

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**A NOVEL METHOD FOR SYNTHESIS OF AN ALKALINE POLYMER
ELECTROLYTE MEMBRANE AND ITS APPLICATION IN A FUEL CELL**

Ph.D. THESIS

Aydın Can ARAL

Department of Chemical Engineering

Chemical Engineering Programme

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(506052002)**

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Thesis Advisor : Assoc. Prof. Dr.Ahmet SİRKECİOĞLU

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**ALKALİ POLİMER ELEKTROLİT MEMBRAN SENTEZLEMELİK İÇİN
YENİ BİR YÖNTEM VE YAKIT PİLİ UYGULAMASI**

DOKTORA TEZİ

**Aydın Can ARAL
(506052002)**

Kimya Mühendisliğı Anabilim Dalı

Kimya Mühendisliğı Programı

Tez Danışmanı : Doç. Dr. Ahmet SİRKECİOĞLU

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Aydın Can Aral, a **Ph.D.** student of ITU **Graduate School of Science Engineering and Technology in Chemical Engineering** student ID **506052002**, successfully defended the **dissertation** entitled “**A NOVEL METHOD FOR SYNTHESIS OF AN ALKALINE POLYMER ELECTROLYTE MEMBRANE AND ITS APPLICATION IN A FUEL CELL**”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assoc.Prof. Dr. Ahmet Sirkecioğlu**.....
İstanbul Technical University

Jury Members : **Prof.Dr. Hüsnü Atakül**
İstanbul Technical University

Prof. Dr. Seniha Güner
İstanbul Technical University

Prof. Dr. Ersan Kalafatoğlu
Marmara University

Assoc.Prof.Dr. Alper Sarioğlu
TÜBİTAK Marmara Research Center
Energy Institute

Date of Submission : 09 September 2013

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FOREWORD

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September 2013

Aydın Can ARAL
(Chemical Engineer)

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ABBREVIATIONS

AAEM	: Alkaline Anion Exchange Membrane
ADEFC	: Alkaline Direct Ethanol Fuel Cell
Aq	: Aqueous
CBT	: Coagulation Bath Temperature
DMM	: Digital Multi Meter
DTA	: Differential Thermal Analysis
EDS	: Energy Dispersive X-ray analysis
EIS	: Electrochemical Impedance Spectroscopy
EOD	: Electro-Osmotic Drag
EOR	: Ethanol Oxidation Reaction
ISP	: Ion Solvating Polymer
MEA	: Membrane Electrode Assembly
MPD	: Maximum Power Density
NMP	: N-Methyl-2-Pyrrolidone
OCV	: Open Circuit Voltage
ORR	: Oxygen Reduction Reaction
PBI	: Polybenzimidazole
PEM	: Proton Exchange Membrane
PES	: Poly Ether Sulfone
SEM	: Scanning Electron Microscopy
SC	: Short Circuit
TGA	: Thermo Gravimetric Analysis
wt	: Weight

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A NOVEL METHOD FOR SYNTHESIS OF AN ALKALINE POLYMER ELECTROLYTE MEMBRANE AND ITS APPLICATION IN A FUEL CELL

SUMMARY

In this work a new method for synthesizing ion conductive polymers from insulating material is demonstrated for use in alkaline direct ethanol fuel cells (ADEFC). Using immersion precipitation technique with polyethersulfone dissolved in N-methylpyrrolidone, cast films are immersed in an aqueous NaOH coagulation bath.

Coagulation bath temperature (CBT) was changed for tailoring the NaOH loading to the membranes. When the CBT was increased from 36 to 66°C, NaOH loading has increased from 3.64wt% to 10wt%. Porosity showed a non-linear relation with CBT and it decreased from 0.62 to 0.55 as the bath temperature was increased from 36 to 56°C but has increased to 0.67 when the bath temperature was further increased to 66°C. The membrane samples with different NaOH loading were kept in distilled water for a duration of three weeks during which weight and pH measurements were recorded and it was shown that only 0.16 to 0.27wt% NaOH has leached out. The pH value has reached its maximum within 24 hours and has stayed constant after on, where as the weight of the samples has reached its maximum within 24 hours but then decreased to an asymptotic value. Although anionically conductive membranes were synthesized during this study, cationically conductive membranes can be synthesized utilizing the same method but using different chemicals.

In-addition, fuel cell performance of composite PES membranes are investigated in relation to the CBT. 2M Ethanol in 1M NaOH fuel is circulated at 53 cc/min at the anode and 828 scc/min O₂ is fed at the cathode. Fuel cell setup was temperature controlled at 60°C.

Maximum power density (MPD) increases from 34 to 46°C CBT and decreases on average from 46 to 66°C. The best MPD obtained with the membranes synthesized at 46°C is 13.04 mW.cm⁻².

Nafion 117 is modified to Na⁺ conducting form for benchmarking and 11.82 mW.cm⁻² MPD is obtained. Composite PES membranes generated higher open circuit voltage around 730 mV, where as the modified Nafion generated around 700 mV. Maximum current density obtained with the composite PES membranes was 104.2 mA.cm⁻² compared to 192.4 mA.cm⁻² obtained with the modified Nafion. In summary composite PES membranes slightly out-performed the modified Nafion in the alkaline direct ethanol fuel cell setup.

ALKALİ POLİMER ELEKTROLİT MEMBRAN SENTEZLEMEK İÇİN YENİ BİR YÖNTEM VE YAKIT PİLİ UYGULAMASI

ÖZET

İyonik olarak yalıtkan bir polimer olan poli ether sulfon (PES) ile başlanarak, iletken membranlar daldırma-çöktürme yöntemi ile sentezlenmiştir. Sodyum hidroksit çözeltisi daldırma banyosu olarak kullanılmış ve PES/N-Methyl-2-Pyrrolidone (NMP) polimer çözeltisi bu banyo içine anyonik olarak iletken membranların (AAEM) sentezlenmesi için daldırılmıştır.

Daldırma banyosu sıcaklığı kontrol edilerek bu parametrenin sentezlenen membranlara yüklenen NaOH miktarı ile membran porozitesi üzerindeki etkisi çalışılmıştır. Banyo sıcaklığı 36°C'den 66°C'ye çıkarıldığında, NaOH yüklemesi ağırlıkça % 3.64 ten % 10'a yükselmiştir. Porozite ise banyo sıcaklığı ile doğrusal olmayan bir ilişki sergileyip, sıcaklığın 36°C'den 56°C'ye yükseltilmesiyle 0.62 den 0.55'e düşmüş, ancak sıcaklığın 66°C'ye çıkartılmasıyla porozite 0.67'ye çıkmıştır. Farklı banyo sıcaklıklarında sentezlenen membranlardan alınan örnekler distile suda üç hafta boyunca bekletilmiş ve bu süre zarfında örneklerin ağırlık değişimleri ve içinde bekletilen suyun pH değerleri kayıt edilmiştir. Sonuç olarak ağırlıkça sadece % 0.16-0.27 arasında NaOH'ın suya salındığı görülmüştür. pH değerleri ilk 24 saat içinde maksimum değere ulaşmış ve daha sonrasında aynı kalmıştır. Ancak numune ağırlıkları ilk 24 saat içinde maksimum değere ulaştıktan sonra asimtotik bir değere doğru azalmışlardır. Bu çalışmada anyonik iletken membranlar sentezlenmiştir, ancak tarif edilen yöntem ile farklı kimyasallar kullanılarak, katyonik iletken membranlar da sentezlenebilir.

Sentezlenen membranların yakıt pili performansları sentez banyo sıcaklığına göre irdelenmiştir. 66°C de sentezlenen membran için yakıt alkalinitesine göre performans ölçümleri yapılmış ve 0.15M, 0.64M ve 1.00M NaOH çözeltileri ile yapılan deneylerde en yüksek performans 1.00M NaOH yakıt alkalinitesi ile elde edilmiştir. Bu sebeple tüm deneyler 1.00M NaOH yakıt alkalinitesi ile yapılmıştır.

2M etanol 1M NaOH yakıtı 53 cc/min debi ile anotda sirküle edilmiş ve 828 scc/min O₂ katoda beslenmiştir. Hücre sıcaklığı 60°C de kontrol edilmiştir.

Zirve birim güç 36°C den 46°C ye olan sentez sıcaklığında artmış, 46° - 66°C aralığında ise ortalama değer düşmüştür. En iyi sonuç 46°C de 13.04 mW.cm⁻² ile elde edilmiştir. Kıyaslama amacı ile Nafion, Na⁺ iletken formuna dönüştürülmüş ve aynı koşullarda 11.82 mW.cm⁻² zirve birim güç elde edilmiştir. Açık devre potansiyeli (OCV) ve zirve birim akım değerleri ise kompozit PES ve Nafion-Na⁺ için sırası ile 730 mV, 104.2 mA.cm⁻² ve 700 mV, 192.4 mA.cm⁻² şeklinde ölçülmüştür. Özetle, kompozit PES membranlar az farkla Nafion-Na⁺ membrandan daha iyi performans göstermiştir.

Nafion, H^+ formundan Na^+ formuna E.H.Yu et. al. ın tanımladığına benzer şekilde dönüştürülmüştür. Nafion önce yarım saat distile suda kaynatıldıktan sonra, 1 saat boyunca 1M NaOH çözeltisi içinde kaynatılmış ve kullanımdan önce distile suyla durulanmıştır.

Kompozit PES membranların yakıt pili performansları karakterizasyon sonuçları ile beraber irdelendiğinde; membran içinde kalan NMP arttıkça yakıt pilinde elde edilen zirve birim güç düşmektedir. Zira artan NMP, membran içindeki gözenekleri işgal etmekte ve iletkenliği sağlayan NaOH çözeltisinin yerini almaktadır.

Yakıt pilinde test edilen membranların TGA analizleri incelendiğinde membran morfolojisinin membranın tuttuğu su miktarı ile değişebildiği anlaşılmıştır. Membranlar atmosfere açık koşullarda saklandığında su kaybetmekte ve içeriğini oluşturan kimyasalların oranları değiştiğinden kırılgan hale gelmektedirler. İyonik iletkenliğin suya doygun haldeki membranlarda daha yüksek olduğu düşünülürse, membranları suya doygun halde hermetik olarak izole edilmiş şekilde saklamak en uygunu olacaktır.

Membran içine yüklenen NaOH'ın iletkenliği sağladığı bilinmekle beraber daha çok NaOH'ın daha yüksek performans sağlamadığıda deneylerle sabitlenmiştir. Burada aynı zamanda membranın morfolojiside rol oynamakta olup gözenek boyutu ve dağılımının kritik önemi vardır. Eldeki veriler incelendiğinde optimum performansın $46^{\circ}C$ deki banyoda sentezlenen membranlar ile elde edilebildiği anlaşılmıştır.

Daldırma-çöktürme yönteminde beş adet bağımsız parametre mevcut olup bunlar; banyo sıcaklığı, banyo kompozisyonu, polimer çözelti kompozisyonu, polimer çözelti film kalınlığı ve daldırma süresidir. Bu çalışmada banyo sıcaklığının membran morfolojisi ve membran yakıt pili performansı üzerindeki etkileri çalışılmıştır. Diğer parametreler ve kullanılan ticari katalizörler Alkali Direk Etanol Yakıt Pili için optimize edilmediğinden elde edilen performans yüksek değildir ancak geliştirilmesi mümkündür.

Na^+ Nafion membranda iletkenliği sağlayan Na^+ iyonu olduğundan bu iyonun sürekli anottan katot a transferi gerçekleşmektedir. Bu sebeple eğer anoda devamlı Na^+ iyonu takviyesi olmaz ise bir süre sonra sistemde Na^+ iyonu dengesi katot lehine bozulacak ve iletkenlik yavaşça düşmeye başlayacaktır. Bunun önüne geçmek için katot ta oluşan NaOH anoda sirküle edilebilir ancak kullanılan sistemde böyle bir mekanizma olmadığından deneyin sonlarına doğru Na^+ Nafion performansında düşüş gözlemlenmiştir. Ancak anotta sirküle eden yakıt uzunca bir süre Na^+ sağlamaya devam etmiş ve kıyaslama yapmaya yetecek kadar veri toplanabilmiştir.

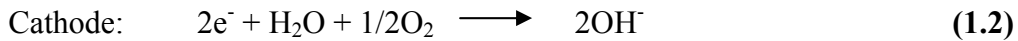
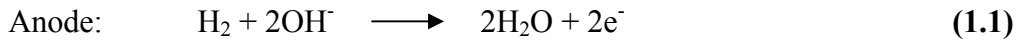
Bir diğer tespit ise OCV değerlerinin tutarlı olarak kompozit PES membranlarda, Na^+ Nafion' a göre daha yüksek ölçülmüş olmasıdır. Bu iki farklı membran tipinde elektrotlar dahil tüm koşullar aynı tutulduğundan bu farkı ancak anottan katoda yakıt kaçışının Na^+ Nafionda daha fazla olması ile açıklayabiliriz. Zira kullanılan ticari katot katalizörü Pt içerikli olup kaçan etanol ile OH^- ın istenmeyen şekilde tepkimeye girmesine ve OCV yi düşürmesine sebep olmaktadır. Buda Na^+ Nafion'un etanol geçirgenliğinin daha yüksek olması ile açıklanabilir.

Bu tip membranların performansları yakıt pilinde denemeden önce genellikle iki parametreye bakılarak ölçülür; iyonik iletkenlik ve yakıt geçirgenliği. Bu iki parametre genelde bir birine oranlanır ve bu, membranın seçiciliği olarak tariflenir. Dolayısı ile sadece iletkenlik yada geçirgenlik pek bir anlam ifade etmemekte bu ikisinin oranına bakılmaktadır.

Bu çalışma esnasında iletkenlik ölçümü için uygun bir ölçüm cihazı bulunamadığından, iletkenlik dolaylı olarak polarizasyon eğrilerinden hesap edilmiştir. Hesaplanan iletkenlik değerleri Na⁺ Nafion için daha yüksek olmakla beraber, OCV farkından anlaşılan geçirgenlik değeride Na⁺ Nafion için daha yüksek olduğundan yakıt pili performansı az farkla kompozit PES membranlar lehine ölçülmüştür.

1. INTRODUCTION

Fuel cells are regarded as a promising technology for many industrial and household applications to preserve the conventional energy stocks and to reduce or eliminate emissions to the environment. The efficiencies of fuel cells which are higher than those of conventional energy technologies, continue improving. Fuel cells can work with a variety of fuels. There are different types of fuel cells, but currently, the direct alcohol polymer electrolyte fuel cell, which is the most mature type of fuel cell, is the most promising in the portable electronics market. The polymer electrolyte membrane type fuel cell also has two subtypes: alkaline anion exchange membrane (AAEM) and proton exchange membrane (PEM) type fuel cells. As their names imply, the AAEM functions in alkaline medium, whereas the PEM functions in acidic medium. In both types, fuel molecules are first adsorbed on the anode catalyst dissociating into carbon and hydrogen complexes. If hydrogen is used as a fuel, the anode and the cathode reactions in an AAEM type fuel cell are:



In contrast to the PEM type fuel cell, water is produced at the anode of the AAEM type fuel cell according to reaction (1.1), and it is consumed at the cathode as a reactant according to reaction (1.2). It is important to establish a water balance such that water is continuously removed from the anode and transferred to the cathode for hydroxide production. Water also plays an essential role for the ionic conductivity of the membranes so the membranes have to be adequately hydrated during fuel cell operation. Water management is thus very important for the efficient functioning of the alkaline direct ethanol fuel cell (ADEFC). Unlike the PEM fuel cell, water flooding of the cathode occurs at intermediate current densities as determined by Li et al. (2011) due to the fact that diffusion flux from anode to cathode outweighs the total water flux due to both the oxygen reduction reaction (ORR) and electro-osmotic drag (EOD). At higher current densities, EOD from cathode to anode dominates and the overall water flux to the cathode is reduced.

The PEM type fuel cell has been studied more extensively than the AAEM type fuel cell, but recently, conditions have started to favor the development of AAEM type fuel cell. Although a vast amount of literature is available on the PEM type fuel cell, a PEM superior to the DuPont®'s Nafion® is yet to be developed. Additionally, the chemical reaction kinetics are 10 to 30 times faster in alkaline medium than they are in acidic medium, the fuel crossover problem is reduced in AAEM due to the migration of OH⁻ ions from the cathode to the anode as illustrated in Figure 1.1, an easier water balance is achieved in AAEMs, and due to faster kinetics, less expensive catalysts can be used in AAEM type fuel cell electrodes (Zhiani et al, 2011).

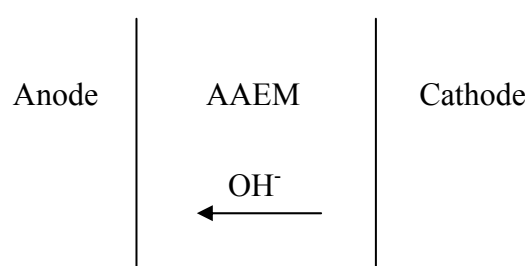
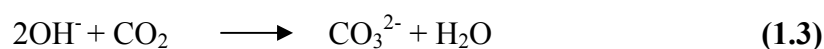


Figure 1.1 : Illustration of hydroxide conduction in AAEM.

Two out of three main problems - fuel leakage from the anode to the cathode and high catalyst cost - that are significant in PEM type fuel cells are greatly reduced in the current AAEM applications. However, when methanol is used as the fuel, the performance of the AAEM type fuel cell, which is in the range of 2 – 20 mW.cm⁻² is lower when compared to that of the PEM type fuel cell, which is in the range of 100 – 300 mW.cm⁻². The lower performance is correlated to the non-optimized electrodes used for AAEM and the carbonation reaction given by equation 1.3:



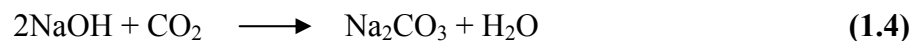
1.1 Ethanol as a Renewable Fuel Source

When ethanol is used as the fuel, the performance loss that results when using methanol is not seen in alkaline AAEM medium, but it is present in acidic PEM medium. This is thought to be related to the faster reaction kinetics occurring in alkaline medium that facilitate the C-C bond cleavage (Rao et al, 2007). Ethanol as a fuel has many distinct advantages over other conventional fuels. The major advantage being the storage, as it can be stored at room temperature as a liquid under atmospheric pressure.

Compared to its rival methanol, it is not poisonous, it is a renewable fuel and its oxidation does not contribute to the green house gases (Kamarudin et al, 2013). Although oxidation of ethanol produces CO₂ if complete, this produced CO₂ is used up during the photosynthesis of plants that are in turn used for producing ethanol. Thus there is no net contribution to the CO₂ cycle. Although it is claimed that if plants such as corn are extensively used for producing ethanol, this will drive the price of corn higher which is also a food product, there are different processes to produce ethanol such as hydrolysis of cellulose. Also ethanol has been demonstrated to have lower crossover rates and affects cathode performance less severely than methanol (Varcoe et al, 2007). Complete oxidation of ethanol molecule yields twelve electrons as compared to six with methanol. Ethanol cross over is a function of operating temperature, current density and ethanol concentration in the fuel. These parameters usually have to be optimized for maximum power output. Considering all these positive aspects, ethanol has started to be a popular fuel in AAEM type fuel cells.

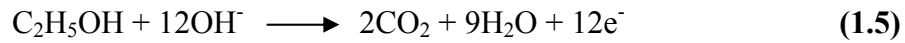
1.2 Ethanol Oxidation Reaction in the Presence of Carbondioxide

Hydroxide depletion in both the electrolyte and the electrodes is still a problem in the AAEM type fuel cell due to the above mentioned carbonation reaction and formation of metal carbonates, when a metal hydroxide is used for creating the alkaline environment. For example, if NaOH is used, Na₂CO₃ is formed according to equation 1.4:



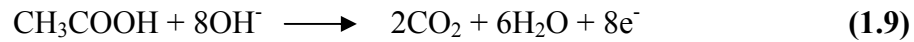
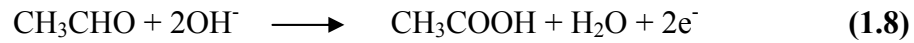
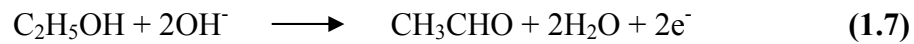
Na₂CO₃ then precipitates on the catalyst surface and hinders the adsorption of fuel molecules on the catalyst. Thus a low operating temperature would decrease the solubility of Na₂CO₃ aggravating the problem. Increasing the operating temperature would both reduce the poisoning effect of CO₂ and would increase the performance of the fuel cell; unfortunately unpressurized systems would need to operate below the normal boiling point of water to achieve adequate conductivities. Also material limitations of composite membranes, especially the ones with functional groups, put a limit usually lower than 100°C (Merle et al, 2011). Hence, the operating temperature needs to be optimized uniquely relevant to the fuel cell system.

When ethanol is used as the fuel, CO₂ is an oxidation product at the anode and it is hard to eliminate it from the anode compartment, but usually the oxidation of ethanol in the anode is not complete yielding by-products such as ethyl acetate and acetic acid. However, if pure O₂ is available as the oxidant, it is preferred over using air which is another source for CO₂. Equations 1.5 and 1.6 are the anode and the cathode reactions respectively for the complete ethanol oxidation-reduction:



The theoretical overall standard cell potential for ethanol oxidation and reduction reactions given above is +1.145 Volts (Song et al, 2007). However, due to incomplete oxidation of ethanol, interfacial resistance in-between the membrane and the electrodes and the mass transport limitation, the actual measured potentials are always lower than the theoretical value. For PEM type direct ethanol fuel cells the measured OCV values range in-between +0.775 to +0.827 Volts (Song et al, 2007).

The complete oxidation of ethanol is thought to occur in three steps:



Reactions 1.7 and 1.8 readily occur with Pt-Ru catalyst in alkaline environment. However, the last step (1.9) involving eight electrons is thought to be relatively much slower and thus occur only in minute amounts (Fujiwara et al, 2008). In addition to the carbonation reaction mentioned above, intermediate product CH₃COOH can react with NaOH, producing CH₃COONa and water, wasting the OH⁻ ions. However, CH₃COONa has a higher solubility in water than Na₂CO₃, 139 gr versus 46 gr in 100 ml water at 60°C. Hence, blocking of the catalyst surface is less of a concern for CH₃COONa.

1.3 Catalysts for EOR and ORR

As for the anode catalysts for EOR, totally Pt free catalysts have been demonstrated such as the HYPERMEC™ of Acta made from clusters of Ni-Fe-Co alloys in a matrix of hydrazone based polymers.

Pd substituted Pt in many works with adatoms such as Pb, Tl, Cd, Ru, Au, Sn and Cu. Cathode catalysts of Ag-W₂C, Pd, Pt-Ru, Pt-Co/C and Pt-Pd/C have been shown to have increased activity for ORR (Kamarudin et al, 2013). Bimetallic alloys of Pt-M and Pd-M where M is Ru, Ti, Sn, Pb, Rh and Ni have been utilized in alkaline environment. Whereas, tri-metallic alloys of Pt-Sn-M where M is Pd, Rh, Ni and Co are used again for EOR this time in acidic media (Beyhan, 2010). Highest activity was observed with the Pt-Sn-Co anode catalyst along with Pt cathode catalyst at 80°C where 34.5 mW.cm⁻² has been reported. Also, totally Pt free catalysts such as Ni-Fe-Co HYPERMEC™ for EOR and Fe-Co HYPERMEC™ for ORR have been used with Ethanol-KOH and A201 Tokuyama membrane where authors claimed 60 mW.cm⁻² at 40°C (Kamarudin et al, 2013). Almost all the time catalyst particles are supported on carbon black.

Power densities as high as 170 mW.cm⁻² with Pd-Ni-Zn anode and Fe-Co cathode with A-006 Tokuyama membrane at 80°C using ethanol-KOH and power densities as low as 1.71 mW.cm⁻² with conventional materials have been reported in the same reference (Kamarudin et al, 2013). Therefore a wide range of performances with different configurations are available in the literature. In this thesis commercial Pt-Ru/C and Pt/C electrodes were used for the anode and the cathode respectively.

1.4 Alkaline Anion Exchange Membrane

The choice of polymer is very important for the application it is intended for. AAEM fuel cell conditions require good ionic conductivity and resistance to heat and chemical attack. Among the candidates, polybenzimidazole (PBI) and polyethersulfone (PES) are the most chemically and thermally stable polymers. These polymers are insulators for ions, however they can be engineered to be ion-conductive via different methods. PBI is relatively expensive and cumbersome to work with. PES on the other hand is abundant and cheap. PES has a long-term thermal stability up to 180°C and is chemically stable in highly alkaline environments (50 wt% NaOH) and alcohols (Mitsui chemicals), which make it a good candidate for AAEM type fuel cells.

AAEM's and PEM's are both classified as solid polymer electrolytes. Solid polymer electrolytes can be differentiated by the ionic mode of conduction within the polymer matrix i.e; ion solvating polymers (ISP) and polyelectrolytes.

ISP membranes conduct ions via migration of anions or cations through the membranes where as polyelectrolytes are polymers on which ionic functions (sulphonate, carboxylate, or quaternary ammonium) are grafted on polymer backbones and ionic conductivity is ensured by the counter ion. Nafion® is an example for a polyelectrolyte. Where as the membranes synthesized via the method mentioned in this study are examples for ISP membranes. ISP membranes are mainly synthesized by immersing a non-conductive membrane such as PBI into a concentrated electrolyte and saturating the membrane with this electrolyte solution (Xing, 2000). Alternatively, ISP's are formed by dissolving a water soluble polymer in water and adding electrolyte to this solution. There is also the combination approach where polyelectrolyte membranes are saturated with electrolytes. This approach enhances the ionic conductivity even further. For instance An et al. (2012) use Tokuyama A201 membrane and measure its ionic conductivity as $5\text{mS}\cdot\text{cm}^{-1}$ in DI water, whereas after saturating the membrane with 5M NaOH its conductivity increases to $30\text{mS}\cdot\text{cm}^{-1}$. This confirmed that both functional groups and alkali doped free volumes contribute to ionic conduction. In this study An et al. (2012) determined that ionic conduction in the AAEM is predominated by alkali doped free volumes. However, there is an optimum electrolyte concentration after which conductivity starts to decrease due to increasing viscosity and decreasing ionic mobility.

1.5 Immersion Precipitation Technique for Membrane Synthesis

There are several methods for membrane preparation such as crystallization, gelation, vitrification, thermal precipitation and immersion precipitation all of which involve phase inversion. Phase inversion and demixing are terms for describing the phase separation phenomena such as a polymer precipitating out from a polymer solution due to compositional or thermal change.

Immersion precipitation technique is a well known method for preparing polymer membranes. A polymer solution consisting of a polymer and a solvent is cast as a thin film upon a support and then immersed in a non-solvent bath i.e coagulation bath. The solvent diffuses into the coagulation bath whereas the non-solvent diffuses into the cast film in a counter current diffusion fashion as illustrated in Figure 1.2.

After a certain period of time the exchange of solvent and non-solvent has proceeded so far that the solution becomes thermodynamically unstable and demixing takes place. Finally a solid polymer film is obtained with an asymmetric structure. Additives such as a second polymer or a low molecular weight substance is not unusual but working with multicomponent systems becomes harder.

The choice of solvent/non-solvent pair has a significant effect on the membrane morphology. Complete miscibility of solvent/non-solvent is usually desired for porous membranes. The NMP/Water pair is known to produce porous membranes. Although addition of NMP to water bath can delay demixing yielding relatively non-porous membranes. The choice of polymer is also important since it limits the solvents and non-solvents that can be used in the phase inversion process. There are mainly five parameters that affect the membrane morphology during an immersion precipitation process. These are; coagulation bath temperature, coagulation bath composition, polymer solution composition, casting thickness of the polymer solution and immersion duration.

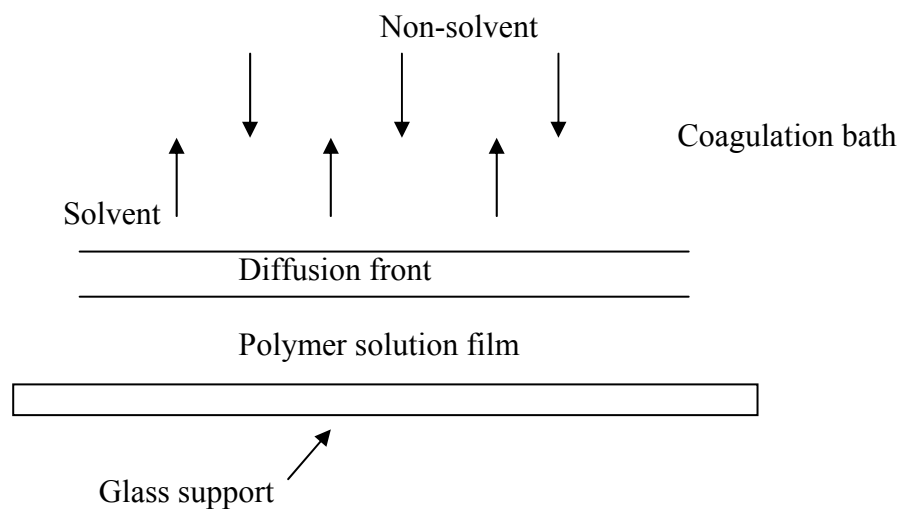


Figure 1.2 : Immersion precipitation illustration.

Higher coagulation bath temperature (CBT) yields faster demixing due to greater diffusion coefficients and lower viscosity which will produce a more porous membrane. Additives such as solvent to the coagulation bath can delay demixing due to lower concentration gradient of the solvent resulting in less porous membranes. Higher polymer concentration in polymer solution will yield less porous membranes because this will cause a higher polymer concentration at the diffusion front.

Thicker polymer solution films yield smaller, closed form pores compared to thinner films. Longer immersion duration yields membranes with less entrapped solvent i.e denser membranes (Mulder, 1996).

The PES-NMP-H₂O ternary system has been studied before by Barton et al, (1997) whereas a new technique for preparing ISP membranes is demonstrated in this study. The system described here is a quaternary system of PES-NMP-H₂O-NaOH which is harder to model thermodynamically.

Initially PES is dissolved in the solvent NMP, forming a polymer solution. Afterwards this polymer solution is cast onto a flat glass plate at desired film thickness via a casting device. The cast polymer solution is then immersed into the so called coagulation bath consisting of an aqueous solution of NaOH. This system favors instantaneous liquid-liquid demixing and transition of the film color from transparent to opaque white is seen within milliseconds. Nevertheless immersion duration is chosen such that the counter diffusion of solvent and non-solvent is complete and a solid membrane is precipitated out of the polymer solution.

Herein, CBT is chosen as the independent parameter and all the remaining parameters are kept constant and the synthesized membranes are investigated in two parts. In part one, the effect of CBT on NaOH loading to the membrane and the membrane porosity were investigated for characterization. In part two, the fuel cell performance of the synthesized membranes were investigated in relation to the CBT. These performances are then benchmarked with a modified Nafion performance.

1.6 Nafion Modification for Alkaline Fuel Cell Operation

Some authors tried to modify Nafion membrane for use in alkaline fuel cells. Yu et al (2006) modified Nafion by boiling first in deionised water for 30 minutes and then in 1M NaOH for 1 hour and rinsing and boiling in deionised water to remove excess NaOH. In Yu et al. (2006) investigation 4.5 mW.cm⁻² power density was achieved with this modified Nafion membrane using air as the oxidant and 2M Methanol and 1M NaOH as the fuel at 60°C operation temperature. Whereas Hou et al. (2011) simply dipped Nafion membrane in 6M KOH solution at room temperature for an undisclosed duration and reported 11.5 mW.cm⁻² with Pt-free catalysts and air breathing cathode and undisclosed fuel composition.

In this dissertation, Yu et al. (2006) approach has been used for modifying the Nafion membrane and its performance is benchmarked with the composite PES membranes synthesized herein. However, reader should be cautioned that cationic membranes such as Nafion can only transport cations. In its regular form Nafion conducts H_3O^+ hydronium ions, whereas in the modified form it conducts Na^+ ions. The redox reactions are essentially the same as mentioned in subsection 1.2, however, the transport of Na^+ ions are exactly in the opposite direction compared to OH^- ions in anionic membranes. Na^+ ions in modified Nafion are transported from the anode to the cathode as illustrated in Figure 1.3 and in effect NaOH is formed at the cathode, continuously depleting the Na^+ ions in the anode. Yu et al. (2006) propose a recirculation line from the cathode to the anode to prevent sodium imbalance, however they do not configure their setup as such. For a thorough discussion on fuel cell operation of Na^+ form of Nafion the reader is referred to (Yu et al, 2006).

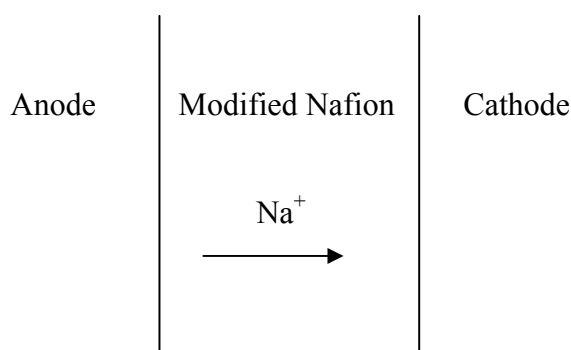


Figure 1.3 : Illustration of Na^+ conduction in modified Nafion.

Another type of fuel cell available in the literature is the alkaline-acid Direct Ethanol Fuel Cell (AADEFC) where an alkaline anode is maintained using NaOH and an acidic cathode is maintained using H_2SO_4 . An and Zhao (2011) report this type of fuel cell in their paper. Although these AADEFC produce high power density, their durability is questioned due to corrosive chemicals and maintenance is an issue due to the formation of Na_2SO_4 .

1.7 Membrane Electrode Assembly

Membrane electrode assembly (MEA) is the heart of the fuel cell where all the electro-chemical activity takes place. MEA's are composed of five parts; namely the anode diffusion layer, anode catalyst layer, electrolyte membrane, cathode catalyst layer and cathode diffusion layer. The diffusion layer provides the basic mechanical structure for the electrodes and serves as a transfer medium for reactants and products as well as a current collector and conductor. The catalyst layer is where the electrochemical reactions takes place for electricity generation. The catalyst layer simultaneously conducts electrons and ions. The electrolyte membrane is an ion conductor only and acts as a selective barrier inbetween the anode and the cathode compartments allowing ions but restricting electrons and fuel. Commonly MEA's are prepared by fixing the catalyst layer directly onto the membrane or seperating the electrode. In the first method the catalyst is directly attached onto the membrane by rolling, spraying, printing or sputtering process after which the MEA is assembled by hot pressing the catalyst coated membrane with the diffusion layer. In the second method a catalyst ink with PTFE or Nafion solution is brushed or sprayed on the diffusion layer forming the electrodes followed by hot-pressing with the membrane inbetween or directly assembling into the cell. The former method is also termed as the decal transfer method and is shown to be more durable compared to the latter conventional method (Kamarudin et al, 2013; Song et al, 2005). Electrode delamination is often encountered in fuel cells due to the differential swelling of the diffusion layer and the membrane. However, decal transfer is the choice of method to overcome this problem. Hot-pressing MEA components or gauged torquing the assembly in the fuel cell is also thought to have an affect on the performance due to contact resistances. Carmo et al. (2013) studied the affect of gauged torquing and found an optimum value for their pressure sensitive FAA-3™ Fumatech membrane. Their MEA showed the best performance at 200 cN.m. As a comparison a fuel cell composed of Nafion 212 is pressed with a torque equivalent of 1800 cN.m.

In this thesis work, commercial Pt-Ru/C and Pt/C electrodes were used for the anode and the cathode respectively and the synthesized membranes were directly assembled with the electrodes into the fuel cell i.e the conventional method without hot pressing.

Equal torque on nuts for each run were assured by first hand tightening in a predetermined sequence and then by using an allen wrench and spanner with semi-circular rotations for each nut in sequence, totalling three full rotations at the end of the procedure.

1.8 Catalyst Binders and their Effect on the Fuel Cell Performance

Catalyst binders which bind discrete catalyst particles to form a porous catalyst layer that facilitates the transfer of reactants, products, ions and electrons has a significant effect on the fuel cell performance. Li et al. (2009a) found that 5wt% addition of PTFE as a binder improves the performance in an ADEFC. In this thesis work, commercial electrodes from Electrochem inc were used as received without further treatment. These electrodes use Nafion solution as the catalyst binder hence may have contributed negatively to the performance of the ADEFC. Although, 1M NaOH fuel alkalinity was used throughout the experiments, it is still thought that use of an alkaline ionomer or PTFE may boost performance of the fuel cell.

Durability is another big concern for the ADEFC, where researchers commonly mention tens of hours of stable operation. Main problem seems to be the agglomeration of the electrocatalysts and cathode flooding. In addition ISP membranes suffer from leaching of the electrolyte during operation, this however is thought to be manageable through the adjustment of fuel alkalinity.

1.9 Ethanol Cross Over Phenomena

Fuel cross over from the anode to the cathode is a daunting problem in acidic fuel cells because the catalysts used in the cathode oxidize this migrating fuel generating counter currents and mixed potential therefore lowering the performance. Especially Nafion is highly permeable to fuels such as methanol and ethanol. One big advantage of the alkaline fuel cells is that due to faster kinetics of the ORR in high pH, precious metal free catalysts can be used in the cathode that are insensitive to the fuel. Therefore, migrating fuel is not such a big concern in these types of fuel cells as it is not oxidized in the cathode but merely wasted.

Zhiani et al. (2011) used Hypermec™ 3020 catalyst on the anode and Hypermec™ K14 catalyst on the cathode both precious metal free catalysts and compared the performance with same anode but Pt/C cathode catalyst in a ADEFC setting. Pt free cathode fuel cell over performed the Pt cathode fuel cell both under oxygen and air cathode feeding. They used a Tokuyama A-006 membrane in OH⁻ form. In the oxygen feeding experiment Pt-free and Pt cathode fuel cells generated 100 mW.cm⁻² versus 90 mW.cm⁻² whereas 90 and 65 mW.cm⁻² power density were generated in the air feeding experiment respectively. These differences in power output are certainly due to cathode catalyst inertness to EOR and selectivity towards ORR in their experiments.

1.10 Ionic Conductivity of the Membranes

Ionic conductivity of the polymer membranes is an important criteria for their applicability in a fuel cell. There is no single theory that thoroughly describes the ionic conductivity in high or low pH range for solid state fuel cells. However, all theories agree that water plays an essential role in ionic conductivity. Therefore the hydration state of a membrane is an essential parameter in determining the conductivity. Widely accepted mechanisms are the Grotthuss (hopping of the hydroxyl ion along the hydrogen bonding water molecules), diffusion and convection. Measurement of ionic conductivity is very difficult because fuel cell conditions are to be applied and the system being measured has to be in a steady-state condition. Most often Electrochemical Impedance Spectroscopy (EIS) is the choice of measurement device. During EIS, AC potential is applied to the specimen that is placed inside a measurement cell with an electrolyte or water. Frequency of the applied potential is varied from couple of hertz to mega hertz and the induced current is measured. This measurement is usually subject to controversy because if the system is not at a steady state, large errors can be generated. Also the membrane inbetween the electrodes do not behave like a simple resistor or a capacitor but like a combination of these. Therefore equivalent circuits are used to model this system. For instance a simplified Randles cell consists of solution resistance R_s , double layer capacitance C_{dl} and polarization resistance R_p as shown below in Figure 1.4.

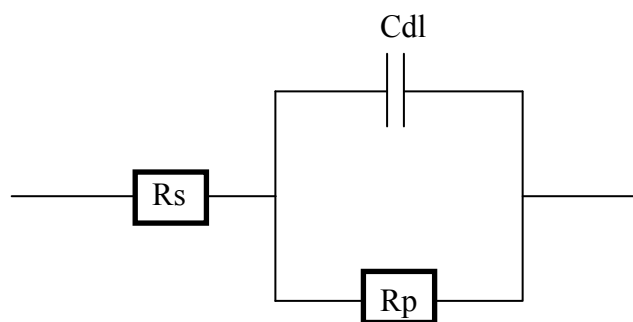


Figure 1.4 : The simplified Randles cell.

Often times a single setup can be represented by multiple models and there is no analytical representation. Therefore parameters extracted from such a model is questionable.

In their review Merle et. al. (2011) report ionic conductivities for ISP class membranes of PEO/KOH as 1 mS.cm^{-1} at 20-25°C to PBI/KOH 100 mS.cm^{-1} at 90°C. To give an idea Nafion conductivity usually range inbetween 50 to 100 mS.cm^{-1} at PEM-FC settings. Due to the unavailability of an EIS device and the ambiguity of the nature of the measurements, ionic conductivity measurements were not attempted in this work.

1.11 Objective of the Works

The aim of this study is to find an easy and economical procedure for synthesizing ion-conductive membranes which can be utilized in applications such as the fuel cell.

Therefore a potential application for the produced membranes, the alkaline direct ethanol fuel cell (ADEFC) has been reported. The fuel cell application is chosen because of its importance due to the current global conditions.

Solid electrolyte membrane is an essential component of the fuel cell and its characteristics such as membrane selectivity, thermal stability and chemical attack resistance has a major impact on the fuel cell performance. Thus there is intense research on synthesizing membranes with superior characteristics to the commercially available membranes. Herein a general method for synthesizing ion-conductive membranes is introduced and its application in ADEFC is demonstrated, however, the synthesized membranes are not optimized for the purpose.

The ion-conductive membrane synthesis method disclosed in this study is a novel and general method which can also be used for synthesizing cationic membranes, these membranes can potentially be used in other applications such as the chlor-alkali process.

2. EXPERIMENTAL

2.1 Materials

PES Ultrason E2010 was supplied by Schneider Ulrich in the form of pellets. N-Methyl-2-pyrrolidone (NMP, 99.5 vol%) was procured from Aldrich. NaOH (99.8 wt%) was procured from Riedel-de Haen and Merck. All materials were used as received. The water used was distilled water.

2.2 Membrane Synthesis

Three sets (batches) of membranes were synthesized at the same controlled conditions. First set was used for characterization of the membranes and the other two sets were used for fuel cell performance testing.

PES pellets were dissolved in NMP under continuous stirring via a magnetic stirrer at room temperature for ca. 24 hours to obtain a homogeneous polymer solution. A casting device with an adjustable blade was used for casting polymer solution films of 400 μm thickness onto a glass support. A stainless steel bath was used to contain 2 liters of an aqueous solution of NaOH. Bath temperature was controlled via a temperature control loop attached to a hot plate where the temperature of the NaOH solution was the measured and the controlled parameter. A uniform temperature distribution was assured by constant stirring and monitoring with an additional thermometer. The casted films were immediately immersed into the coagulation bath, in which an instantaneous phase inversion took place for all the samples. The synthesis parameters for the membrane samples are shown in Table 2.1, where the only independent variable was the bath temperature. Polymer solution film thickness was fixed at 400 μm , polymer solution composition at 20wt% PES in NMP, non-solvent composition at 4 M NaOH and immersion duration at 10 minutes for all the membranes. The casted films shrunk in thickness after phase inversion.

The formed membranes are rinsed with distilled water and kept in hermetically sealed jars prior to usage. The synthesized membranes are coded such that the first character C stands for characterization and F stands for fuel cell, the second character is a number indicating the batch number, the remaining three characters are for determining the CBT. The membranes synthesized for characterization are coded only with three characters since there is only a single batch for characterization purposes. For instance F1M66 indicates that this membrane is used for fuel cell application, is produced from the first batch and it is phase inverted in a CBT of 66°C. In a given batch consisting of a set of membranes each membrane is immersed in the coagulation bath at a different bath temperature, sequentially from low to high bath temperature. F0M34 is an exception to the above mentioned sets, which is yet from another batch with the same parameters and was initially used for fuel cell investigation. Immersion of subsequent polymer solution films into the same bath in a given batch will cause minor changes in the bath composition such as slightly lower NaOH concentration and very low amounts of introduced solvent, however, the effects of these minute compositional changes on phase inversion dynamics are neglected as the bath solution volume is big enough to act as a reservoir.

Table 2.1 : CBT's used during the synthesis of composite PES membranes.

Bath Temperature (°C)	Membrane Sample Code		
34	F0M34	F1M34	F2M34
36	CM36	N/A	N/A
46	CM46	F1M46	F2M46
56	CM56	F1M56	F2M56
66	CM66	F1M66	F2M66

The fuel cell membrane sets CBT were started at 34°C to be able to make comparison with the F0M34 sample that was synthesized earlier. No membranes at 36°C CBT were synthesized for the fuel cell application purposes since a 2°C temperature difference will not have an appreciable effect on the membrane morphology. Therefore when interpreting the effect of the membrane morphology on the fuel cell performance the CBT's of 34 and 36°C respectively for the fuel cell membranes and the characterization membranes were treated to be approximately equivalent.

2.3 Characterization of the Samples

Initially, SEM images were obtained and energy dispersive X-ray analysis (EDS) with Ka line, 10kV and 16.0° take-off angle was performed on a selected sample; CM50 which was casted 200 μm from a 20wt% PES in NMP solution, immersed in a 4 M NaOH bath for 2.5 minutes at 50°C.

Netzsch STA 409C/CD Thermogravimetric/Differential Thermal Analysis device was used for sample analysis. Samples taken from the membranes were heated from room temperature to 1100°C at the rate of 10°K/min and then held at 1100°C for an hour under dry air flowing at 50 cc/min.

Leaching tests and porosity calculations were also conducted on the portions taken from the same membranes. The samples were dried in an oven at 50°C until their weights remain unchanged. Each of these samples were then immersed in 100 mL distilled water in separate, sealed jars. Ino-Lab pH 720 WTW 82362 device with pH electrode Sen Tix 81 was used for pH measurements. The pH of the distilled water was also recorded for each jar prior to the immersion of the samples. The weight change of the samples and the pH values in the jars were then monitored for 3 weeks. Care was taken not to cross-contaminate the samples and they were dabbed dry before each weighing. Prior to each set of pH measurements, the pH electrode was tested with calibration solutions. Thickness measurement of the membranes were performed by a magnetic micrometer, byko test 8500 basic NFe (Germany).

2.4 Fuel Cell Application

2.4.1 Membrane Electrode Assembly

Initially a single membrane F0M34 was used for fuel cell investigation. Afterwards, two sets of synthesized membranes were used for MEA preparation. Also commercial Nafion 117 was treated to Na^+ form and was tested for benchmarking. Fresh electrodes were used for each membrane including the modified Nafion. Electrodes were purchased from Electrochem Inc., the anode electrode contained 30 wt% Pt-Ru/C with 2 mg Pt-Ru/ cm^2 catalyst loading on hydrophobic carbon cloth, and the cathode electrode contained 20 wt% Pt/C with 1 mg Pt/ cm^2 catalyst loading on hydrophilic carbon cloth.

Water is produced at the anode and consumed at the cathode therefore to preserve the water balance, the anode electrode is chosen as hydrophobic and the cathode electrode is chosen as hydrophilic.

Concerning F0M34, Nafion solution was used as a binder between the anode and the membrane, whereas no binder was used between the membrane and the cathode. The anode-membrane-cathode components were hot pressed under 100 bar at 50°C for a duration of 3.5 minutes. Whereas the rest of the membranes including the treated Nafion were directly assembled into the fuel cell without using any binders or hot-pressing.

2.4.2 Nafion 117 Treatment to Na⁺ form

The procedure mentioned in Yu et. al. (2006) was used for the treatment of Nafion 117. As received Nafion membrane was initially boiled in distilled water for 30 minutes. Afterwards it was immersed in a boiling 1M NaOH aqueous solution for 1 hour. However, in the final step, membrane was only rinsed with distilled water at room temperature and immediately used. During the NaOH boiling step, water continuously evaporated and the solution got more concentrated. A few times fresh 1M NaOH solution was added slowly to the boiling solution, however it is most likely that the boiling NaOH solution got more concentrated than 1M.

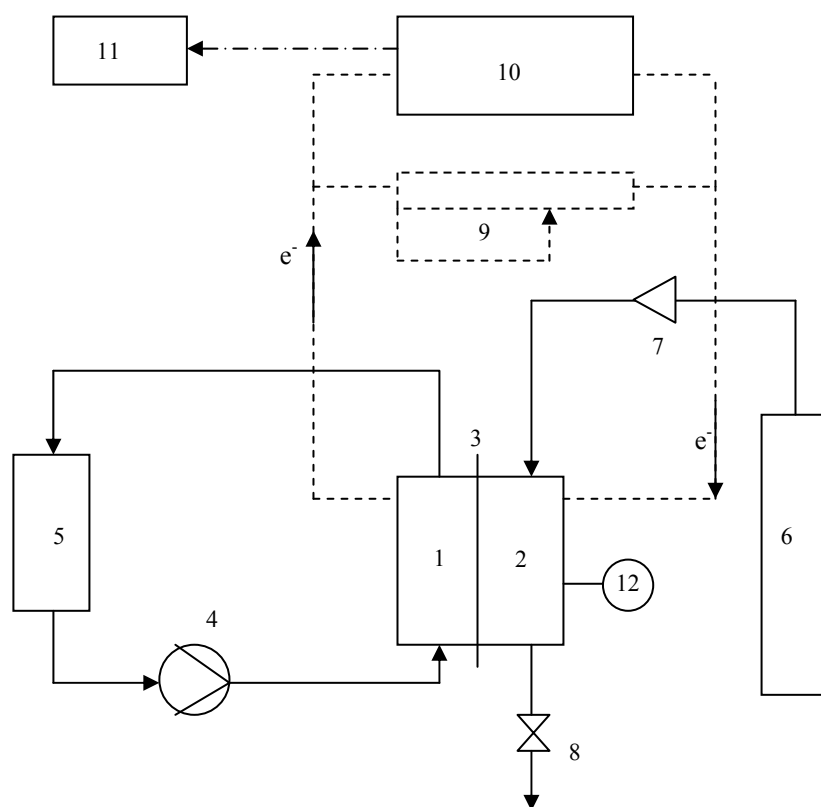
In the alkaline fuel cell setup, Nafion membrane is conducting the Na⁺ ions instead of the H₃O⁺ ions, where there is a continuous transfer of Na⁺ ions from the anode to the cathode. Therefore a sodium imbalance is expected after certain operation time. Yu et. al. (2006) is suggesting a NaOH circulation from cathode to anode to overcome this issue. In this setup such a circulation was not overseen. For the operation duration a gradual performance loss was observed, however, enough data were recorded to be able to do a benchmarking with the synthesized membranes during the course of experiments.

2.4.3 Fuel cell performance tests

Membranes were tested inside a fuel cell with 5cm² active area utilizing a serpentine pattern grooved on graphite blocks with gold plated current collectors that is procured from Electrochem Inc.

This fuel cell was then turned into a test station by in-house integration of closed fuel circulation system including a reservoir and a pump, oxidant feeding, flow measurement and exhaust system, electronic circuitry including a potentiometer, temperature controls with a PID controller and resistor heating and data recording via WT 230 Yokogawa digital multimeter.

This test station is shown schematically in Figure 2.1. 2M ethanol + 1M NaOH was circulated as the liquid fuel through the anode at 53 cc/min and 828 scc/min GC grade dry O₂ was fed continuously to the cathode. The temperature of the fuel cell was kept at 60°C. Exceptionally, F0M34 membrane was tested in a 25 cm² electrochem fuel cell.



1. Fuel cell anode compartment
2. Fuel cell cathode compartment
3. MEA
4. Fuel circulation pump with speed control
5. Fuel tank
6. Oxygen cylinder
7. Rotameter
8. Cathode back pressure regulator
9. Potentiometer
10. Digital multi meter
11. Computer
12. Temperature controller with resistor heaters

Figure 2.1 : The constructed fuel cell system.

3. RESULTS AND DISCUSSION

3.1 Results on the Characterization of Samples

3.1.1 EDS and SEM results

EDS and SEM analysis were conducted initially, to see if the synthesis method did provide samples which were effectively penetrated by NaOH. It was clear from a single selected sample (CM50) that NaOH did indeed effectively penetrated into the polymer matrix and therefore it was decided to proceed further with the synthesis method.

Sodium was detected both on the surface and in the cross section of the sample (see Figures 3.1-3.2). A different phase within the PES polymer is clearly visible in the SEM images which is marked with red circles. CM50 was first dipped in liquid nitrogen and then was broken prior to cross-sectional SEM-EDS analysis. It is thought that this separate precipitate phase may have occurred when the composite membrane lost its absorbed water over time. In Figure 3.2 lower bright section shows the support side of the membrane and the edge line is where the bright and dark regions meet, diffusion front corresponds to the porous top layer.

In Table 3.1 EDS analysis results are shown for the lateral surface and the cross-section of CM50. It should be noted that the sodium concentration is higher at the cross-section of the membrane compared to its lateral surface. This is expected as the synthesized membranes are rinsed with distilled water prior to preservation.

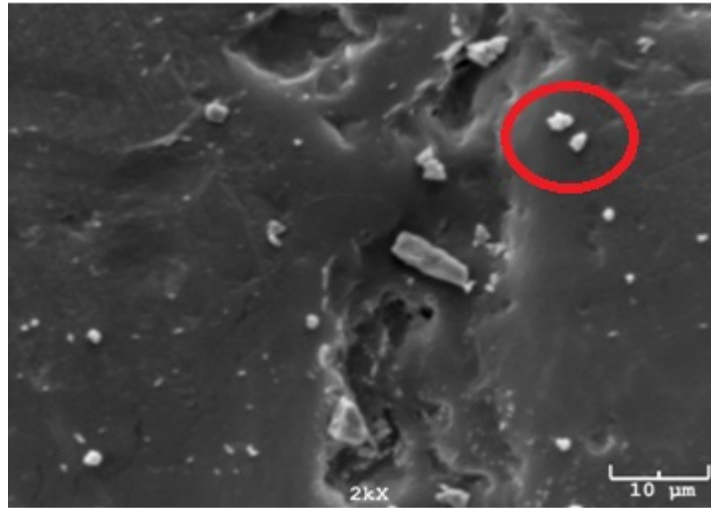


Figure 3.1 : CM50 lateral surface SEM image.

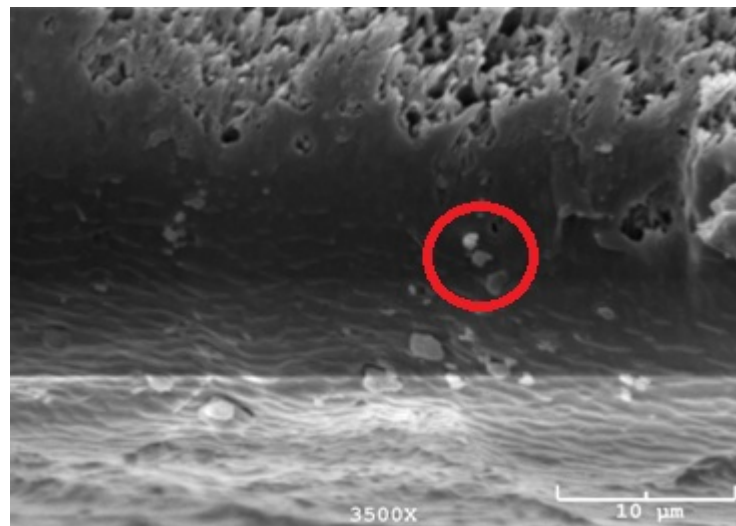


Figure 3.2 : CM50 cross section SEM image.

Table 3.1 : EDS results for the lateral surface and cross section of CM50.

Element	Concentration wt%	
	Lateral	Cross section
C	48.32	42.62
O	32.56	35.87
S	15.76	14.71
Na	3.36	6.81

The PES/NMP/H₂O ternary system has been thermodynamically modeled previously by Barton et al. (1997) however, the composite PES membranes synthesized using the method discussed here utilizes a quaternary system that cannot be represented with a classical ternary diagram.

3.1.2 TGA results

Initially, the lean PES polymer used in membrane synthesis was analyzed for potential incombustible impurities that would affect the experiment. As seen in Fig. 3.3a, the untreated PES sample was combusted to depletion, verifying that the used polymer was free of any incombustible impurities.

The results are tabulated in Table 3.2, where W_0 is the initial sample weight. T_{df} is the temperature, which corresponds to the second inflection point of weight loss curve where rapid degradation slows down. Residual weight, W_r is the recorded weight after one hour at 1100°C.

Table 3.2 : TGA results of the NaOH impregnated PES membranes.

Sample	W_0 (mg)	T_{df} (°C)	W_r (wt%)
CM36	22.01	787	3.64
CM46	24.31	748	7.50
CM56	17.59	725	7.24
CM66	20.57	729	10.09

TGA weight loss curves of the membranes are plotted in Figures 3.3a and 3.3b (and Appendix A). TGA analyses proved that the NaOH loading to the membranes increases as the CBT is increased. The initial weight loss of about 15-20 wt% taking place up to 200°C, which can be seen in Fig. 3.3b, was mainly attributed to water. NMP has a normal boiling point of 202°C but since it is dissolved within the membrane matrix its desorption may be taking place at higher temperatures of up to 400°C, where actually the rapid degradation of PES starts. In between 200-400°C, this residual NMP and possibly some other residual volatile compounds are desorbed from the membrane matrix which accounts for a loss of 3.5-5.5 wt%. Although the rapid degradation of PES inevitably starts at 400°C for all the membranes, the end of rapid degradation and thus the flattening of the weight loss curve were seen to take place at a decreasing temperature (T_{df}) as the residual weight (W_r) is increased. Hence, as the NaOH loading to the membrane increased, the degradation became faster.

This effect of faster degradation due to the loading of an ionizing chemical to a membrane matrix has also been reported previously (Salmon et al, 1997). Interestingly, Nafion does not behave in a similar fashion as reported by Hou et al. (2011) where the degradation of KOH saturated Nafion 112 is delayed significantly compared to H-Nafion 112 in a TGA. This opposite effect in Nafion is explained by the self catalysis of the acid causing the lower thermal stability of H-Nafion 112.

The residual weight increased almost linearly with increasing CBT as seen in Figure 3.4 given below. For a CBT of 66°C, over 10 wt% of the synthesized membranes consisted of NaOH.

The hydration states of the synthesized membranes constantly change. Even inside a hermetically sealed containment it will take a while for the membrane hydration state to reach equilibrium with the isolated environment. Post TGA analysis of the membrane sets that were used for fuel cell performance testing revealed that water composition ranged in between 40 to 60 wt%. Post TGA analyses also revealed that these samples generated residual weights in the range 3.5 to 9 wt% with a positive almost linear relationship with CBT.

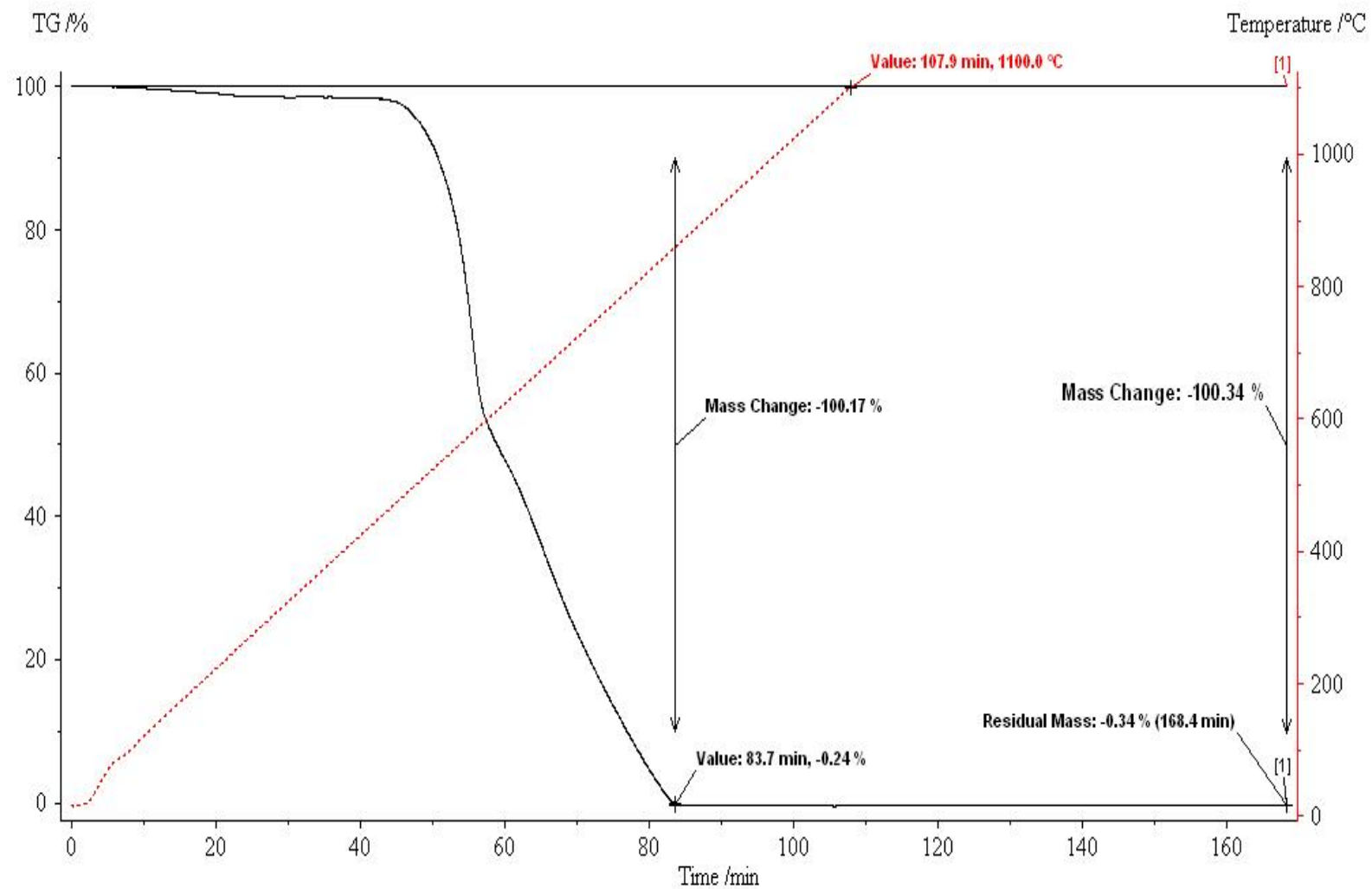


Figure 3.3a : TGA weight loss curve for untreated PES polymer.

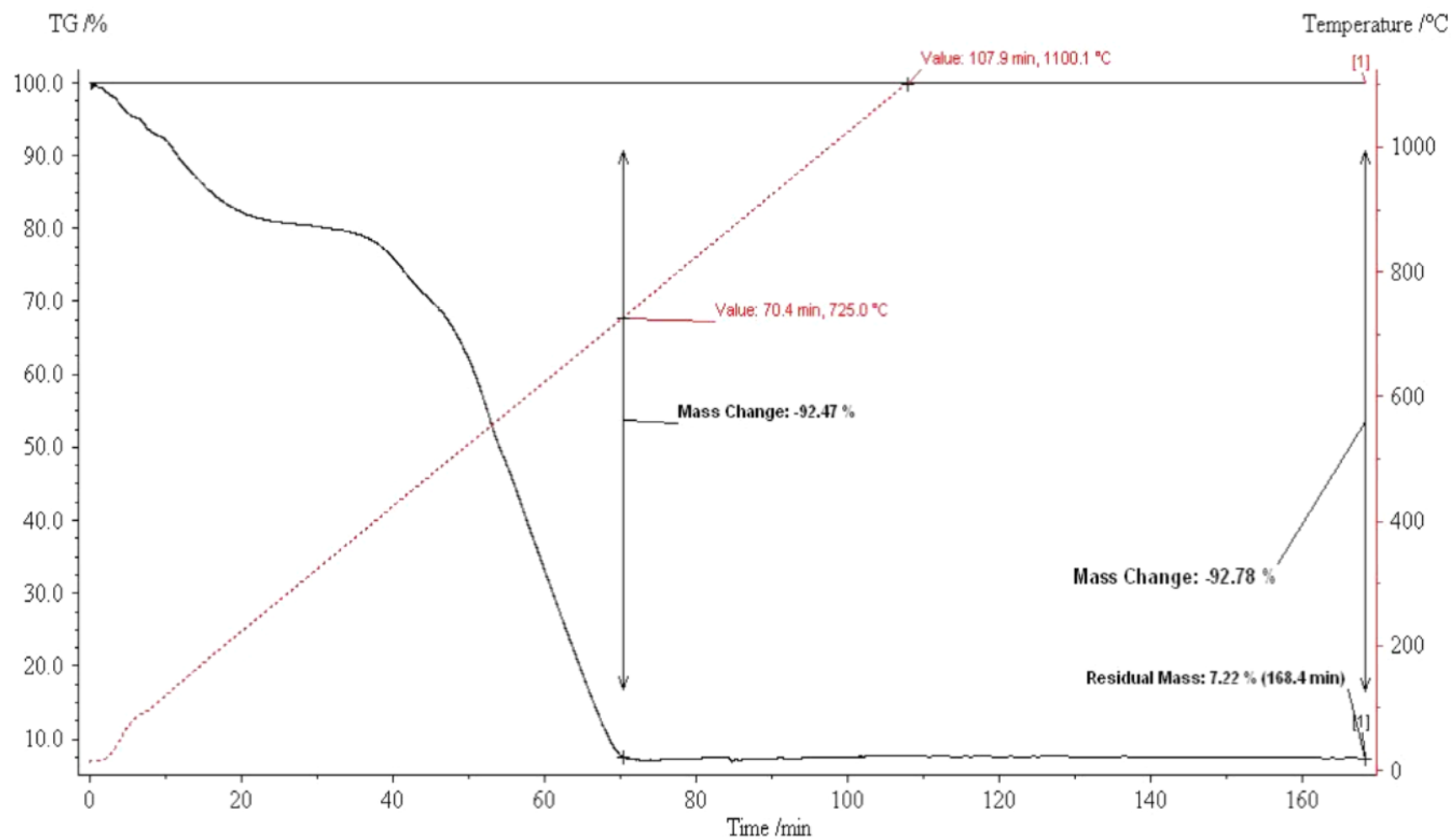


Figure 3.3b : TGA weight loss curve for membrane CM56.

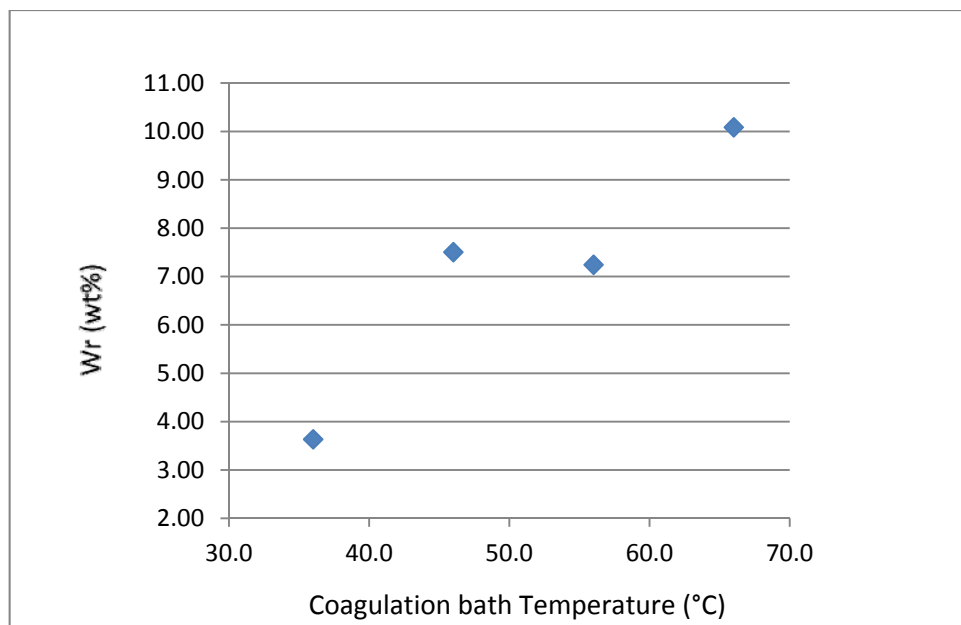


Figure 3.4 : Residual weight in relation to CBT.

The slight decrease of residual weight from 46 to 56°C CBT can be attributed to morphological changes in the synthesized membranes which will be apparent in later figures. NaOH has a normal boiling point of 1390°C and as expected loss of NaOH due to evaporation or decomposition was not observed.

3.1.3 Leaching Test and Porosity

Weight changes for samples of composite membranes all followed the same trend, where a sharp increase in weight was recorded within the first 24 hours and then a gradual decrease to an asymptotic value was observed, which can be seen from Figure 3.5. Since, pH value has reached to an equilibrium just after 24 hours, the variation in weight after 24 hours can not be attributed to NaOH leaching out from the membrane. The percent change in sample weights after 24 hours was most likely due to diffusion of residual NMP out of the membrane. The largest weight percent change was observed for CM66 membrane which has the highest NaOH loading and porosity. The increasing change in weight percent for the membranes exactly followed the increasing porosity which will be shown in the following subsection.

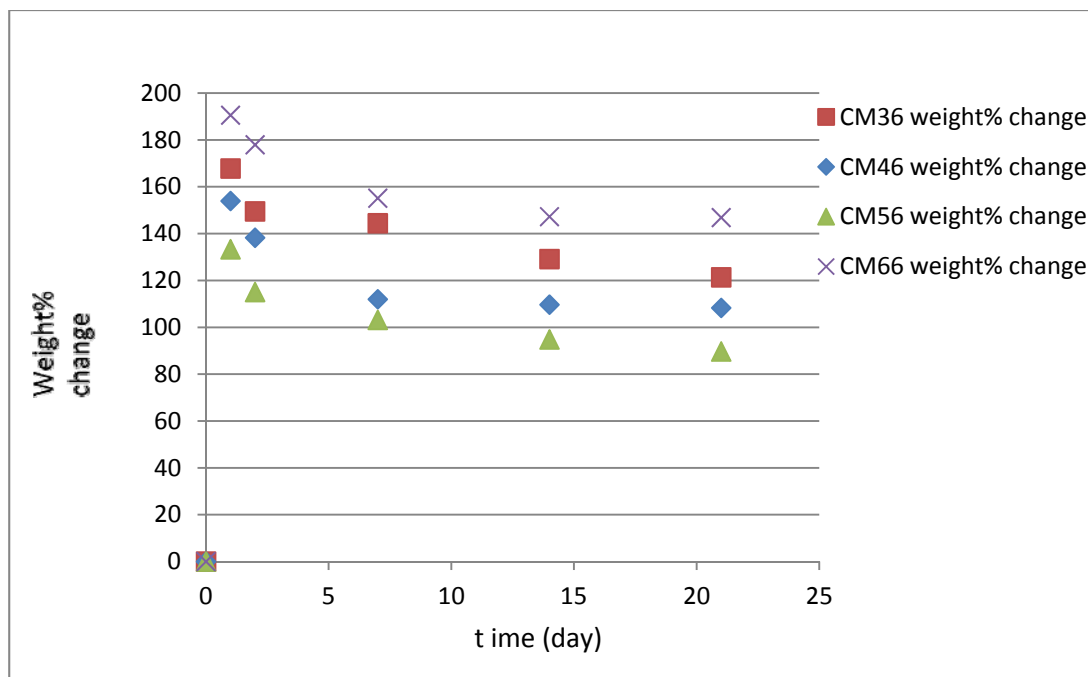


Figure 3.5 : Weight percent change for the samples in distilled water.

The pH value has reached its maximum within the first 24 hours too, after which it stayed constant. The trend for the variation of the pH values with time was the same for all of the samples. Figure 3.6, shows the variation of the pH with time for the aqueous media containing characterization samples.

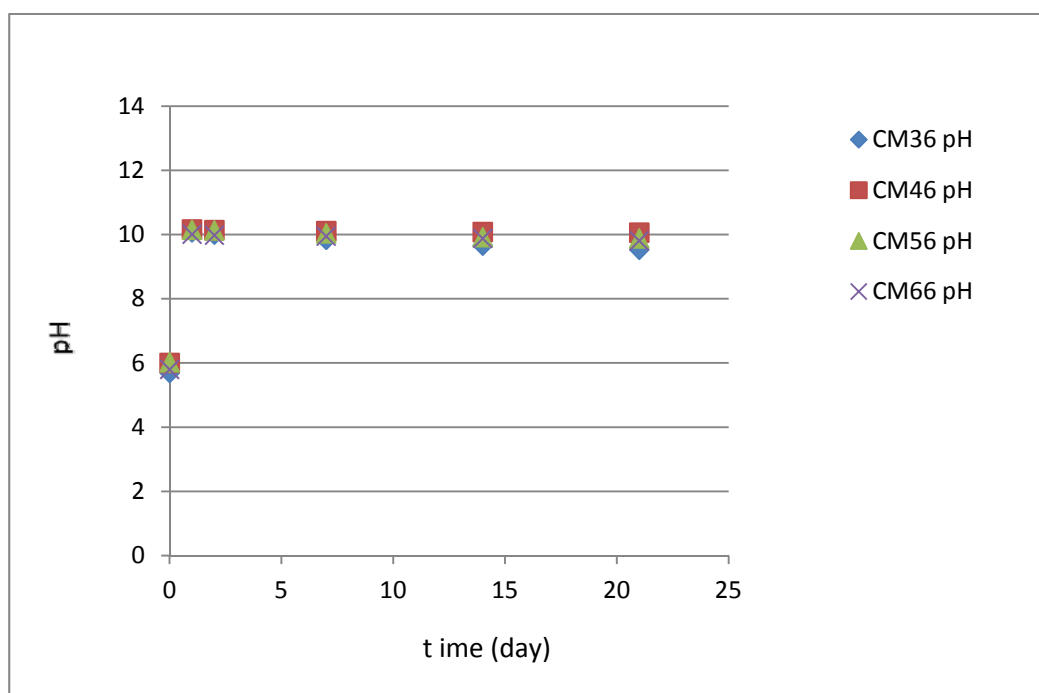


Figure 3.6 : pH change of the aqueous media containing the samples.

Porosity was calculated according to equation 3.2, where W_w is the wet weight of the sample at the end of 21 days, W_d is the oven dried weight of the sample, ρ_w is the density of distilled water and ρ_p is the density of the polymer. Oven drying does not remove any noticeable amount of NMP, therefore the calculated porosity values refer to water free pores.

$$\varepsilon = \frac{\frac{W_w - W_d}{\rho_w}}{\frac{W_w - W_d}{\rho_w} + \frac{W_d}{\rho_p}} \quad (3.2)$$

Figure 3.7 shows the porosity of samples in relation to the CBT. The porosity in the temperature range of 36-66°C shows a minimum at 56°C. This non-linear behavior may be related to the complex membrane formation dynamics of the quaternary system. However, as expected, porosity displays an inverse relation with NMP content. As the residual NMP increases, porosity decreases, whereas, when NMP content decreases in the highest bath temperature, porosity increases. Figure 3.7 is also consistent with Figure 3.4 such that the slight decrease of residual weight from 46 to 56°C CBT coincides with decreasing porosity and increasing NMP. This effect is related to the competition of NMP and NaOH for the pores of the membranes.

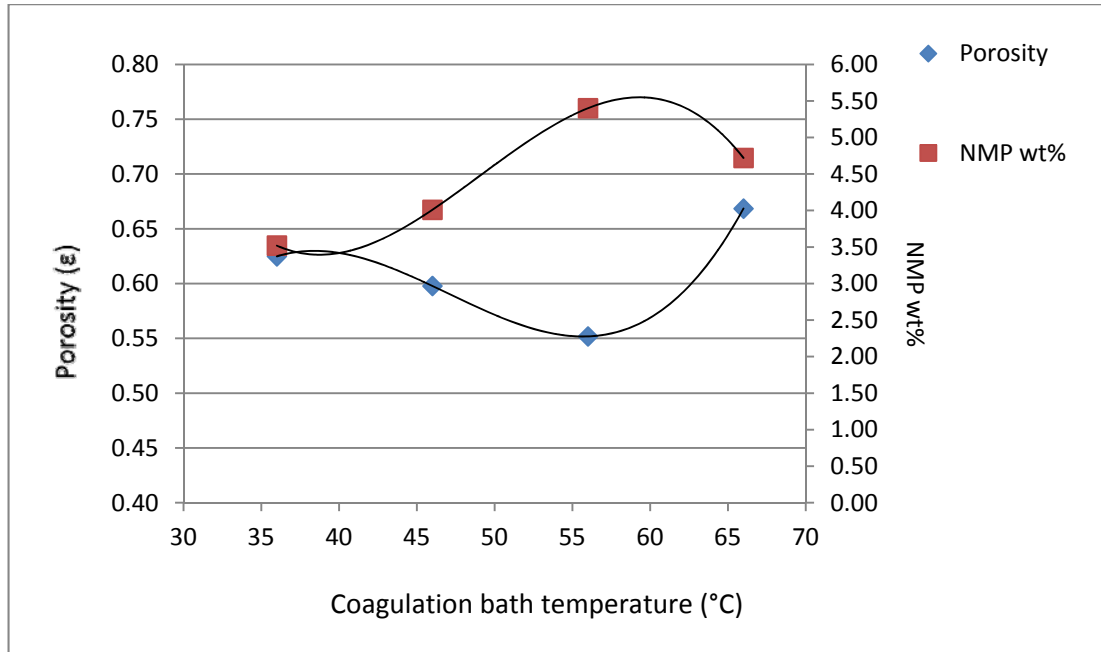


Figure 3.7 : Porosity and NMP content of the samples in relation to CBT.

An interesting outcome was that when the amount of NaOH released to the distilled water was back calculated from the pH value and the solution volume, it turned out that only a minute fraction of what had been loaded to the membranes had leached out of the membranes. This shows that a major fraction of the NaOH has been trapped within the pores of the membrane.

The results of the leaching tests are summarized in Table 3.3, where the dry weight, W_d is the weight of the oven dried samples prior to the leaching test, Δm is the amount of NaOH that has leached out of the membrane; W_r is the residual weight percent as explained previously and the last column is the leaching ratio (LR).

Table 3.3: Leached out NaOH versus loaded NaOH for the samples.

Sample	W_d (mg)	Δm NaOH (mg)	$(\Delta m / W_d) * 100\%$	Wr wt%	LR%
CM36	295	0.47	0.16	3.64	4.40
CM46	217	0.58	0.27	7.50	3.60
CM56	252	0.56	0.22	7.24	3.04
CM66	254	0.41	0.16	10.09	1.59

Another interesting fact is that the ratio of the leached out NaOH percent to loaded NaOH percent mentioned in Table 3.3, the LR, is decreasing with increasing bath temperature. This means that as the bath temperature is increased lesser portion of the loaded NaOH is being leached out of the membranes. Possibly due to the effect of CBT on the membrane morphology.

3.1.4 Membrane thickness measurement

Membrane thickness is especially important when comparing membrane performances in a fuel cell setting because the thickness is related to the conductivity via equation 3.3:

$$\sigma = \frac{d}{R.A} \quad (3.3)$$

Where, σ is conductivity, d is membrane thickness, R is the membrane resistance and A is the effective lateral area of the membrane. Membrane thicknesses were measured from at least five points on the surface with a magnetic micrometer. Thickness of the Na^+ Nafion and the synthesized membranes were withing close proximity.

Measurements were done after fuel cell disassembly when the membranes were in a hydrated state. Thickness results are shown in Table 3.4.

Table 3.4 : Measured membrane thicknesses.

Sample	Thickness (μm)	% Deviation from Nafion Na+
F1M34	197	21
F1M46	144	-12
F1M56	142	-13
F1M66	156	-4
F2M34	142	-13
F2M46	137	-16
F2M56	164	1
F2M66	166	2
Na ⁺ Nafion	163	0

3.2 Fuel Cell Performance

As mentioned earlier F0M34, sample was phase inverted in a separate batch and was hot pressed with Nafion binder on the anode side thus it should be regarded as a separate MEA from the rest of the MEA's. Concerning F0M34 the peak values recorded were +1.067 V open circuit voltage (OCV), 15.3 mA.cm⁻² short circuit current density (SC) and 3.6 mW.cm⁻² maximum power density (MPD).

For deciding on the fuel alkalinity, MEA from F1M66 was run at three different fuel NaOH concentrations.

Table 3.5 : Performance of F1M66 at different fuel NaOH concentrations.

NaOH (M)	0.15	0.64	1.00
MPD (mW.cm ⁻²)	5.40	6.94	7.00
SC (mA.cm ⁻²)	68	101	69
OCV (V)	0.707	0.741	0.775

There was a marked performance difference in between F0M34 and F1M66 with 3.6 and 5.4 mW.cm⁻² MPD's respectively at 0.15M NaOH concentration in fuel. F1M66 performance further improved with higher fuel alkalinity.

Looking at the results it was decided to use 1M fuel NaOH concentration throughout the experiments. Apart from the F0M34, two sets of membranes totalling eight MEA's were benchmarked with the modified Nafion and the synthesis bath temperature affect on the membrane fuel cell performance was observed. The catalyst loadings of the anode and the cathode for Na⁺ Nafion were exactly the same as those of the synthesized membrane electrodes. As can be seen from Figure 3.8, 12.42 and 13.04 mW.cm⁻² MPD's are obtained respectively with F2M34 and F2M46, whereas 11.82 mW.cm⁻² MPD is obtained with the modified Nafion. Taking the arithmetic average of these two sets, Nafion performed slightly better, however stability of Nafion was worse, possibly due to the constant migration of Na⁺ ions from the anode to the cathode, causing sodium imbalance.

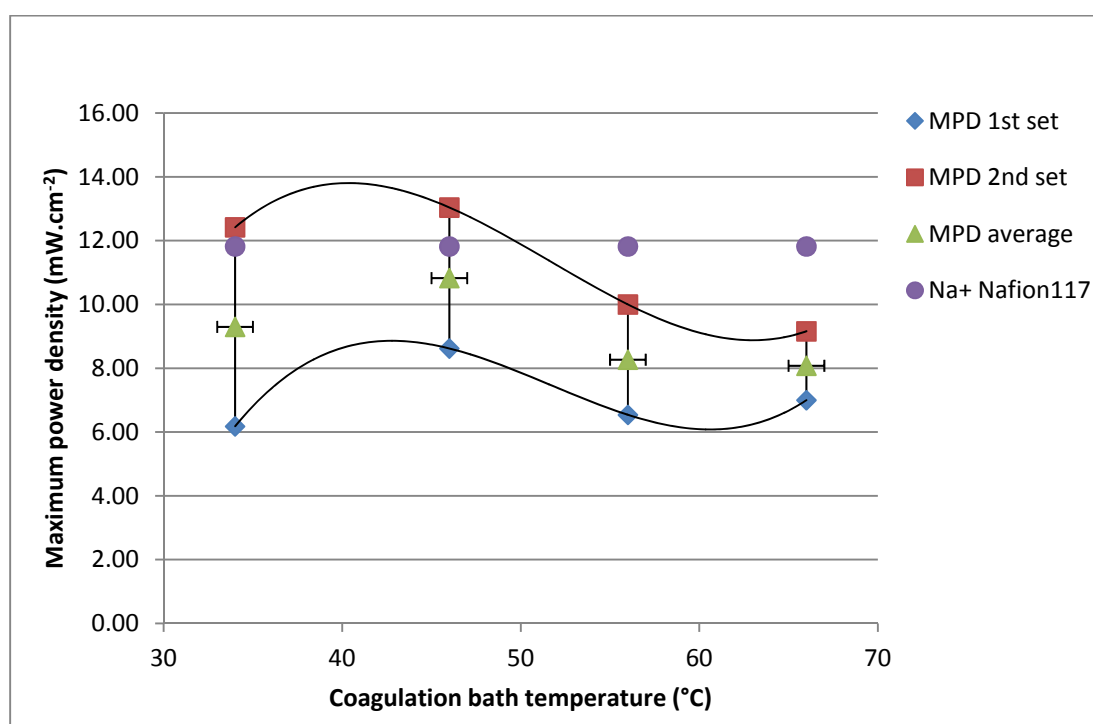


Figure 3.8 : MPD v.s CBT for the composite PES membranes and Na⁺ Nafion performance. (Fuel cell operated at 60°C)

In terms of MPD both sets of synthesized membranes displayed similar trend where maxima obtained at 46°C CBT and minimum at 56 and 66°C respectively for the first and the second sets. This observation is in line with Figure 3.7 where the NMP content increases with increasing bath temperature producing a peak value at 56°C corresponding to minimum power density in the first set of membranes. Infact, the NMP content curve is nearly symmetrical along the vertical axis with the maximum power density curve.

This makes sense such that as the NMP content increases, porosity decreases, making the NaOH filled pores less available for ion conduction. The maximum power density for both set of synthesized membranes occur at a corresponding porosity value of 0.6. Any higher or lower porosity negatively affects the power density. This may seem like a high porosity value, however for adequate ionic conduction, connected networks of pores are required in this application. In a similar composite alkaline membrane fuel cell application, Cao et al. (2012) use an 80% porous PTFE and saturate this substrate with quaternized poly-vinyl-benzyl hydroxide. Although, they use this membrane in a H_2/O_2 alkaline fuel cell, to reach adequate conductivities they need a very porous substrate as in our case. Figure 3.9 is a comparison of the F2M46 run with the modified Nafion run. It is clearly seen that the OCV value of F2M46 is over 100 mV higher compared to the modified Nafion. Although, modified Nafion in general produced higher current density towards short circuit, initial pairs of voltage and current density generated higher power density for the F2M46 membrane.

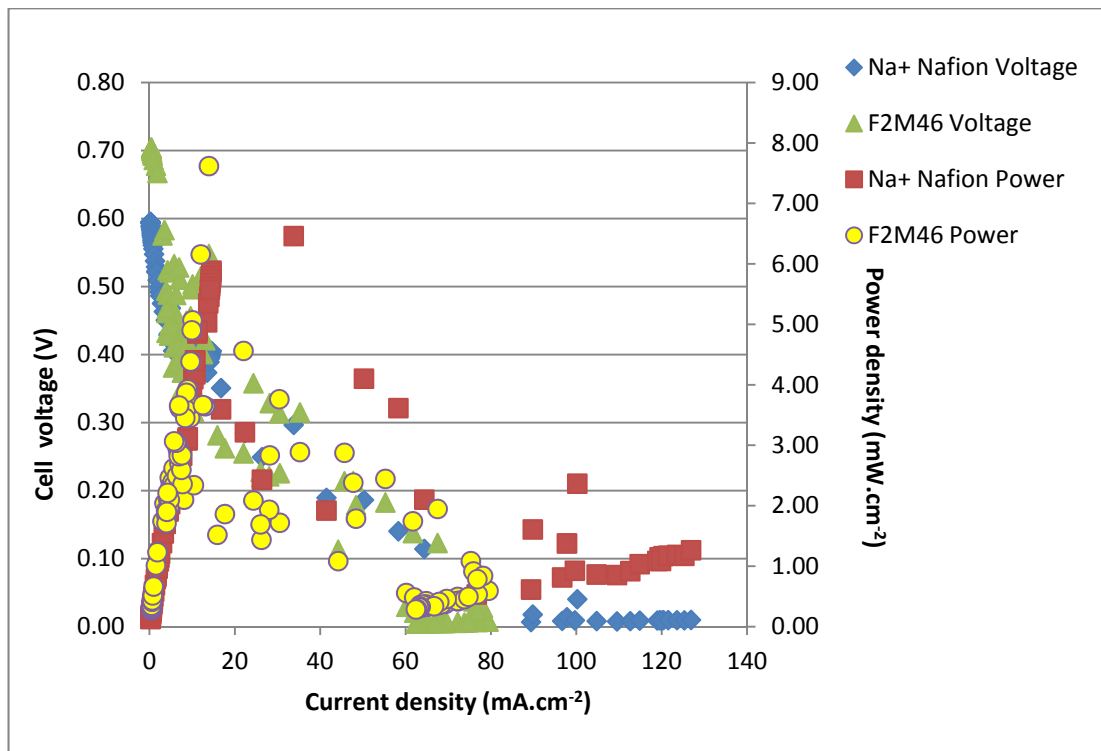


Figure 3.9 : Polarization and power curves for F2M46 and modified Nafion.

It should also be noted that the mobility of the Na^+ ions is much lower than the mobility of the OH^- ions.

For instance the ionic mobility of the OH^- is reported to be 2.69 relative to the K^+ (Merle et al, 2011). The Na^+ mobility relative to the K^+ is reported to be 0.682. Therefore OH^- ion is 3.94 times more mobile than Na^+ ion. Ofcourse, there are other factors contributing to the overall ionic conductivity other than the ionic mobility, such as coordination of the ions with water molecules, membrane morphology in regards to ion conducting paths etc. However, in this work even with a lower ionic mobility cation, Nafion seems to be more conductive compared to the synthesized membranes. Figure 3.10 is a comparison of the F2M34 run with the modified Nafion run. Several polarization curves are generated during the course of a run and only selected curves are shown here.

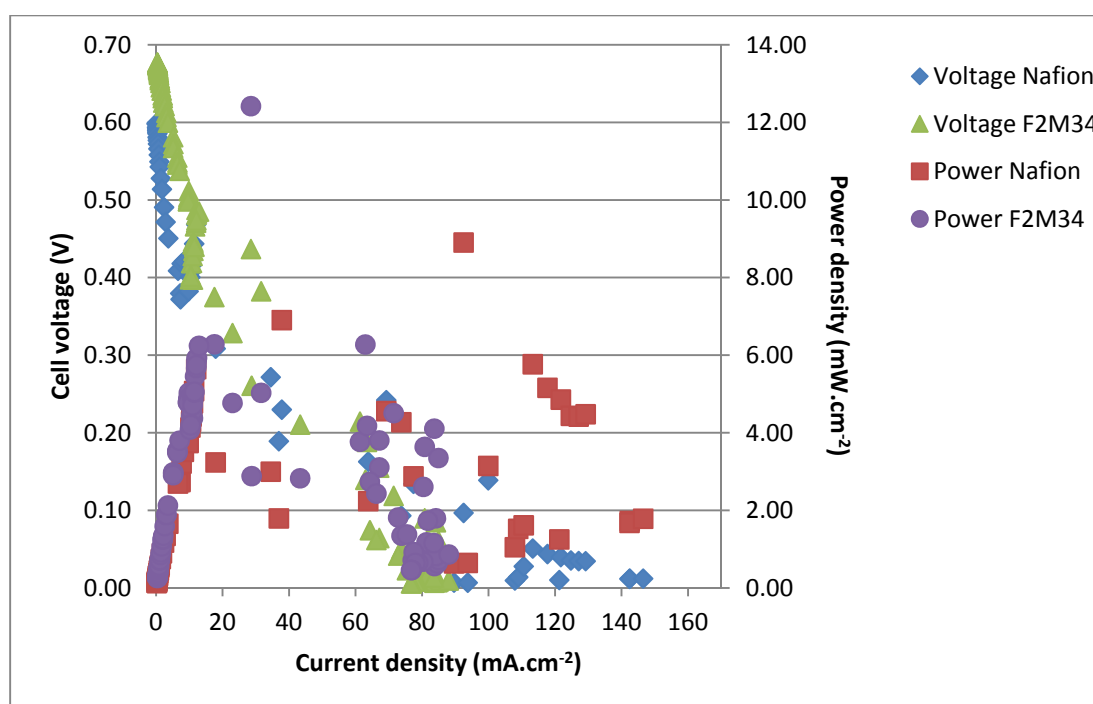


Figure 3.10 : Polarization and power curves for F2M34 and modified Nafion.

Similar trends to Figure 3.9 are visible in Figure 3.10. Generally, lower OCV (cell voltage at zero current density) is a sign of higher fuel crossover as mentioned in Kim et al. (2009), therefore it is highly likely that the synthesized membranes have lower ethanol crossover rates compared to the modified Nafion membrane. Higher OCV and SC behaviour for the composite PES membranes and the modified Nafion respectively, repeat consistently through out the runs.

Also as mentioned in An et al. (2012) both functional groups and alkali doped free volumes contribute to the ionic conduction in modified Nafion, whereas alkali doped free volumes are the only possible contributor to the ionic conduction in the synthesized membranes, which may explain the higher measured current density in the modified Nafion run.

It is possible that a fuel cell with a less conductive membrane generate higher power density compared to a fuel cell with a higher conductivity membrane because there are other factors contributing to the power output other than the membrane conductivity itself. Membrane selectivity, electrode-membrane interface and MEA structure are all determining factors for power output. In the Merle et al. (2011) review, examples of fuel cells with lower membrane conductivity generating higher power density compared to higher conductivity membrane fuel cells, all in alkaline setup are present. Figure 3.11 is a superposition of polarization curves for the first set of membranes to see the CBT affect on the membrane performances and also compare modified Nafion performance.

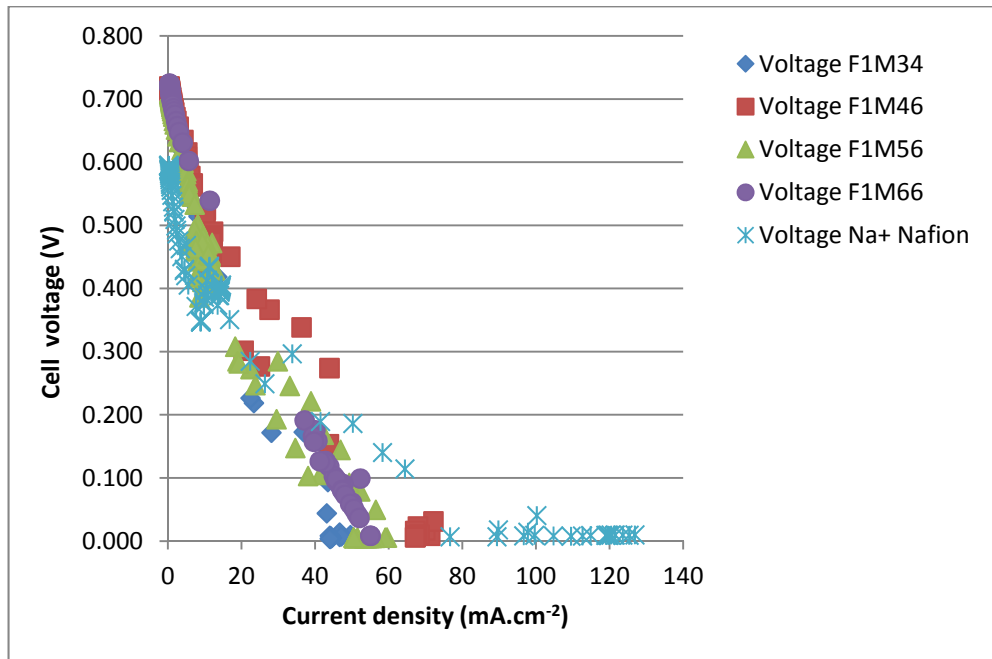


Figure 3.11 : Superposed polarization curves for the 1st set of synthesized membranes and Na⁺ Nafion.

F1M56 has the lowest and F1M66 has the highest OCV, whereas, F1M46 has the highest SC value. F1M46 corresponds to the membrane that was synthesized in the first batch at 46°C CBT which also has the peak power density in this batch.

The potential decay with current density is the fastest for F1M34 which also has the lowest power density in the first batch. The remaining membranes fall inbetween the F1M34 and F1M46 in terms of potential decay speed with current density. Na⁺Nafion starts off with a 120 mV lower OCV but generates over 50mA.cm⁻² higher SC.

Referring to the previous discussion this translates to higher ethanol cross over and ionic conductivity for the modified Nafion. Higher fuel crossover for the modified Nafion is expected as Na⁺ ions migrate from the anode to the cathode creating an EOD. The polarization curves in Figure 3.11 obey the exponential decay form:

$$V = V_o \cdot \exp(-a \cdot i) \quad (3.3)$$

Where V_o is the OCV, i the current density and a is a lumped parameter that accounts for all the mass transfer and electrical resistances. The greater the value of a the faster the potential will decay with increasing current density translating to higher transport and electrical resistances. In our case lower NMP means, higher amount of aqueous NaOH filled pores which is thought to reduce electrical and transport resistances contributing positively to the ionic conductivity hence power output. To give an idea, in Figure 3.9 the value of a is calculated as 0.060 for F2M46 ($R^2 = 0.8595$) and 0.036 for modified Nafion ($R^2 = 0.9559$) whereas values of a are calculated as 0.044 ($R^2 = 0.8781$) and 0.027 ($R^2 = 0.8639$) for F2M34 and modified Nafion respectively in Figure 3.10. For each polarization curve of the same membrane during different times of the same run it is possible to end up with different values of a as local compositions of reactants and temperature distribution will be different, also fitting error will be different for each set of data. Nevertheless, calculated values of a for modified Nafion are consistently lower at the beginning of the run compared to the calculated values of a for the synthesized membranes, but towards the end of the modified Nafion run, resistances increase possibly due to sodium imbalance and calculated values of a break even. This means at the beginning of the run modified Nafion MEA has lower overall resistance compared to the MEA's of the synthesized membranes, however, as time progresses overall resistance increase and become equal to that of the MEA's of the synthesized membranes.

Figure 3.12 is a similar illustration to Figure 3.11, here the polarization curves for the second set of membranes are superposed. F2M34 has the lowest OCV, whereas, F2M66 has the highest OCV. F2M34 has the highest SC in this set.

Higher performance membranes F2M34 and F2M46 can be distinguished from their relatively slower potential decay compared to the other membranes. Na⁺ Nafion generates 100 mV less OCV but 40 mA.cm⁻² higher SC.

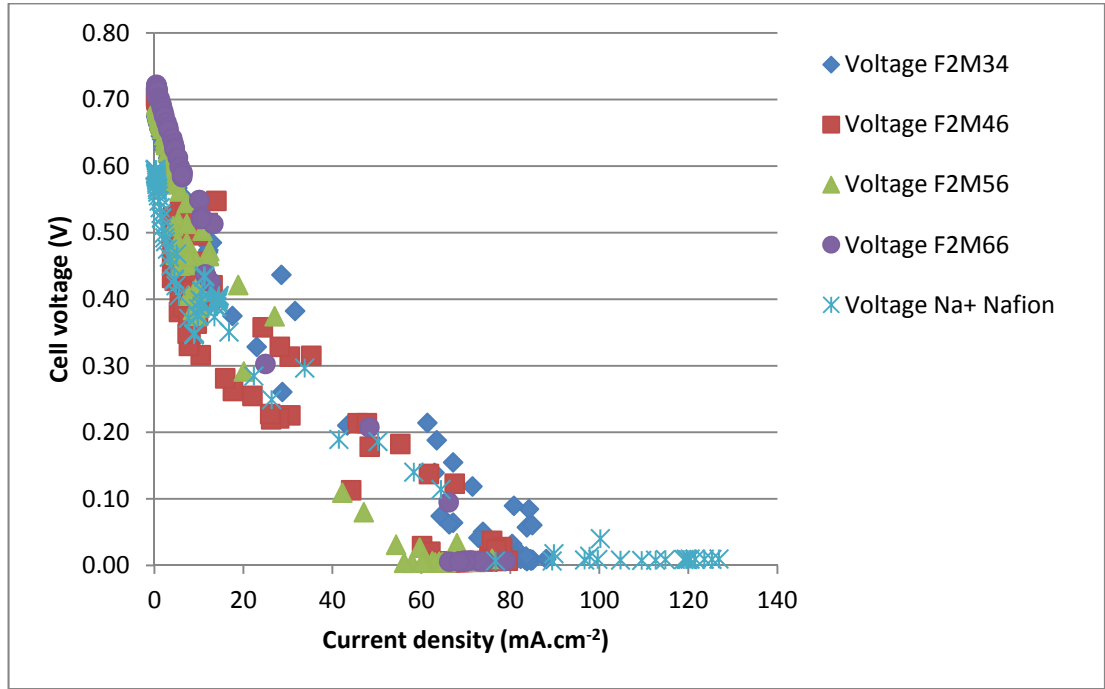


Figure 3.12 : Superposed polarization curves for the 2nd set of synthesized membranes and Na⁺ Nafion.

To see the aging affect on the synthesized membranes, a one year old membrane that was phase inverted in a 66°C coagulation bath and kept in filter paper was regenerated in a 4M NaOH solution at 55°C for two hours. 4.88 mW.cm⁻² maximum power density, 54 mA.cm⁻² SC current density and 0.708 V OCV were generated with this membrane. These power and current densities are superior to F0M34 performance which at the time of testing was a relatively fresh membrane. This outcome clearly underlines the effect of MEA preparation on performance as this one year old membrane was directly assembled into the fuel cell without using any binders or hot pressing. Therefore, it can be reasoned that hot pressing and Nafion binder has a negative effect on the fuel cell performance of the synthesized membranes in this study. Regeneration of the old membranes are necessary due to the carbonation reaction mentioned in the introduction chapter (subsection 1.2).

Atmospheric carbondioxide slowly transforms NaOH into Na_2CO_3 unless the membranes are hermetically sealed from the atmosphere.

The alkalinity of the fuel used in this study was much lower than those reported in the literature (Li et al, 2009b). It is thought that a higher performance can be attained through the use of optimized catalysts, such as Acta's ® hypermec® catalysts, combined with optimized membrane synthesis parameters.

Also, useage of an alkaline ionomer such as Acta's I2® rather than Nafion solution for the catalyst ink may improve the power density. Figures 3.13 and 3.14 respectively show the OCV and SC variation with CBT. Particularly OCV shows a non-linear relation with a minumum at 56 and a maximum at 66°C. It is important to note the similarity of the porosity curve in Figure 3.7 and OCV curves in Figure 3.13, where OCV display a parallel relation with porosity. This is possibly due to the fact that a membrane having more pores filled with aqueous NaOH will have lesser spacing in-between the pores generating a higher electrical potential at open circuit conditions. OCV curves for the two sets of membranes overlap at all bath temperatures but 56°C.

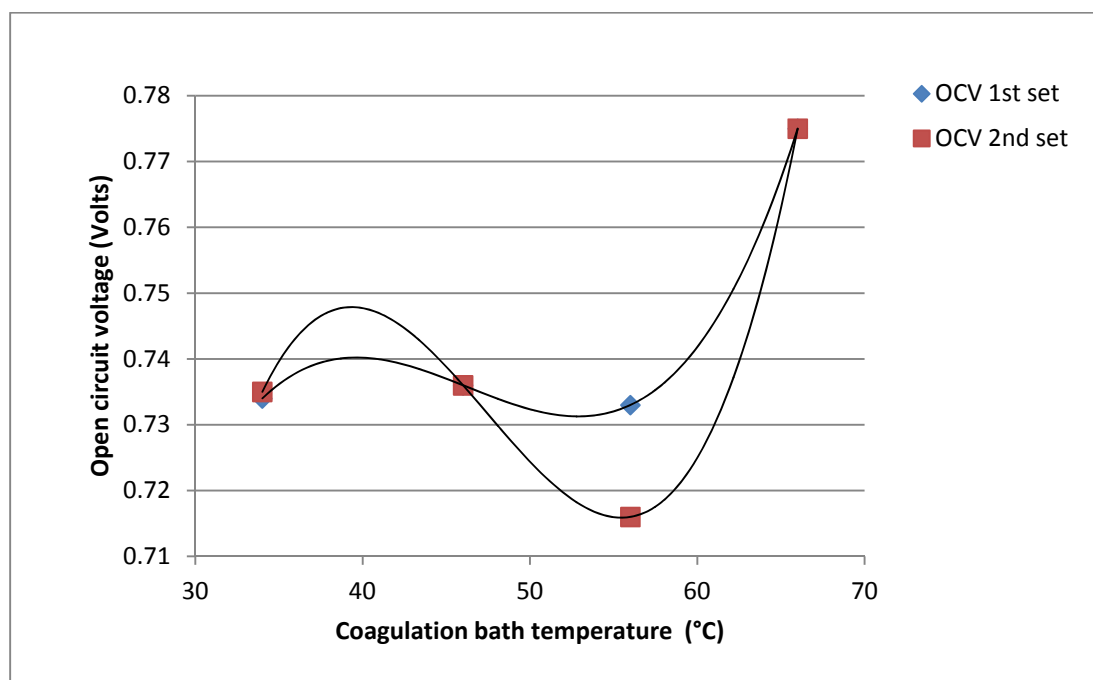


Figure 3.13 : OCV values in-relation to CBT.

Concerning the SC relation with CBT in Figure 3.14, SC for the second set of membranes decrease linearly with increasing CBT but the first set of membranes behave differently and produce a maximum at 46°C then decrease relative to 46°C but to a higher value than the one with 34°C. SC curves intersect at 46°C bath temperature.

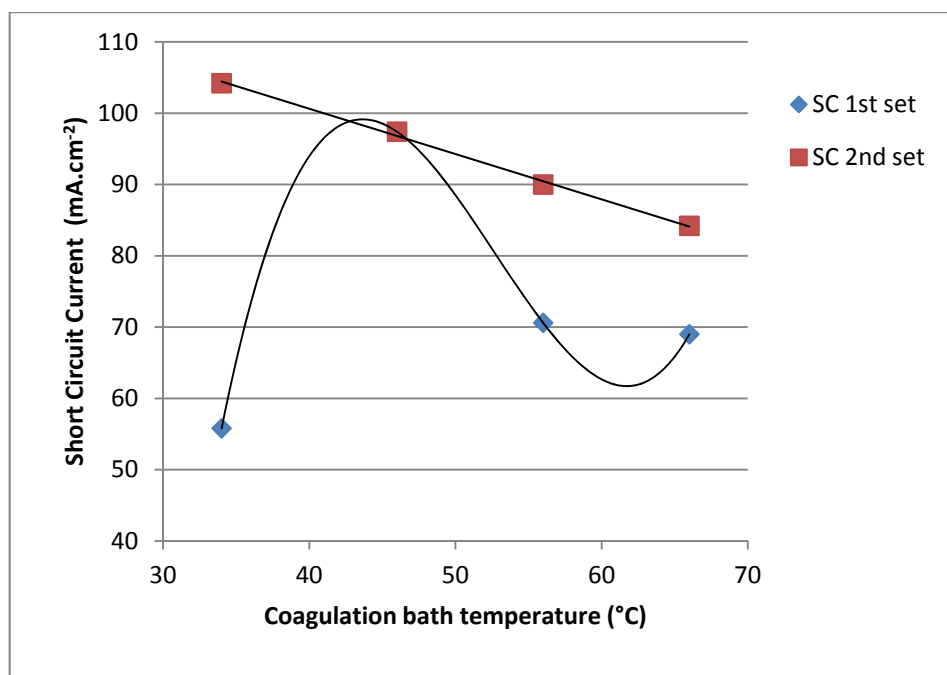


Figure 3.14 : SC values in-relation to the CBT.

It appears that membrane morphology favoring maximum power density conditions are achieved at a CBT of 46°C, whereas, highest OCV values are achieved with membranes synthesized at a CBT of 66°C. This is possibly due to the generation of a morphology permitting less ethanol crossover, however, this does not translate to the highest conductivity and power density. Infact the morphology favoring less ethanol crossover may well be less favorable for higher conductivity due to higher NMP content compared to 46°C membrane. At higher CBTs, skin layer on the polymer solution film is expected to develop faster, inhibiting further counter diffusion compared to lower bath temperatures. This does not necessarily mean less NaOH loading to the membrane but a morphology that is less favorable to ion conduction may be realized. In Figure 3.15, F0M34 performance can be viewed in relation to successive runs with corresponding fuel alkalinities.

It can be seen from Table 3.3 that only 1/20 to 1/60 of the loaded NaOH had leached out of the membranes.

Even though this ratio may increase during the actual fuel cell conditions due to the continuous flow of fuel, the performance loss does not seem attributable to leaching phenomena at all. Infact, leaching may be controlled via fuel alkalinity.

Therefore the performance loss following successive runs was most likely due to the fuel crossover to the cathode, carbonation reaction as explained in the introduction chapter and possibly the delamination of the electrodes from the PES composite membrane. It is thought that if ethanol insensitive cathode catalysts are utilized better stability could be obtained.

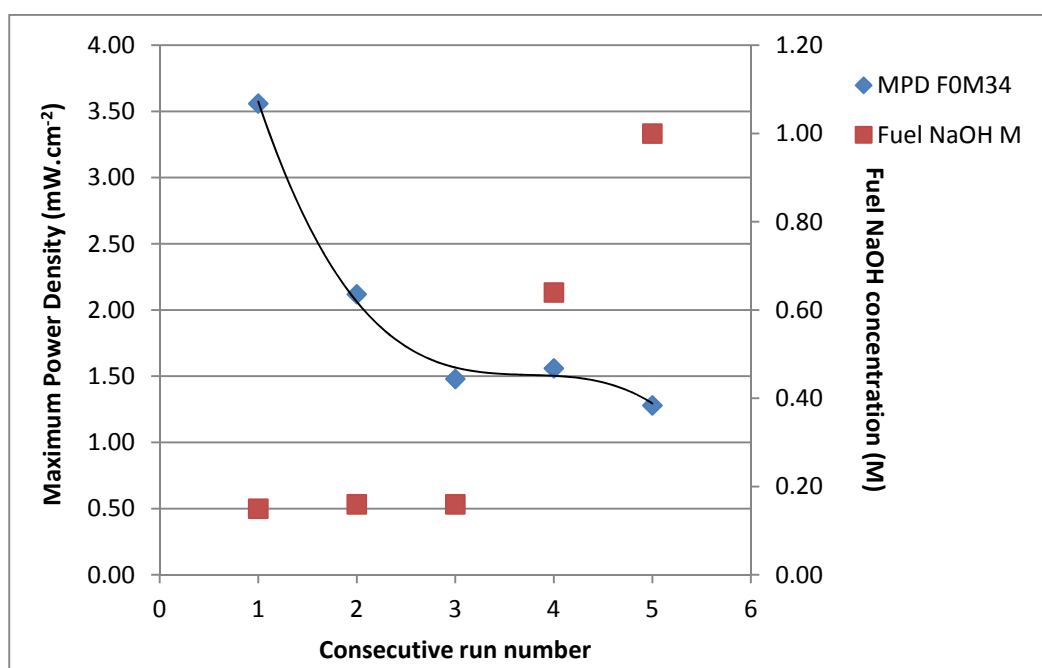


Figure 3.15 : F0M34 performance in relation to successive runs and fuel alkalinity.

It should also be kept in mind that Figure 3.15 is obtained with a hot pressed MEA utilizing Nafion binder, different stability results may be obtained with the current approach of direct assembly of MEA components into the fuel cell without hot pressing or using Nafion binder. It is possible that during the harsh conditions of hot pressing membrane morphology is being negatively effected.

4. CONCLUSIONS

A novel method for synthesizing ion conductive membranes has been demonstrated. The effect of the CBT on membrane NaOH loading and porosity have been studied. A potential application, the alkaline direct ethanol fuel cell has been explored. The effect of the CBT on membrane fuel cell performance has also been studied. The synthesized membranes have been benchmarked with the Na⁺ form of Nafion 117. The main results can be summarized as:

1. Synthesis bath temperature and NaOH loading to the membrane show a positive nearly linear relationship.
2. Synthesis bath temperature and membrane porosity show a non-linear behaviour such that from 36 to 56°C porosity decreases from 0.62 to 0.55, whereas from 56 to 66°C it increases to 0.67.
3. Residual NMP content and membrane porosity are inversely related, such that as the NMP content increases, porosity decreases, whereas when NMP content decreases upon further increasing of the bath temperature, porosity increases.
4. As the NaOH loading to the membrane increases, its decomposition/combustion in TGA becomes faster.
5. As the synthesis bath temperature is increased, the leaching of NaOH from the membranes in proportion to loaded NaOH decreases.
6. Characteristics of the membrane change depending on its hydration state.
7. 13.04 mW.cm⁻² peak power density is obtained with the synthesized membranes compared to 11.82 mW.cm⁻² peak power density of Na⁺ Nafion.
8. Peak power density is obtained with the membranes synthesized at 46°C CBT for both sets.
9. Peak power density curve and NMP content curve are symmetrical along the vertical axis. This observation is in line with expectations as higher NMP content translates to lower aqueous NaOH filled pores causing decreased performance.

10. An optimum porosity of 0.6 is determined with the given set of conditions for peak power density output.
11. Highest OCV is achieved with membranes synthesized at 66°C, however, highest power density is achieved with membranes synthesized at 46°C. The membrane morphology favoring highest OCV is not similar to the morphology favoring highest power density output.
12. It is thought that a higher performance can be attained through the use of optimized catalysts, such as Acta's ® hypermec® catalysts, combined with optimized membrane synthesis parameters and use of an alkaline ionomer as catalyst binder.

As a suggestion further characterization of the synthesized membranes such as ethanol permeability and ionic conductivity measurements can be performed. Concerning the fuel cell performance, non-precious metal catalysts with alkaline ionomers such as Acta Hypermec™ catalysts can be utilized, stability runs with different fuel alkalinities and optimization of the remaining membrane synthesis parameters for maximum power density output can be carried out.

REFERENCES

- An L. and Zhao T.S.** (2011). Performance of an alkaline-acid direct ethanol fuel cell, *Int. J. Hydrogen Energ.*, 36, 9994.
- An L., Zhao T.S., Wu Q.X., and Zeng L.** (2012). Comparison of different types of membrane in alkaline direct ethanol fuel cells, *Int. J. Hydrogen Energ.*, 37, 14536.
- Barton, B.F., Reeve, J.L., and McHugh, A.J.** (1997). Observations on the dynamics of nonsolvent-induced phase inversion, *J. Polym. Sci. B: Polym. Phys.*, 35, 569.
- Cao Y.C., Scott K., and Wang X.** (2012). Preparation of polytetrafluoroethylene porous membrane based composite alkaline exchange membrane with improved tensile strength and its fuel cell test, *Int. J. Hydrogen Energ.*, 37, 12688.
- Carmo M., Doubek G., Sekol R.C., Linardi M., and Taylor A.D.** (2013). Development and electrochemical studies of membrane electrode assemblies for polymer electrolyte alkaline fuel cells using FAA membrane and ionomer, *J. Power Sources*, 230, 169.
- Hou H., Wang S., Jin W., Jiang Q., Sun L., Jiang L., and Sun G.** (2011). KOH modified Nafion 112 membrane for high performance alkaline direct ethanol fuel cell, *Int. J. Hydrogen Energ.*, 36, 5104.
- Kamarudin M.Z.F., Kamarudin S.K., Masdar M.S., and Daud W.R.W.** (2013). Review: Direct ethanol fuel cells, *Int. J. Hydrogen Energ.*, 38, 9438
- Kim J., Momma T., and Osaka T.** (2009). Cell performance of Pd-Sn catalyst in passive direct methanol alkaline fuel cell using anion exchange membrane, *J. Power Sources*, 189, 999.
- Li Y.S., Zhao T.S., and Liang Z.X.** (2009a). Effect of polymer binders in anode catalyst layer on performance of alkaline direct ethanol fuel cells, *J. Power Sources*, 190, 223.
- Li, Y.S., Zhao, T.S., and Liang, Z.X.** (2009b). Performance of alkaline electrolyte-membrane-based direct ethanol fuel cells, *J. Power Sources*, 187, 387.
- Li Y.S., Zhao T.S., and Chen R.** (2011). Cathode flooding behaviour in alkaline direct ethanol fuel cells, *J. Power Sources*, 196, 133.
- Merle G., Wessling M., and Nijmeijer K.** (2011). Anion exchange membranes for alkaline fuel cells: A review, *J. Membr. Sci.*, 377, 1.
- Mulder M.** (1996). *Basic principles of membrane technology*. Dordrecht, the Netherlands : Kluwer Academic Publishers.

- Mitsui Chemicals Inc.** (n.d.). PES Technical literature. Date retrieved: 01.02.2010, address: http://bdml.stanford.edu/twiki/pub/Haptics/MaterialSelection/Polyethersulfone_PES.pdf
- Rao, V., Hariyanto, Cremers, C., and Stimming, U.** (2007). Investigation of the Ethanol Electro-Oxidation in Alkaline Membrane Electrode Assembly by Differential Electrochemical Mass Spectrometry, *Fuel Cells*, No. 5, 417.
- Salmon E., Guinot S., Godet M., Fauvarque J.F.** (1997). Structural Characterization of New Poly(ethylene oxide) Based Alkaline Solid Polymer Electrolytes, *J. Appl. Polym. Sci.*, 65, 601.
- Song, S., Wang, Y., Shen, P.** (2007). Thermodynamic and kinetic considerations for ethanol electrooxidation in direct ethanol fuel cells, *Chinese J. Catal.*, 28, 752..
- Song, S., Wang, G., Zhou, X., Sun, G., Xin, Q., Kontou, S. and Tsiakaras, P.** (2005). The effect of the MEA preparation procedure on both ethanol crossover and DEFC performance, *J. Power Sources*, 140, 103..
- Varcoe, J.R., Slade, R.T.C., Yee, E.L.H., Poynton, S.D., and Driscoll, D.J.** (2007). Investigations into the ex situ methanol, ethanol and ethylene glycol permeabilities of alkaline polymer electrolyte membranes, *J. Power Sources*, 173, 194.
- Xing, B., and Savadogo, O.** (2000). Hydrogen / oxygen polymer electrolyte membrane fuel cells (PEMFCs) based on alkaline-doped polybenzimidazole (PBI), *Electrochem. Commun.*, 2, 697.
- Yu, E. H., Scott, K., and Reeve, R. W.** (2006). Application of sodium conducting membranes in direct methanol alkaline fuel cells, *J. Appl. Electrochem.*, 36, 25.
- Zhiani M., Gasteiger H.A., Piana M., and Catanorchi S.** (2011). Comparative study between platinum supported on carbon and non-noble metal cathode catalyst in alkaline direct ethanol fuel cell (ADEFC), *Int. J. Hydrogen Energ.*, 36, 5110.

APPENDICES

APPENDIX A: TGA Analysis of the Synthesized Membranes

APPENDIX B: Mass and pH change for the samples in distilled water

APPENDIX C: Raw and Processed data of the Fuel Cell Runs (CD)

APPENDIX A: TGA Analysis of the Synthesized Membranes

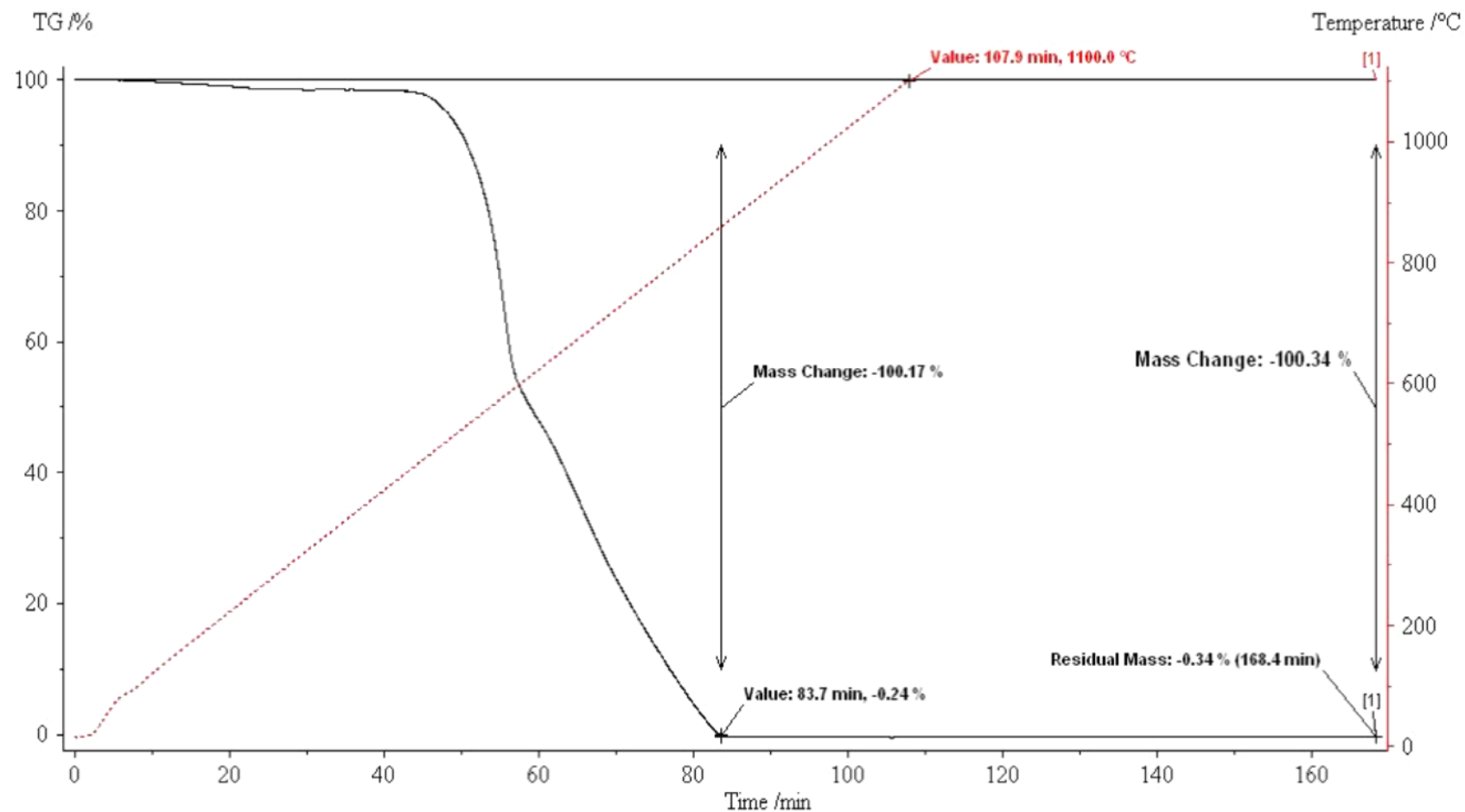


Figure A.1 : TGA weight loss curve for untreated PES polymer.

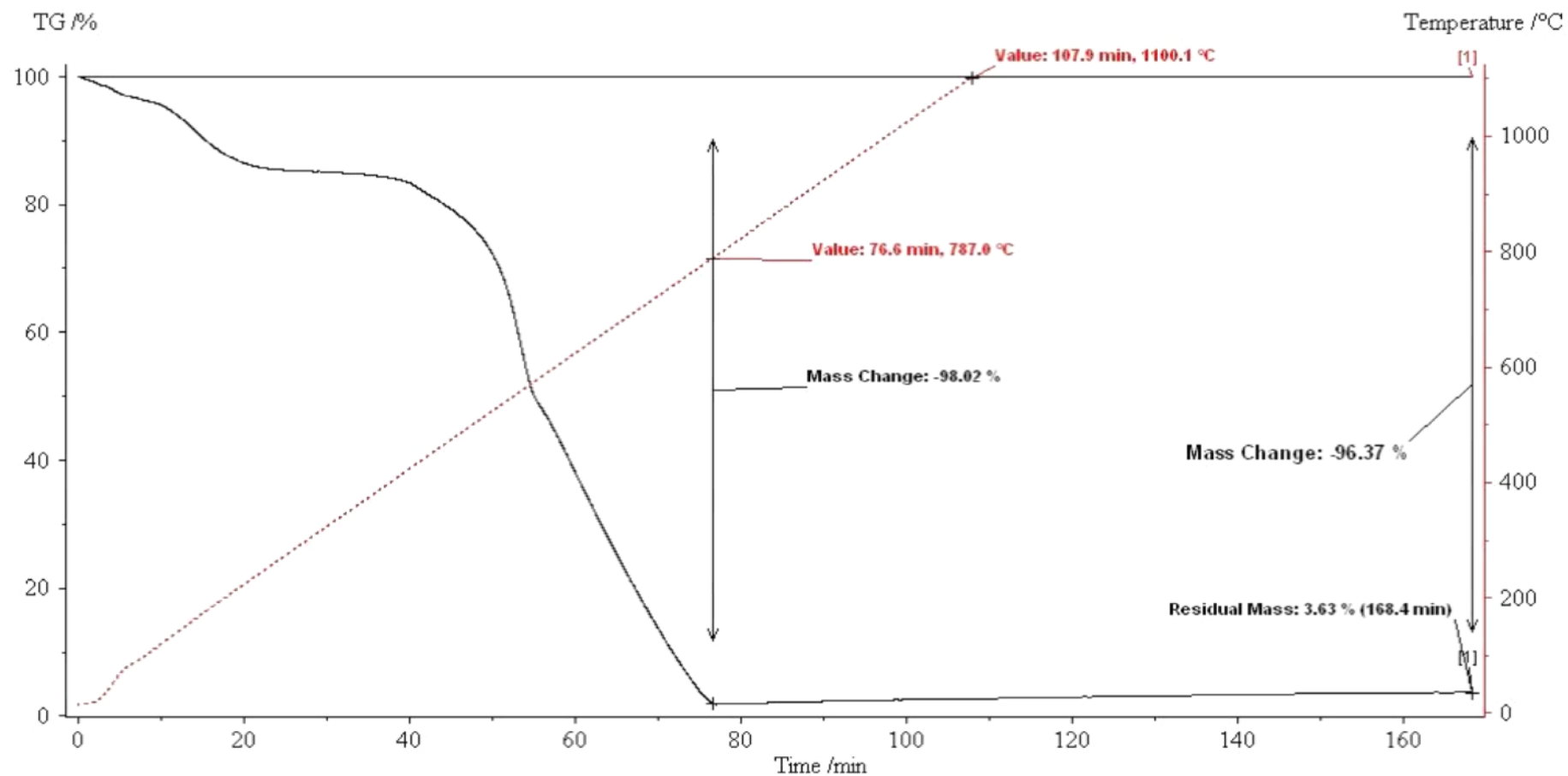


Figure A.2 : TGA weight loss curve for membrane CM36.

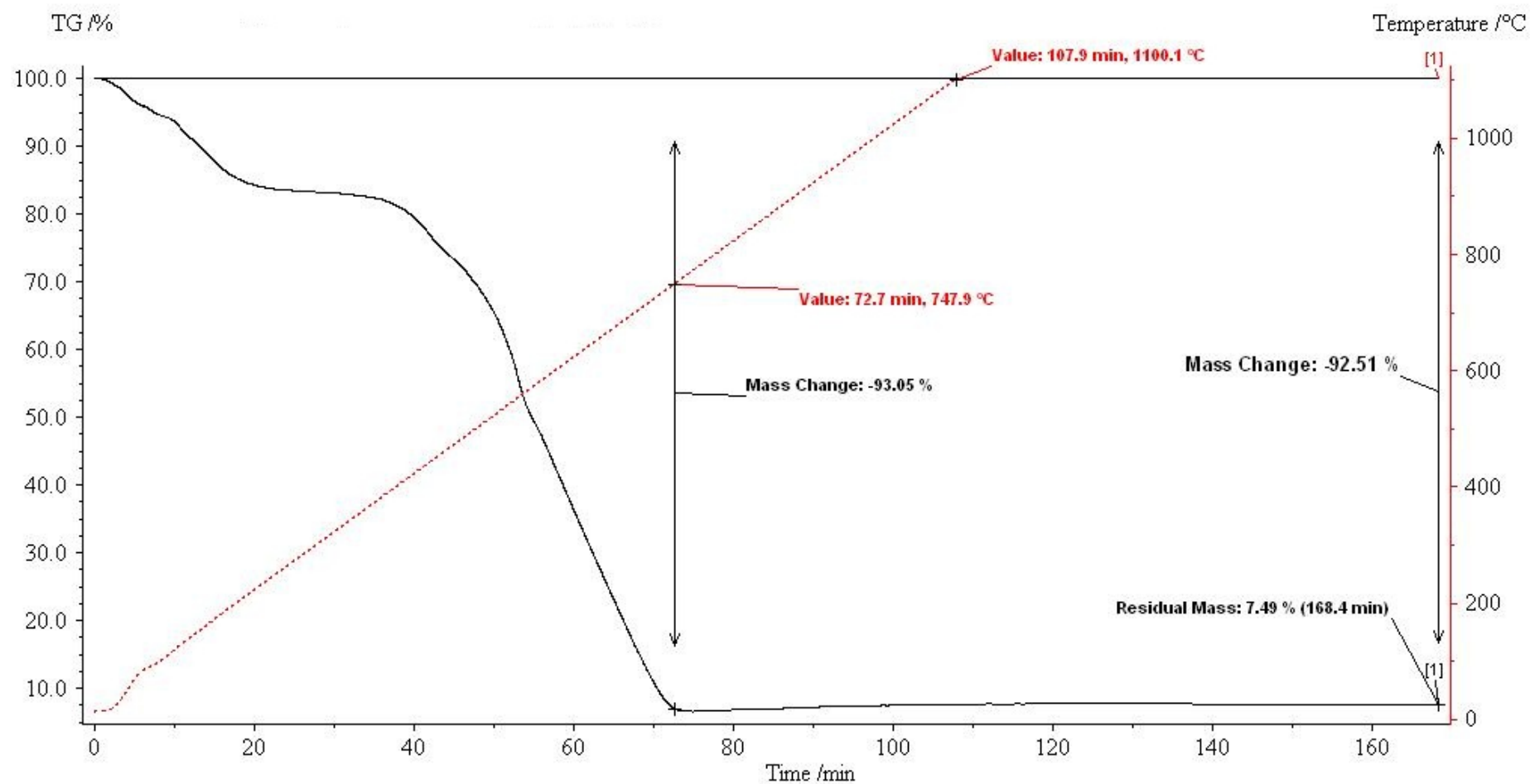


Figure A.3 : TGA weight loss curve for membrane CM46.

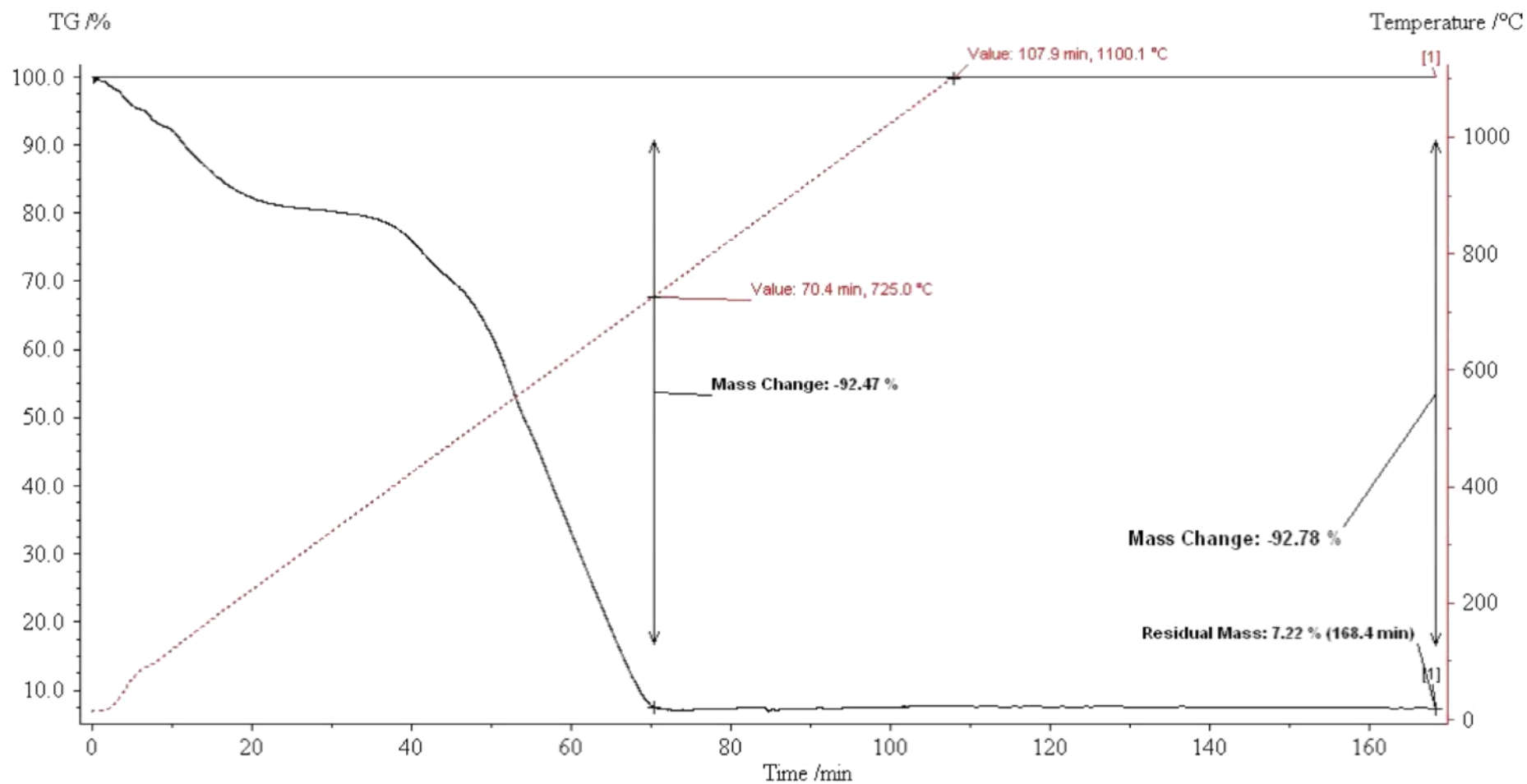


Figure A.4 : TGA weight loss curve for membrane CM56.

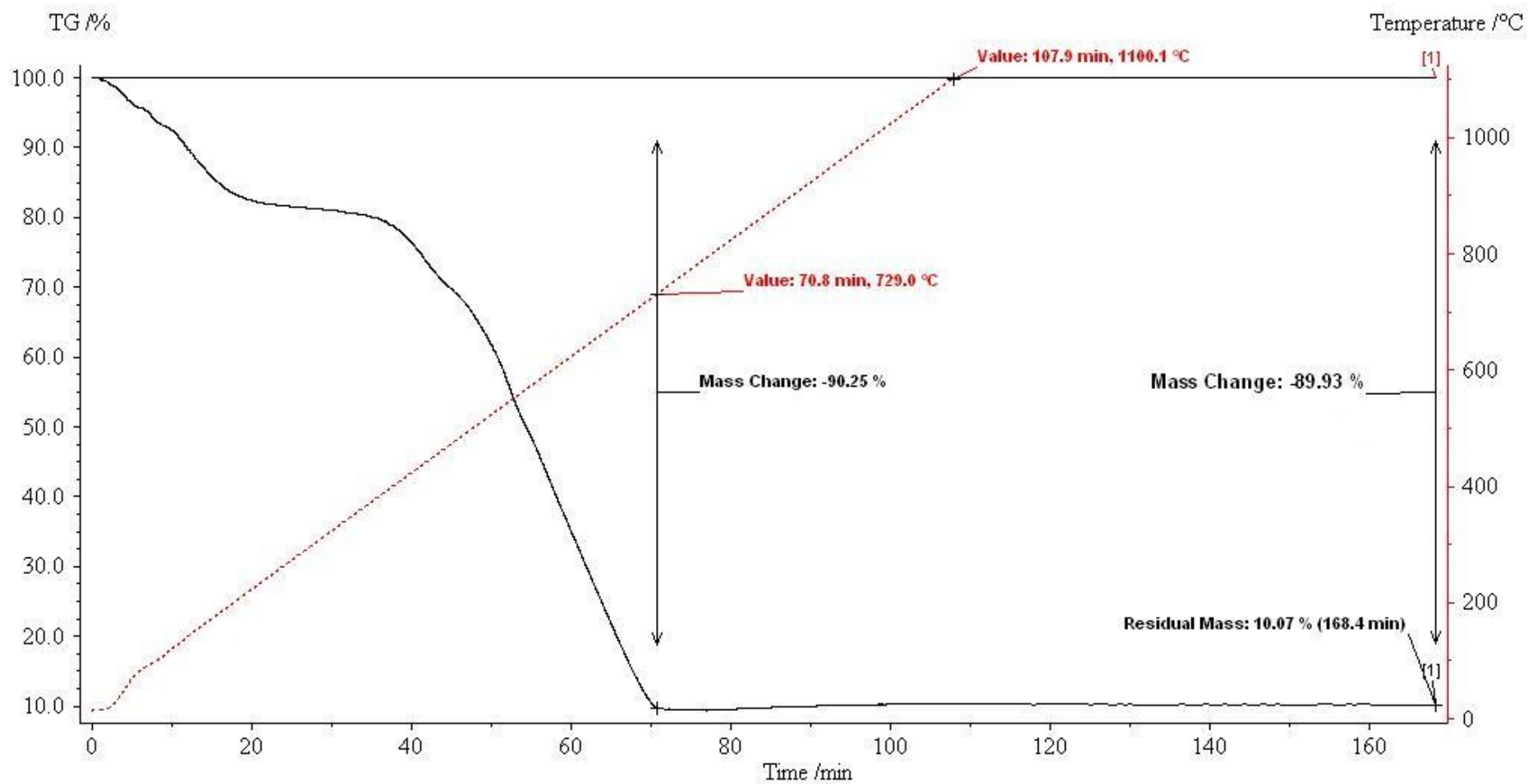


Figure A.5 : TGA weight loss curve for membrane CM66.

APPENDIX B: Mass and pH change for the samples in distilled water

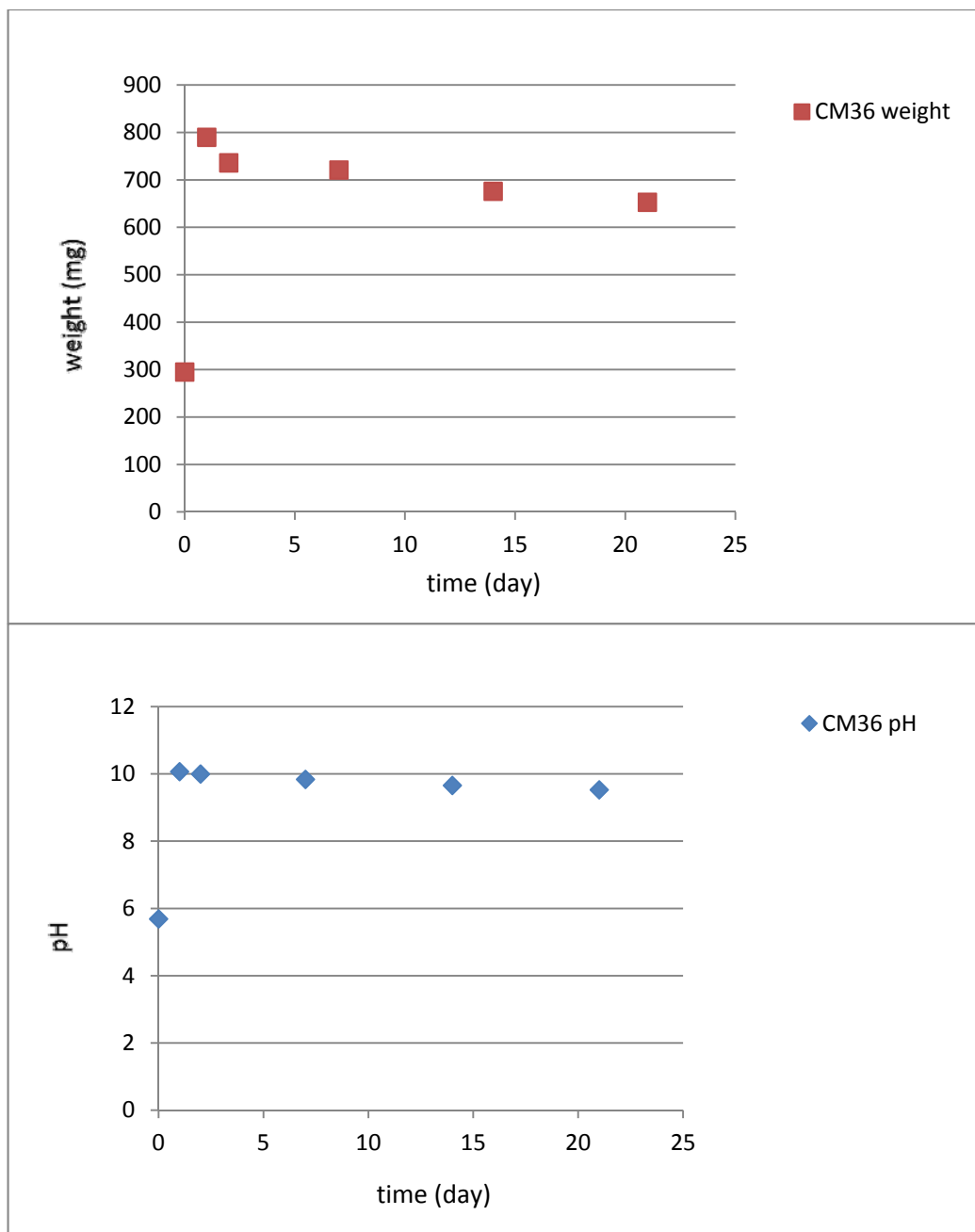


Figure B.1 : Mass and pH change for the sample taken from membrane CM36 in distilled water.

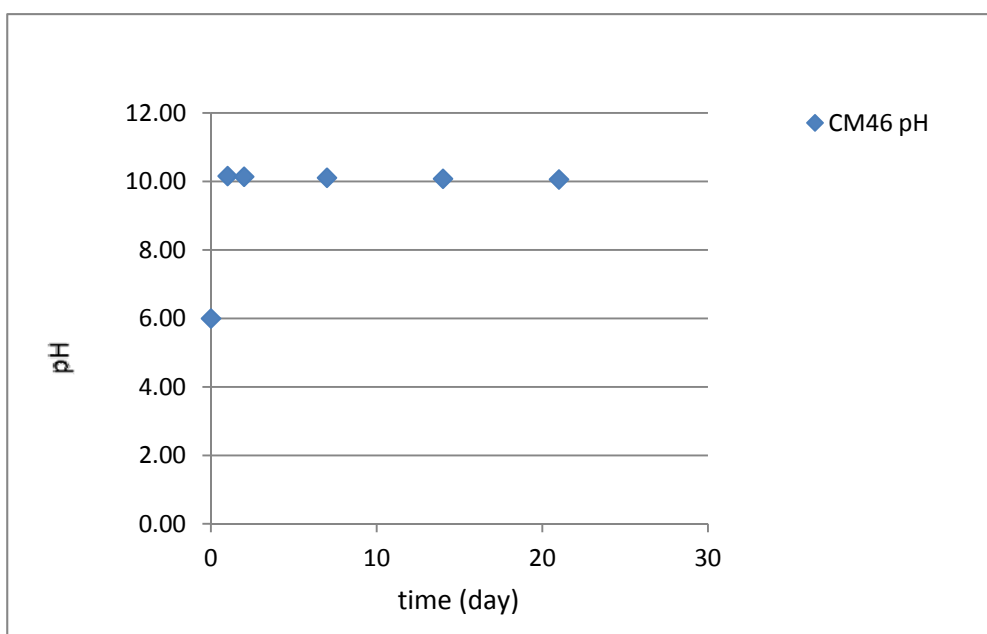
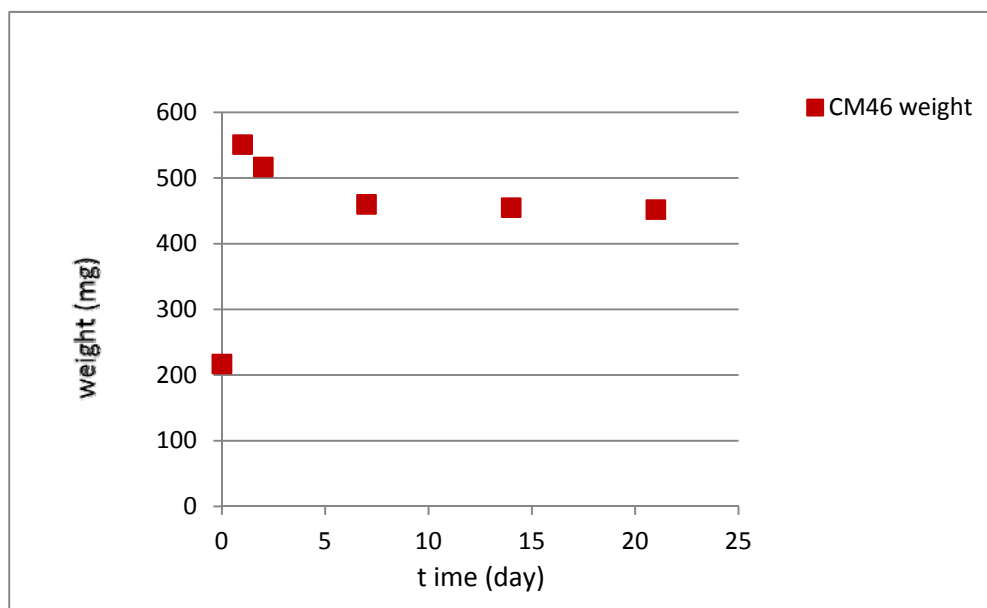


Figure B.2 : Mass and pH change for the sample taken from membrane CM46 in distilled water.

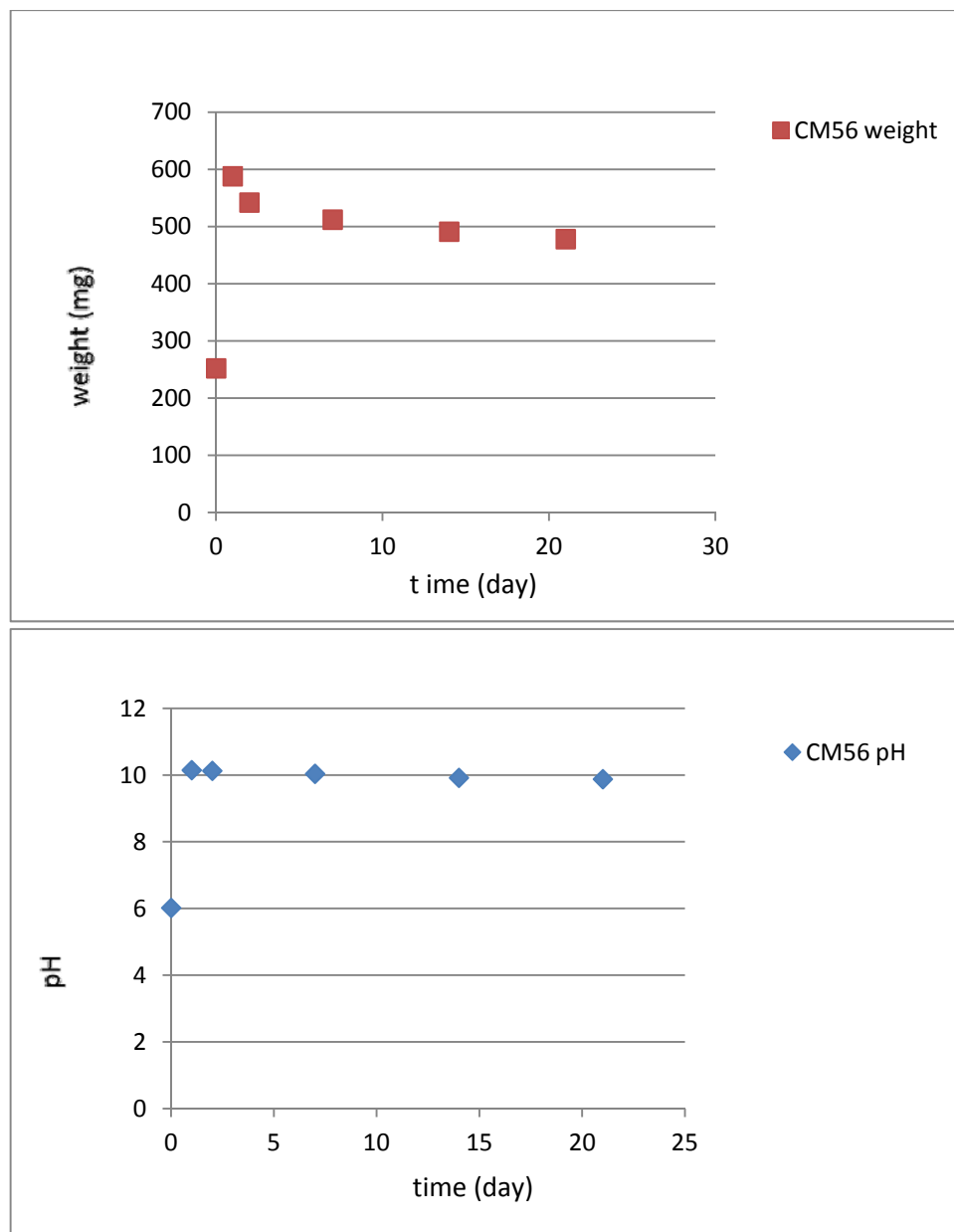


Figure B.3 : Mass and pH change for the sample taken from membrane CM56 in distilled water.

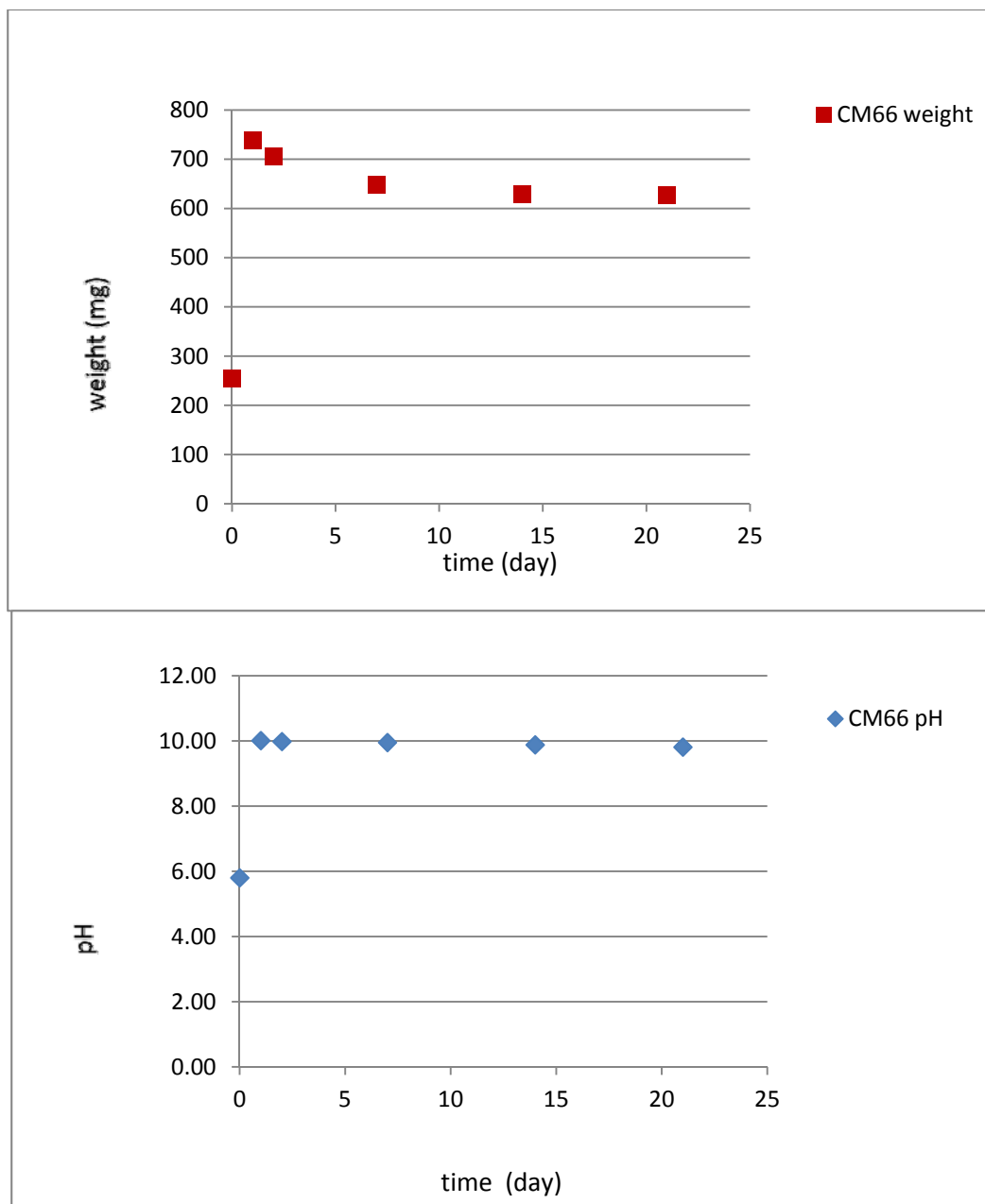


Figure B.4: Mass and pH change for the sample taken from membrane CM66 in distilled water.



CURRICULUM VITAE

Name Surname : Aydın Can Aral
Profession : Chemical Engineer
Date of Birth: 1976
Correspondence: Beşiktaş, Istanbul.
aydinaral@yahoo.com
Nationality: Turkish Citizen

Higher Education

- Boğaziçi University, B.Sc. Chemical Engineering, 1999
- University of South Florida, M.Sc. Chemical Engineering, 2001
- Istanbul Technical University Ph.D. Chemical Engineering 2013

Foreign Languages : English (Advanced level), French (Beginner level)

Professional Experience :

Jan 2013 – Currently ENKA

Employed as senior process engineer in the Power Plants Engineering Group

- Joined the Power Plants Engineering group recently. This group will undertake the complete engineering for Power, Oil&Gas EPC projects of ENKA. Currently West Qurna GTTP is being undertaken. This power plant is to serve early oil production facilities of LukOil Middle Eastern. 3x GE 6B dual fuel GTG's will have a gross output of 100 MWe. Expansion of another set of 3x GE 6B is expected to start soon. Currently I am working on the fuel gas buffer tanks capacity check during fuel switchover. Also an interesting FEHA case is studied where I predict the duration of uncontrolled decompression of buffer tanks during a leak and blowdown simultaneously. Also I review the P&ID and HMB documents.

Jan 2012 – Dec 2012 General Systems Design Inc.

Employed as senior process engineer in the proposal department.

- GSD is an EPC firm in Energy sector. It specializes on HRSG design and manufacturing under Nooter Eriksen license.

- However, GSD also undertakes complete EPC of thermal power plants. In the proposal department my functions are performing heat and mass balance, feasibility studies and preliminary design using GE gate cycle software.

2010 - 2011 BGM Group, Istanbul

Employed as Project Leader

- Repowering of Ambarlı EÜAŞ Power Plant Units 40 and 50. Originally rated 150 MW x2 Escher-Wyss-Oerlikon Steam turbines with fired boilers are being converted to CCPP with 280 MW x 2 Siemens GTG's and old STG's rerated at 125 MW x2 with AEE HRSG's. Mainly working as the process lead.
- 1000MW Aksa Antalya CCPP Project Stress Analysis calculations using Autopipe Plus version.
- 75MW upgrading of Zorlu Lüleburgaz CCPP plant, control philosophy and P&ID work.
- Technical evaluation of offers for equipment purchasing for various projects.

2004 - 2010 Boral Eng. and Consulting Ltd., Istanbul

- Alarko, Kırklareli 82MW combined cycle power plant, stress analysis using Caesar II, 2009-10.
- Rohm and Haas Co. Startup team process engineer for the Gebze Plastic Additives Plant. Various services including process controls, automation testing and commissioning, fire sensing system testing and commissioning, 2008-09.
- Kiplasma Hazardous Waste Treatment and Power Plant. Process calculations for mass and energy balance using flowsheet simulator chemcad, Gebze, Istanbul, 2008.
- Kromsan Plant, process calculations for the Sodium Sulfate Production from waste streams, Mersin, 2007-08.
- Kromsan Plant, neutralization of Solid Waste, Process Calculations, Mersin, 2008
- Borçelik Cold reversing mill and continuous galvanizing mill interconnecting piping, design and calculations, Gemlik, Bursa, 2008.
- AD Demirel Natural gas Separator and heat exchanger design using chemcad flowsheet Simulator, 2008.
- Tüpraş DHRP unit piping stress calculations and supporting of piping using Algor pipepak software, Izmit, 2005-06.
- Kroman iron and steel mill reclamation of process water, 2005.
- PETKİM Petrochemical Co. 2005 investment, process and instrumentation engineer.

1999-2004 University of South Florida

- Teaching and Research assistant in Chemical Engineering department.

1998-1999 Boral Eng. and Consulting Ltd., Istanbul

- HVAC Calculations for the 480 MW Unimar Power Plant.
- Process instrumentation for LAB sulfonation Plant in Kaynarca.

Honor Societies

- The Society of Omega Chi Epsilon, Beta Kappa Chapter, February 2002.
- Phi Kappa Phi, USF Chapter, October 2001.

Certificates

- Pressurized Equipment design:

TUV Rheinland - 08.05.2010

"EN 13445 European Standard for Unfired Pressure Vessels" course on contents and design.

- SITRAIN Simatic S7-300/400 System 1, Course on physical structure, basic operation and programming of Siemens Simatic PLC system, September 2008.
- Aspen Hysys Process Modeling Course EHY-101, 23-25 February 2014.

PUBLICATIONS/PRESENTATIONS ON THE THESIS

- **Aral A.C.** Bir Alkali Polimer Elektrolit Membranın Sentezlenmesi için Bir Metot. *Türk Patent Enstitüsü.* 2009/03467.

