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PROCEEDING



The 8th International Conference
on Membrane Science and Technology
ITB Bandung, Indonesia | 29th Nov - 1st Dec 2010

"Surtainable Technology for Water and Wartewater Treatment.

Energy and Environment"

The 8th International Conference on Membrane Science and Technology

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The 8th International Conference on Membrane Science and Technology

Foreword

The International conference on Membrane Science & Technology is an annual event jointly organized by ITB, Indonesia; PSU, Thailand; UNDIP, Indonesia; UTM, Malaysia; NUS, Singapore and NTU, Singapore. The first MST were held in 1996 at ITB, Bandung. This year, Institut Teknologi Bandung, Indonesia is given the honour to host this 8th regional symposium after University Teknologi Malaysia in 2009.

MST 2010 is dedicated to Prof. AG Fane, as one of the most influential figures in membrane science and technology. His long time works on membrane which is started since more than 40 years ago, has achieved prestigious awards such as Distinguished Visiting Fellow, RAEng, Oxford [2008], Oliver Smithies Lectureship-Balliol College, Oxford [2006], European Membrane Society – Honorary life membership [2003], Centenary Medal for service in Chemical Engineering and Environmental Science [2003], Esso Award of Excellence in Chemical Engineering [1996], Whiffen Medal of IChem.E for Developments in Membrane Technology [1989]. Prof. AG Fane is a key person in the early development of membrane science and technology in South East Asia.It is an honor for ASEAN Association on Membrane as organizing committee of MST 2010 to commemorate retirement of Prof. AG Fane.

This conference was attended representatives from industries, private-sector organizations, academia, and other governmental agencies to accomplish four objectives: to highlight advances and new findings in membrane science & technology and their impacts on technology development, to develop a great mutual appreciation of related disciplines apart from the state-of-the art exposure in the areas of direct interest to different participants, to foster international collaborations and joint ventures, and to promote and facilitate the growth of scientific and technical development in the field of membrane technology development in Indonesia and the ASEAN region. The conference agenda included an opening session, parallel open presentation sessions, and keynote presentations session. In total, there were fourteen keynote speakers, and seventy seven general presentations. The papers and presentations in this document were produced primarily from electronic files provided by the authors. They have been neither refereed nor extensively edited. The conference Proceedings is provided to participants on CD.

Finally, I would like to thank to all Speakers, all Participants, the Session chairs and Moderators, Scientific committees and Organizing committees for their help in making this conference a success. I would also like express our gratitude to all sponsors for their generous support. This Symposium would not have been successful without assistance received from our main sponsor, GDP FILTER (www.gdpfilter.co.id).

Dr. I G. Wenten Chairman of MST 2010

The 8th International Conference on Membrane Science and Technology

List of Content

	Page
A. MEMBRANE PREPARATION	
A-1	
The Effect of Functionalization Carbon Nanotubes (CNTs) as a Composite Material for Membrane Application	
A-2	
The Effect Of Added Plasticizer Compound Dibutyl Phtalat To Mechanically Nature And Cellulose Diasetate Membrane Performance From Pineapple Leaf Fiber (Ananas Comosus)	15
A-3	
Effect of Dope Extrusion rate (DER) in Spinning Process of Hollow Fiber Membrane for Ultrafiltration Using CFD	16
A-4	
Perfluorosulphonated Composite Membranes for the Direct Ethanol Fuel Cell Working at Higher Temperature (>100°C)	17
A-5	18
PVA/XSBR Blending For Desalination of Aqueous Salt Solutions	
A-6	10
The Effect of Dispersion State of Cloisite 15A® on the Performance Properties of SPEEK/Cloisite15A®/TAP Nanocomposite Membrane for DMFC Application	19
A-7	20
In-situ Synthesis of Cubic Silver Nanoparticles in Polyethersulfone for Antibacterial UF Membrane	
A-8	
Carbon Hollow Fiber Membrane Fabrication from Polyetherimide/Polyvinylpyrrolidone (PEI/PVP) for Gas Separation	21
A-9	
Polyfurfuryl Alcohol Based Carbon Molecular Sieve Membranes: Effect of Carbonization Temperature on CO ₂ /CH ₄ Selectivity	22
A-10	
Application of Response Surface Methodology for Optimization of Carbon Molecular Sieve Membrane Synthesis from Polyfurfuryl Alcohol for O ₂ /N ₂ Selectivity	23
	Page
A-11	24

The 8th International Conference on Membrane Science and Technology

A-23				
Optimization of CO ₂ /CH ₄ Ideal Selectivity by Carbon Molecular Sieve Membranes Derived from Polyetherimide Using Response Surface Methodology				
A-24				
Surface Modification of <i>Polyacrylonitrile</i> Membrane with Inorganic Particles for Ultrafiltration Application				
A-25	39			
Membrane Surface Modification for Anti-Adhesion and Anti-Bacterial Properties	39			
A-26	14.191			
Influence of Dope Extrusion Rate (DER) to Polyethersulfone Hollow Fiber Membranes Added With Surface Modifying Macromolecules (SMM)	40			
A-27				
Surface Properties Effects on Filtration Performance of PVDF Composite Hollow Fiber Membrane	41			
A-28	42			
Is Single-step Radiation Grafting Method Better Than Its Counterpart Conventional Two- step Method in Preparation of Proton Exchange Membranes for Fuel Cell?				
A-29				
Study of Crystallinity and Phase Behavior of PVDF-GPPS Blends Membranes from X- Ray Diffractometry and Fourier Transform Infra Red Spectroscopy (In Atr Mode)	43			
A-30	44			
High performance flat sheet NF type forward osmosis membrane				
A-31				
influence of Silica/Sulfonated Polyether-Ether Ketone as Polymer Electrolyte Membrane for Hydrogen Fueled Proton Exchange Membrane Fuel Cells	45			

Nanocomposite Electrolyte Membrane for Moderate Temperature and Low Relative Humidity Hydrogen Proton Exchange Membrane Fuel Cell (hpemfc) Application

Page

The 8th International Conference on Membrane Science and Technology

Keynote Speaker:

- 1. Prof. Anthony Gordon Fane, NTU, Singapore "MEMBRANE FOR A WATER CYCLE"
- 2. **Prof. William Bernard Krantz,** *University of Colorado, USA* "POLYMERIC MEMBRANE FORMATION"
- Prof. Kang Li, Imperial College London, United Kingdom
 "CERAMIC HOLLOW FIBRE MEMBRANES FOR SEPARATION AND CHEMICAL REACTION"
- Prof. Kazuo Yamamoto, University of Tokyo, Japan
 "ADVANCEMENT IN SUBMERGED MBR: ZERO SLUDGE DISCHARGE OR MAXIMUM SLUDGE PRODUCTION"
- Prof. Zbigniew J. Grzywna, SUT, Poland
 "RECENT ADVANCES IN AIR ENRICHMENT BY POLYMERIC MAGNETIC MEMBRANES"
- Prof. S. M. Javaid Zaidi, King Fahd University, Saudi Arabia
 "DEVELOPMENT OF COMPOSITE MEMBRANE FOR FUEL CELL APPLICATIONS"
- 7. **Prof. Ahmad Fauzi Ismail,** *UTM, Malaysia* "MIXED MATRIX MEMBRANE FOR SEPARATION PROCESSES: THE NEED, CHALLENGES AND FUTURE PROSPECTS"
- Prof. Hamdani Saidi, UTM, Malaysia
 "MEMBRANE TECHNOLOGY FOR DECARBONIZATION OF ENERGY"
- Prof. Wirote Yauravong, PSU, Thailand
 "MEMBRANE AS CLEAN TECHNOLOGY IN FOOD PROCESSING"
- 10. Prof. Pikul Wanichapichart, PSU, Thailand
 "SURFACE ANALYSIS AND MODIFICATIONS OF CHITOSAN MEMBRANE"
- 11. Prof. Mohamed Mahmoud El-Sayed Nasef, UTM, Malaysia
 "IS SINGLE-STEP RADIATION GRAFTING METHOD BETTER THAN ITS
 COUNTERPART CONVENTIONAL TWO-STEP METHOD IN PREPARATION OF
 PROTON EXCHANGE MEMBRANES FOR FUEL CELL?"
- 12. Dr. I G Wenten, ITB, Indonesia "DEVELOPMENT OF MEMBRANE IN INDONESIA"

NANOCOMPOSITE ELECTROLYTE MEMBRANE FOR MODERATE TEMPERATURE AND LOW RELATIVE HUMIDITY HYDROGEN PROTON EXCHANGE MEMBRANE FUEL CELL (HPEMFC) APPLICATION

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Nowadays PEMFC with hydrogen fuel has developed to commercialize to replace the conventional machine. Several limitations in PEMFC commercialization are its low efficiency, viability of hydrogen fuel supply and problem of controlling fuel and water as reaction products. Effective effort to increase efficiency and water management include elevating temperature of PEMFC operation near water boiling point to increase energy produced, prevent water flooding, enhanced cooling efficiency and also the possibility to use hydrogen and air under lower humidity in order to make simples PEMFC design. But at elevated temperature and low relative humidity, Nafion membrane that during the time still used as electrolyte will shrink and at high humidity and high temperature above 80°C membrane will swell and irreversibility decay occur. Membrane shrinking and swelling will reduce PEMFC performance. The objective of this study is to investigate the usage of Nafion-SiO2-PWA nanocomposite membrane NS10W, NS15W and NS20W with the ratio of Nafion:SiO2-PWA = (1:0.0288:0.0154), (1:0.0432:0.0173) and (1:0.05768:0.023) respectively as PEMFC electrolyte to improve PEMFC performance at moderate temperature and low relative humidity. The Fuel cell test (FCT) station (FCT-2000 ElectroChem, USA) was used for the cell polarization test and determination of the internal resistance of the membrane. The gas flow of H2/O2 was fixed at the stoichiometric ($H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O$) mole ratio 0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was varied between 30-90°C. The relative humidity (RH) was controlled by using the water temperature of the H2 and O2 gas humidifiers. During the (V-I) measurement, the testing system was stabilized for about 1 h in order to obtain constant value for all the parameters of interest and the resistance of the membranes was measured by optimizing the (V-I) experiments. The electrochemical performance of the composite membrane with dry and humidified reactants are compared with those of the native Nafion membrane to identify the operating condition with low relative humidity condition. The results show that at temperature of 30-90°C and 100% RH humidity, the Nafion membrane performance is higher compare to composite membrane under same temperature value. But at 40% RH and same temperature, the composite membrane performance is higher compared to Nafion membrane. The result of data analysis and optimized polarization curve model shows that the mechanism of proton transfer in the Nation membrane followed the vehicular model, which is as in the composite membrane is close to the proton hopping model. The performance of the Nafion-SiO₂-PWA composite membrane is stable at low relative humidity operating at 30-90°C temperature. Since the humidity is low and operating temperature are high, the PEMFC using the nanocomposite membrane can run with lower humidity and with higher power compared to a PEMFC using the pure Nafion membrane.

1.Introduction

Operation of proton exchange membrane fuel cells (PEMFC) at elevated temperatures can alleviate the anode electro catalyst poisoning and accelerate the oxygen reduction reaction (ORR) kinetics of the fuel cells. Common perfluorosulfonic acid (PFSA) membrane, such as Nafion, is widely used as the polymer electrolyte membrane under low-temperature because of its excellent chemical, mechanical and thermal stability. However, the proton conductivity of the Nafion membrane depends strongly upon the water content in the membrane. Thus, development of proton-conducting membranes with high water-retention ability is crucial for elevated temperature PEMFCs and high power output [1].

Much work been conducted to modified the Nafion membrane with incorporated hygroscopic and high conductivity material such as Silicon oxide and heteropolyacid in the Nafion matrix [2], to increase water absorbstion of the membrane and conductivity. Many report have evident the Nafion-inorganic composite membrane more stable than pure Nafion membrane at low relative humidity condition [3, 4, 2, 5]. But in those reported papers, phenomenon behind the conductivity improvement not fully described in detail.

This research was conducted to investigate the role of inorganic component in the Nafion membrane to the electrochemical properties. To know the effect on addition of inorganic component to the electro-chemical property, the Nafion-SiO₂-PWA membrane was synthesized with varies the ratio of Nafion: SiO₂: PWA in the range of (1:0.0288:0.0154); (1:0.0432:0.0173) and (1:0.05768:0.023) respectively. Hopefully, incorporated inorganic compound like PWA that is hygroscopic and has high proton conductivity properties in the Nafion cluster strongly increase the amount of structural water in the film, improve the conductivity of the membrane and PEMFC performance especially at higher temperature and low relative humidity condition [5]

2. Experiment

2.1 Membrane preparation and membrane electrode assemblies

Material and method of the Nafion-SiO₂-PWA composite membrane and membrane electrode assemblies (MEA) have been reported in the previous paper [5] and a brief description described in Fig.1

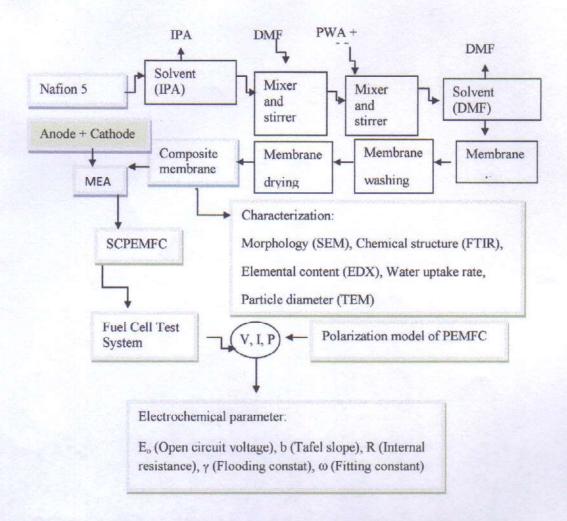


Fig. 1 Material and method synthesis and characterization of Nafion-SiO₂-PWA composite membrane

2.2. Single cell of PEMFC

The MEA is combined with bi-polar plate, current collector, and end plate with arrangement of end plate, current collector, bi-polar plate, MEA, bi-polar plate, current collector and end plate respectively form single cell proton exchange membrane fuel cell (SCPEMFC) system. The arrangement of SCPEMFC is figured out by Figure 2 and the specification of every part is pointed out by Tabel 1. The components of SCPEMFC as shown in Fig. 1 include (1) current collector (CC), (2) bipolar plate (BP), (3) gas diffusion layer (GDL), (4) anode (A), (5) electrolyte membrane (EM) and (6) cathode (C). The specification of each component of SCPEMFC have been presented in [Mahreni et al. 2009][5].

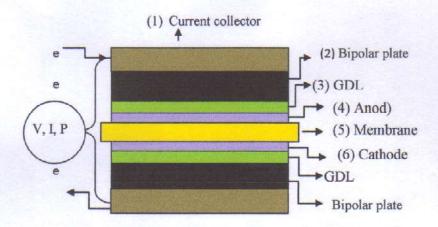


Fig. 2 The single cell of proton exchange membrane fuel cell (SCPMFC)

2.3 Physical-chemical characterization

Physical-chemical property as well as membrane morphology, chemical structure, element content and the diameter of SiO₂-PWA particle in Nafion-SiO₂-PWA composite membrane which was synthesized using the sol-gel method [5]. The diameter of the particle is analyzed using two methods, i.e. TEM and UV-VIS. TEM was used to measure the real particle diameter while the UV-VIS was used to measure the transparency of composite membrane and theoretical particle diameter [5].

2.4 Determination of internal resistance, conductivity and cell performance

The Fuel cell test (FCTS) station (FCT-2000 ElectroChem, USA) was used for the cell polarization test and determination of the internal resistance of the membrane. The gas flowrate of H_2/O_2 was fixed at the stoichiometric ($H_2 + 1/2O_2 \leftrightarrow H_2O$) mole ratio of 0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was varied between 30°C - 90°C.

The relative humidity was controlled by controlling the water temperature in the H₂ and O₂ gas humidifiers. During the (V-I) measurement, the testing system was stabilized for about 1 h in order to obtain constant value for all the parameters of interest and the resistance of the membranes was measured by optimizing the (V-I) experiments. A mathematical model for polarization curve was used to correlate voltage and current (V-I) at 100° relative humidity (RH) and 40% RH based in a single fuel cell system, which include the flooding parameter as given in Eq. (1) [6].

$$E = E_o - b \log(i) - R(i) - \exp(\omega i)$$
 (1)

where E, E₀, b, R, γ and ω are the cell voltage, open circuit voltage, Tafel constant, internal resistance, flooding constant and fitting constant, respectively. The internal resistance of the cell is assumed to be same as the conductivity of the composite membrane. Hence, Eq. (2) was used to calculate the membrane conductivity as [7]

$$\sigma = (1/R)(1/S) \tag{2}$$

$$P = V_X i \tag{3}$$

where σ is the conductivity of the composite membrane (S cm⁻¹), R the resistance (ohm), i is thickness of the membrane (cm) and S is contact surface area of the electrode (cm²), P is power density, V is cell voltage and I is the current density [7, 8].

3. Results and discussion

3.1 Particle diameter of inorganic component in the Nafion matrix.

Solution phase sol-gel method had been used to produce Nafion-SiO₂-PWA composite membrane and could improve the membrane structure from micro structure to nano structure. Analysis using TEM found the particle diameter of SiO₂ and PWA in the NS10W, NS15W and NS20W composite membrane are 6.9, 7.86 and 12.64 nm respectively.

The particle size of SiO_2 and PWA in the NS10W, NS15W composite membranes found less than the size of the Nafion cluster. Therefore, it can be concluded that SiO_2 and PWA particles are in the Nafion cluster. The presence of inorganic particles in the Nafion cluster increase water uptake rate of the membrane. The water uptake rate of N112 (pure Nafion) membrane is 26.52% weight, meanwhile of NS10W, NS15W are 30.25 g%, 33.43 g%, respectively. The increase of water uptake rate is identical to the increase in the membrane conductivity. At 90° C of temperature and at 40% RH, the conductivity of NS15W membrane is 2.85×10^{-3} S cm⁻¹ while compared to Nafion membrane under the same condition to be only at 1.16×10^{-3} S cm⁻¹.

3.2 Performance of PEMFC

The performance of the single cell MEA using N112, NS10W, NS15W and NS20W membranes were obtained from the cell voltage versus current density measurement. The results of the test at temperature range of 30 – 90°C of two different relative humidity, namely those are 40% RH and 100% RH, were recorded and presented as power density (m W cm⁻²) vs current density (mA cm⁻²) as shown in Fig. 3 (from a to g). All of the data are presented with the mathematical model of polarization curves. The electrochemical parameters was found from the optimization and experimental data in fitting with mathematical model to measure internal resistance (R), open circuit voltage (E₀), Tafel slope (b) and flooding constant (γ) as presented elsewhere [5]. Conductivity values were calculated from electrochemical parameters in which obtain from graphs in Fig.3 and the data is listed in table 1. The best cell performance was recorded 90°C, 1.7 atm at 40% RH with using NS15W membrane.

Table 1 Values of conductivity (σ) and maximal power (P_{max}) for N112, NS10W, NS15W and NS20W membranes, with membrane thickness 70 μm and surface area 50 cm².

30°C, 100% RH			60°C, 100% RH	
Membrane	σ (S cm ⁻¹) 10 ³	P (watt)	σ (S cm ⁻¹) 10 ³	P _{maks} (watt)
N112	2.69	0.79	2.79	0.83
NS10W	2.40	0.68	2.49	0.75
NS15W	2.19	0.58	2.31	0.82
NS20W	2.12	0.50	2.19	0.66
80°C, 100% RH			90°C, 100% RH	
N112	3.03	1.42	3.33	2.04
NS10W	2.64	1.20	3.04	1.55
NS15W	2.97	1.24	3.29	1,75
NS20W	2.64	1.13	3.02	1.47
60°C, 40% RH			80°C, 40% RH	
N112	1.66	0.65	1.53	0.55
NS10W	2.32	1.13	2.41	0.73
NS15W	2.22	1.02	2.37	1.26
NS20W	2.00	0.73	2.12	0.77
90°C, 40% R	H			
N112	1.16	0.55		
NS10W	2.51	0.86		
NS15W	2.85	2.66		
NS20W	2.32	1.81		

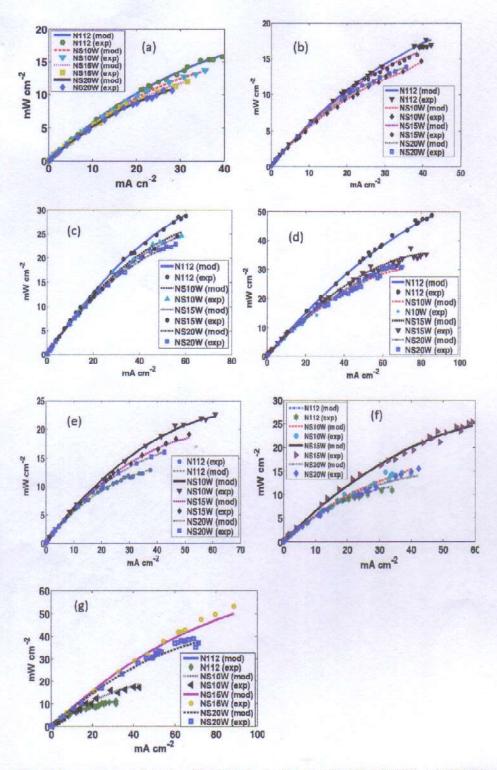


Fig. 3. Power output of single cell PEMFC using N112, NS10W, NS15W and NS20W membranes as electrolyte at temperature of: (a) 30°at 100% RH; (b) 60°C, 100%RH; 80°C, 100% RH; (d) 90°C, 100% RH; (e) 60°C, 40% RH; (f) 80°C, 40% RH and (g) 90°C, 40% RH.

The performance of N112 Nafion membrane was exhibited best performance at saturation humidity at all temperature range in this study. While composite membrane was performing better than Nafion membrane at 40% relative humidity. The best performance among all these membrane was a composite NS15W.

It was observable that the presence of inorganic compounds in the Nafion cluster may create a capillary condensation that making the composite membrane has more hygroscopic properties in compare with Nafion membrane. The conductivity of the composit membrane stable at reduced relative humidity.

4. Conclusion

Nafion-PWA –SiO₂ composite membrane was fabricated to improve the water-retention ability of the membrane with the assistance of the hydrophilic capillary. The PWA-SiO₂ was characterized to be ordered meso-structure with pores size of 3.5 nm. The proton conductivity through the Nafion-PWA-SiO₂ composite membrane has little change under elevated temperature and low humidity. As a result, the Nafion-PWA-SiO₂ composite membrane (NS15W), presented a steady performance under 90°C, 40 % RH. The power of the cell assembled with Nafion-PWA-SiO₂ composite membrane reached a peak value of 2.66 Watt, which is much higher than pure Nafion membrane.

References

- [1] Xue-Min Yan, Ping Mei, Yuanzhu Mi, Lin Gao, Shaoxiong Qin. 2009. Proton exchange membrane with hydrophilic capillaries for elevated temperature PEM fuel cells. Electrochemistry Communications 11:71–74.
- [2] Shao, Z.G., Joghee, P., Hsing, I.M. 2003. Preparation and characterization of hybrid Nafionsilica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells. *Journal of Membrane Science* 229: 43-51.
- [3] Ramani, V., Kunz, H.R. & Fenton, J.M. 2004. Investigation of Nafion/HPA composite membranes for high temperature/low relative humidity PEMFC operation. *Journal of Membrane Science* 232: 31-44.
- [4] Ramani, V., Kunz H.R. and Fenton, J.M. 2005. Effect of particle size reduction on the conductivity of Nafion/phosphotungstic acid composite membranes. *Journal of Membrane* Science 266: 110-114.
- [5] Mahreni, A., Mohamad, A.B., Kadhum A.A.H., W.R.W. Daud., S.E. Iyuke. 2009. Nafion/silicon oxide/phosphotungstic acid nanocomposite membrane with enhanced proton conductivity. Journal of Membrane Science. 327: 32–40.
- [6] Baschuk, J.J., Li X. 2000. Modelling of polymer electrolyte membrane fuel cells with variable degree of water flooding. Journal of Power Sources 86:181.
- [7] Sancho, T., Soler, J., Pina, M.P. 2007. Conductivity in zeolite-polymer composite membranes for PEMFCs. Journal of Power Sources 169: 92.
- [8] Jang, W., Choi, S., Lee, S., Shul, Y., Han, H. 2007. Characterizations and stability of polyimideephosphotungstic acid composite electrolyte membranes for fuel cell, Polym. Degrad. Stab. 92: 1289.