

**İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

**DEVELOPMENT OF ZEOLITE-NAFION  
COMPOSITE MEMBRANES FOR PEM FUEL CELLS**

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## **LIST OF ABBREVIATIONS**

|            |                                          |
|------------|------------------------------------------|
| <b>PEM</b> | : Proton Exchange Membrane               |
| <b>EIS</b> | : Electrochemical Impedance Spectroscopy |
| <b>SEM</b> | : Scanning Electron Microscopy           |
| <b>AFM</b> | : Atomic Force Microscopy                |
| <b>EDX</b> | : Energy Dispersive Spectroscopy         |

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## **DEVELOPMENT OF ZEOLITE-NAFION COMPOSITE MEMBRANES FOR PEM FUEL CELL**

### **Summary**

Proton Exchange Membrane (PEM) fuel cells are the most preferred type of fuel cells due to their high energy densities, low polluting emissions and long life times. The most widely used proton exchange membranes are perfluoro sulphonic acid membranes, such as Dupont's Nafion, because of their excellent proton conductivity, mechanical strength, thermal and chemical stability. However, their high preparation cost, low ion conductivity at high temperatures and high methanol permeability limit their commercialization in fuel cells.

The purpose of this study is to develop zeolite-Nafion composite membranes that have high mechanical strength, thermal and chemical stability and high proton conductivity at elevated temperatures at relatively low cost. For this purpose, Nafion ionomer was used as proton conducting matrix and clinoptilolite as zeolitic filler. The membranes were converted into the  $H^+$  and  $Na^+$  forms after the preparation of membranes with different zeolite content. The characterizations of the membranes were done by impedance spectroscopy, microscopic and electrochemical methods. The proton conductivities were measured in the temperature range of 25-80  $^{\circ}C$ . The results showed that proton conductivities increased with temperature. Also from SEM and EDX results, we observed that the zeolite particles were evenly dispersed in the Nafion matrix. Finally, we found that modification of Nafion with zeolites resulted in notable changes in its characteristics when compared with sole Nafion.

## PEM YAKIT HÜCRELERİNDE ZEOLİT NAFYON KOMPOZİT MEMBRANLARIN GELİŞTİRİLMESİ

### Özet

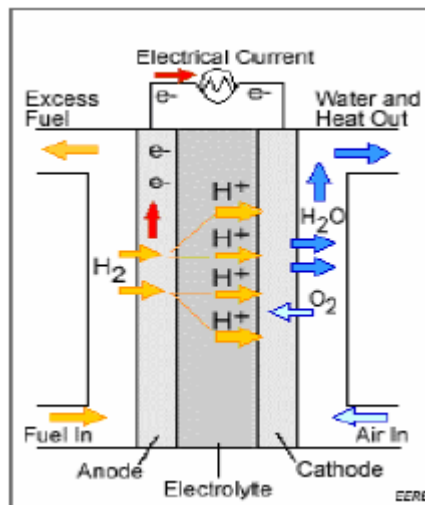
Proton geçirgen membran yakıt hücreleri sahip oldukları yüksek enerji verimliliği, uzun kullanım ömrü ve düşük kirlilik emisyonu gibi karakteristik özelliklerinden dolayı günümüzde en çok tercih edilen yakıt hücrelerindendir. En yaygın olarak kullanılan proton geçirgen membranlar Dupont firmasının ürettiği Nafion olarak bilinen perfluoro sülfonik asit membranlarıdır. Bu membranlar oldukça yüksek proton iletkenliğine, yüksek mekanik dayanıklılığa ve kimyasal ve termal kararlılığa sahiptir. Ancak Nafyon membranının üretim aşamasındaki yüksek maliyeti, yüksek sıcaklıklardaki düşük proton iletkenliği ve metanol geçirgenliği gibi özelliklerinden dolayı yakıt hücrelerindeki kullanım alanları kısıtlanmaktadır.

Bu çalışmanın amacı, düşük maliyet ile yüksek mekanik güce, kimyasal ve termal kararlılığa sahip ve yüksek sıcaklıklarda yüksek proton iletkenlik gösterebilen zeolit-Nafion kompozit yapıda yakıt hücresi membranları geliştirmektir. Bu amaçla, proton iletken matriks olarak Nafion iyonomeri, zeolitik dolgu olarak da doğal zeolitlerden klinoptilolit zeoliti kullanılmıştır. Değişik zeolit miktarlarıyla hazırlanan membranlar  $H^+$  ve  $Na^+$  formlarında yapılara dönüştürülmüştür. Karakterizasyon deneyleri için empedans spektroskopisi, SEM ve AFM kullanılmıştır. Proton iletkenlik ölçümleri ise 25- 80  $^{\circ}C$  arasında yapılmış ve iletkenliğin sıcaklıkla arttığı gözlenmiştir. SEM ve EDX sonuçları da bize zeolit parçacıklarının Nafion yüzeyine iyi bir dağılım gösterdiğini kanıtlamıştır. Son olarak, Nafion un zeolit ile modifikasyonu ticari Nafion membranları ile karşılaştırıldığında karakteristik yapısında ayırt edilebilir değişiklikler olduğu gözlenmiştir.

## 1. INTRODUCTION

### 1.1 Fuel Cells

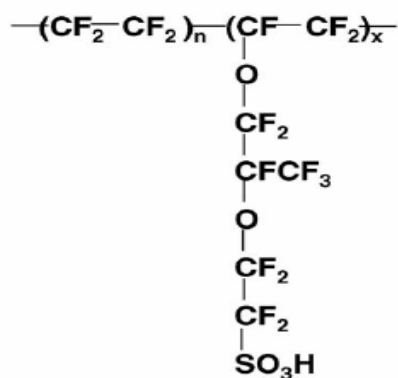
A fuel cell is an electrochemical device which directly converts the chemical energy of a reaction between a fuel (on the anode side) and an oxidant (on the cathode side) into electrical energy. It consists of an electrolyte and two electrodes, one negative and the other positive. The fuel and oxidant are externally fed into the fuel cell. At the anode side, the fuel is converted into its protons and electrons and the electrons are carried to the cathode side by external circuit while protons are carried through the electrolyte.



**Figure 1.1 : Pem Fuel Cell**

The proton exchange membrane fuel cell (PEMFC) is one of the most promising power sources, especially for portable electronics and stationary applications due to its relatively high energy density, low polluting emission and low cost. One of the vital component of PEMFC is the proton exchange membrane which transports proton while blocking electrons. Nafion, the perfluorinated membrane from DuPont,

or similar membranes manufactured from Asahi and Down are the most widely used and successful proton conducting materials. They exhibit high proton conductivity, good thermal, mechanical and chemical stability in hydrated state. The hydrophilic nature of the sulphonic acid groups attached to the polymer backbone provides proton conduction. Water is essential for proton conductivity because it promotes the dissociation of the proton from the sulfonic acid group and provides highly mobile hydrated protons.



**Figure 1.2 :** Structure of Nafion

Besides these advantages, unmodified nafion membranes are unstable at high temperatures, are very expensive due to their complicated synthesis procedures and exhibit high methanol permeability. Additionally, their high methanol crossover rate reduces fuel utilization efficiency and decreases cathode performance. They tend to dehydrate very fast at high temperatures leading to poor performance, and also with dehydration, shrinkage of the membrane can occur leading to a poor contact between the membrane and the electrodes.

## 1.2 Purpose of the Research

Sustainable and renewable energy sources are being developed due to the depletion of fossil fuels and the increasing threat of global warming. Fuel cells are one of the most energy-efficient and environmentally friendly power sources. They have the potential to replace the conventional combustion engines because they are more efficient and they produce no greenhouse gases. Extensive research is being carried out in order to expand the applications of PEM fuel cells. Most important challenges include making the membrane durable at high temperatures and methanol-resistant as well as

chemically and mechanically stable while achieving further cost reductions. There are two different ways to improve the performance of Nafion membranes, the first being the development of proton conducting membranes based on alternative polymers, the second being the modification of Nafion membranes.

In this work, zeolite/Nafion composite membranes were prepared. Clinoptilolite, from natural zeolites was chosen for the durability of the membrane at high temperatures. The prepared membranes were then converted into the  $H^+$  and  $Na^+$  forms. Finally, the characterizations of the membranes, such as impedance spectroscopy and microscopic measurements were performed.

## **2. LITERATURE REVIEW**

### **2.1. Previous Studies on Composite Membranes**

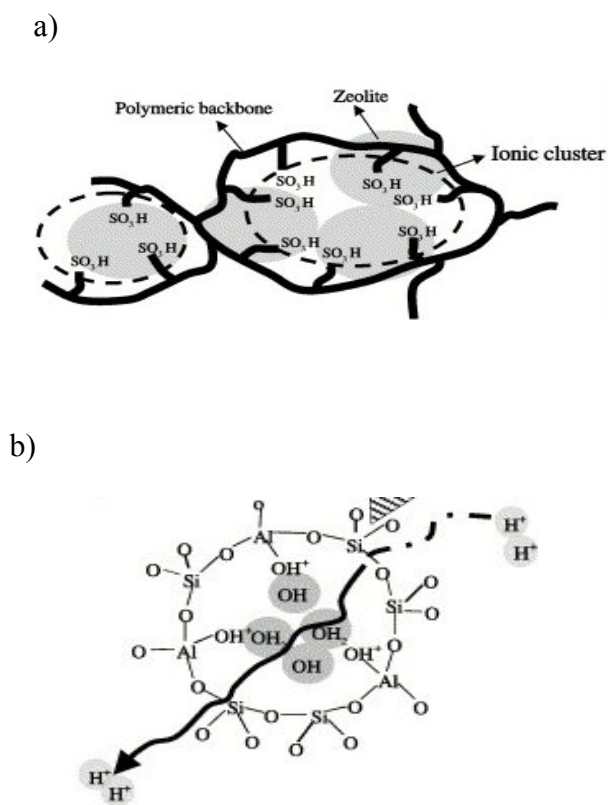
The idea of forming composite membranes is based on to utilize polymer materials, such as Nafion, polyetherketone, polybenzimidazole etc. as a matrix and some inorganic crystals as filler. The polymer should be proton conductive and the filler should be both proton conductive and poorly permeable to methanol. The synthesis of inorganic phases, such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ -to mention just a few- inside the pore of nafion membrane has been an effective modification in order to get high selectivities [1-3]. These compoiste membranes were prepared by sol-gel synthesis of tetraethoxysilane (TEOS) within Nafion membrane and additionally treated in acid. In none of those reports were the membranes at high temperatures investigated.

Some other studies have been attempted to operate membranes at high temperatures. The loss of water from the ionic regions of the membranes lowers the proton conductivity at elevated temperatures. To increase the water affinity, one attempt is to incorporate the hydrophilic inorganic fillers into nafion membrane in the case of heteropolyacids. These acids provide the hydration of membrane up to  $120^\circ\text{C}$  [4]. A second attempt is to use a non-aqueous, low volality solvent, such as sulphuric acid, imidazole, butyl methyl imidazolium[5-7]within Nafion.

Although the research field related to composite membranes is very diversified, zeolite-nafion composite membranes are very promising due to their natural narrow pore size distributions, high water retention ability and high surface acidity [8-11]. In addition, their molecular sized pores and channels make them very selective for seperations based on molecular size. One other characteristic property of zeolite is to seperate components due to the preferential adsorption. They adsorp one component while blocking the passage of other.

On the other hand, composite membranes with pure zeolites can cause cracks and gaps leading poor mechanical properties like brittleness and fragility.

In order to see the structure of zeolite-Nafion membrane, a clear schematic diagram (figure 2.1) is illustrated. It can be seen from figure that zeolite particles exist within ionic cluster channel.



**Figure 2.1 :** Schematic diagrams of zeolite-Nafion composite membranes  
(a) Structure of the membranes and (b) movement of proton

## 2.2. Composite Membranes

### 2.2.1. Proton Conductivity

Ionic conductivity is the heart of PEM fuel cells. Nafion membranes have excellent proton conductivities differing from  $10^{-2}$  to  $10^{-3}$  S/cm but they decrease at high temperatures which limits their usage. Several research groups have focused on the improvement of conductivity. Composite membranes prepared by dispersion of tin mordenite crystals in acrylic acid polymer exhibits stable and high protonic conductivity of  $1 \times 10^{-2}$  S/cm at room temperature [11]. Other reports based on poly(tetrafluoroethylene)-mordenite composite membranes with high zeolite contents exhibited good ionic conductivity but their mechanical stability was poor. Later on, membranes based on poly(vinylalcohol) with mordenite crystals were produced. As polyvinylalcohol is not adequately ion conductive, the membranes had to be doped with acid to improve ion conductivity [12]. Composite membranes based on natural zeolites, such as clinoptilolite, chabazite and mordenite for high temperatures were studied [9, 14]. Those membranes showed good properties for high temperature fuel cell application due to their improved water retention abilities. Tricoli et al. [13] investigated chabazite and clinoptilolite/Nafion composite membranes in medium temperature range. The membranes were converted into the  $\text{Na}^+$  and  $\text{H}^+$  forms. The conductivity of  $\text{H}^+$  form membrane was almost four times smaller with respect to the same membrane in the  $\text{Na}^+$  form. Commercial zeolites were also studied [8]. Kim et al. [15] investigated the effect of solvent and crystal size on the selectivity of ZSM-5/Nafion composite membranes. The type of solvent with high boiling point have led to higher mechanical strength of composite membrane. Also, the proton conductivity of Na-ZSM-5 was higher than that with H-ZSM-5. The difficulty while studying with zeolites is the lack of control of pore structure, surface acidity and zeolite particle. Some researcher are developing methods in order to control over the inorganic particle properties [16].

### 2.2.2 Methanol Permeability

Crossover of methanol from anode to the cathode site is the main obstacle for direct methanol fuel cells using proton exchange membrane. The results of this crossover are the loss of fuel, reduced energy and power densities, catalyst poisoning and hence a reduced performance. Methanol transport through Nafion membranes were investigated [17,18]. In order to reduce methanol crossover, there are many approaches, such as changing the operational parameters and cell designs, using different cathode catalysts or developing composite membranes showing high resistivity to methanol. For this reason a number of different composite membranes were proposed [19-21]. Hsing et al. [19] prepared a membrane containing polyvinylalcohol and Nafion. The permeation current density,  $i_d$  of this composite membrane decreased significantly compared to Nafion membrane, but as mentioned before its proton conductivity decreased due to the non-proton conductive PVA [12]. Also, Nafion membrane coated with poly(vinylidene fluoride) was studied [20]. The coated layer reduced methanol crossover but proton conductivity was little lower than that of Nafion. Wang et al. [21] used polbenzimidazole doped with phosphoric acid and their methanol crossover rates were about an order of magnitude less than for Nafion membrane. In another report, Nafion modification with poly(1-methyl pyrrole) was investigated [22] and the results indicated that modification of Nafion lowered methanol permeability by ~50%. In another work, similar results were obtained with Nafion-poly(1methyl pyrrole) [23]. Kim et al. [15] fabricated composite membranes based on Nafion and zeolite, ZSM-5. Low methanol permeabilities were obtained due to the blocking effect of HSM-5 for ionic clustered channels so that transport of methanol through zeolite pores became more difficult. Some other researchers investigated the effect of pre-conditioning of zeolite-Nafion composite membranes on permeability [13]. It was observed that pre-conditioning in hot water increased the permeability which was ascribed to membrane swelling.

### **3. EXPERIMENTAL**

#### **3.1. Materials**

Nafion solution was purchased from Electrochem, Inc. as 5 wt.% solution. Clinoptilolite was received from Faculty of Chemical and Metallurgical Engineering as powder (10  $\mu\text{m}$ ). Ethanol, N,N-dimethylformamide (DMF),  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were purchased from Merck.

#### **3.2. Preparation of Clinoptilolite/Nafion Composite Membranes**

5 g of the as-received clinoptilolite powder was suspended in 250 ml deionized water by stirring, and sonicating in an ultrasonic bath (Azaklı, M600). In order to eliminate the bigger particles, the suspension was allowed to decant for 60 h. The bigger particles which settled down were removed and water was evaporated. The remaining zeolite powder was used as zeolitic filler in the membrane. Then predetermined amount of zeolite powders (4 mg and 1 mg individually) were mixed with the solution of 5 ml of Nafion, 5 ml of ethanol and 3 ml of DMF. This suspension was sonicated to form a homogeneous dispersion at room temperature in an ultrasonic bath for 3 h. Following this step, the suspension was spread on a petri dish and allowed to air dry for 2 h and after that it was placed in a vacuum oven at 80  $^{\circ}\text{C}$  for 3 h until complete evaporation of the solvent. Before investigation, the membranes were converted into  $\text{H}^+$  form (by treating in  $\text{H}_2\text{SO}_4$  solution of  $\text{pH}>3$ ) and  $\text{Na}^+$  form (by treating in 1 N  $\text{Na}_2\text{SO}_4$  solution made acid at pH 3.4 by addition of  $\text{H}_2\text{SO}_4$ ) and all membranes were pre-conditioned in deionized water at 80  $^{\circ}\text{C}$  for 3 h. Obtained membranes in  $\text{H}^+$  and  $\text{Na}^+$  form were stored in deionized water till further use [13].

For comparison of composite membranes, a commercial Nafion 117 membrane used as the standard sample. This Nafion membrane was cleaned by boiling for 45 min in 3% hydrogen peroxide, followed by boiling for 45 min in 1M sulphuric acid, and

finally 15 min in deionised water (repeated twice). Between all steps it was rinsed with deionized water, then stored in deionized water till further use [24].



**Figure 3.1** Picture of the prepared clinoptilolite/Nafion composite membrane

The thickness of the membranes was measured by means of a micrometer in hydrated state.

### **3.3 Membrane Characterization**

#### **3.3.1 Impedance Spectroscopy Measurements**

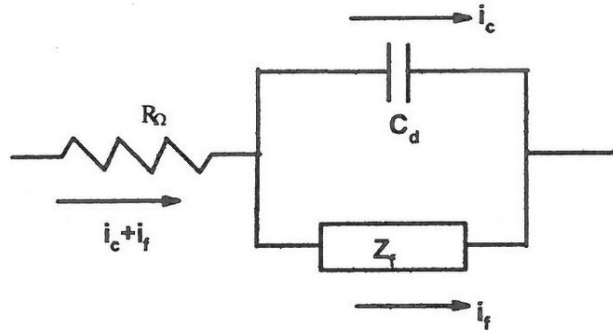
The general approach in impedance spectroscopy is to apply an electrical stimulus (a known voltage or current) to the electrodes and observe the response (the resulting current or voltage). One of the basic purposes of IS is to determine the properties of the electrode-material system, their interrelations, and their dependences on controllable variables such as, temperature, applied hydrostatic pressure, and applied static voltage or current.

The most common approach in EIS, is to measure impedance by applying a single-frequency voltage or current to the interface and measuring the phase shift and amplitude, or real and imaginary parts, of the resulting current at that frequency using either analog circuit or fast Fourier transform (FFT) analysis of response. Commercial instruments are available which measure the impedance as a function of frequency automatically in the frequency ranges of about 1 mHz to 1 MHz. The advantages of this technique are the availability of these instruments and the ease of

their use, also the experimentalist can achieve a better signal-to-noise ratio in frequency range of interest.

After the general shape of the impedance spectrum is obtained, it may be modelled in terms of an equivalent circuit. This equivalent circuit should contain these components:

- The double layer, a pure capacitor of capacity,  $C_d$ ,
- The impedance of faradaic process  $Z_f$ ,
- The resistance  $R_\Omega$  which is assumed the solution resistance between working and reference electrodes



**Figure 3.2:** Equivalent electrical circuit of an electrochemical process.

The measured total impedance of the cell,  $Z$ , is expressed as the series combination of the real and imaginary components of  $Z$ . For the simple charge transfer reaction such as,  $M^+(aq) + ne^- \rightarrow M$ , the  $Z_{Im}$  and  $Z_{Re}$  can be expressed as:

$$Z_{RE} = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2}}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2} \quad (3.1)$$

$$Z_{IM} = \frac{\omega C_d (R_{ct} + \sigma\omega^{-1/2})^2 + \sigma\omega^{-1/2} (\omega^{1/2} C_d \sigma + 1)}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2} \quad (3.2)$$

Where  $\omega$  is angular frequency and  $\sigma$  is defined as

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left( \frac{1}{D_0^{1/2} [O]_{\infty}} + \frac{1}{D_R^{1/2} [R]_{\infty}} \right) \quad (3.3)$$

Where R is gas constant, F is Faradat constant, A is the area of electrode,  $D_O$  and  $D_R$  are diffusion coefficients of oxidized and reduced species respectively,  $[O]_{\infty}$  and  $[R]_{\infty}$  are bulk concetrations of this species.

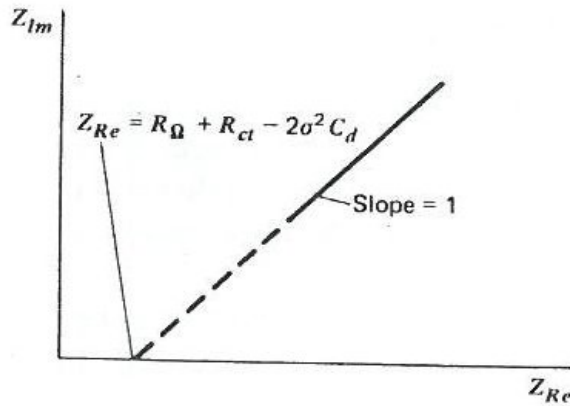
Chemical informations can be extracted by plotting  $Z_{Im}$  vs.  $Z_{Re}$  for diffrenent  $\omega$  values.

- For low frequency limit, as  $\omega \rightarrow 0$ , the functions (1) and (2) approach the limiting forms:

$$Z_{Re} = R_{\Omega} + R_{ct} + \sigma \omega^{-1/2} \quad (3.4)$$

$$Z_{Im} = \sigma \omega^{-1/2} + 2\sigma^2 C_d \quad (3.5)$$

The plot of  $Z_{Im}$  vs.  $Z_{Re}$  should be linear and have unit slope, as shown in Figure 3.3. The extrapolation to the real axis gives an intercept of  $(R_{\Omega} + R_{ct} - 2\sigma^2 C_d)$ . This line comes only from Warburg impedance; thus it is a characteristic of a diffusion-controlled electrode process.



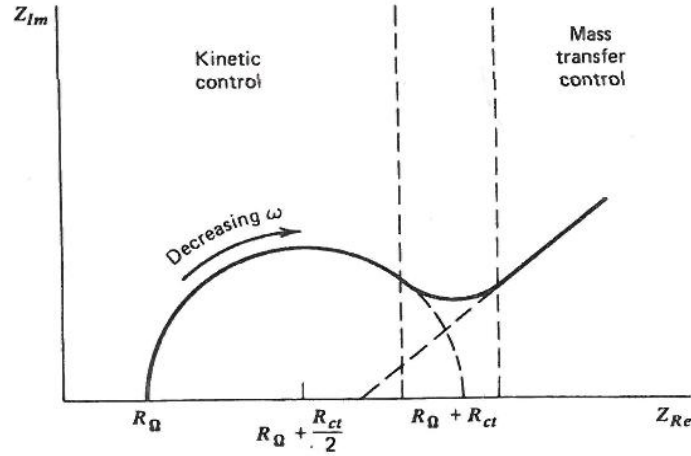
**Figure 3.3:** Impedance plane plot for low frequencies.

- At high frequencies, as  $\omega \rightarrow \infty$ , the functions (1) and (2) approach the limiting forms:

$$Z_{RE} = R_{\Omega} + R_{ct} + \sigma\omega^{-1/2} \quad (3.6)$$

$$Z_{IM} = \sigma\omega^{-1/2} + 2\sigma^2 C_d \quad (3.7)$$

The Warburg impedance becomes unimportant. All of the current is charging current and the only impedance it seems the ohmic resistance,  $R_{ct} \gg Z_w$ .



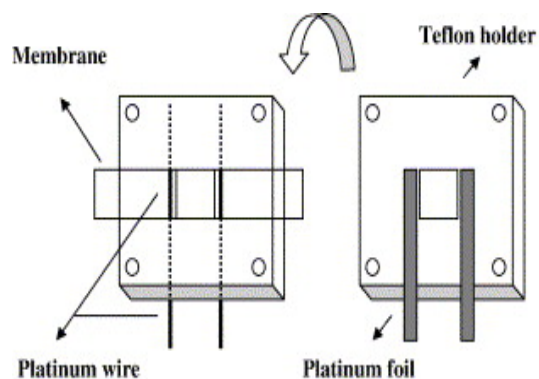
**Figure 3.4 :** Impedance plot of an electrochemical systems

### 3.3.1.1 Conductivity Measurements

The proton conductivity of the zeolite composite membranes was measured by impedance analyzer (Votalab PGZ 301). Before measurements, the membrane in the  $H^+$  form was immersed in a very dilute ( $10^{-5}$  M)  $H_2SO_4$  solution and the  $Na^+$  form in a very dilute  $Na_2SO_4/H_2SO_4$  equilibration solution (which was diluted  $10^5$ -times in deionized water) for 2 days. The resistivity was obtained from a Nyquist plot over the frequency range from 100 kHz to 10 mHz. The proton conductivity was calculated according to the following expression:

$$\kappa = \frac{L}{R \times V \times D} \quad (3.8)$$

where  $\kappa$ ,  $L$ ,  $R$  represent the proton conductivity, the distance between the electrodes to measure the potential (1 cm), the impedance of the membrane respectively.  $W$  and  $D$  are the width (1cm) and the thickness of the membrane respectively. A schematic diagram of the cell is given in Fig 3.5.



**Figure 3.5 :** A conductivity cell [15].

### 3.3.2 Microscopic Measurements

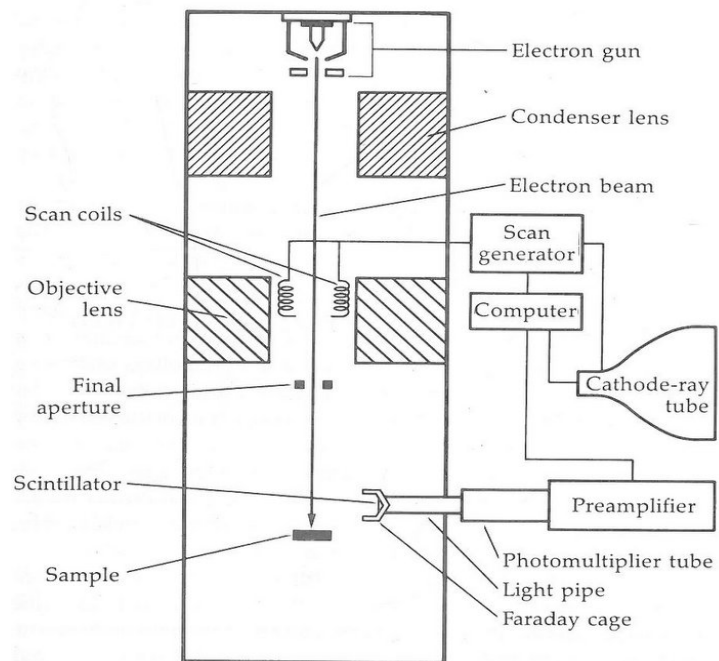
#### 3.3.2.1 SEM Measurements

Scanning electron microscopy is the technology of using electron beam to form magnified species of specimen. The principle advantage of using electrons, rather than light, to form images is that electrons provide as much as thousandfold increase in resolving power. SEM can resolve detail to approximately 3 nm for specially designed instruments. The SEM has a large depth of field, which can be up to four hundred times greater than of a light microscope. Also, most techniques for the preparation of samples for the SEM are considerably easy because the surface of whole sample is examined and no sectioning is required [25]. The interaction of electrons with the atoms in sample produces signal that contain information about the sample's surface topography, composition and other properties like electrical conductivity.

A schematic diagram of SEM is shown in Figure 3.6. The electron gun produces a beam of electrons. These electrons are condensed by condenser lens and then focused as a very fine point on the specimen by the objective lens. The scan coils in objective lens are energized by a varying voltage produced by the scan generator and create a magnetic field that deflects the beam of electrons back and forth in a controlled pattern called raster. The varying voltage from the scan generator is also applied to deflection coils in cathode-ray tube (CRT). The magnetic field causes the deflection of a spot of light back and forth on the surface of CRT.

When the beam of electrons strikes the sample, secondary electrons are produced from the sample, which are collected by detector, converted to a voltage, and

amplified. The amplified voltage is then applied to the CRT and changes the intensity of the spot of light on the surface. The SEM image consists of varying intensity on the face of a CRT that correspond to the topography of the sample.



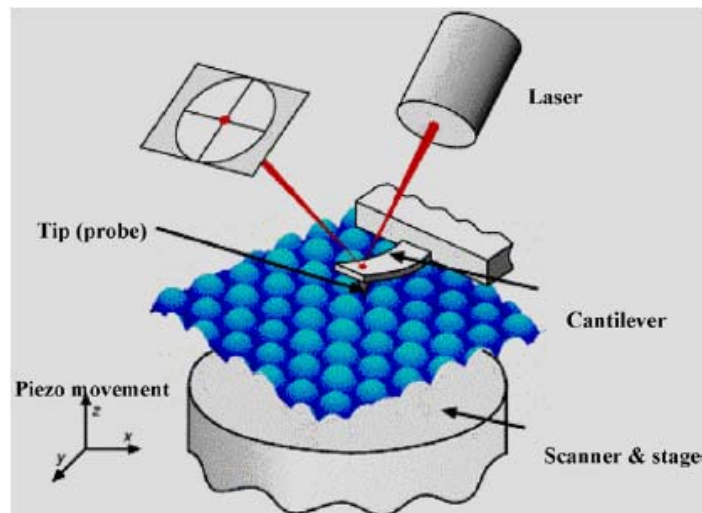
**Figure 3.6 :** Schematic diagram of a scanning electron microscopy [25]

Energy Dispersive Spectroscopy (EDX) is a part of SEM. It is used for identifying and quantifying elemental composition of sample which relies on the investigation of the sample through the interaction between electromagnetic radiation and matter. The emitted X-rays from the matter are analyzed in response to being hit with the electromagnetic radiation. The atomic structure of the elements are identified uniquely from each other because every element has a unique atomic structure which allows x-rays.

### 3.3.2.2 AFM Measurements

Atomic Force Microscope is based on the attractive and repulsive forces that exist between atoms and molecules. A very fine mechanical tip scans the whole surface with a high resolution and great sensitivity. The tip is mounted on a triangular piece of metal foil which is called cantilever. The piezoelectric device moves the sample under the tip. The variation of forces between the tip and sample cause the movement

of cantilever. A laser beam is also directed at an angle toward the surface of cantilever. The reflected beam of the laser is detected by a photodiode. The movement of cantilever causes variation in the current in photodiode. Finally, this variation in current produces an image on cathode-ray tube.

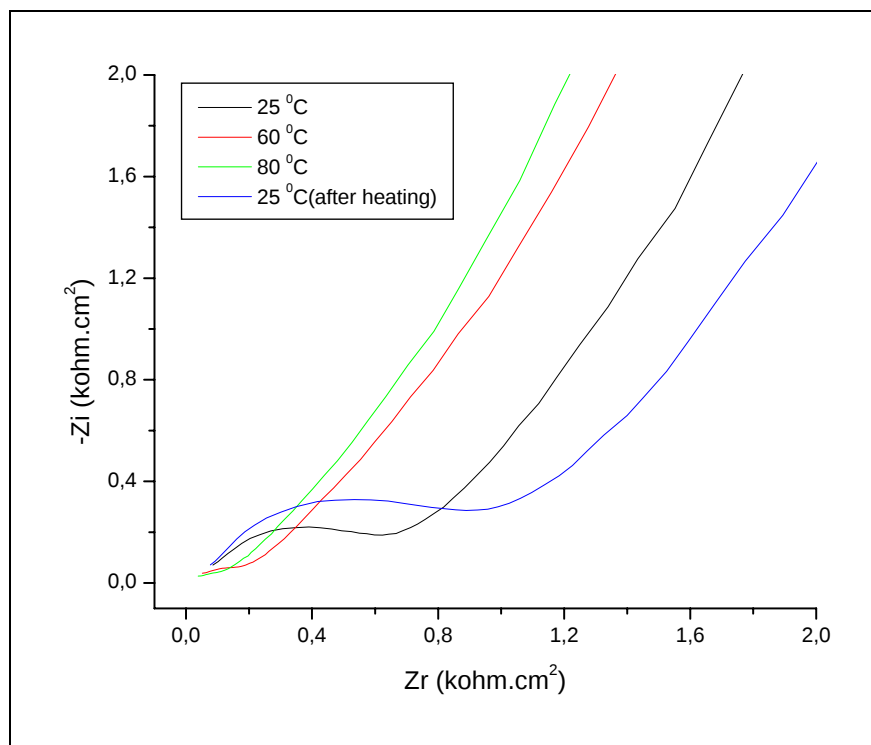


**Figure 3.7 :** A Schematic drawing of an atomic force microscope [26]

According to the type of forces between the tip and the sample, AFM can be operated generally at two different modes, such as contact and dynamic modes. In contact mode, the tip is brought into physical contact with the sample surface and the system uses repulsive forces. This mode is used for atomic scale imaging of flat and rigid samples. However, in this mode samples can be easily damaged or moved. In dynamic mode, the cantilever is vibrated to its free resonance frequency. Upon interaction of the tip with the sample surface, the vibrational characteristics are altered and used as a feedback signal for surface topography of sample.

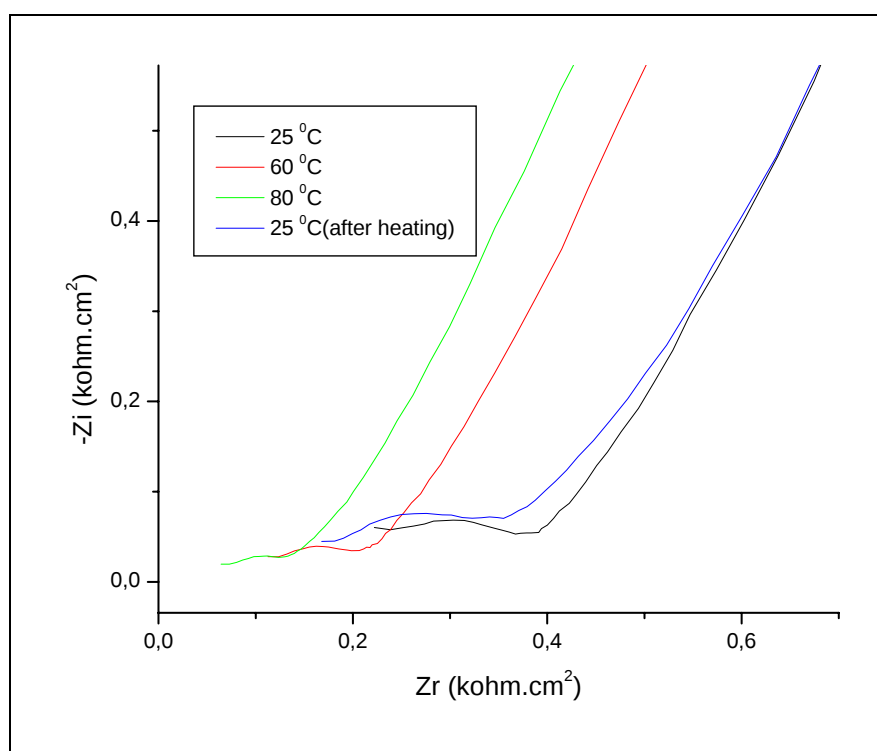
## 4. RESULTS AND DISCUSSIONS

### 4.1 Impedance Measurements



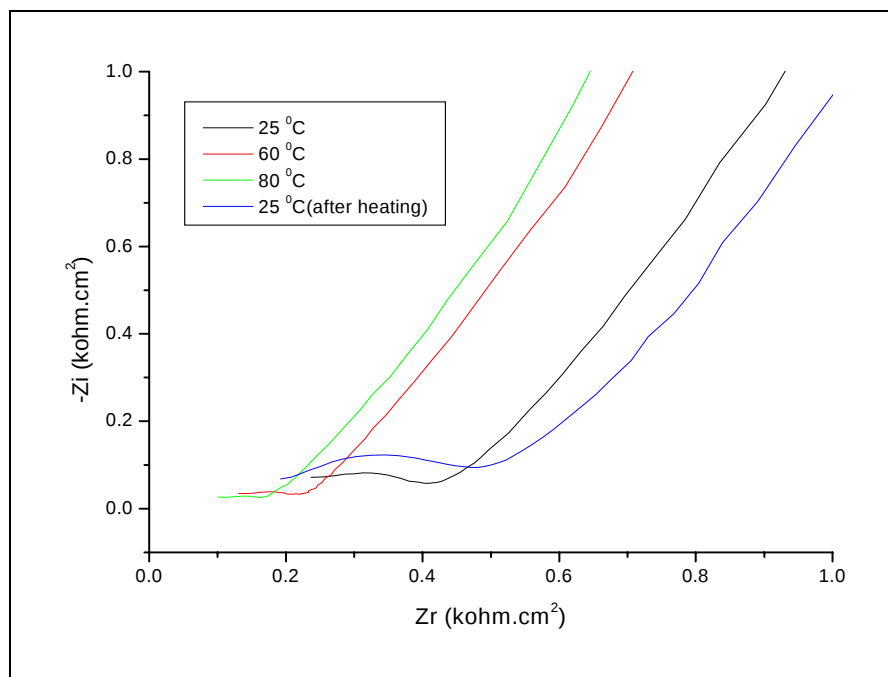
**Figure 4.1 :** Impedance Measurements of 30% (w/v) H<sup>+</sup> - Clinoptilolite membrane

When temperature increases, the curve shifts to left and becomes narrower. So that the resistivity of the membrane decreases with temperature. After testing the membrane at 80 °C, the temperature was lowered to 25 °C, in this time it showed a quite high resistivity than the value of the first measurement at 25 °C.

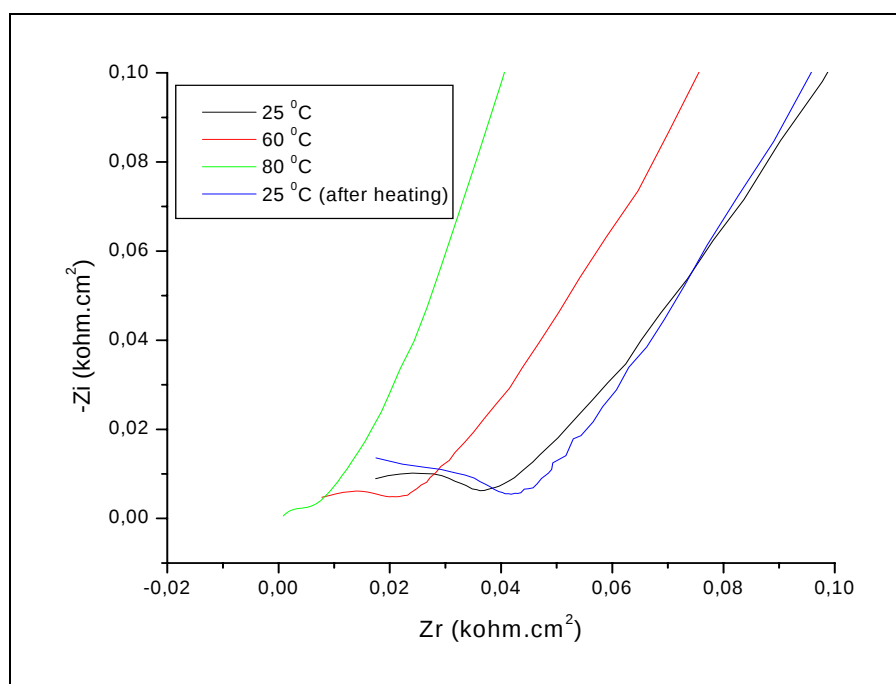


**Figure 4.2 :** Impedance measurements of 30% (w/v) Na<sup>+</sup>-clinoptilolite membrane

Na<sup>+</sup> form of the 30% (w/v) clinoptilolite membrane showed lower resistivities than that of H<sup>+</sup> form.

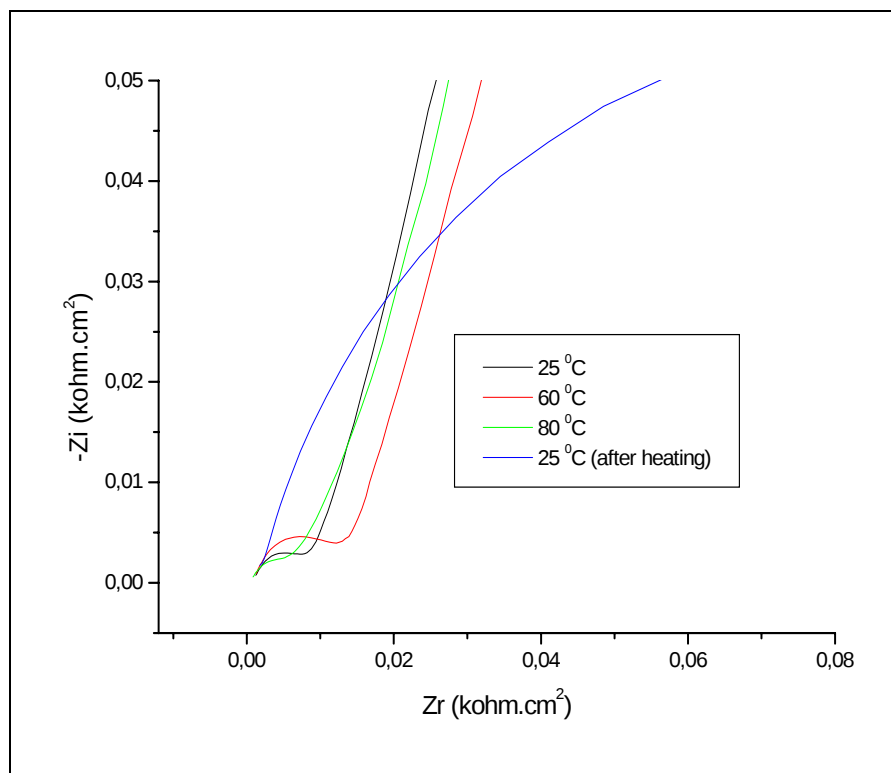


**Figure 4.3 :** Impedance measurements of 7.7% (w/v) H<sup>+</sup>-clinoptilolite membrane



**Figure 4.4 :** Impedance Measurements of 7.7 % (w/v) Na<sup>+</sup>-clinoptilolite membrane

Na<sup>+</sup> form of 7.7 % (w/v) clinoptilolite membrane showed lower resistivity values than H<sup>+</sup> form which is similar with the situation of 30 % (w/v) membranes.



**Figure 4.5 :** Impedance measurements of Nafion 117 membrane

The impedance analysis of Nafion 117 shows us the resistivity of Nafion increases evidently after the high temperature measurements. This lead to a notable decrease in its proton conductivity value.

**Table 4 :** Proton conductivities of Nafion 117 and Nafion composite membranes

| <b>Membrane Identification</b>              | <b>Proton Cond.<br/>(S cm<sup>-1</sup>)<br/>25 °C</b> | <b>Proton Cond.<br/>(S cm<sup>-1</sup>)<br/>60 °C</b> | <b>Proton Cond.<br/>(S cm<sup>-1</sup>)<br/>80 °C</b> | <b>Proton Cond.<br/>(S cm<sup>-1</sup>)<br/>25 °C<br/>(after heating<br/>up to 80 °C)</b> |
|---------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------------------------------------------|
| <b>Nafion 117</b>                           | 4.84 x 10 <sup>-4</sup>                               | 6.62 x 10 <sup>-4</sup>                               | 1.22 x 10 <sup>-3</sup>                               | 3.28 x 10 <sup>-5</sup>                                                                   |
| <b>H<sup>+</sup> Memb.<br/>(30%, w/v)</b>   | 3.02 x 10 <sup>-5</sup>                               | 7.08 x 10 <sup>-5</sup>                               | 1.52 x 10 <sup>-4</sup>                               | 2.18 x 10 <sup>-5</sup>                                                                   |
| <b>Na<sup>+</sup> Memb.<br/>(30%, w/v)</b>  | 7.13 x 10 <sup>-5</sup>                               | 1.23 x 10 <sup>-4</sup>                               | 1.61 x 10 <sup>-4</sup>                               | 6.83 x 10 <sup>-5</sup>                                                                   |
| <b>H<sup>+</sup> Memb.<br/>(7.7%, w/v)</b>  | 6.03 x 10 <sup>-5</sup>                               | 1.01 x 10 <sup>-4</sup>                               | 1.21 x 10 <sup>-4</sup>                               | 5.24 x 10 <sup>-5</sup>                                                                   |
| <b>Na<sup>+</sup> Memb.<br/>(7.7%, w/v)</b> | 6.55 x 10 <sup>-4</sup>                               | 8.88 x 10 <sup>-4</sup>                               | 1.11 x 10 <sup>-3</sup>                               | 4.93 x 10 <sup>-4</sup>                                                                   |

Table shows the proton conductivity values of composite membranes and Nafion 117 membrane at different temperatures. It can be seen that the proton conductivity behaviours of Na<sup>+</sup>-clinoptilolite composite membranes at higher temperatures are higher than that of H<sup>+</sup>-clinoptilolite composite membranes. This can be explained by the hydrophilic groups of zeolites. The outer surface of H<sup>+</sup> form membranes is more hydrophilic than of Na<sup>+</sup> form membranes. During the heat treatment of Nafion dispersion, the hydrophilic parts of Nafion with SO<sub>3</sub>H groups tend to inversely orient and H<sup>+</sup> groups of zeolites with more hydrophilic outer surface are more likely to be surrounded by these Nafion micelles. Finally, this results in the blocking of ionic clustered channels. The proton conductivity decreases with zeolite content because of the effect of inversely orientation.

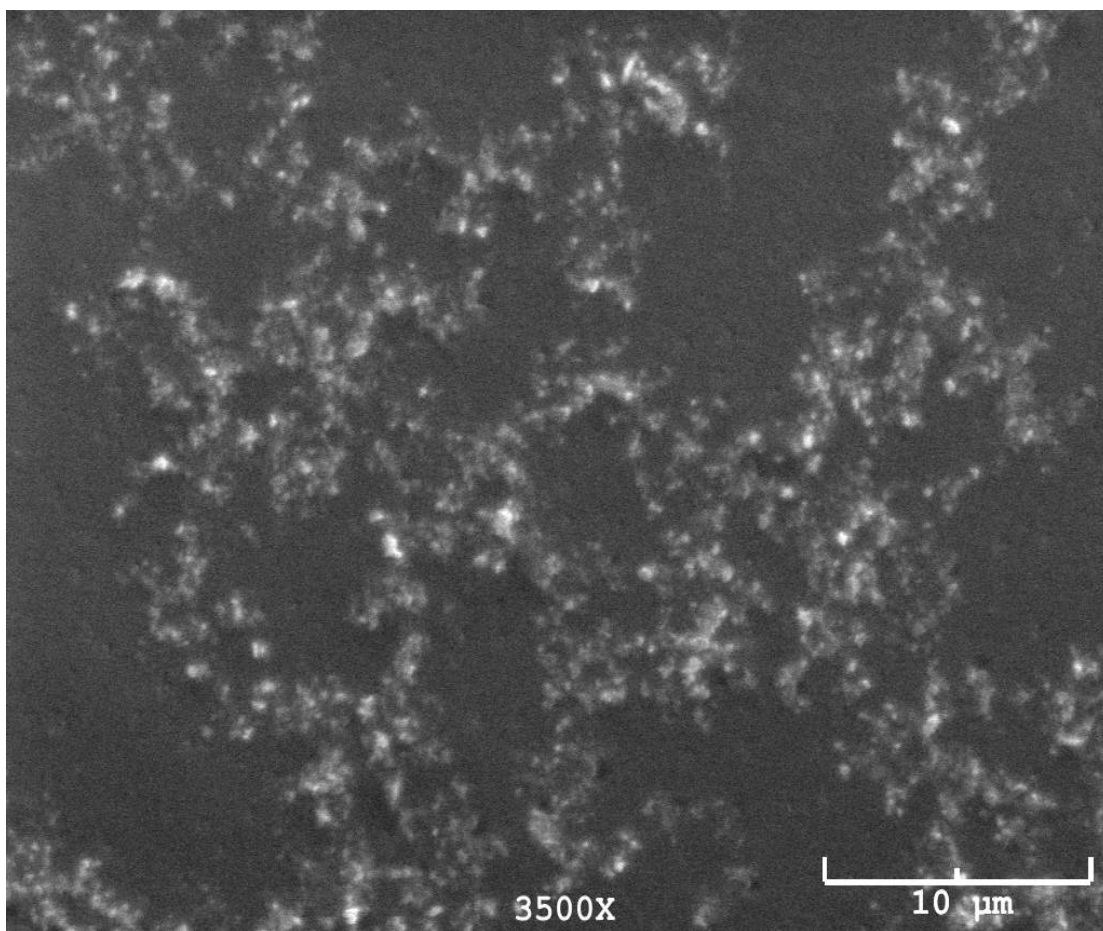
We also see in Table 4 that proton conductivities increase with temperature. After measuring the membranes at 80 °C, we decreased the temperature to 25 °C to test the thermal and chemical stabilities of the membrane. We observed that, all of the

conductivities of the composite membranes decreased slightly but Nafion 117 showed an evident decrease in its conductivity value.

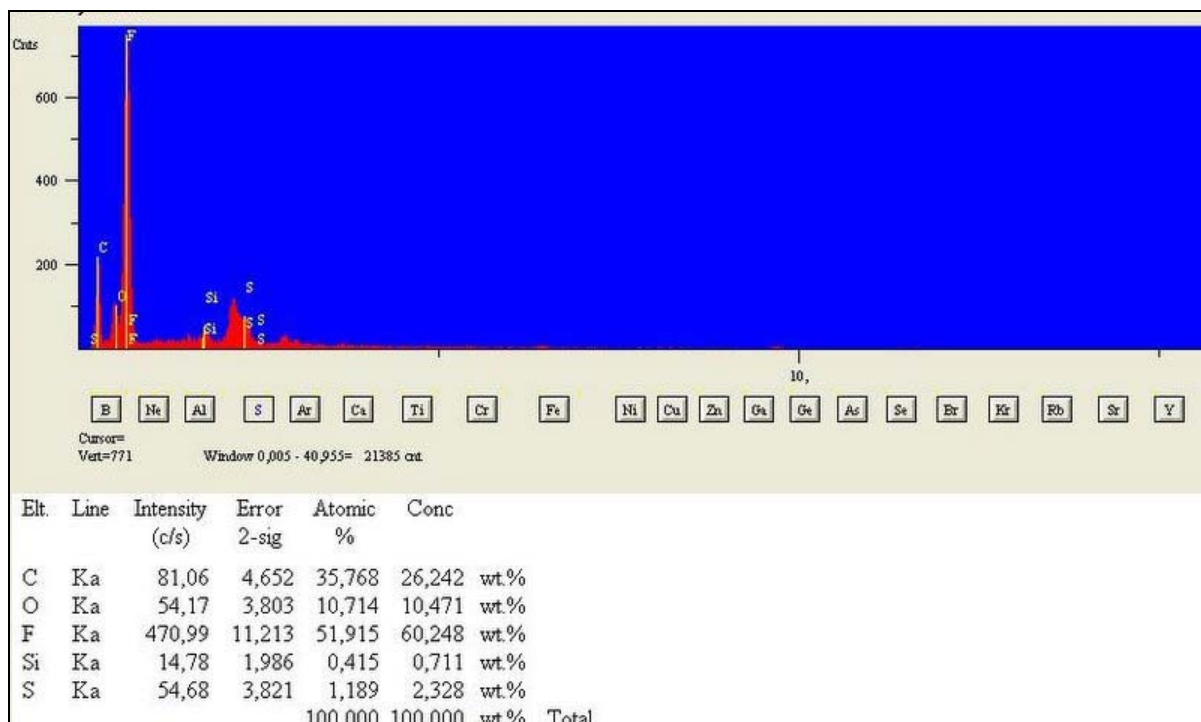
## **4.2. Microscopic Measurements**

### **4.2.1 SEM and EDX Results**

SEM and EDX analysis were performed by Jeal JSM-T330 Scanning Microscope.



**Figure 4.6 :** SEM image of clinoptilolite-Nafion dispersion

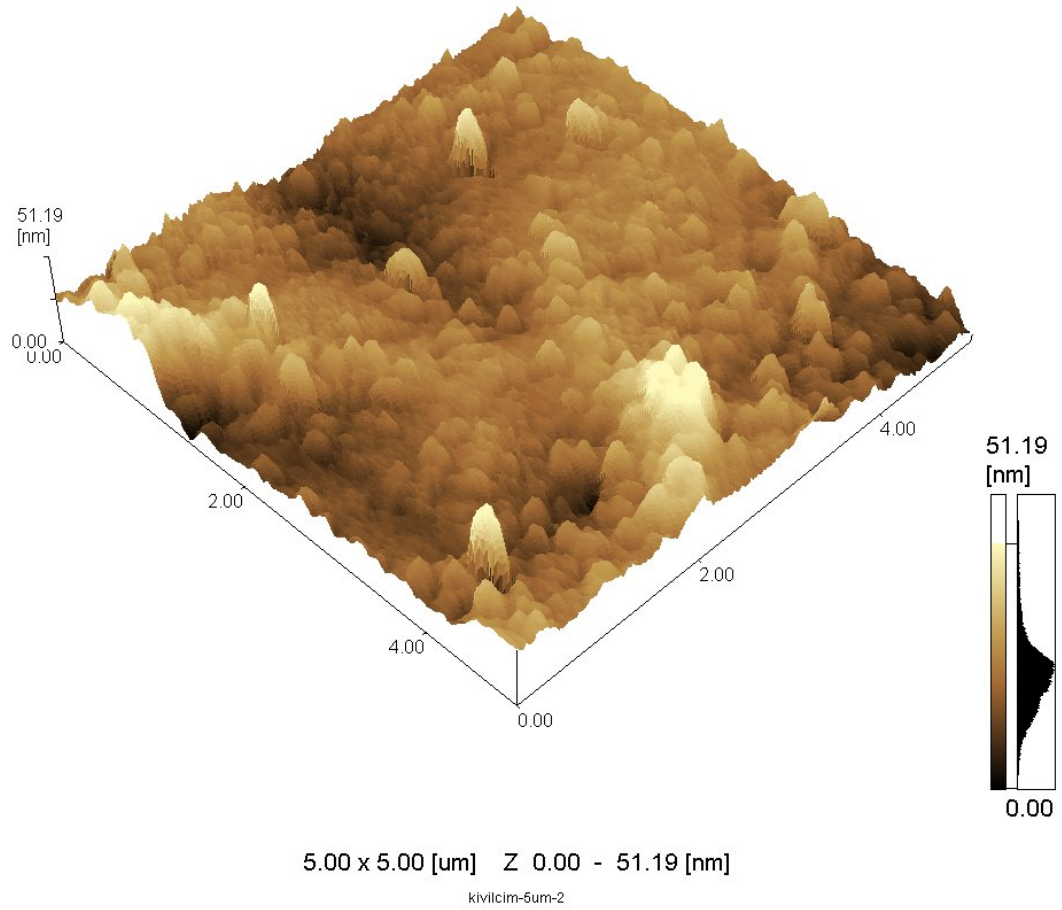


**Figure 4.7 :** EDX results of clinoptilolite-Nafion Dispersion

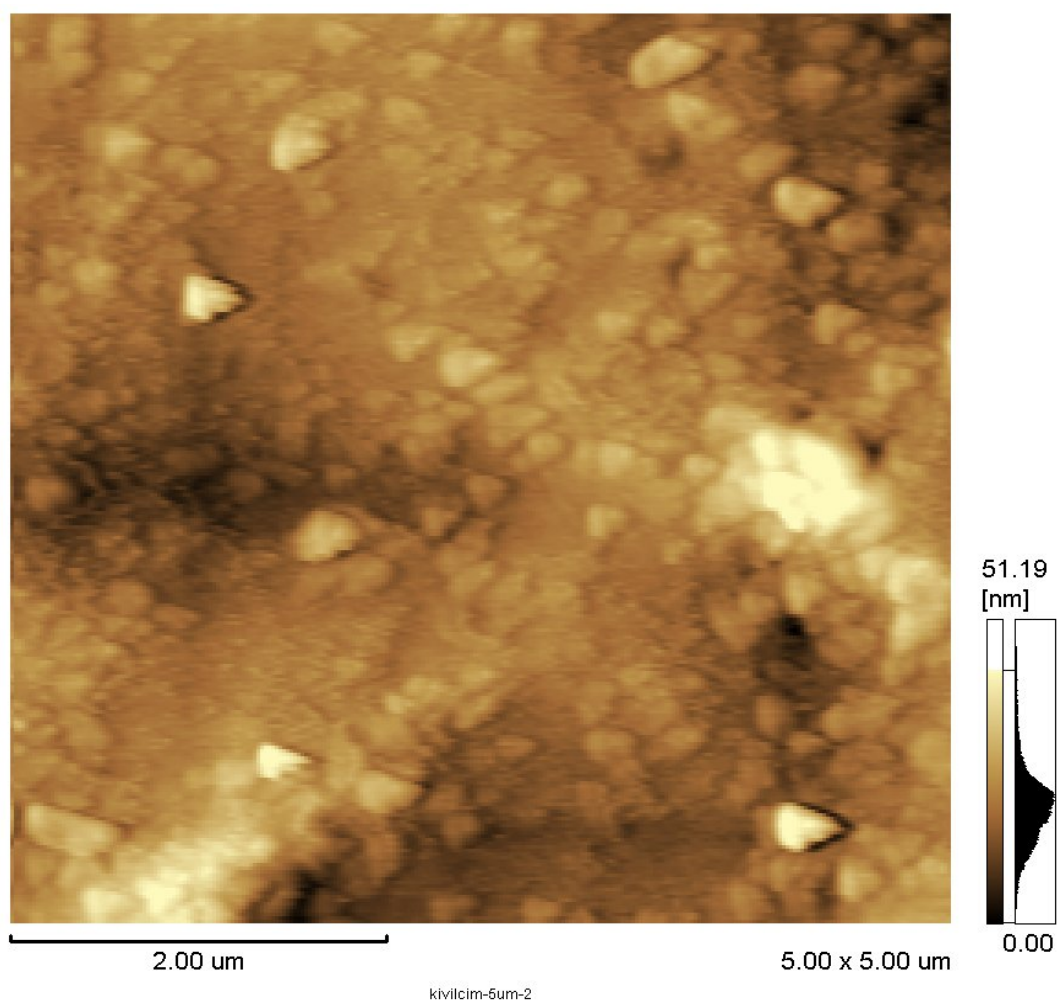
The SEM image of the composite membrane is presented in Figure 4.6. It shows the zeolite fillers are evenly well dispersed in the Nafion matrix in the size range of 0.3-1  $\mu\text{m}$ . Figure 4.7 shows the EDX results which monitors the concentration of carbon, oxygen, fluorine, silicon and sulfur. Fluorine is an indicative of Nafion while silicon is an indicative of zeolite.

#### 4.2.2 AFM Results

AFM images were obtained by Shimadzu SPM- 9500J3 in dynamic mode. The membranes were scanned on two scan sizes (2.50  $\mu\text{m}$  x 2.50  $\mu\text{m}$  and 5.00  $\mu\text{m}$  and 5.00  $\mu\text{m}$ )

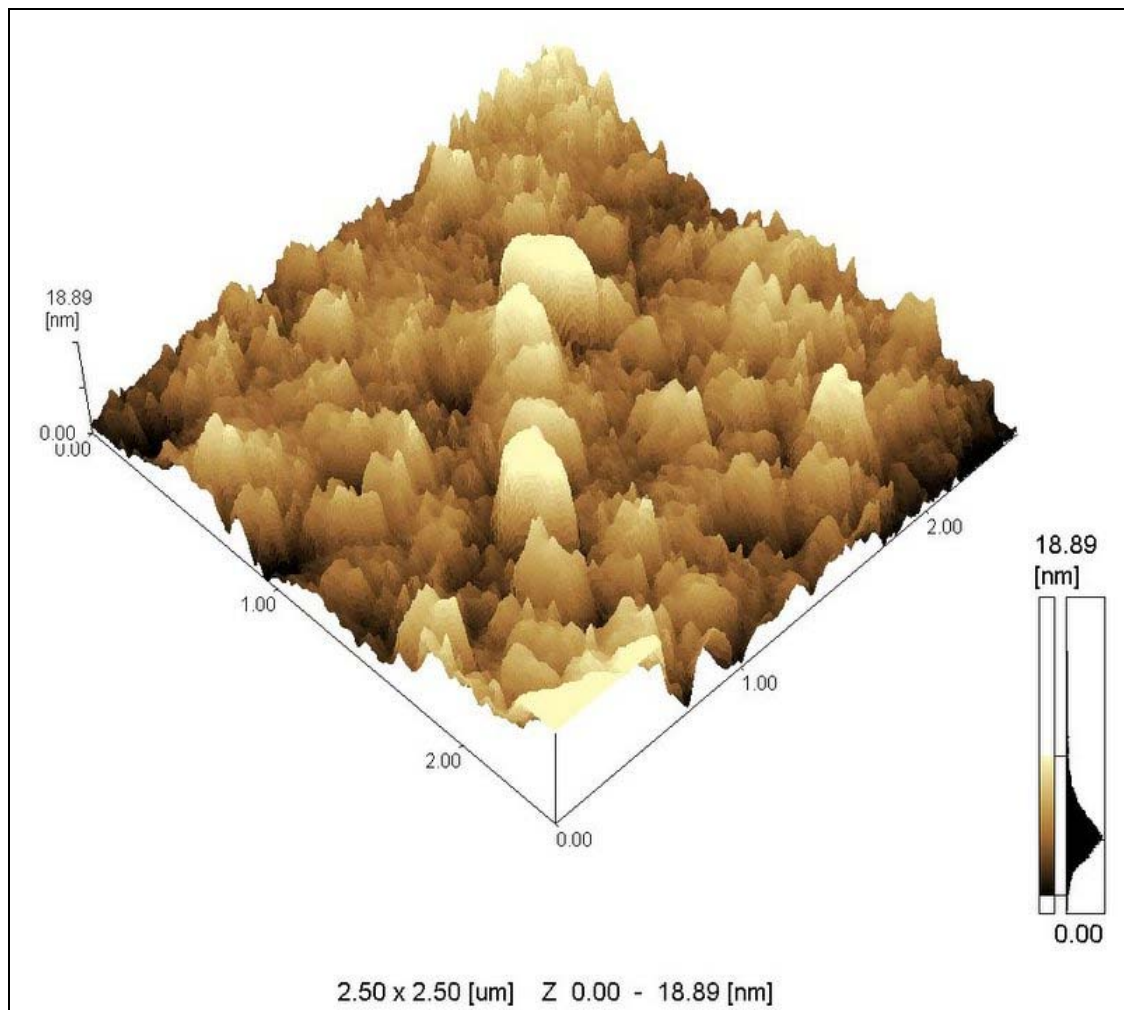


**Figure 4.8 :** 3 dimensional AFM image ( 5.00 μm x 5.00 μm) of clinoptilolite-Nafion membrane



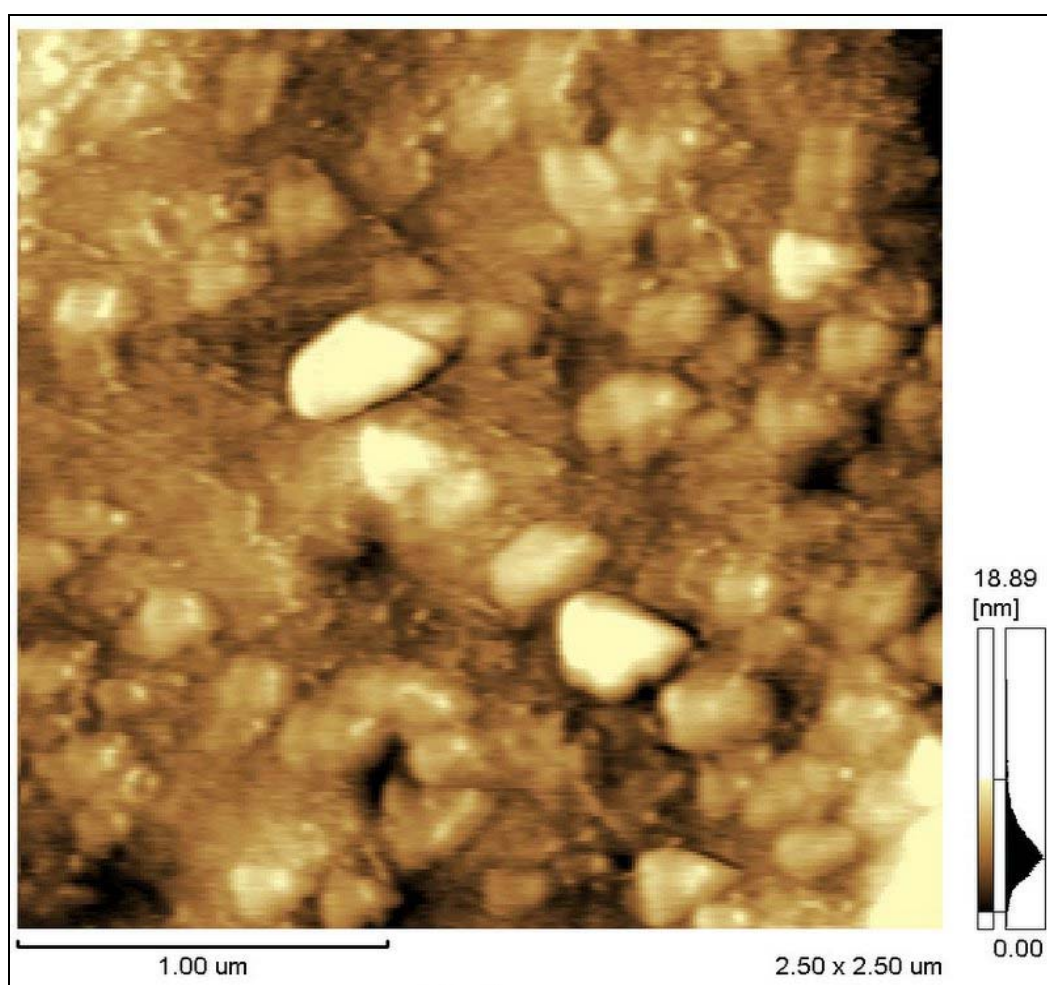
**Figure 4.9 :** 2 dimensional AFM image ( 5.00  $\mu\text{m}$  x 5.00  $\mu\text{m}$ ) of clinoptilolite-Nafion membrane

AFM images provided information about the surface of composite membrane. In figure 4.8, a 3 dimensional image is monitored in coordinates of x, y, z. The z axis shows the height of rough surface of the membrane. The darker parts are the low regions of the membrane. Figure 4.9 is the image of the membrane from top view.



**Figure 4.10:** 3 dimensional AFM image (2.50  $\mu\text{m}$  x 2.50  $\mu\text{m}$ ) of clinoptilolite-Nafion membrane

When the image is zoomed to the size of 2.50  $\mu\text{m}$  x 2.50  $\mu\text{m}$  dimensions, we can see the roughness in more detail.



**Figure 4.11 :** 2 dimensional AFM image (2.50 μm x 2.50 μm) of clinoptilolite-Nafion membrane

## 5. CONCLUSION

The aim of this study was to develop zeolite-Nafion composite membranes that have high mechanical strength, thermal and chemical stability and high proton conductivity at elevated temperatures at relatively low cost. Clinoptilolite was chosen as zeolitic filler because it is fairly low cost and it is chemically stable in aqueous solutions within the pH range of 3-12. It was expected that, zeolitic fillers will contribute to the mechanical strength, thermal stability and proton conductivity of the membrane. The conductivity results showed that the  $\text{Na}^+$  form membranes exhibited higher proton conductivity value than that of  $\text{H}^+$  form membranes. The highest proton conductivity was measured as  $1.11 \times 10^{-3} \text{ Scm}^{-1}$  at  $80^\circ\text{C}$  which is very comparable to Nafion 117. It was also seen that the conductivity values decreased with zeolite content which was attributed to the blocking effect of zeolites. Additionally, the composite membranes showed high thermal and chemical stability. SEM and AFM analysis proved that zeolitic fillers were well dispersed in Nafion matrix. During the synthesis of zeolite-Nafion composite membranes, the difficulty was that natural zeolites do not allow control of pore structure and particle size.

In conclusion, the composite membranes resulted in adequate mechanical strength, thermal and chemical stability. However, their proton conductivity values were slightly less than the values of Nafion 117.

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## **BIOGRAPHY**

Kıvılcım Topbaş was born in İzmir in 1984. She graduated from Bornova Anatolian High School in 2002. She took her Bachelor's Degree from the Department of Chemistry, İzmir Institute of Technology in 2006.

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