB CNF |
|------------------|---------|--------|--------|----------|--------|
| scan rate [mV/s] | C [Q/g] |        |        |          |        |
| 2                | 127.78  | 134.65 | 117.58 | 172.20   | 33.38  |
| 5                | 93.80   | 87.18  | 61.94  | 133.57   | 18.27  |
| 10               | 80.12   | 45.48  | 28.61  | 108.63   | 13.69  |
| 20               | 74.82   | 26.43  | 14.11  | 78.99    | 10.59  |
| 50               | 53.68   | 8.86   | 4.95   | 31.11    | 7.38   |
| 100              | 29.29   | 4.00   | 2.60   | 12.16    | 5.17   |

The lower capacity of doped CNF implies that doping materials do not have an influence on the capacity of the electrode. However, they did change the potential limits for hydrogen and oxygen evolution. As mentioned before, the potential limit for Sn CNF, Mn CNF and PB CNF moved slightly towards more positive values, while those of SnMo CNF towards more negative values. However, the shift of the potential limits is not as big as expected. It seems that despite the addition of doping elements, the carbon-based structure of the fibers dominates and thus dictates the potential limits.

### 7.3.3 Electrochemical properties of symmetric supercapacitor cells with doped CNF electrodes

After investigating the electrochemical properties of individual doped CNF electrodes, their cycling capabilities were investigated in a 2-electrodes symmetric supercapacitor cells. Symmetric cells were assembled using the same doped CNF as positive and negative electrodes. The cells are denoted as Sn//Sn (for a cell with Sn CNF as positive and negative electrode), Mn//Mn (for a cell with Mn CNF as positive and negative electrode), SnMo//SnMo (for a cell with SnMo CNF as positive and negative electrode) and PB//PB (for a cell with PB CNF as positive and negative electrode). In order to maximize the the potential utilization of the positive and the negative electrodes their mass was balanced [247], [307]. Mass balancing was done using the formula  $\frac{m^+}{m^-} = \frac{E^- - V_{OC}}{E^+ - V_{OC}}$ , where  $m^+$  and  $m^-$  are the mass of the positive and the

negative electrode, respectively;  $E^+$  and  $E^-$  are the positive and negative potential limits of the given doped CNF electrode determined with CV measurements; while  $V_{OC}$  is its open circuit voltage of the electrode. The calculated balanced mass ratios ( $m^+/m^-$ ) were 1.1 for Sn CNF and Mn CNF, 0.8 for SnMo CNF and 1.5 for PB CNF (all values needed for calculation are summarized in Appendix C, Table C.1). The total mass of both electrodes in each cell was kept 25 ( $1\pm$ ) mg/cm<sup>2</sup> and thickness in the range from 250 to 412  $\mu$ m (detailed mass and thickness values of the electrodes used are given in Appendix C, Table C.2). The voltage window determined by each doped CNF electrode was used as maximum operating voltage window of the symmetric cells. So, accordingly Sn//Sn and Mn//Mn were tested in a voltage range from 0 to 1.3 V; SnMo//SnMo from 0 to 1.2 V and PB//PB from 0 to 1.5 V. For comparison, symmetric cell with neat CNF electrodes was also assembled (total electrode mass of 25 mg/cm<sup>2</sup>,  $m^+/m^-=1.5$ ). Taking into account the pseudocapacitive character of all electrodes, all capacity values of the cells are given in mAh/g (taking into account the weight of both electrodes).

Figure 7.7-a) shows the gravimetric capacity of symmetric supercapacitor cells obtained at the 10<sup>th</sup> cycle at current rates from 0.01 to 1 A/g (based on the mass of both electrodes in the cell). Among all cells, maximum capacity in the range from 11.9 to 19.2 mAh/g was calculated for Sn//Sn. It was followed by Mn//Mn (10.5  $\div$  16.4 mAh/g), PB//PB (7.4  $\div$  13.9 mAh/g) and then SnMo//SnMo (8.3  $\div$  11.0 mAh/g). Compared to neat CNF symmetric cell (9.3  $\div$  18.5 mAh/g), all symmetric cells containing doped CNF as electrodes show smaller gravimetric capacity, which was expected taking into account the capacity values obtained from the CV measurements of individual electrodes (Table 7.3). Galvanostatic charge/discharge profiles of each cell at different currents (Figure 7.8 a-d) show symmetric triangular curves indicating reversible capacity at all currents.

Cycling stability (Figure 7.7-b) of the cells was determined by galvanostatic charge/discharge tests at 1 A/g (based on the mass of both electrodes in the cell) for 10000 cycles. Among all cells, Sn//Sn showed the highest capacity loss (-17 %), while Mn//Mn and SnMo//SnMo retained 92 % and 93 % of their initial capacity, respectively. Similarly to CNF//CNF, there is almost no capacity loss for PB//PB. Coulombic efficiency (Figure 7.7-c) of the cells was 99.98 % for Sn//Sn, 100 % for Mn//Mn, 99.95 % for SnMo//SnMo and 98.46 % for PB//PB. Galvanostatic

charge/discharge profiles of the cells before and after the cycling stability tests (Figure 7.8 e÷h) show that the cells keep their capacitive behavior and confirm their capacity retention. Constant ohmic drop through whole cycling life was noted for Mn//Mn, SnMo//SnMo and PB//PB (0.17 V, 0.07 V and 0.40 V, respectively), while an increased ohmic drop for +0.05 V (from 0.18 V at the first to 0.25 V at 10000<sup>th</sup> cycle) was registered for for Sn//Sn.

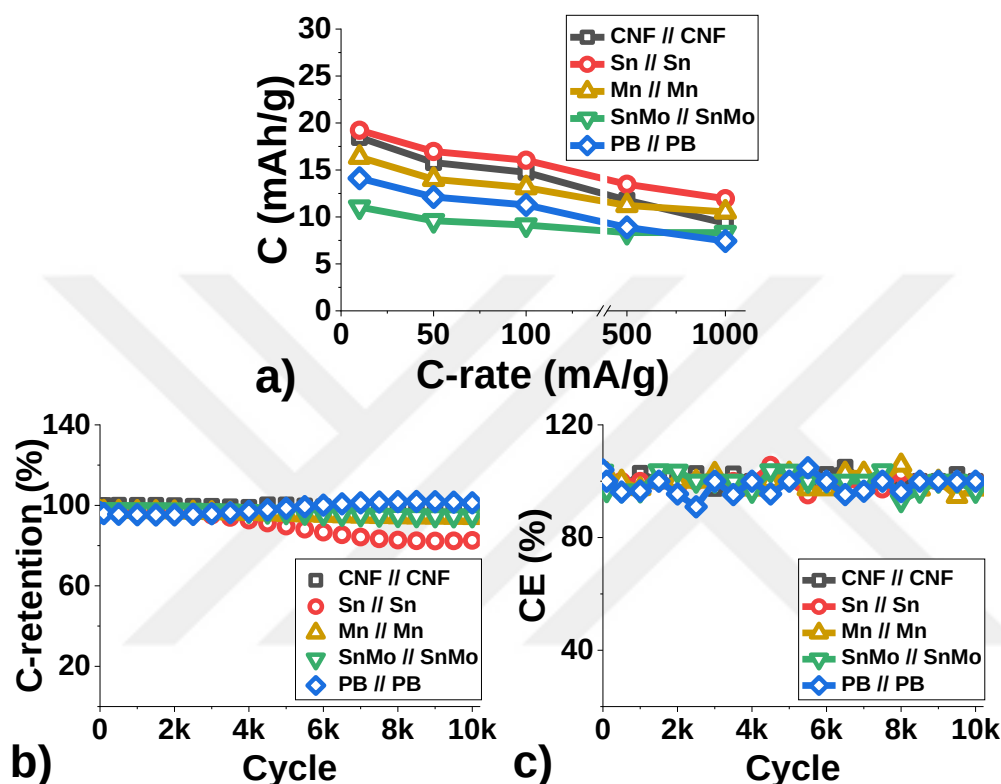


**Figure 7.7 :** a) Gravimetric capacity of symmetric CNF supercapacitor cells at different C-rates; b) Capacity retention and c) Coulombic efficiency of symmetric CNF supercapacitor cells at C-rate of 1 A/g for 10000 cycles.

To further investigate the cycling behavior of the cells CV and EIS analysis were performed on new and cycled cells. CV curves obtained from the cycled cells (Figure 7.9 a÷d) show typical supercapacitor shape similar to that from the new cells, and does not show signs for hydrogen nor oxygen evolution after cycling. The difference is only in the total area occupied by the curves, which is narrower after cycling for all cells and is consistent to the capacity loss registered during the charge/discharge cycling tests.

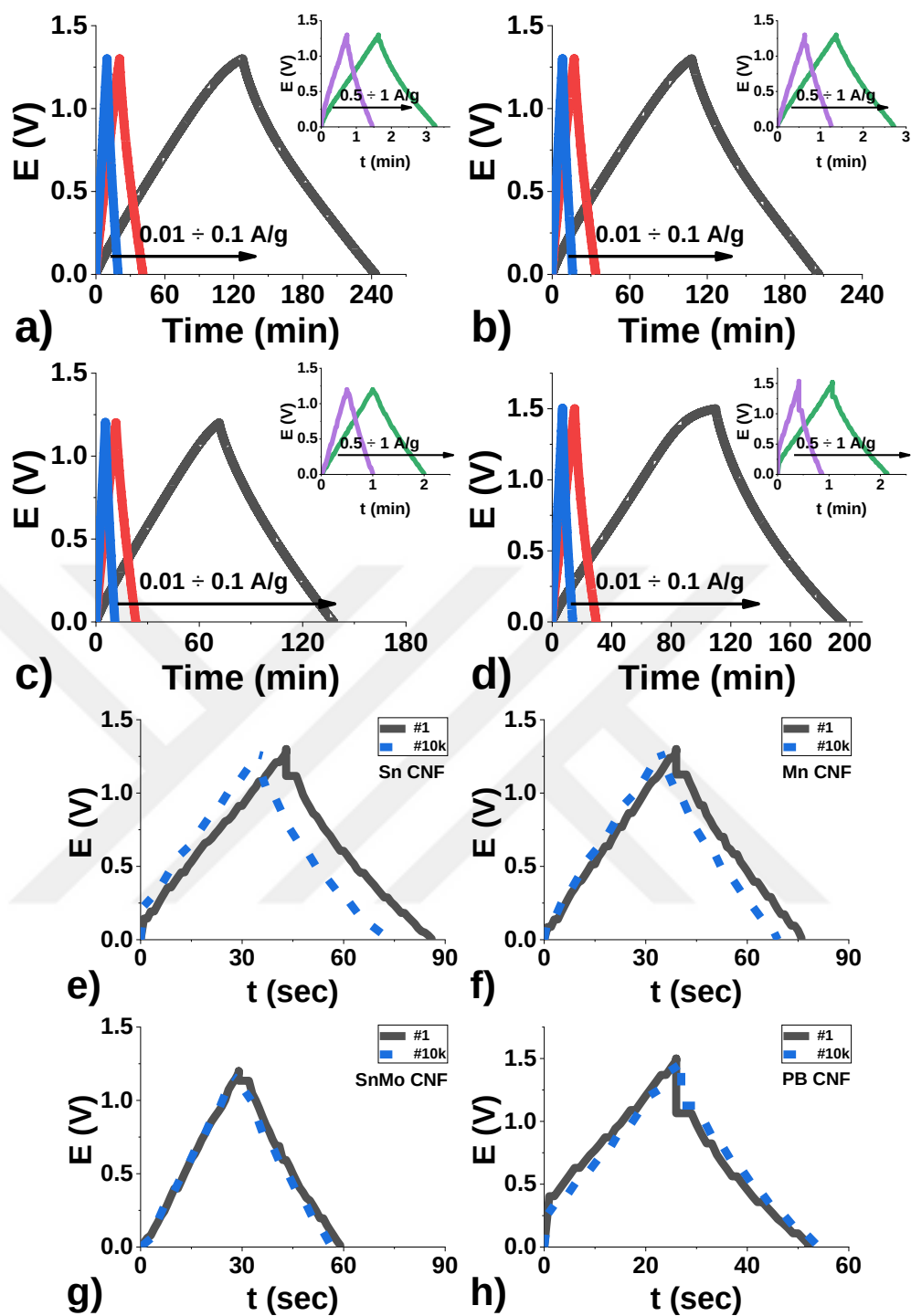


**Figure 7.8 :** Charge-Discharge profiles of symmetric CNF supercapacitor cells a)-d) at different currents, and e)-h) before and after 10000 cycles at 1 A/g. [a) & e) Sn//Sn; b) & f) Mn//Mn; c) & g) SnMo//SnMo; d) & h) PB//PB].

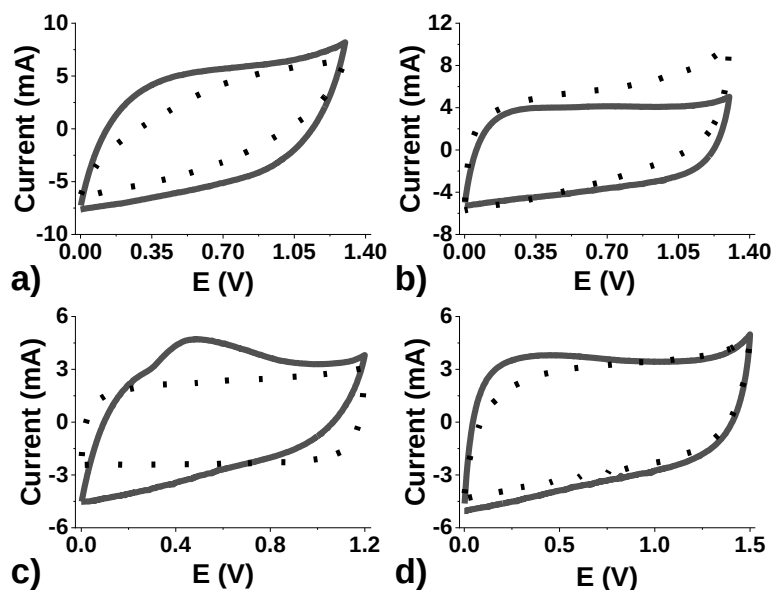


**Figure 7.9 :** a)-d) Cyclic voltammograms of symmetric CNF supercapacitor cells before and cycling after (scan rate: 20 mV/s; full line: before cycling; dashed line: after 10000 cycles at 1 A/g). [a) & e) Sn//Sn; b) & f) Mn//Mn; c) & g) SnMo//SnMo; d) & h) PB//PB].

Complex bode plots, obtained from EIS measurements of new and cycled cells were used to understand the cycling behavior of the cells. Figure 7.10-a) and -b) represent the bode plot -  $C'$  vs frequency - that explain how the ion transport into the electrodes changes with cycling [355]. Low frequency region of the plot for the new cells (Figure 7.10-a) is characterized by plateau for each cell, indicating the whole electrode thickness is accessible for ions. Despite, the areal capacity values calculated here correspond to those obtained from the charge/discharge tests. After cycling (Figure 7.10-b), the length of these plateaus decreases but does not disappears, indicating decreased ion transport through the electrode. On the other hand, the ion diffusivity ( $W_0$ ) values obtained from the fitted Nyquist plots (Figure 7.10 e÷h) suggest that the addition of active materials favors the ionic diffusivity during cycling (Table 7.4). This is especially emphasized in the cells containing SnMo CNF and PB CNF, where the ionic diffusivity increased 7 and 9 times, respectively. Exception for this was the cell with Mn CNF electrodes whose ion diffusivity decreased 7 times. Taking into account the formation of carboxylic acid salts (discussed in Chapter 6) and the assumption that Mn CNF has higher porosity, the decreased ion diffusion in this cell can be attributed to decreased porosity as a result of the layer of carboxylic acid salts deposited on the surface of the Mn CNF. However, post-mortem analysis is required to confirm this hypothesis.

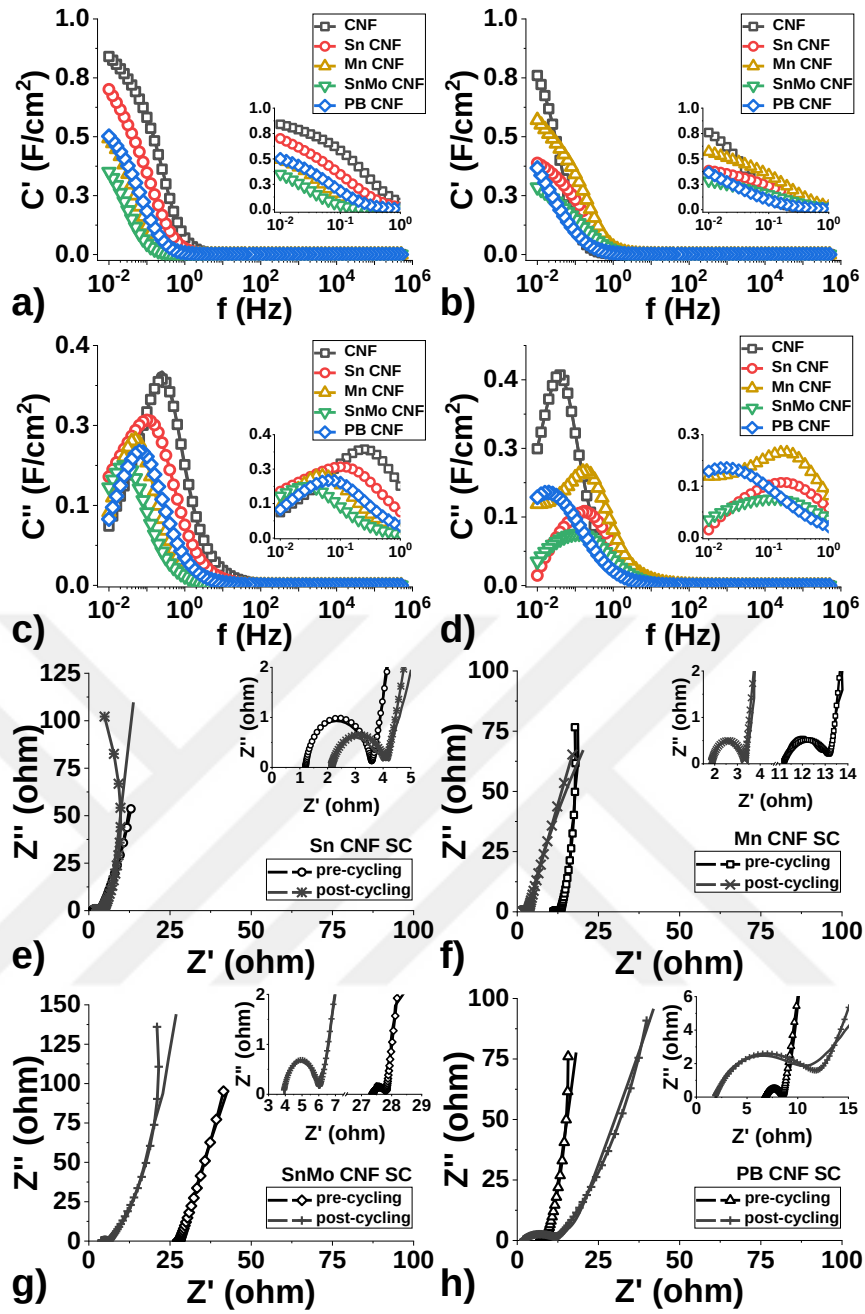


**Figure 7.10 :** Complex Bode plots a)-b)  $C'$  vs frequency, c)-d)  $C''$  vs frequency of symmetric CNF supercapacitor cells (a, c) before and (b, d) cycling after and e)-h) Nyquist plots of symmetric CNF supercapacitor cells before and cycling after. [a) & e) Sn//Sn; b) & f) Mn//Mn; c) & g) SnMo//SnMo; d) & h) PB//PB].

Despite the improved ionic diffusivity, the overall internal resistance ( $R_i = R_s + R_{ct}$ ) of most of the cells also improved after cycling. The main reason for this was the significant decrease of electrolyte resistance ( $R_s$ ) during cycling, which can be attributed to complete penetration of the electrolyte through the whole electrode thickness. This was emphasized for Mn//Mn, SnMo//SnMo and PB//PB. In terms of charge transfer resistance ( $R_{ct}$  in Table 7.4), it seems to be more dependent on the

type of dopant used. Namely, charge transfer resistance of CNF electrodes doped with salts slightly decreased after cycling. It seems that the highly organized carbonaceous structure of these electrodes remains during cycling allowing constant charge transfer. On the other hand, both cells containing electrodes doped with nanoparticles show significant five-folded increment of  $R_{ct}$ . In the case of PB CNF, which according to Raman analysis has highly ordered carbonaceous structure, it was expected to follow the behavior of the Sn CNF and Mn CNF. However, the presence of PB nanoparticles that did not acted as nuclei for formation of larger graphitic domains, can be the reason for discontinued charge transfer and thus higher  $R_{ct}$ . Similarly, the presence of Sn and MoS<sub>2</sub> nanoparticles in SnMo CNF, contribute to the increase of  $R_{ct}$  during cycling, even though here the carbonaceous matrix was the most disordered (Table 7.2).

**Table 7.4 :** Impedance values obtained from EIS measurements before and after cycling of symmetric and asymmetric CNF SCs.

|              | Cell       | $R_s (\Omega \cdot \text{cm}^2)$ | $R_{ct} (\Omega \cdot \text{cm}^2)$ | $W_o (\text{S} \cdot \text{s}^{1/2} \cdot \text{cm}^{-2})$ | $\tau (\text{sec})$ |
|--------------|------------|----------------------------------|-------------------------------------|------------------------------------------------------------|---------------------|
| pre cycling  | CNF//CNF   | 1.72                             | 0.90                                | 0.0121                                                     | 4.000               |
|              | Sn//Sn     | 1.85                             | 3.66                                | 0.0135                                                     | 9.980               |
|              | Mn//Mn     | 17.16                            | 3.26                                | 0.0113                                                     | 19.948              |
|              | SnMo//SnMo | 42.11                            | 0.70                                | 0.0024                                                     | 39.809              |
|              | PB//PB     | 10.43                            | 2.73                                | 0.0154                                                     | 15.830              |
|              | SnMo//CNF  | 12.40                            | 0.75                                | 0.0128                                                     | 19.948              |
| post cycling | CNF//CNF   | 5.01                             | 1.25                                | 0.0109                                                     | 25.1                |
|              | Sn//Sn     | 3.27                             | 3.06                                | 0.0239                                                     | 6.293               |
|              | Mn//Mn     | 2.84                             | 2.29                                | 0.0015                                                     | 6.293               |
|              | SnMo//SnMo | 5.97                             | 3.32                                | 0.0183                                                     | 7.937               |
|              | PB//PB     | 2.79                             | 15.46                               | 0.1395                                                     | 31.616              |
|              | SnMo//CNF  | 1.24                             | 3.3                                 | 0.1822                                                     | 39.809              |

$C''$  vs frequency plot (Figure 7.10 c and d) is another complex bode plot that gives important information about the cell conditions. The time constant ( $\tau$  in Table 7.4), calculated as the period at which maximum imaginary capacity ( $C''$ ) can be achieved, is an indicator for the discharge power of a given cell. It can be seen that all new cells have slow relaxation time, but it decreases significantly during cycling, reaching values comparable to those of active carbon supercapacitors [128], [356].

Exception for this is only PB//PB whose relaxation time increases even more during cycling. The reason behind this will be discussed later.

### 7.3.3.1 Post-mortem Analysis of Doped CNF Electrodes

SEM imaging and FTIR analysis were performed on the cycled electrodes in order to investigate their structural changes after cycling. SEM images (Figure 7.11) show presence of crystal-like structures on both positive and negative cycled electrodes.

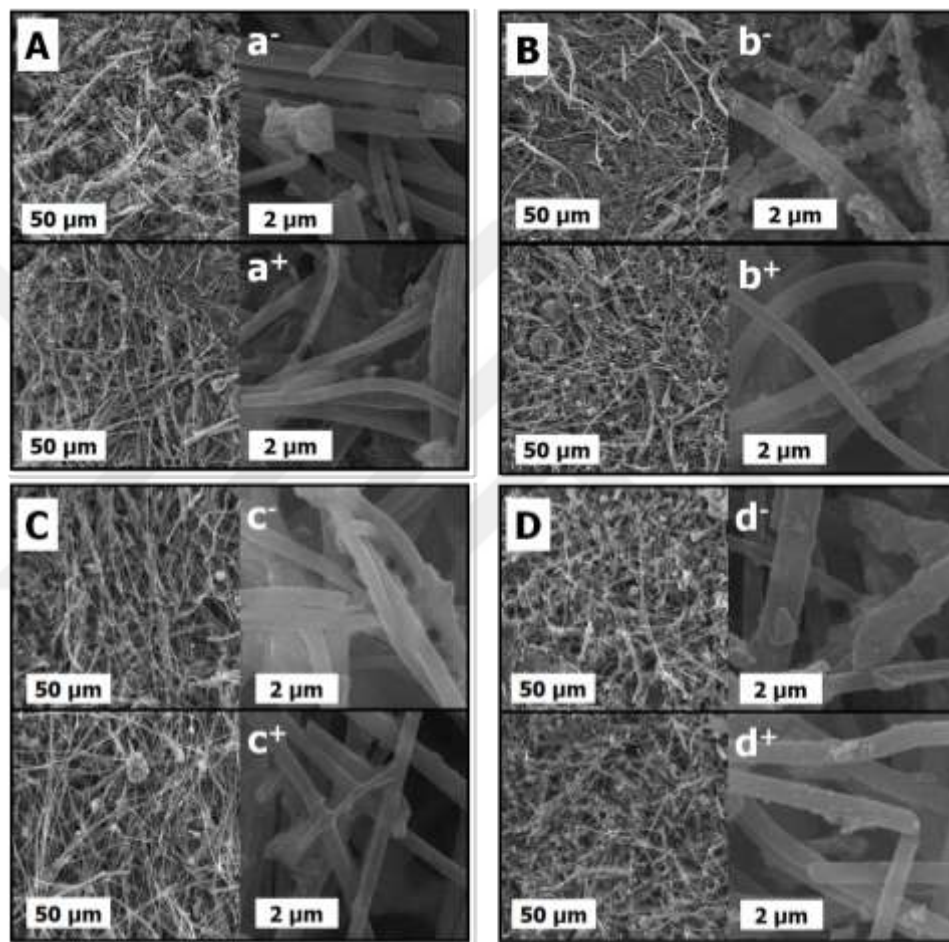


**Figure 7.11** : Post-mortem SEM images of positive (lower row, <sup>+</sup>) and negative (upper row, <sup>-</sup>) A) Sn CNF, B) Mn CNF, C) SnMo CNF and D) PB CNF electrodes.

As discussed in Chapter 6, these structures are results of formation of carboxylic acid salts that form during decomposition reactions between the electrode and the electrolyte. The presence of the side-products was firstly noticed by an increment in the average fiber diameter of the electrodes after cycling. Among all doped CNF, it is the most emphasized in Mn CNF and PB CNF (increment for 130 and 150 nm, respectively), where the diameter increased double than that of Sn CNF and SnMo CNF (+65 nm). The small fiber diameter increase of Sn CNF and SnMo CNF

indicates deposition of thin layer of carboxylic acid salts, which apparently does not affect the ionic diffusion (Table 7.4). Besides, SEM images of post-mortem Sn CNF (Figure 7.11-a) and SnMo CNF (Figure 7.11-c) show smooth fiber surface and isolated crystal-like structures, being less in the later sample. On the other hand, SEM images of post-mortem Mn CNF (Figure 7.11-b) show small crystal-like structures stack on fiber surface, while those of post-mortem PB CNF (Figure 7.11-d) show fibers with larger crystal-like structures stack on their surface. The larger increment of the diameter (measured only on the smooth areas of the fibers) of these doped CNF suggests that besides the crystals, whole fiber surface is covered/deposited with thick layer or carboxylic acid salts.

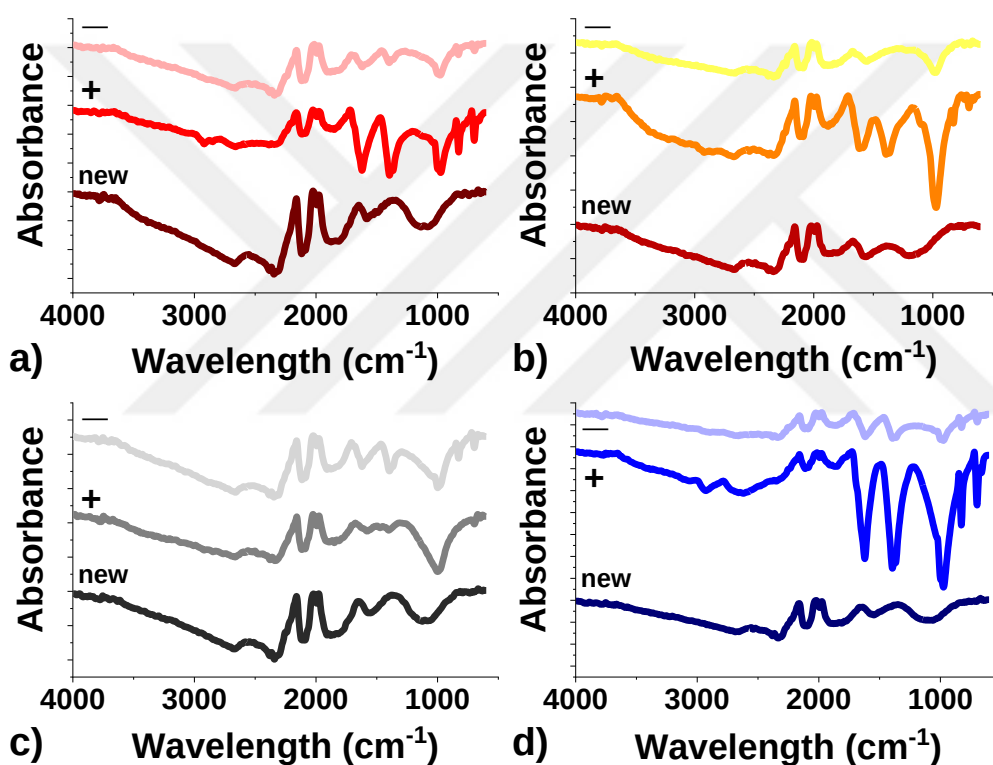


**Figure 7.12** : Post-mortem FTIR analysis of positive and negative a) Sn CNF, b) Mn CNF, c) SnMo CNF and d) PB CNF electrodes.

Post-mortem FTIR analysis (Figure 7.12) of the electrodes revealed that doped CNF tend to prevent, or at least to decrease the formation of carboxylic acid salts, when compared to neat CNF. The peaks at about 1400 and 1615  $\text{cm}^{-1}$ , almost disappeared from the negative doped CNF indicating significantly less formation of carboxylic acid salts on their surface [323], [329]. Additionally, from the three peaks in the region below 1000  $\text{cm}^{-1}$ , only the one at about 960  $\text{cm}^{-1}$  (characteristic for aromatic C-H out-of-plane groups [327]) remained its intensity which indicates there is also

chemisorption and storage of  $H_2$  during cycling [323]. Analyzing each doped CNF individually, it can be noted that SnMo CNF (Figure 7.12-c) is the least affected by the carboxylic acid salts, which coincide with the observations from the post-mortem SEM images. On the opposite side of the list is PB CNF (Figure 7.12-d), which show peaks with highest intensity, similar to those of post-mortem neat CNF – meaning it is the most affected one by the formation of carboxylic acid salts and confirms the increase of the average fiber diameter of this sample. It also explains the doubled time ( $\tau$ ) for relaxation of the cell, but contradicts the increased ion diffusivity (Table 7.4). This can be attributed to the presence of protruding PB particles, which are not affected by the carboxylic layer and thus attract ions and increase their diffusion into the electrode. Similar effect can be attributed to SnMo CNF where Sn and  $MoS_2$  particles, despite the thin crystal layer over the fibers, the particles protruding through them are able to significantly improve the ionic diffusivity and keep it high during cycling. EDAX analysis of the cycled SnMo CNF (Figure 7.13-a) and PB CNF electrodes (Figure 7.13-b) confirmed that the particles are free from the carboxylic layer. Regarding Sn CNF electrode, despite the thin layer on its surface, the side-carboxylic-products are more emphasized as crystal-like structures, therefore it shows stronger carboxylic peaks (Figure 7.12-a). In the case of Mn CNF (Figure 7.12-b), the small crystals stuck on the surface of the fiber block the pores and do not allow new ions to penetrate during cycling and thus its ionic diffusivity decreases significantly. However, it can be assumed that the blocked pores are filled with electrolyte, which even limited allow fast relaxation time and higher power rates during cycling.

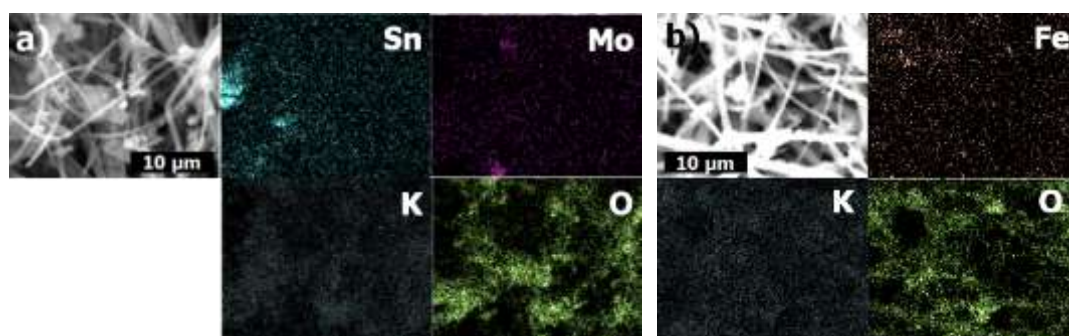


**Figure 7.13 :** EDAX mapping of cycled a) SnMo CNF and b) PB CNF.

### 7.3.4 Electrochemical properties of asymmetric supercapacitor cells with doped CNF electrodes

For formation of asymmetric cell that would maximize the operating potential and use the whole capacity of each individual electrode, electrodes that operate at potentials that does not overlap is preferred [199]. However, the potential limits of all CNF electrodes developed here, ether doped or not, does not differ significantly. The point of the thesis was assembling hybrid cell in which one electrode is neat CNF and the other one doped CNF. Therefore, the second electrode was selected so that maximum working potential and the lowest possible potential overlap can be achieved. Among the doped electrodes, SnMo CNF showed potential limits that in combination with those of neat CNF give the largest voltage window of 1.6 V (Figure 7.14).

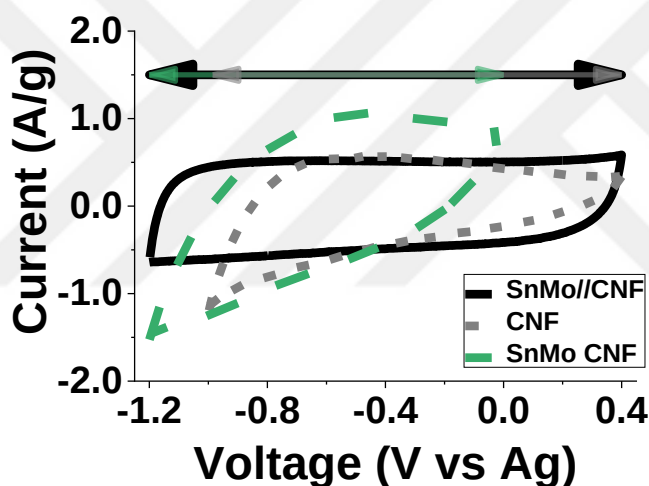


**Figure 7.14 :** Cyclic voltammograms of individual CNF (-1.2 V÷0 V) and SnMo CNF (-1 V÷0.4 V) electrodes and asymmetric SnMo//CNF cell ( $\Delta U = 1.6$  V).

Asymmetric cells were assembled using one SnMo CNF as positive and neat CNF as negative electrode in the supercapacitor cell. In order to maximize the the potential utilization of the positive and the negative electrodes their mass was balanced using the formula  $\frac{m^+}{m^-} = \frac{Q^- \cdot E^-}{Q^+ \cdot E^+}$  [247], [307], where  $m^+$  and  $m^-$  are the mass of the positive and the negative electrode, respectively;  $E$  and  $Q$  are the working potential and capacity of either the positive (+) or the negative (-) electrode determined with CV measurements. The calculated balanced mass ratios ( $m^+/m^-$ ) was 1.3 (all values needed for calculation are summarized in Appendix C, Table C.1). The operating voltage window of the asymmetric cell was determined as a union of the maximum

operation voltage windows of each of the two electrodes within the cells. So, accordingly SnMo//CNF cells were tested in a voltage range from 0 to 1.6 V.

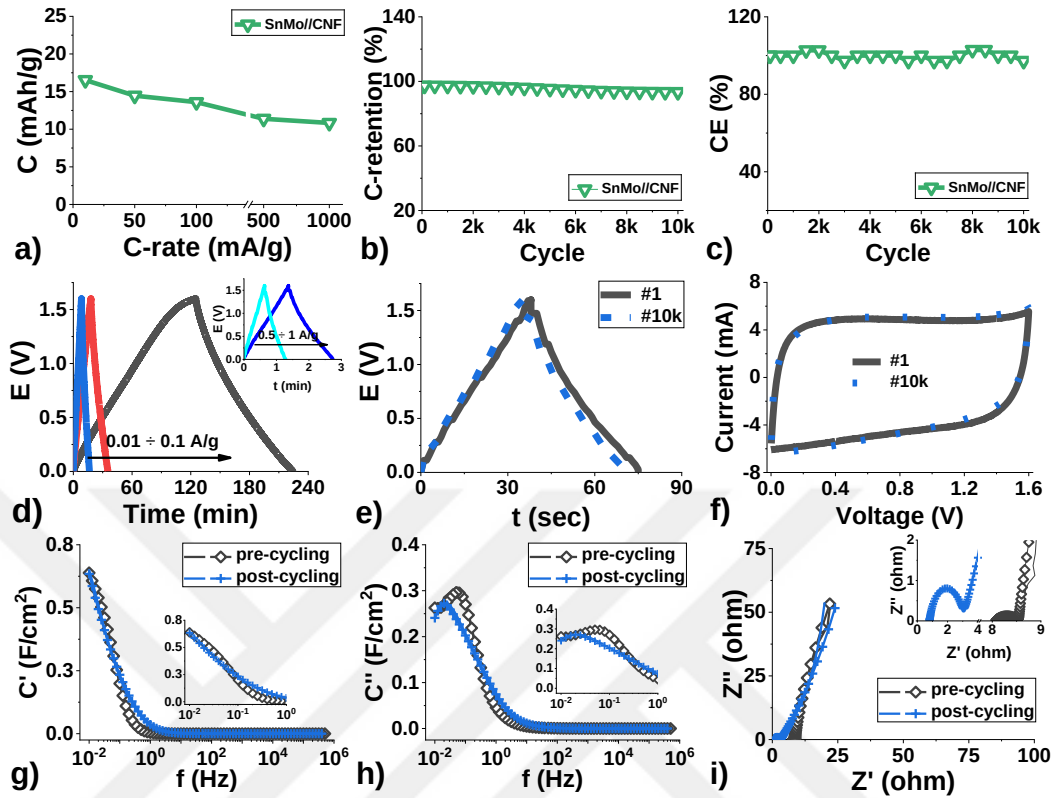


**Figure 7.15 :** a) Gravimetric capacity at different C-rates; c) Capacity retention and d) Coulombic efficiency at C-rate of 1 A/g for 10000 cycles; d)-e) Charge-Discharge profiles of asymmetric CNF supercapacitor cells d) at different currents and e) before (black) and after (blue) 10000 cycles at 1 A/g; f) Cyclic voltammograms; g)-h) Complex Bode plots g)  $C'$  vs frequency, h)  $C''$  vs frequency and i) Nyquist plots of asymmetric SnMo//CNF supercapacitor cells before (black) and after (blue) cycling after.

Rate capability of the asymmetric cell was investigating by cycling it at c.rates from 0.01 to 1 A/g (taking into account the weight of both electrodes) and cut-off voltage from 0 to 1.6 V. Discharge capacity (Figure 7.15-a) from 16.5 mAh/g (at 0.01 A/g) to 10.8 mAh/g (1 A/g) were registered. They correspond to areal capacity from 0.40 to 0.26 mAh/cm<sup>2</sup>. Compared to the symmetric SnMo//SnMo, the asymmetric cell shows better performance, but similar to those of symmetric CNF//CNF. The cell also showed good coulombic efficiency (Figure 7.15-c) of 99.9 % and cycling life (Figure 7.15-b), losing only 7 % of its initial capacity after 10000 cycles at 1 A/g. Ohmic voltage drop of 0.17 V was constant through all 10000 cycles. Charge/discharge profiles show symmetric triangles at each current (Figure 7.15-d)

and also throughout the whole cycling test at 1 A/g (Figure 7.15-e) confirming reversible cycling.

Pseudocapacitive shape of the cyclic voltammograms obtained before and after cycling confirmed the capacitive behavior of the cell throughout the whole cycling life. While the retention of the small plateau on the complex bode plot “C” vs frequency” indicates ion accessibility through the whole electrode thickness even after 10000 cycles. The ionic accessibility is followed by a large ionic diffusivity during cycling (Table 7.4), which can be attributed to the presence of SnMo CNF electrode. As discussed above, SnMo CNF electrode is capable of attracting high amount of ions, so it can also release large amount of ions towards the negative electrode. However, the response time of neat CNF electrode becomes slower during cycling, as a result of formation of crystal-like structure on its surface (discussed in Chapter 6). Therefore, neat CNF electrode defines the relaxation time ( $\tau$ ) of the asymmetric cell. On the other hand, the influence of the positive electrode is also dominant on the internal resistivity of the asymmetric cell, especially on its electrolyte resistivity ( $R_s$ ).

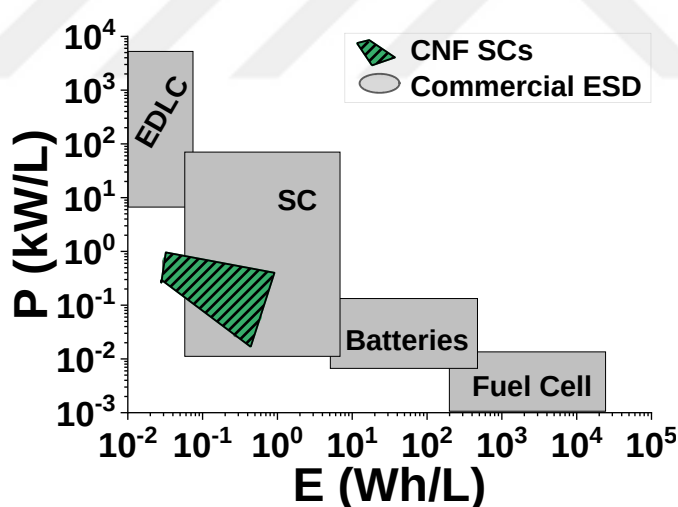


**Figure 7.16 :** Ragone plot of asymmetric CNF supercapacitor cells along with various commercial energy storage devices.

Gravimetric energy and power of the asymmetric cell was calculated based on the total mass of both electrodes in the cell. Asymmetric SnMo//CNF can deliver energy up to 10.6 Wh/kg, Table 7.5 which is higher than that of symmetric CNF//CNF and SnMo//SnMo cells. However, its gravimetric power (1.2÷14.2 kW/kg) is between the two symmetric cells. Moreover, the gravimetric power of SnMo//CNF is comparable to asymmetric cells based on CNF electrodes (Table 7.5), though its gravimetric

energy is low. It was discussed above, that the performances of an asymmetric cell can be maximized when matching electrodes whose potentials does not overlap, which is not the case here. Therefore, the increment of energy and power does not differ significantly compared to those of symmetric cells. Ragone plot (Figure 7.16) of the asymmetric SnMo//CNF cell shows that its volumetric energy and power are in the range of commercial supercapacitors. It is worth mentioning that, commercial supercapacitors have an operating potential of at least 2.3 V due to its organic electrolyte, which is about 50 % higher than that of SnMo//CNF with aqueous KOH electrolyte.

**Table 7.5 :** Characteristics and performances of symmetric and asymmetric CNF-based supercapacitors reported in literature.

| Positive // Negative Electrode [precursor] | Electrolyte                            | Electrode details                           | $\Delta V$ | F/g (C-rate)              | E (Wh/kg)                   | P (kW/kg) | Ref   |
|--------------------------------------------|----------------------------------------|---------------------------------------------|------------|---------------------------|-----------------------------|-----------|-------|
| Fe-CNF (sym)                               | 1M H <sub>2</sub> SO <sub>4</sub>      | /                                           | 1          | 10÷80<br>(10÷0.5 A/g)     | 1÷10                        | 0.1÷10    | [295] |
| CNF (sym) [PAN/PVP]                        | 2M KOH                                 | /                                           | 1.6        | 7÷22<br>(5÷0.5 A/g)       | 7.8÷2                       | 0.4÷4     | [292] |
| MoN-CNF (sym)                              | 1M H <sub>2</sub> SO <sub>4</sub>      | 1 cm <sup>2</sup>                           | 1.3        | 20÷30<br>(5÷0.5 A/g)      | 4.5                         | 0.25      | [311] |
| CNF (sym) [PAN/PMMA]                       | 6M KOH                                 | 2 mg                                        | 1          | 95÷140<br>(50÷0.5 A/g)    | 14÷20                       | 0.2÷40    | [357] |
| Porous CNF (sym) [PAN/ZnCl <sub>2</sub> ]  | 6M KOH                                 | 2.7 mg/cm <sup>2</sup>                      | 1          | 100÷175<br>(60÷1 A/g)     | 5÷7                         | 0.1÷10    | [315] |
| CNF (sym) [Lignin/PEO]                     | 6M KOH                                 | 0.5-1 mg/cm <sup>2</sup>                    | 1.2        | 140÷195<br>(100÷1 A/g)    | 5÷10                        | 0.05÷60   | [358] |
| CNF (sym) [coal/PAN]                       | 6M KOH                                 | 1.5 mg/cm <sup>2</sup>                      | 1          | 103 (100 A/g)             | 2÷4.7                       | 0.25÷9    | [316] |
| AC (sym)                                   | 0.1-1M Na <sub>2</sub> SO <sub>4</sub> | 2.6-3.5 mg/cm <sup>2</sup> ; 50-300 $\mu$ m | 1          | 87÷92.5 F/g <sub>AC</sub> | 5.7÷6.1 Wh/kg <sub>AC</sub> |           | [359] |
| K-MnO-CNF//Activated CNF                   | 0.5M K <sub>2</sub> SO <sub>4</sub>    | 1 cm <sup>2</sup>                           | 1.8        | /                         | 23.5                        | 0.2÷9.5   | [360] |
| Ni-CNF//CNF                                | 4M KOH                                 | /                                           | 1.5        | 15÷80<br>(5÷0.5 A/g)      | 46÷91                       | 1.3÷2.7   | [361] |
| MnO <sub>2</sub> -CNF//Porous CNF          | 1M Na <sub>2</sub> SO <sub>4</sub>     | /                                           | 2          | 32÷65<br>(10÷0.5 A/g)     | 15÷20                       | 0.7÷10    | [362] |
| Bi-N-CNF//S-N-CNF                          | 6M KOH                                 | /                                           | 1.4        | 60÷90<br>(8÷1 A/g)        | 15÷22                       | 0.8÷8     | [363] |
| MOF-PPNF//Ni-PPNE                          | PVA/KOH                                | /                                           | 1.5        | 25÷90<br>(10÷3 A/g)       | 51÷8                        | 7.5÷1.5   | [364] |

**Table 7.5 (continued) :** Characteristics and performances of symmetric and asymmetric CNF-based supercapacitors reported in literature.

| Positive // Negative Electrode [precursor]  | Electrolyte                                                   | Electrode details       | $\Delta V$ | F/g (C-rate)                                                           | E (Wh/kg) | P (kW/kg) | Ref       |
|---------------------------------------------|---------------------------------------------------------------|-------------------------|------------|------------------------------------------------------------------------|-----------|-----------|-----------|
| Ni-Co-S-N-porous CNF//AC-N-porous CNF       | NKK/KOH                                                       | /                       | 1.5        | 30÷70 (1÷0.1 A/g)                                                      | 7÷22      | 0.1÷1.2   | [365]     |
| NiMoO-CNF//AC                               | 3M KOH                                                        | 1.3 mg/cm <sup>2</sup>  | 1.6        | 85÷125 (10÷1 A/g)                                                      | 30÷45     | 0.8÷8     | [296]     |
| NaMnO-CNF // AC                             | 1 M Na <sub>2</sub> SO <sub>4</sub> & 4 mM NaHCO <sub>3</sub> | 1 cm <sup>2</sup>       | 2          | /                                                                      | 10÷21     | 1÷32      | [366]     |
| MoO <sub>2</sub> -MoS <sub>2</sub> -CNF//AC | 6M KOH                                                        | /                       | 1.5        | 147 (3 A/g)                                                            | 46        | 2.25      | [367]     |
| FeCoS-CNF//AC                               | 3M KOH                                                        | /                       | 1.6        | 120÷250 (10÷1A/g)                                                      | 40÷90     | 0.8÷8     | [368]     |
| AC//MnO-CNF                                 | 1M Na <sub>2</sub> SO <sub>4</sub>                            | 2 cm <sup>2</sup>       | 2          | /                                                                      | 11÷36     | 1÷12      | [369]     |
| CNF//CNF [PAN]                              | 6M KOH                                                        | 25 mg/cm <sup>2</sup> ; | 1.4        | 23.8÷47.5 (1÷0.01 A/g <sub>(m<sup>+</sup> &amp; m<sup>-</sup>)</sub> ) | 2÷8.6     | 1÷23.1    | This work |
| SnMo//SnMo [PAN]                            | 6M KOH                                                        | 25 mg/cm <sup>2</sup> ; | 1.2        | 23.6÷32.8 (1÷0.01 A/g <sub>(m<sup>+</sup> &amp; m<sup>-</sup>)</sub> ) | 0.6÷3.4   | 0.4÷7.1   | This work |
| SnMo CNF//CNF [PAN]                         | 6M KOH                                                        | 25 mg/cm <sup>2</sup> ; | 1.6        | 25.5-37.2 (1÷0.01 A/g <sub>(m<sup>+</sup> &amp; m<sup>-</sup>)</sub> ) | 1.2÷10.6  | 1.2÷14.2  | This work |

## 7.4 Conclusion

In this chapter, precursor fibers containing two types of doping agents, precursor salts (SnCl<sub>4</sub> and Mn-acetate) and nanoparticles (Sn, MoS<sub>2</sub>, Prussian blue) were produced via solution blowing method and then carbonized. The effect of doping agent on the structure of the carbonized fibers was investigated via FTIR, Raman and XRD analysis. It was concluded that the type of doping agents has an important role on the organization of the carbonaceous structure and the size of graphitic domains. Precursor salt, as doping agents, significantly improve the structural order of carbonaceous material. In the case of nanoparticles, it depends on their interaction with the polymer chains. The type of nanoparticles, such as PB, that make strong intermolecular bonds with PAN even before stabilization, improves the organization of carbonaceous structure even better than the precursor salts. On the other hand, Sn

and MoS<sub>2</sub> nanoparticles that does not get trapped between the polymer chains by secondary bonds have no significant effect on the carbonaceous structure.

Electrochemical analysis of single doped CNF electrodes, reveals that doping agents does not affect the capacity significantly. The more organized carbonaceous structure dominates over the doping elements and reduces the capacitive behavior of the CNF. However, doping elements does move the potential limits for hydrogen and oxygen evolution in aqueous KOH electrolyte, and thus changes the operating voltage window of the CNF. When used in symmetric supercapacitor cells, doped CNF electrodes does not show significant change in capacity than neat CNF, which was anticipated from their previous analysis. However, most of them do show high cycling stability. EIS analysis of cycled cells reveals that doped CNF have great impact on the ion diffusivity and internal resistance during cycling, which was not the case in neat CNF cells. Post-mortem FTIR analysis showed that doping CNF prevent the formation of carboxylic salts during cycling. This was mostly emphasized for SnMo CNF cell where the particles protruding through the CNF matrix are not affected by the side-carboxylic-products and thus allow high ion diffusion and low internal resistance even after 10000 cycles at 1 A/g.

Taking into account the potential differences between neat CNF and SnMo CNF, asymmetric supercapacitor cell was assembled using these two electrodes. The SnMo//CNF cell, was characterized with high ionic diffusivity and low internal resistance during cycling, which was attributed to the presence of SnMo CNF electrode. Though, its capacity higher than that of symmetric SnMo, and similar to symmetric CNF cell, it showed high cycling stability. Its extended voltage window (1.6 V) resulted in improvement of the specific energy, compared to the symmetric cells. Moreover, the volumetric energy and power of the asymmetric cell is comparable to that of commercial supercapacitors.

In summary, doping materials change the physical-chemical properties of CNF and have an impact on their electrochemical properties. It was shown that selected doping materials do not affect the capacity of individual doped CNF electrodes, however they do changed the operational potential limits. They can be used as electrodes for symmetric and asymmetric supercapacitor cells that deliver power and energy comparable to the commercial supercapacitors. Furthermore, doped CNF also prevent the formation of side-products during cycling. This would have positive

effect on the volumetric performances of supercapacitors containing thick doped CNF as electrodes.



## 8. DISCUSSION, CONCLUSION AND RECOMMENDATIONS

Organic wastes are abundant and with environmentally friendly character under debate, but for sure are renewable energy source. Biomass is also an interesting starting source for obtaining new materials. This is mostly emphasized when producing carbon materials. Among all of it, lignin is second most abundant polymer, which despite its complex extraction, can be found as side products in many industries. Due to its aromatic structure and high carbon content is the perfect candidate to replace the expensive polyacrylonitrile as main carbon precursor. Therefore, lignin was used as main material for the formation of fibrous carbon structures in this thesis. With focus on obtaining porous fibrous materials, in the first part of this thesis, lignin based carbon fibers with submicron diameter were produced via electrospinning technique. The study showed a feasible route to produce carbon fibers with controllable porous structure from natural sources, which can be applied as anodes for Li- and Na-ion batteries. However, the long fiber production process, followed by stabilization step including iodine vapor which interfere with the potential doping materials (deduced from a preliminary study), forced me to find an alternative route towards more practicable production.

Solution blowing as an alternative spinning methods provided faster production rates of large amount fibrous mats containing fibers with diameters of about 500 nm, in most of the cases with optimized polymer solutions. Albeit, the relatively high fiber diameter distribution (SD  $\pm 35$  %) of the fibrous mats obtained can be mentioned as a negative aspect. Spinning rates used with this system were 5 to 7 times higher than those used for the production of lignin based fibers via electrospinning. Besides, the system allows using multi (8) nozzle set up (not used in this thesis) which can speed up the production for at least 2.5 times when compared to commercial nozzle-less electrospinning system.

The use of bio-waste was further investigated, but for development of active carbon particles. In this regard, peanut shell showed to be suitable precursor, which with chemical pretreatment can be easily converted into carbon particles with micro and mesoporous structure and high specific surface area (1167 m<sup>2</sup>/g). Finish processing

step involving ball milling allowed controlling the particle size ( $\sim 580$  nm) and increasing the mesoporous fractions. Such particles resulted suitable for electrochemical energy storage, and were further used for development of specific polymer/particle fibrous structures. This unique architecture consisting of a binder (PVDF) wrapping up large amount of peanut shell-based carbon particles into fibers with diameter of  $708 (\pm 211)$  nm. This type of fibrous materials, scarcely reported in literature, were for first time – to the best of my knowledge – used as electrodes for supercapacitor devices in either aqueous or organic electrolyte. Controlling the thickness of the fibrous electrodes it was possible to achieve areal capacitance of  $1.12 \text{ F/cm}^2$  in aqueous electrolyte. Whilst, optimized peanut shell based carbon-to-commercial carbon particles ratio enabled high cycling stability in both, aqueous and organic systems.

Despite the importance of electrode thickness and/or mass loading on the feasibility of a potential electrode material/structure for its industrial application, limited number of research published pays attention on it. The typical industrial demand for electrodes with mass loading of about  $10 \text{ mg/cm}^2$  (which corresponds to a thickness of about  $150 \mu\text{m}$ ) is rarely applied when reporting new potential high performance electrodes. Having into account the feasible production of large amounts of nanofibers for a relatively short time, using solution blowing system, it was possible to produce and analyze CNF electrodes with thicknesses up to  $1.2 \text{ mm}$  (or mass loading of  $45 \text{ mg/cm}^2$ ). In this regard, chapter 6 of this thesis gives answers about the effect of the thickness of nanofibrous carbon electrode over the overall properties of a symmetric supercapacitor. As in conventional film electrodes, increasing the thickness of CNF results in increased internal resistance of the device, however here the maximum thickness can be moved up to about  $700 \mu\text{m}$  ( $20 \text{ mg/cm}^2$ ) which – in comparison to the electrode requirements for commercial cell - means 50% higher amount of electrode material within the cell which would result in higher energy and power densities of the same. This, plus the fact that CNF are binder-free electrodes that can be used without current collector contributes to decreasing the cell weight and also the cost for materials. Increasing the electrode thickness above this limit results in low ionic diffusivity and low cycling stability due to formation of larger amount of side products (carboxylic acid salts) during cycling. On the other side, composite CNF embedded with active materials showed to be an alternative to

suppress this negative effect. The type of doping – precursor salt or nanoparticles – resulted to play an important role on the formation of the carboxylic side products. Proper selection of doping material can be considered as a strategy to improve the cycling stability of thick electrodes.

It has to be mentioned that fiber-to-void ratio is a key factors to be satisfied in the production of fibrous electrodes. The porous structure of the fibrous mats, independently on the material they are made of, positively affects the ion diffusion through the whole electrode thickness. However, large void portion results in loose network for electron transfer and thus high electrical resistivity of the electrode. This is especially important when the fibrous electrodes are based on a nonconductive polymers, such in the case of the polymer/carbon particle fibrous electrode. Increasing the thickness of the fibrous electrode - as in the case of CNF electrodes with fiber-to-void ratio of 45% - leads to exponentially proportional relation between electrode thickness and its ion absorption in very thick electrodes, which can be positive in given circumstances. Compact fibrous mats can be achieved with a simple controlled hot or cold press. Hot press is preferred for polymer/particle electrodes due to their polymer nature. Whilst cold press of stabilized precursor fibers is more suitable for CNF in order to avoid self-hardening of PAN nanofibers or volume expansion during stabilization.

Though the addition of doping elements was expected to boost the capacity of the electrodes and to impart battery-like property, all of the doped CNF showed pseudocapacitive behavior, without signs for redox reactions in aqueous 6M KOH electrolyte. However, they did improve the capacity at lower currents on expense of that at high currents. Besides, doping elements embedded into CNF contributed to the formation of carbonaceous structure that changes the limits for hydrogen and oxygen evolution on the electrode surface. This effect was used find the best possible match that allows assembly of an asymmetric cell that operate at the largest possible potential window. Among all doped CNF developed here, the one containing Sn and MoS<sub>2</sub> nanoparticles was the best pair for neat CNF. Such asymmetric supercapacitor that operates at cut-off voltage of 1.6 V, did improve the energy density of the CNF-based supercapacitor cells.

Despite that the energy and power densities obtained with the symmetric and asymmetric cells are comparable to the commercial supercapacitors, the capacity of

the individual electrodes is relatively low. To further improve the performances of either polymer/particle or CNF electrodes, materials with higher electrochemical activity in aqueous electrolyte can be selected and tested. Introduction of materials with battery-like (redox) behavior should significantly boost their capacity. Changing the type (pH) of the electrolyte may be another approach towards the same goal. On the other hand, development of electrodes that operate on more positive potentials, would be more suitable pair for any of the developed CNF, in this thesis, since that would enlarge the overall potential window of a possible asymmetric or hybrid cell.

In summary, the research conducted in this thesis demonstrates:

- The possibility to develop fibrous structure with controllable porosity using biomaterials as main carbon precursor and its application in battery storage systems.
- The possibility to develop fibrous architecture combining a binder and bio-waste carbon particles with controllable porosity as flexible and free-standing supercapacitor electrode.
- The importance of electrode mass loading on the performances of the energy storage device
- That fibrous structures can be produced via industrially scalable technique which makes feasible their industrial application in energy storage devices.
- The possibility to control structural characteristics of carbon-based fibrous materials so that they may be suitable for energy storage applications.
- The feasible application of free standing fibrous electrodes in both, batteries and supercapacitors; and the possibility to combine fibrous electrodes with different structures into one hybrid energy storage device.

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## **APPENDICES**

**APPENDIX A:** Supporting data for Chapter 5.

**APPENDIX B:** Supporting data for Chapter 6.

**APPENDIX C:** Supporting data for Chapter 7.



## APPENDIX A

The details provided in Appendix A are supporting data for Chapter 5.

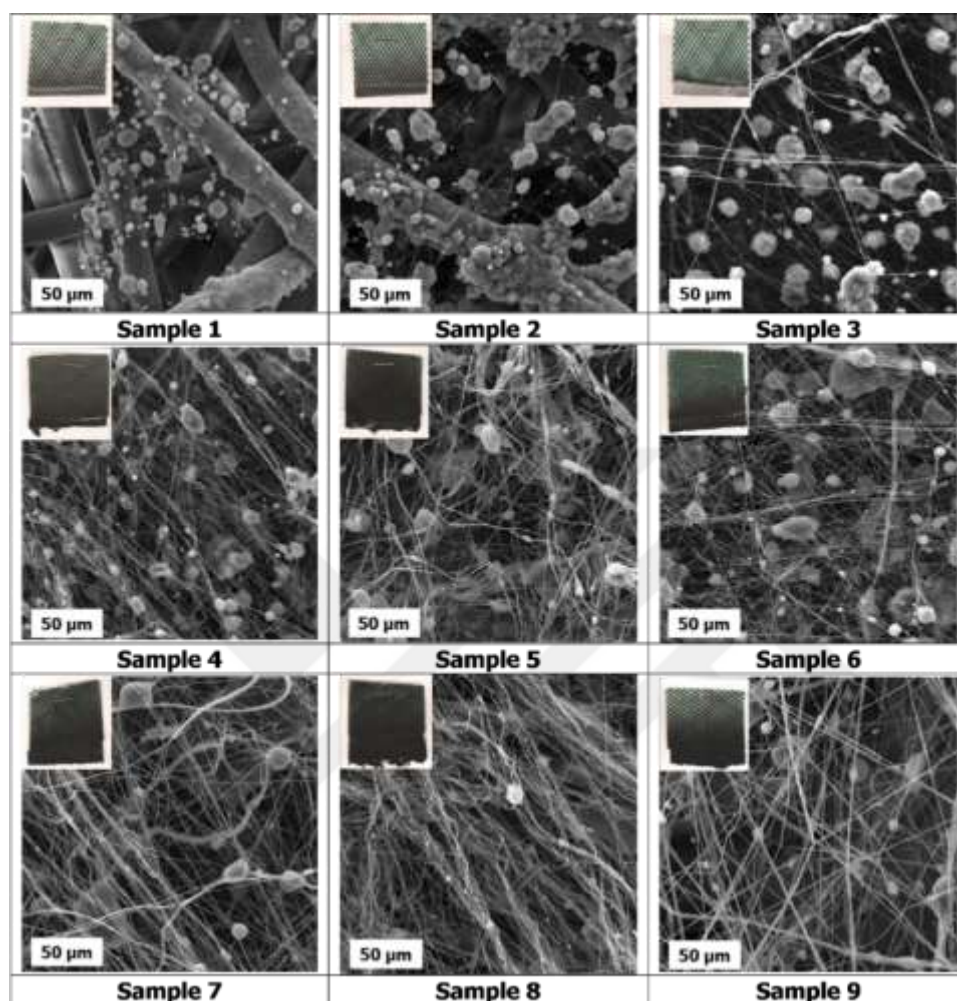


**Figure A.1** : SEM images of the fibers produced from the nine trial solutions (magnification 1000x). (NOTE: the thick fibers on Samples 1 and 2 are from the PE mesh on which solution blown fibers were collected). Insets: real images of the fibrous mats.

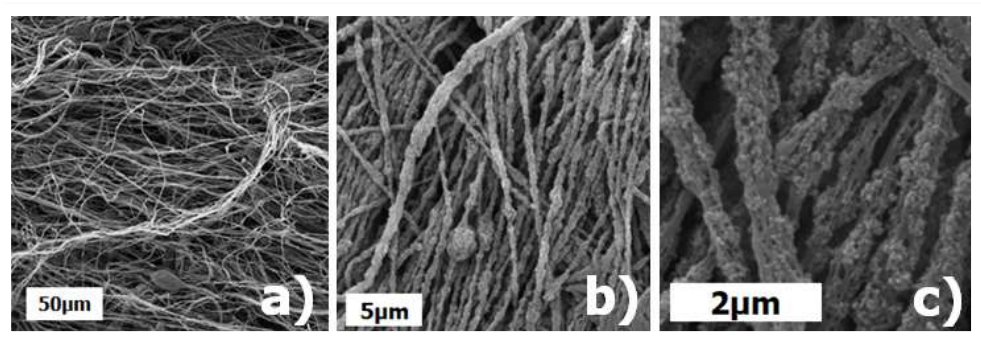


**Figure A.2** : SEM images of PVDF/C nanofibers produced with optimal process parameters at different magnifications.

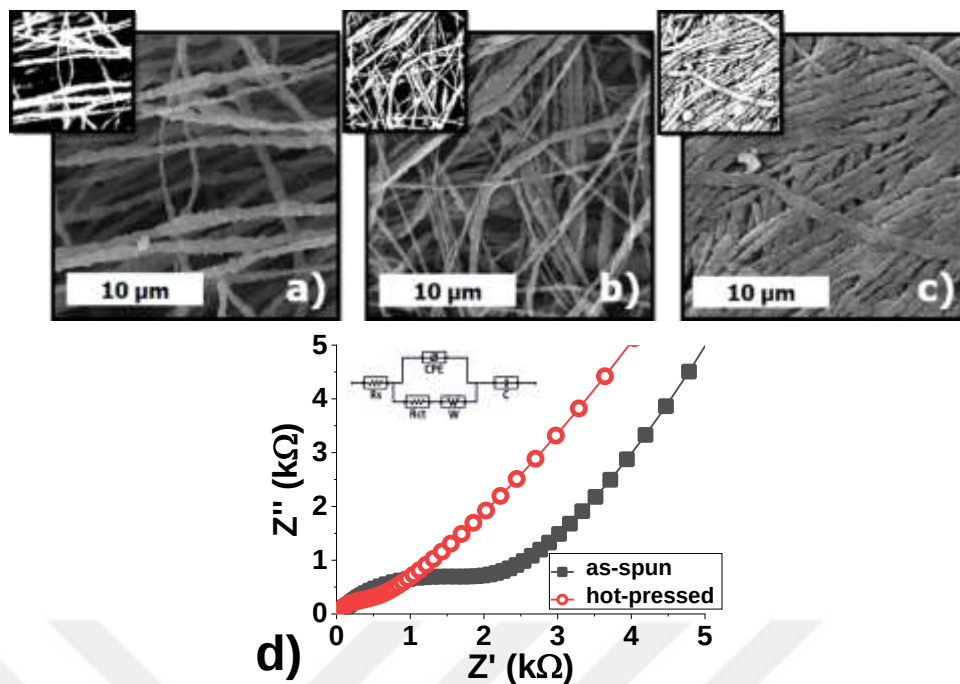


**Figure A.3** : SEM images of a) as spun and pressed PVDF/C nanofiber mats at b) room temperature, and c) at 50  $^{\circ}\text{C}$  for 3 minutes under 4.5 MPa. d) Nyquist plots of as-spun (red circled symbols) and hot-pressed (grey squared symbols) PVDF/C nf electrodes in half-cell against Li-metal reference electrode and EtAN electrolyte.

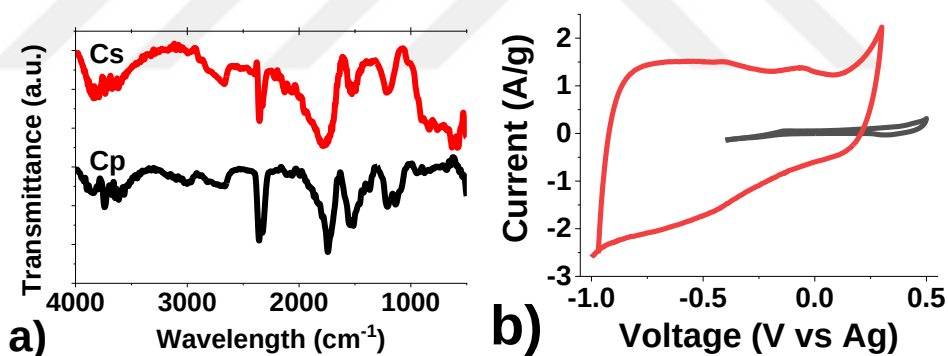


**Figure A.4** : a) FTIR spectra of Cp and Cs powders and b) cyclic voltammograms of electrodes made of casted Cp and Cs base slurries in a 3-electrode system with 6M KOH as electrolyte.

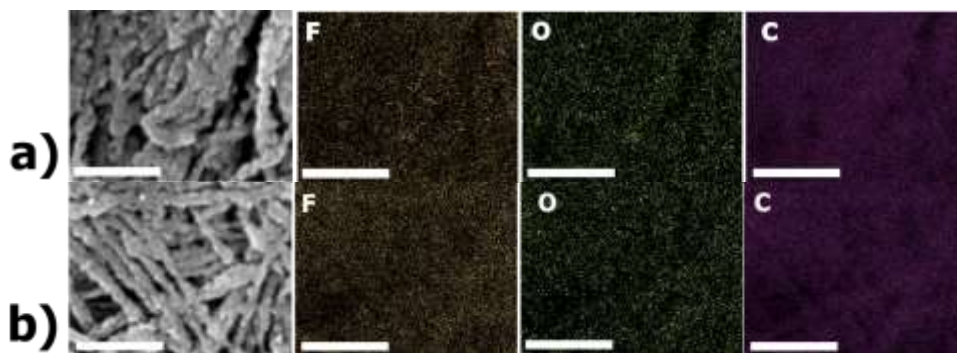


**Figure A.5 :** EDX analysis of a) Cp nf and b) CpCs nf (scale bar 5  $\mu\text{m}$ ).

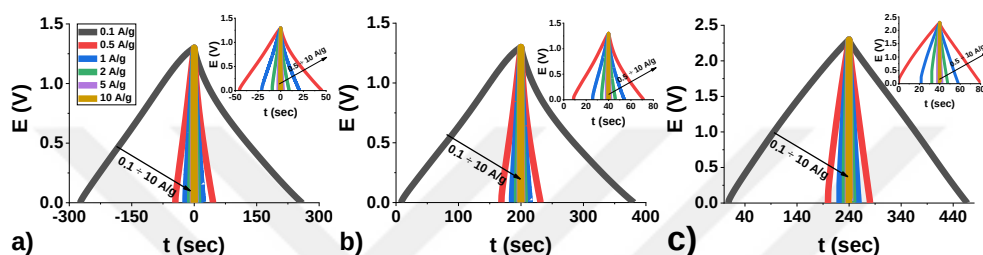


**Figure A.6 :** Galvanostatic charge-discharge profiles of a) symmetric Cp nf and b) CpCs nf supercapacitor cells in aqueous electrolyte at different current rates. (Electrode mass loading: 20//10  $\text{mg cm}^{-2}$ ); and c) symmetric CpCs nf supercapacitors in organic electrolyte at different current rates. (Electrode mass loading: 11//10  $\text{mg cm}^{-2}$ ).

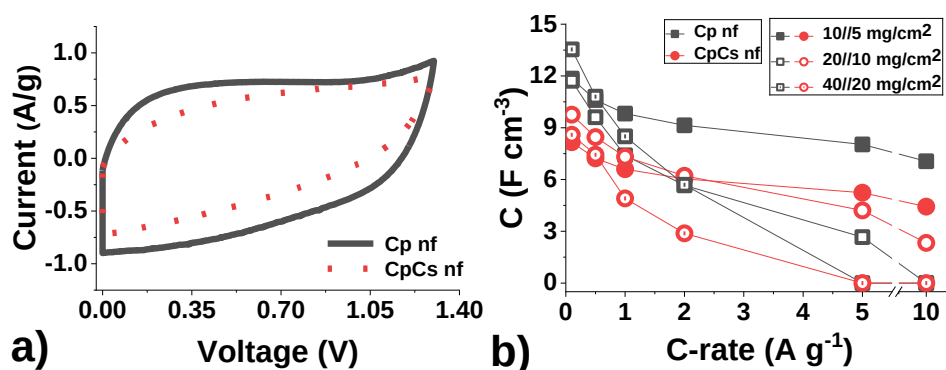


**Figure A.7 :** a) Cyclic voltammograms of new Cp nf (solid line) and CpCs nf (dashed line) symmetric supercapacitor cells in aqueous electrolytes at scan rate of 50 mV/s. (Electrode mass loading: 20//10  $\text{mg cm}^{-2}$ ). b) Volumetric capacitance of symmetric Cp nf and CpCs nf supercapacitor cells with different electrode mass loading in aqueous electrolyte.

## APPENDIX B

The details provided in Appendix B are supporting data for Chapter 6.

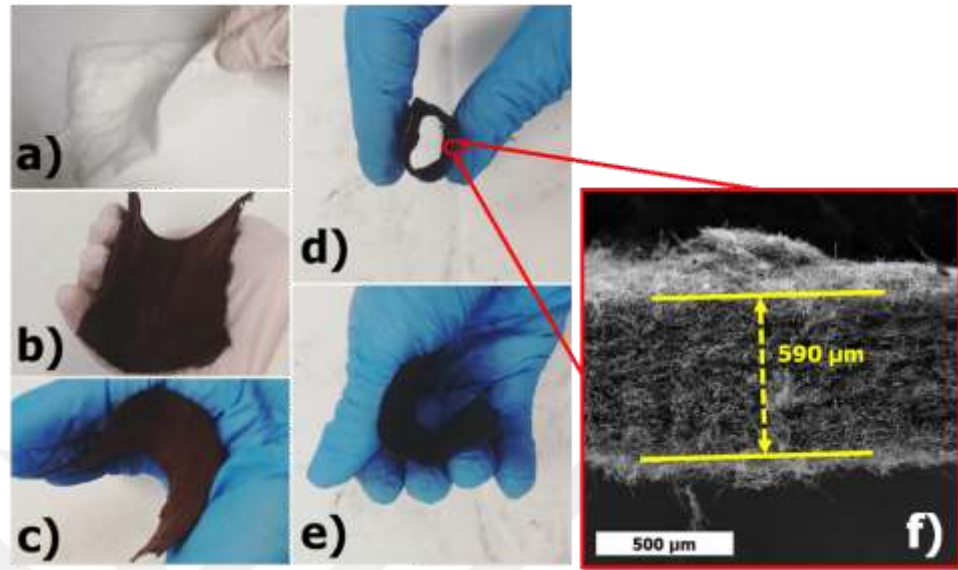


**Figure B.1 :** Real images of a) As-spun PAN nanofibrous mat (~1 mm thickness), b) stabilized PAN nanofibrous mat, c) stabilized and pressed PAN nanofibrous mat, d)-e) carbonized nanofibrous mat. f) SEM image of cross section of CNF electrode.

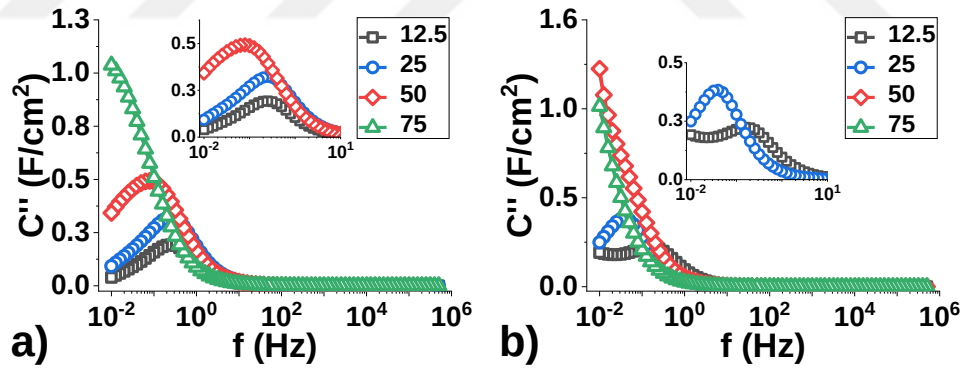


**Figure B.2 :** Complex Bode plots of symmetric CNF supercapacitor cells with different mass loadings a) before and b) after 10000 cycles at 2 A/g. (The circuit used to fit the data is same as in Figure 6.5; solid line: measured, symbols: fitted values).

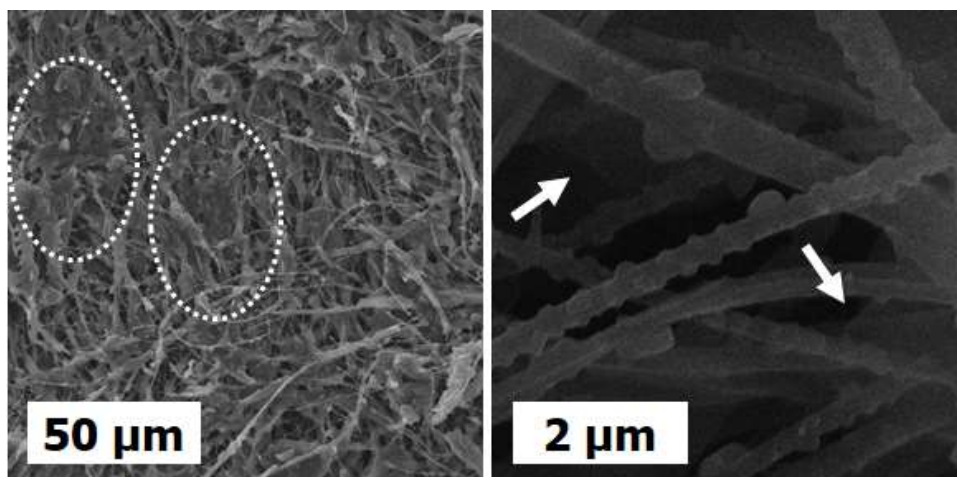


**Figure B.3 :** SEM images of cycled CNF electrode with cell mass loading of 75 mg/cm<sup>2</sup>.

## APPENDIX C

The details provided in Appendix C are supporting data for Chapter 7.

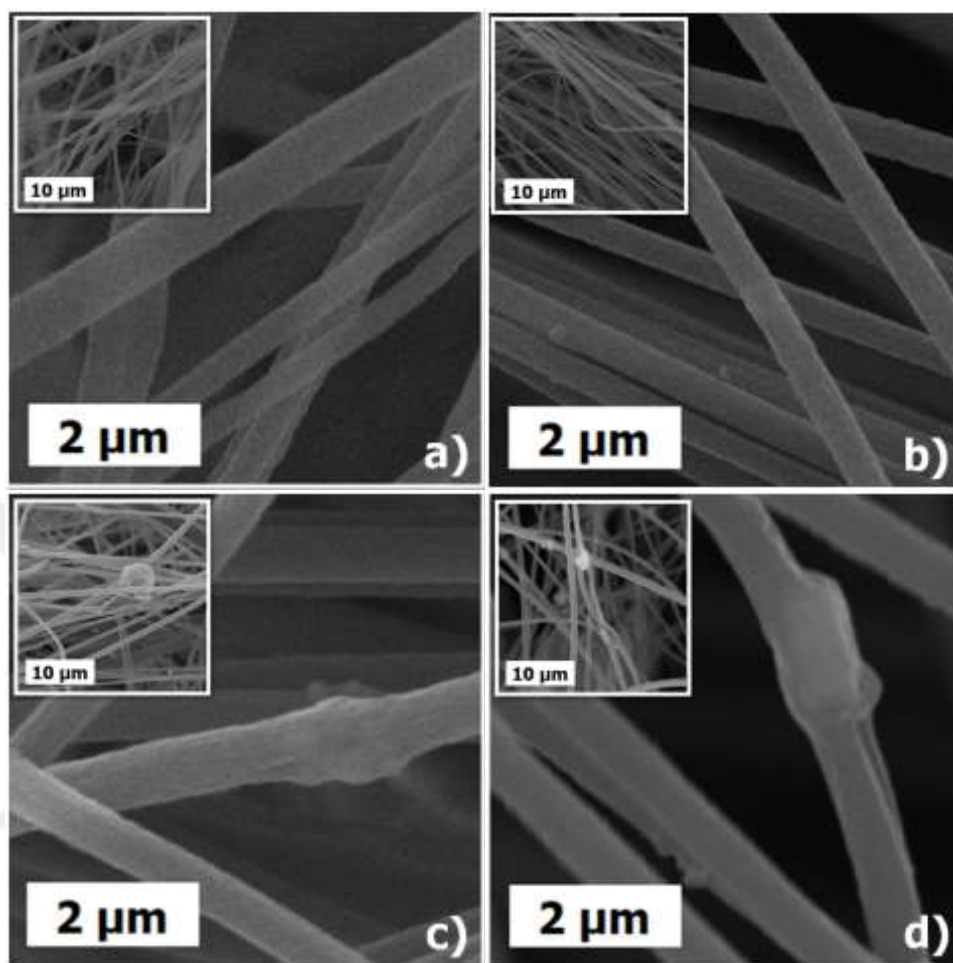


**Figure C.1 : SEM images of as-spun a)  $\text{SnCl}_4$  PAN nf, b)  $\text{MnAc}$  PAN nf, c)  $\text{SnMoS}_2$  PAN nf and d) PB PAN nf.**

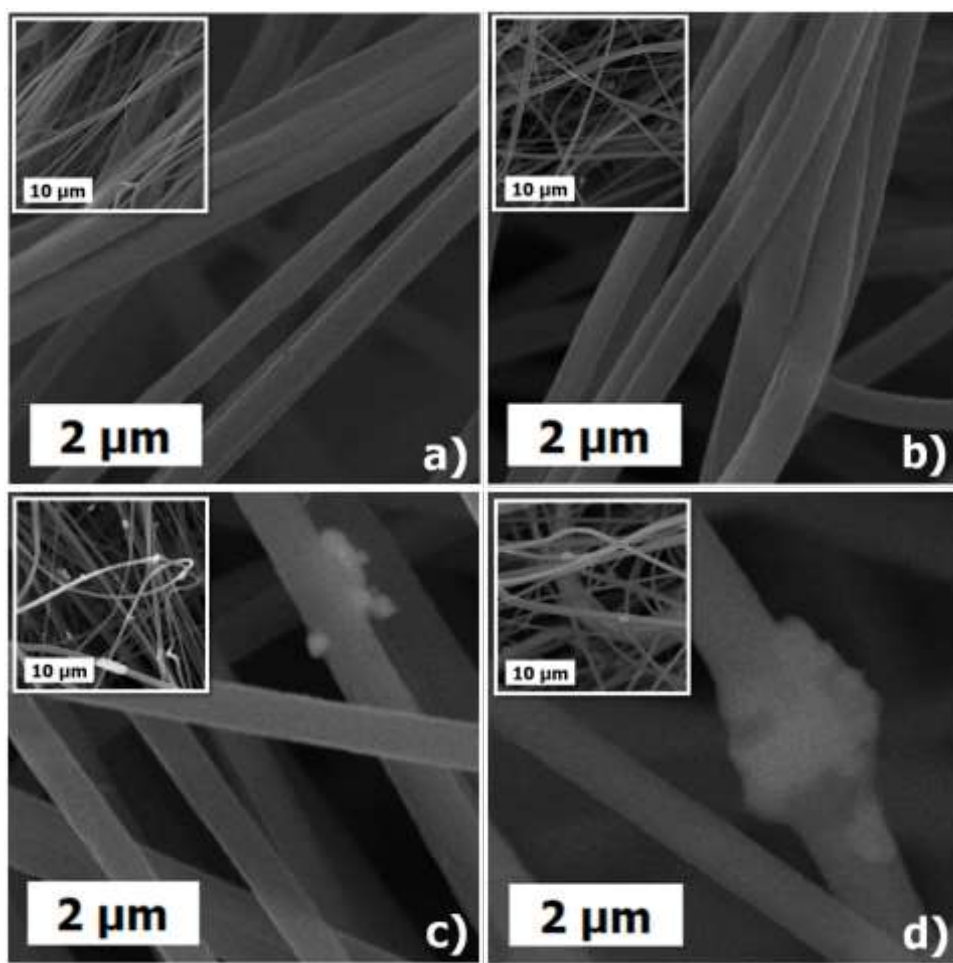


**Figure C.2 : SEM images of stabilized a) SnCl<sub>4</sub> PAN nf, b) MnAc PAN nf, c) SnMoS<sub>2</sub> PAN nf and d) PB PAN nf.**

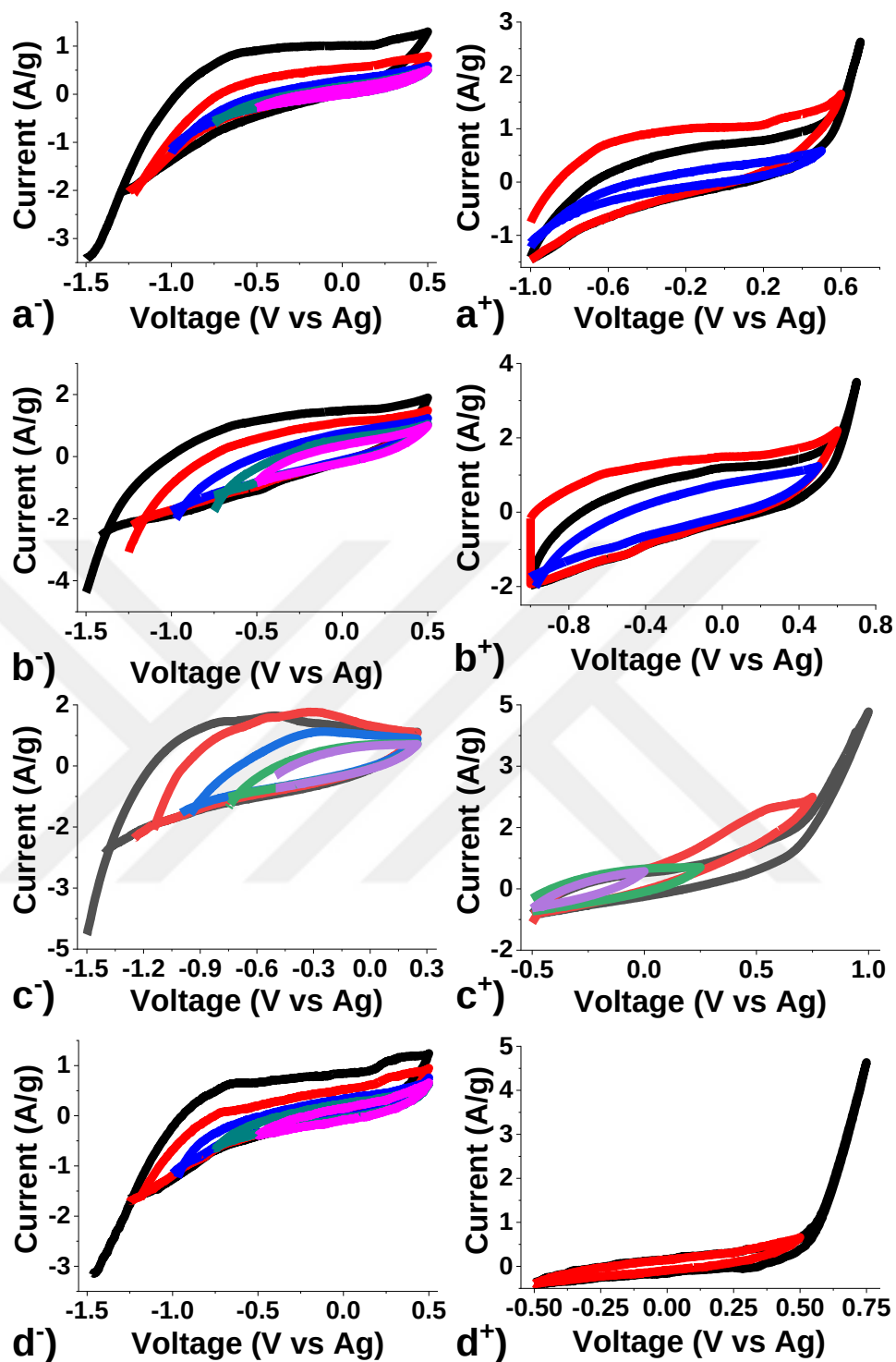


Figure C.3 : Cyclic voltammograms for positive and negative voltage opening for a) Sn CNF, b) Mn CNF, c) SnMo CNF and d) PB CNF (scan rate 10 mV/s).

**Table C.1 : Positive ( $E^+$ ) and negative ( $E^-$ ) potential limits and open circuit voltage ( $V_{oc}$ ) values of doped CNF obtained from CV measurements.**

| sample   | $E^-$ [V] | $E^+$ [V] | $V_{oc}$ [V] |
|----------|-----------|-----------|--------------|
| CNF      | -1.00     | 0.40      | -0.154       |
| Sn CNF   | -0.8      | 0.5       | -0.129       |
| Mn CNF   | -0.8      | 0.5       | -0.116       |
| SnMo CNF | -1.2      | 0         | -0.671       |
| PB CNF   | -1        | 0.5       | -0.092       |

**Table C.2 : Mass and thickness of CNF electrodes used for assembly of symmetric and asymmetric cells.**

| sample          | m [mg/cm <sup>2</sup> ] | t [ $\mu$ m] |
|-----------------|-------------------------|--------------|
| <b>CNF</b>      | 10 $\pm$ 0.7            | 291 $\pm$ 53 |
|                 | 15 $\pm$ 0.6            | 567 $\pm$ 51 |
| <b>Sn CNF</b>   | 11 $\pm$ 0.1            | 286 $\pm$ 49 |
|                 | 12 $\pm$ 0.2            | 331 $\pm$ 43 |
| <b>Mn CNF</b>   | 11 $\pm$ 0.3            | 291 $\pm$ 32 |
|                 | 12 $\pm$ 0.1            | 358 $\pm$ 47 |
| <b>SnMo CNF</b> | 10 $\pm$ 0.7            | 295 $\pm$ 28 |
|                 | 12 $\pm$ 0.1            | 305 $\pm$ 31 |
|                 | 13 $\pm$ 0.5            | 312 $\pm$ 38 |
| <b>PB CNF</b>   | 10 $\pm$ 0.9            | 253 $\pm$ 40 |
|                 | 15 $\pm$ 0.3            | 412 $\pm$ 52 |

## CURRICULUM VITAE



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