Hydrogen Production by Using Composite Membrane (Nafion/Al₂O₃) in PEM Water Electrolysis

E. L. Santhi Priya¹, V. Himabindu²

¹Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad-500 085, A.P, India

² Associate Professor, Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Hyderabad – 500 085, A.P, India

Abstract: In the present study, Nafion/Al₂O₃ composite membrane is prepared and evaluated as electrolytes in PEM water electrolysis. A composite membrane is obtained by mixing 5Wt% Nafion which have a SO₃H group as a proton conductor with inorganic material (Al_2O_3) , using casting method. In addition, by using adequate catalysts, the performance of prepared Composite membrane has been tested using in-house fabricated single cell PEM water electrolysis cell with $10cm^2$ active area at different temperatures and at 1 atmosphere pressure by varying voltage range from 1.7–3.2V with respect to hydrogen yield and at current density 0.1, 0.2, 0.3, 0.4, and 0.5(A cm⁻²). Experiments have shown that 99.9% purity of hydrogen Gas is evolved, and also the fabricated composite membrane have shown the significant improvement of all tested properties compared to that of pure Nafion115 membrane. The physicochemical properties of the composite membranes such as water uptake, ion-exchange capacity, X-ray diffraction (XRD), Fourier transform infrared spectroscopy and Gas Chromatography is determined.

Keywords: Al₂O₃, Nafion, catalysts, Composite membrane, PEM water Electrolyser, Hydrogen.

1. Introduction

Conversion of energy has huge impact on quality of our environment, and main intention is to supply economical, adequate energy conversion with few negative environmental impacts to our society. Hydrogen as an energy carrier is an attractive option, because it is environmentally friendly, affordable in nature, flexible and its significance in all sectors of the economy.Hydrogen is the lightest and most abundant element on the planet (Hanslmeier et al. 2011) .Hydrogen is considered as the key to a clean energy for future. It doesn't occur naturally in its useful form, it has to be generated using fossil fuel, nuclear or renewable energy. The use of hydrogen could eventually eliminate greenhouse gas emissions from the energy sector. Ongoing research efforts and challenges in the hydrogen technology areas are spanning the fields of hydrogen production and storage, fuel cells. Nowadays hydrogen has been widely used in industrial applications to processing the petrochemicals and fertilizers, but not producing hydrogen as an energy carrier or as a fuel for energy generation, except for pilot scale R&D projects. Proton transport is one of the most fundamental phenomena in nature and it also plays key role in proton exchange membrane (PEM) fuel cells and water electrolyzers. Therefore the electrolysis of water using proton exchange membrane (PEM) can be a novel approach for developing a technology for hydrogen production(E.L.Santhi priya et al. 2012).

In water electrolysis the major components are PEM and electrocatalysts, the most commonly used PEM is Nafion and Composite membrane (Nafion/TiO₂) and Nafion/ZnO₂) etc. Perfluorosulfonate ionomer membranes such as Nafion are specifically used in several industrial applications that require an ion-conducting polymer membrane with good

thermal and chemical stability (K.D kreuer et al. 2001 and A. and J Appleby et al. 1989). The conventional proton conducting polymer electrolyte membrane is mechanically unstable at temperatures above 100°c (H. Nikhil Jalani et al. 2005). Nafion also have a few disadvantages such as high cost, water dragging during operation. An attempt to develop these higher temperature membranes includes changes of the conventional host polymers via incorporation of various hygroscopic inorganic particles or by developing alternate new polymer system (T.A Zawodzinski et al. 1995, S.Malhotra et al. 1997, G. Alberti et al. 2000, and K. A Mauritz et al. 2000). The inorganic fillers increases the water retention inside the composite membrane permit to operating at high temperatures (Watanabe M et al. 1996 and Arico A et al. 2003). One of the inorganic membranes among the new polymer system in Nafion/Al₂O₃ (A.M. Herring et al. 2006, A.K. Sahu et al. 2007, and D.E Alessandra et al. 2010). The Nafion membrane has strong electrochemical stability satisfactory mechanical strength and high proton conductivity (L. J. M. J Blomen et al. 1993, EG&G Services Fuel Cell Handbook 2000, S.Srinivasan et al. 1993).

So far used electrocatalysts in PEM electrolyser are Pt and Ru. Pt is used as a hydrogen electrocatalyst (cathode) for PEM water electrolysis processes, enhances its performance for the evolution of hydrogen (Moreira J et al. 2004). Pt is considered to be most economical. This drawback, together with the need for low cost effective method, encouraged many researchers to use Pd as alternative, Pd more abundant than Pt (Grigoriev SA, et al. 2006).Recently some studies have been reported in the literature on the use of Pd catalyst in PEM water electrolysis.

Hence, research and development is very important to enhance the performance and lower costs of hydrogen production. So far less amount of work has been reported on inorganic composite membranes with Pd on activated carbon support to produce hydrogen. Accordingly, the present study an attempt has been made to assess the performance of inorganic membrane with Pd on activated carbon in water electrolysis process for the production of hydrogen. The conductivity of the PEM is measured at 30°C .The characterization studies of the Composite membrane is done by ion exchange capacity (IEC), FT-IR, and Water uptake,.

2. Material and Methods

2.1. Materials

Nafion 115 membrane and 5 wt% Nafion solution is procured from M/s.Ion power Inc, USA, Al_2O_3 , NaCl, NaOH, and10 wt% Pd on Activated carbon, RuO₂, N, N-Dimethylacetamide are purchased from SRL Chemicals India. De-ionized water was used in all experiments.

2.2 Membrane Preparation

For the method of preparation of the Al_2O_3 Composite membrane was based on casting method (E.L.Santhi priya et al. 2012), in this procedure, a known amount of Al_2O_3 is dissolved in solution DMAc and added to 5wt% Nafion solution and then sonicated in an ultrasonic water bath to get fine dispersion of Al_2O_3 in the Nafion solution. Clear solution obtained at RT is then cast on a petri dish and the solvent was evaporated at 100°C without vacuum. The solvent when completely evaporated, then the Composite membrane is annealed at 120° C for 1 hour [K.A.Mauritz et al. 1995]. The prepared Composite membrane (Nafion/ Al_2O_3) and commercial Nafion membrane115 is pretreated with a standard treatment procedure mentioned below (S.Srinivasan et al. 1993).

• Firstly the membranes boiled in solution 3% hydrogen peroxide (H2O2) for 1h to oxidize organic impurities.

- Rinsing with boiling water.
- Boiling in 0.5M H2SO4 for 1h to remove ionic impurities.

• And finally the membranes is washed with deionized water to remove any excess acid and flattened.

2.3 Preparation of Membrane Electrode Assemblies (MEAs)

The composite membrane used in this study is given in figure 1.10 wt% Pd on activated carbon is mixed with isopropyl alcohol and 5 wt% commercial Nafion solution an equal proportions, mixed well and then sonicated for 30 min in a sonicator thus formed (Cathode) catalyst ink is coated on a composite membrane on one side as hydrogen electrode and RuO2 is mixed with isopropyl alcohol and nafion solution thus formed a (Anode) catalyst ink. This anode catalyst ink is coated on another side as oxygen electrode. Similarly the same procedure has been used to Nafion 115 membrane. The prepared both MEAs are tested in-house single cell PEM water electrolysis.



Figure.1 Composite membrane (Nafion/Al₂O₃)

2.4 Description of single cell PEM water electrolyser

The PEM water electrolyser 10 cm² single cell is fabricated with Stainless Steel 316 material. Current collectors used are perforated titanium sheets. 20 mm thickness of each two end plates, with a provision for inlet/outlet for water/gases for the respective electrodes. Each end plate has horizontal and vertical flow fields so as to hold water and for the free flow of produced gases during electrolysis operation (Naga Mahesh K., et al. 2009). The prepared MEA is fixed in single cell and operated in electrolysis mode at 1 atm pressure and at different temperatures (30°C, 45°C, 65°C, 85°C.). The purified (Millipore Milli Q equipment) water used for this experiment. The obtained pure water is supplied from water reservoir atop and supplied on the both sides of the single cell. The produced hydrogen and oxygen gases are evolved from top of the cell at respective electrodes. Thus evolved water, gases are lifted by circulating water on both sides of the single cell and collected in vessels atop of the electrolyser.

2.5 Performance of the Membrane electrode assembly (MEA)

The performance of prepared Membrane Electrode Assembly is evaluated in single cell assembly. The 10 cm^2 single cell is kept under experimental condition for 2 hrs. A DC voltage of 1.8 to 3.2V is applied during PEM water electrolysis operation. The performance is evaluated by current and voltage (I-V) characteristics curves (Sawada S., et al. 2008 and Ioroi T., et al. 2002).

Membrane characterization 2.6 Water uptake

The water uptake of the composite membrane is measured by suspendinging a dry membrane of known weight in purified (Millipore Milli Q equipment) water for 24 hours. After, the membrane is removed from water and then the membrane is quickly wiped by filter paper to avoid excess of water from the surface (Lepakshi Barbora et al. 2009). The wet membrane weight is measured. Water uptake of the membrane is calculated by the following equation (1)

$$Water - uptake = \frac{(W_w - W_d)\mathbf{X}100}{\mathbf{W}_d} \dots (1)$$

Where, Ww and W_d are the weight of wet and dry membranes, respectively.

2.7 Ion Exchange Capacity

The ion exchange capacity (IEC) by using an acid –base titration method (M.Barclay Scatterfield, et al. 2006) .The membrane is dried at 80° c over night and then immersed in 0.1 M solution NaCl at 65° c overnight under stirring, which would replace H⁺ ion of the polymer acid side chains could be replaced by Na⁺ ion. The solution is then titrated with 0.1M NaOH by using phenolphthalein indicator.IEC was calculated by the following equation

$$IEC = \frac{V_{\text{NaOH}} X C_{\text{NaOH}}}{W_{\text{Sample}}} \qquad \dots (2)$$

Where V_{NaOH} is the added titrant volume at the equivalent point (ml). C_{NaOH} is the molar concentration of the titrant, W_{sample} is the dry mass of the sample (g).

2.8 XRD analysis.

The x-ray diffraction (XRD) analysis of the membrane was investigated by using Shimadzu X ray diffractometer.

2.9 Hydrogen Production

In electrolysis operation, hydrogen is produced and then it is collected in vessels provided at the top of the single cell electrolyser .The theoretical yield of hydrogen is calculated using Faraday laws equation(Eq:3) as given below (Alsheyab M., et al. 2008)

$$\mathcal{W}_{H_2} = \frac{ItM}{FN_e} \quad \dots \quad (3)$$

Where w is the weight of the hydrogen produced at the cathode,

I the applied current intensity (A),

t is the time (s),

M is the molecular weight of hydrogen $(\underline{g} \text{ mol}^{-1})$,

F is the faraday's constant (96485 C mol⁻¹) and

 N_{e} the number of electrons involved in the reaction.

The experimental yields of the hydrogen with Composite membrane and10 wt% of Pd on activated carbon is calculated. The experiments were run for 2hours at current densities 0.1, 0.2, 0.3, 0.4, 0.5 A/cm² at different temperatures and the produced hydrogen and oxygen gases were collected in respective vessels. The yield of hydrogen is calculated by taking the length and volume of the vessel and length of the vessel occupied by hydrogen gas at 1 atm pressure.

2.9 Gas chromatography

Hydrogen gas purity, investigated by using Gas chromatography.

3. Results and Discussion

3.1 Water uptake

Water uptake is closely related to the basic membrane properties and plays an essential role in the membrane behavior. Presence of water in the membrane influences the ionomer microstructure, cluster, channel size, plasticizes and modifies the mechanical properties (Lepakshi Barbora, et al. 2009) .Water uptake properties of the composite membrane and Nafion membrane 115 was evaluated with de-ionized water. Nafion/ Al_2O_3 composite membrane have higher water uptake (29%)than Nafion membrane115 (26%).The enhanced water uptake can be attributed to the hygroscopic nature of Al_2O_3 . A significant number of water molecules can be coordinated by hydrogen bonding with the OH groups present on the surface of Al_2O_3 particles. Therefore, the water uptake of the composite membrane with the addition of the Al_2O_3 in the membrane. Water uptake is more than the Nafion membrane 115.

3.2 Ion Exchange Capacity Measurement

The important property of PEM is Ion exchange capacity (IEC). The acid-base titration method reveals that the Composite membrane exhibited IEC value (0.92 meq g⁻¹) in comparison to that of Nafion membrane 115 (0.90 meq g⁻¹) by using (Eq: 2), indicating an active contribution of the synthesized fillers in providing free acid groups to the membrane, as expected from the proton conductivity features of the sulfated oxides itself. However Composite membrane was found to higher than Nafion membrane.

3.3 FT-IR

The characteristic peaks in FT-IR spectra [Figure 2] present near at 3467.27 cm-1, 1634.5 cm-1 indicate the stretching vibration and bending vibration of hydroxyl group peaks on the Al2O3 particles'. Moreover, the band at 2918.5 cm-1 is the C-H band stretching vibration. The Al-O-Al band is observed at 400-800 cm-1. The bands near 1623 are also assigned to the Al-O stretching mode. 1045 cm-1, assigned to the Al-O stretching of the surface component. The characteristic peak of -SO3- group of Nafion is 1238.8 and 1152.81 cm⁻¹. Also the adsorption band of Nafion at 1238cm⁻¹, attributed to -SO₃- asymmetric stretch, shifted to 1238.8 cm-1 and that at 1152.81 cm⁻¹ attributed to -SO₃symmetric stretch shifted to 1152.81cm-1. The peaks 1100cm^{-1} and 1200cm-1 confirms symmetric and asymmetric stretching of the CF₂ bonds. The obtained peak at 1634 cm-1 was due to the formation of CF=CF bonds in the polymer. The most common peaks that can be identified in this spectrum are symmetric S-O stretching at 1061.80 cm⁻¹.



Figure.2 FT-IR spectra for Composite membrane (Nafion/ Al₂O₃)

Volume 4 Issue 5, May 2015 <u>www.ijsr.net</u> Licensed Under Creative Commons Attribution CC BY

3.4 XRD Analysis

According to the XRD analysis of Nafion/Al₂O₃. The Nafion pattern displays a broad diffraction feature at $2\theta = 12-22^{\circ}$, one of the peak assigned to the amorphous form ($2\theta = 17^{\circ}$) in Figure 3,the most stable alumina phase has been identified with the strong peaks of Al₂O₃ main crystal planes at diffraction angles of 27.379, 35.875, and 54.221. Confirms that inorganic fillers are incorporated into the Nafion® dispersion. X-ray spectra related to the developed composite membranes show the peaks of the considered Al2O3 powder confirming the presence of the inorganic compound within the Nafion polymeric matrix.



Figure.3 XRD for Composite membrane (Nafion/Al₂O₃)

3.5 Performance of prepared composite membrane (Nafion/Al_2O_3) in 10 \mbox{cm}^2 single cell

The performance of the current-voltage (I-V) characteristics curves for the prepared composite membrane (Nafion/



 Al_2O_3) (Figure 1) and Nafion 115 is studied in PEM single cell water electrolysis system using 10 wt% palladium on activated carbon.. Hydrogen yield is calculated by using Faradays law, the experimental yields of hydrogen with respect to current densities at different voltages and at temperature 30°C, 45°C, 65°C and 85°C are studied (Figures 4a, 4b) and Table 1,

Table 1. Experiments carried out for 10wt% Pd/AC for Nafion Membrane 115.

Experimental	Current	Time	Voltage during electrolysis					
Hydrogen yield	density	(hours)	process (V)					
$(\operatorname{cc} \operatorname{min}^{-1})$	$(A \text{ cm}^{-2})$		30°C	45°C	65°C	85°C		
6.45	0.1	2	1.96	1.88	1.81	1.78		
12.29	0.2	2	2.19	2.12	2	1.9		
19.92	0.3	2	2.32	2.2	2.1	2		
24.10	0.4	2	2.44	2.30	2.2	2.1		
30.20	0.5	2	2.56	2.44	2.31	2.22		

shows that The performance of Nafion membrane 115 (Figure 4a&b) shows the decrease in voltage from 2.4V-1.9V when temperatures increased from 30 to 85oC at current density 0.3 A cm⁻² respectively.



Figure 4(a). Polarization curves for 10 wt% Pd on activated carbon 30°C, 45°C , 65°C and 85°C for Nafion membrane 115 Figure 4(b). Hydrogen yield with respect to cell voltages at different temperatures and current densities for Nafion membrane 115

(Figures 5a, 5b) and Table 2, Similarly the performance of composite membrane (Figure 5a&b) is better than the former as it shows the decrease in voltage from 2.0 to1.8 V at current density of 0.3 Acm⁻², the decrease in overvoltages are because of the decrease in temperatures from 30°C, 45° C, 65° C and 85° C respectively during single cell. The corresponding yields of hydrogen for 10wt% Pd/AC at current densities 0.1 (6.45), 0.2 (12.4), 0.3 (19.2), 0.4 (24.1) and 0.5 (30.2) have been represented. The prepared composite membrane with Pd on carbon support demonstrates better performance than Nafion 115 membrane during the electrolysis operation.



Figure. 5(a) Current density Vs Cell voltage for Composite membrane (Nafion/Al₂O₃)

temperatures and current densities for Nation memorane 115

Table 2: Experiments carried out for 10wt% Pd/AC for Composite membrane (Nafion/Al₂O₂)

Composite memorane (Nation/Al ₂ O_3).											
Experimental	Current	Time	Voltage during electrolysis								
Hydrogen yield	density	(hours)	process (V)								
$(\operatorname{cc} \operatorname{min}^{-1})$	$(A \text{ cm}^{-2})$		30°C	45°C	65°C	85°C					
6.45	0.1	2	1.8	1.77	1.75	1.73					
12.29	0.2	2	1.9	1.86	1.82	1.77					
19.92	0.3	2	1.98	1.93	1.88	1.83					
24.10	0.4	2	2.06	2.01	1.94	1.88					
30.20	0.5	2	2.12	2.07	2	1.92					



Figure. 5(b) Cell voltage Vs Hydrogen Yield for Composite membrane (Nafion/Al₂O₃)

Gas chromatography

By using Gas chromatography 99.9% purity of Hydrogen gas is evolved.

4. Conclusion

- The experiments reveal that the composite membrane is performed better than Nafion membrane115
- This results in an improvement in cell performance as well as hydrogen yield.
- A novel modified Composite membrane is prepared by casting method is having good proton conductivity.
- The composite membrane shows a good electrical conductivity and also shows sustainability hydrogen yields with respect to cell voltage and current density.
- The lower over potential saves the energy (current) consumption in electrolysis process which is important for industrial application.
- This study concluded that composite membrane is obtained 99.9% purity of Hydrogen gas

5. Acknowledgments

We would like to thank Board of Research in Nuclear Sciences (BRNS), Bhabha Atomic Research Centre, Department of Atomic Energy, Government of India for providing financial support for this work.

References

- [1] A. Hanslmeier, Water in the Universe, Springer Netherlands, Dordrecht, 2011, pp. 1-24.
- [2] A.J Appleby, F.R Foulkes, Fuel cell Handbook, Van Nastrand Rein-hold, New York, 1989.
- [3] A.K. Sahu, G. Selvarani, S. Pitchumani, P. Sridhar, A.K.Shukla, A sol-gel modified alternative Nafionsilica composite membrane for polymer electrolyte fuel cells, J Electro chem. Soc.154 (2007) B123-132.
- [4] Arico A.S, Baglio V, Di Blasi A, Antonucci V, 2003 *Electrochem. Commun.* 5, 862.
- [5] A.M. Herring, Inorganic–Polymer Composite Membranes for Proton Exchange Membrane Fuel Cells, Polymer.Rev. 46 (2006) 245-296.
- [6] D.E Alessandra, Maria Assunta Navarra, F. Christoph Weise, Barbara Mecheri, Jaime Farrington, Silvia Licoccia, Steve Greenbaum, Composite Nafion/Sulfated Zirconia Membranes: Effect of the Filler Surface Properties on Proton Transport Characteristics, Chem. Mater. 22 (2010) 813–821.
- [7] D. Jiang, Y.Xu, Bo Hou, D. Wu, Y.H Sun, Synthesis of visible light-activated TiO₂ photo catalyst via surface organic modification, J Solid State Chemistry. 180 (2007) 1787-1791.
- [8] EG&G Services, Fuel Cell Handbook, U.S. Department of Energy, Morgantown, WV. (2000) 312.
- ^[9] E.L.Santhi priya, C.Mahendar, K.Naga Mahesh, V.Himabindu, Y.Anjaneyulu,Production of hydrogen using composite membrane in PEM water electrolysis, International Journal of Energy and Environment 3(2012)
- [10] Fa.Tang Li, Di.Shun Zhao, Qing.Zhi Luo, Rui.Hong Liu, Rong Yin, Research on surface-modification of

nano-Tio₂ by span 60, J Ceramic Processing Research. 9 (2008) 398-400.

- [11] G. Alberti, M .Casciola, P.Palombari, Inorganic-organic proton conduction membranes for fuell cells and sensors at medium temperatures, J Membr Sci. 172 (2000) 233– 239.
- [12] Grigoriev SA, Lyutikova EK, Martemianov S, Fateev VN. On the possibility of replacement of Pt by Pd in a hydrogen electrode of PEM fuel cells. Int J Hydrogen Energy 2007;32: 4438–42.
- [13] H. Nikhil Jalani, Katherine Dunn, Ravindra Datta, Synthesis and characterization of Nafion- Synthesis and characterization of Nafion-Mo₂ (M=Zr, Si, Ti) nano composite membranes for higher temperature PEM fuell cells, Electrochim Acta. 51 (2005) 553-560.
- [14] K.D kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuells, J Membr.Sci.185 (2001) 29.
- [15] K. A Mauritz, J.T Payne, [perfluorosulfonate ionomer]/silicate hybrid membranes via base –catalysed in .situ sol-gel processes for tetraethylorthosilicate, J Membr Sci.168 (2000) 39–51.
- [16] K.Naga Mahesh, J. Sarada Prasad, M. Venkateswer Rao, V. Himabindu, Anjaneyulu yerramilli, P.Raghunathan Rao, Performance of Pd on activated carbon as hydrogen electrode with respect to hydrogen yield in a single cell proton exchange membrane (PEM) water electrolysis, Int. J Hydrogen Energy .34 (2009) 6085 – 6088.
- [17] L. J. M. J Blomen, M. N .Mugerwa, Plenum, Fuel Cell Systems, New York. (1993) 614.
- [18] Lepakshi Barbora, Simadri Acharya, Anil Verma, Synthesis and Ex-situ Characterization of Nafion/TiO2 Composite Membranes for Direct Ethanol Fuel Cell, Macromolecular Symposia, <u>277</u>, (2009) 177–189.
- [19] Mo₂ (M=Zr, Si, Ti) nano composite membranes for higher temperature PEM fuell cells, Electrochim Acta. 51 (2005) 553-560.
- [20] M.Barclay Scatterfield, P.W.Majsztrik, Hitoshi Ota, J.B.Benziger, A.B.Bocarsly, Mechanical properties of Nafion and Titania/Nafion composite membranes for polymer electrolyte membrane Fuel cells. J Poly.Sci: Part-B:Polymer Physics.44(2006) 2327-2345.
- [21] M.Alsheyab, J.Jia-Qian, C.Stanford, Risk assessment of hydrogen gas production in the laboratory scale electro chemical generation of ferrate (VI), J Chem. Health Saf September/October (2008)16-20.
- [22] N.H.Jalani, P.Choi, R.Datta, TEOM: A novel technique for investigating sorption in proton-exchange membranes, J Membr Sci. 254(2005) 31-38.
- [23] R.B Moore (III), C.R Martin, Chemical and morphological properties of solution-cast perfluorosulfonate ionomers, Macromolecules. 21 (1988) 1334.
- [24] Sawada S, Yamaki T, Maeno T, Asano M, Suzuki A, Terai T, Solid polymer electrolyte water electrolysis systems for hydrogen production based on our newly developed membranes, part I: analysis of voltage– current characteristics. Prog Nucl Energy 2008;50:443– 8.
- [25] S.Malhotra, R.Datta, Membrane-Supported Nonvolatile Acidic Electrolytes Allow Higher Temperature Operation of Proton-Exchange Membrane Fuel Cell,

- [26] S.Srinivasan, B.Dave, K. A Murugesamoorthi, A.Parthasarathy, A. Appleby, L. J.M. J. Mugerwa, M. N., Eds.Plenum, In Fuel Cell Systems, Blomen, M.N.Eds,Plenum, New York. (1993) 37–72.
- [27] T.A Zawodzinski, J.Davey, Valerio, The water content dependence of electro-osmotic
- [28] Tianzhong Tong, Jinlong Zhang, Baozhu Tian, Feng Chen, He Dannong, Preparation and characterization of anatase TiO₂ microspheres with porous frameworks via controlled hydrolysis of titanium alkoxide followed by hydrothermal treatment, Materials Letters.62 (2008) 2970–2972.
- [29] T.Ioroi, K.Yasuda, Z.Siroma, N. Fujiwara, Y. Miyazaki, Thin film electro catalyst layer for unitized regenerative polymer electrolyte fuel cells, J Power Sources. 112 (2002) 583–7.
- [30] Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P, 1996 *Electrochem. Soc.* 143, 3847.