International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.11 pp 157-163, 2016

Development of Sulfonated Latex Membranes and Modified with $Va_2O_5$for Application in PEM Fuel Cells

Álvaro Realpe*, Yina Pino, María T. Acevedo

Department of Chemical Engineering, Research Group of Modeling of Particles and Processes, Engineering Faculty, Universidad de Cartagena, Colombia

Abstract : Proton Exchange Membranes were prepared with sulfonated natural latex and modified with different loaded percentages (0,2,4 and 6%) of vanadium pentoxide for analyzeits application in fuel cells. Physicochemical properties as water uptake, ionic exchange capacity, oxidative capacity and FTIR analysis were evaluated. Membranes loaded with 2% and 6% of vanadium pentoxide presented the highest values of water uptake andexchange ionic conductivity with 23.9% and 0.33 meq/g, respectively. Mechanical properties values for tensile stretch and elongation average are lower than Nafion 117; however ,these membranes have potential for applications in fuel cells.

Keywords- fuel cell, membrane, natural latex, sulfonation, Vanadium pentoxide.

1. Introduction

Last years has been very noticeable, the development of new energy sources to supply the non-distant necessity due to the extinction of fossil fuel, considering that this type of energy sources are more friendly to the environment and it could provide a better quality of life[1].

The fuel cell is presented as an alternative to generate energy, from the chemical energy present in a fuel(usually hydrogen) and an oxidant (oxygen), it is cleanly, silently and efficiently converted directly into electrical energy[2] generating water from this reaction[3].Otherresearchers have developed the synthesis of hydrogen from water electrolysis and the study of this[4-8]and other sources of energy as wind of Cartagena city[9.]

Among existing fuel cell systems, the proton exchange-membrane (PEM) fuel cell is the most promising alternative with a variety of targeted applications ranging from miniature power supplies to large-scale power plants[10], especially for terrestrial applications such as local power generation and transportation, due to of its simple design and low temperature operations[11]. Over the past decade, studies related to proton exchange membranes (PEMs) for polymer electrolyte fuel cells have focused, mainly on perfluorosulfonic acid membranes such as DuPont's Nafion® and Dow's, due to the exhibition of a number of desirable properties, such as a high ionic conductivity, mechanical strength, chemical/thermalstability, and reasonably low water swelling[12], However, the commercialization of fuel cell is limited considering its low conductivity at relatively low humidification, high permeably in methanol, poor mechanical properties at high temperatures and the amount of platinum required as catalyzer[13].

According to previous research, which has synthesized new membranes that may be used as electrolyte in a fuel cell[14], like as membranes from: polymer SEBS modified with TiO_2 and Sulfonation[15,16], in satured polyester and natural rubber[17,18], copolymers of Vinyl Acetate Acrylic Ester and Styrene-Acrylic Ester, and sulfonation of copolymer Acrylic Ester and Styrene[19]. In this research were obtained sulfonated membranes and modified with vanadium pentoxide at 2,4,6% w/w.Membranes were characterized to determine properties such as water uptake, ion exchange capacity, oxidative stability, infrared spectroscopy and the evaluation of mechanical properties.

2. Method and Materials

2.1. Materials

Latex natural from Ladecol S.A Colombia was used for preparing membranes, Vanadium pentoxide, was used to load membrane; for the sulfonation were used acetic anhydride, sulfiric acid, metylene chloride and ethyl alcohol.Hydrogen pentoxide, chloriodric acid, sodium hydroxide and sodium chloride were used for characaterizations of the membranes.

2.2. Synthesis of Membranes

Acetyl sulfate was used as sulfonating agent to prepare the sulfonated membranes. Initially acetic anhydride reacts with sulfuric acid to produce acetyl sulfate[20].After, 100 ml of methylene chloride was cooled in an ice bath during 10 minutes and 4.73 ml of acetic anhydride was addedin the methylene chloride and wait for 10 minutes in the ice bath, then 2.67 ml of sulfuric acid was added to the solution and wait for 10 minutes, subsequently was added slowly in a solution of latex natural and distilled water 10% W/V, finally was stirred for 3 hours. Ethyl alcohol was used to stop the reaction, then the sulfonated polymer was precipitated, filtered and washed with deionized water until neutralize, the resultant polymer was dried at 80°C in an oven for half hour then was dissolved in toluene and verted in petri dishes to evaporate the solvent[16].

2.3. Characterization

Water Uptake was carried for samples of each membrane which were dried in a vacuum oven for 24 hours, after they were weighed. Then, they were submerged in distilled water for 24 hours; the water in the surface was removed and weighed again. The water uptake is calculated by the next equation[21]:

$$\%\ WaterUptake = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) x\ 100 \qquad (1)$$

Wwere W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Proton Exchange Capacity in the membraneswas characterized by the ion Exchange capacity, a titration technique was used to determine the ion-exchange capacity (IEC) of the membranes. First, the membranes were converted to the acid form by immersion into HCl 1 M solution for 24 h [22].Consequently, membranes were immersed in a NaCl 1 M solution for 24 h to exchange H+ ions with Na+ ions. Finally, the exchanged H+ ions within the solutions were titrated with a NaOH 0.01 Msolution using phenolphthalein as an indicator [23]. The IEC values were obtained by the following equation:

$$IEC\ \left(\frac{mequiv}{g}\right) = \frac{consumed\ NaOH\ x\ molarity\ NaOH}{Weight\ of\ dried\ membrane} \qquad (2)$$

Fourier Transform Infrared (FTIR) spectra were collected on Thermo Nicolet 6700 with a resolution of 4cm^{-1} in the wavelength range of 400-4000cm^{-1}. [24] Mechanical properties determined were such as tensile strength, elongation and modulus, using universal machine instron 4411.

3. Results and Discussion

Figure 1 shows the four types of prepared membranes, sulfonated membrane and loaded (0, 2, 4, and 6 % W/W), each membrane was characterized.

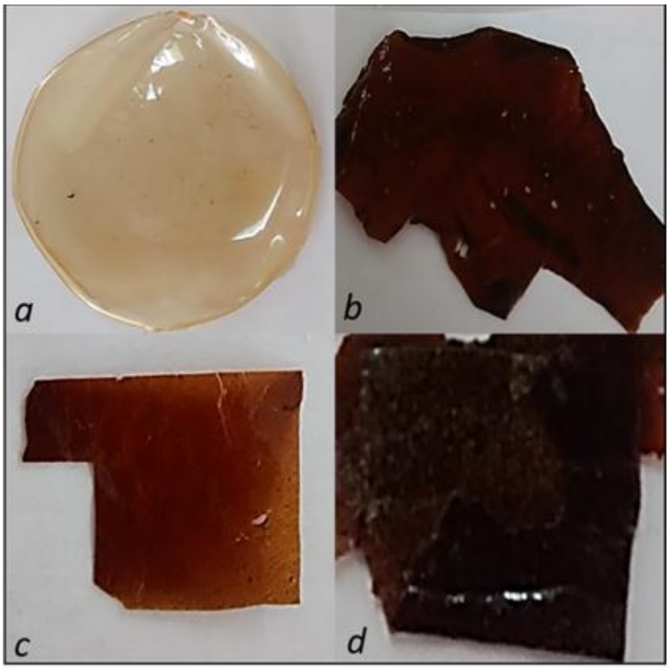

Figure 1.Proton Exchange Membrane from Sulfonated Natural Latex; a) Load 0%, b) Load 2%, c) Load 4%, d) Load 6%

3.1. Water uptake

Water uptake is important due to proton exchange reaction requires a lot of water to cross the membrane[25].However, the absorbed water by the membrane affects mechanical properties[18].

Figure 2 shows water uptake for each samples, loaded membrane with 2% has the highest value (23,99%), while membrane without load has lowest value (11,21%) this due to the characteristic hydrophobic of the polymer[18].

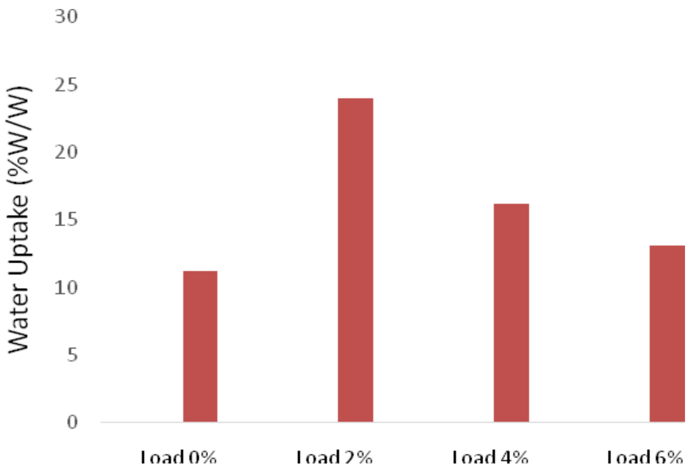

Figure 2. Water Uptake

The addition of sulfonic groups in the sulfonation increase the water uptake, the addition of a Va2O5, also increase the water uptake according to[16], however in this research this the effect is only relevant to small quantities, due to the water uptake decreases with the addition of load. The action of an inorganic load reduces the free volume in the membrane surface and the ability to moisten[20].

3.2. Ionic Exchange Capacity

The efficiency in a fuel cell is directly related with the ability of the electrolyte transporting ionsfrom anode to cathode[26]. Ion exchange capacity was carried by titration technique andin the figure3is observed values for each samples, loaded 0% shows lowest valueof 0.134 meq/g while membranes loaded with 2,4,6 % increase with respect the amount of the load, in values of 0.164, 0.234 y 1.329 meq/g respectively.

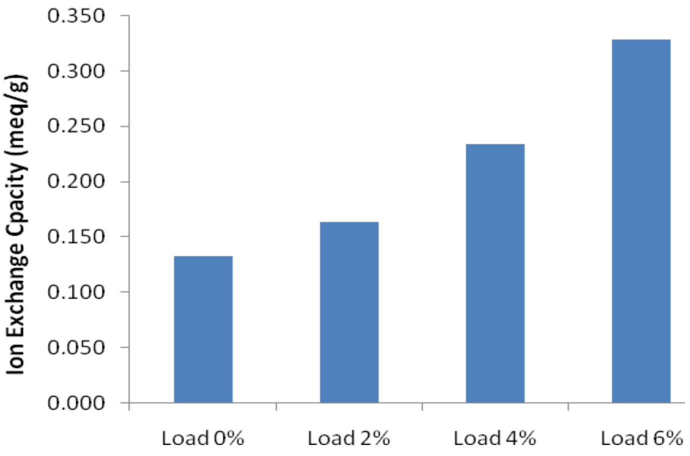

Figure 3. Ionic Exchange Capacity

The sulfonic groups constitute available sites to exchange of proton into membrane[17],due to the ion exchange capacity is related with the water uptake by the methods of proton migration that is presents in the membranes by the Grotthus method[27].The mixture among sulfonics groups and load, contributed the IEC, this verifies the existences of the functional groups in the vanadium to promote the ionic exchange, however these values are lower than Nafion 115[26].

3.3. Oxidative Stability

Oxidative stability was determined by the procedure described above, each sample was submerged in an oxidative solution (H_2O_2).Figure 4shows the weight loss of the membrane at the time.The sample more stable is sulfonated membrane without load due to the type of load produces sites available for oxygen absorption and to generate an oxidation in the polymeric chains[14].

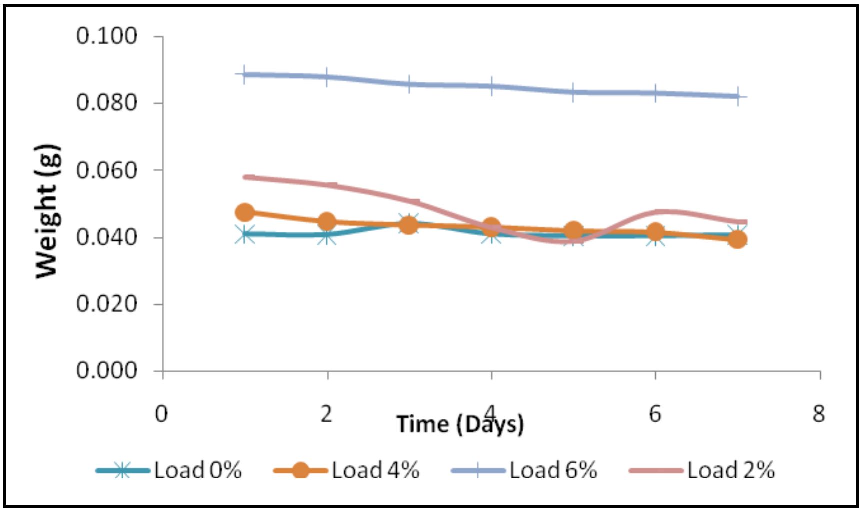

Figure 4. Oxidative stability

The sulfonic groups give a high chemical stability and resistance to the oxidation, in the polymeric chains the oxidation occurs due to the attack of OH^- radicals, because these radicals have a free electron, that are considered electron donors[28].Thesulfonic groups (SO_3-) of membrane is responsible for repelling the negative groups and the positive part is responsible for the cationic flow[29].

3.4. FTIR

Spectroscopy analysis was carried out for each membrane was used to confirm the functional groups on the copolymers.Figure5 shows the spectra wherethe region covered by 1600-1670 cm^{-1}picks corresponding to the tension C=C bond and the tension out the plane $C=CH_2$, presents in the natural rubber[25]. The stretching of the Va=O is close the peak 1020 cm^{-1}, which is not presented in the spectra by the interaction of the sulfonics groups, which break the Va=O bond into membrane. Thus 1400 a 950 cm^{-1} region corresponding to SO_3H groups only can see in sulfonated membrane without load[30].

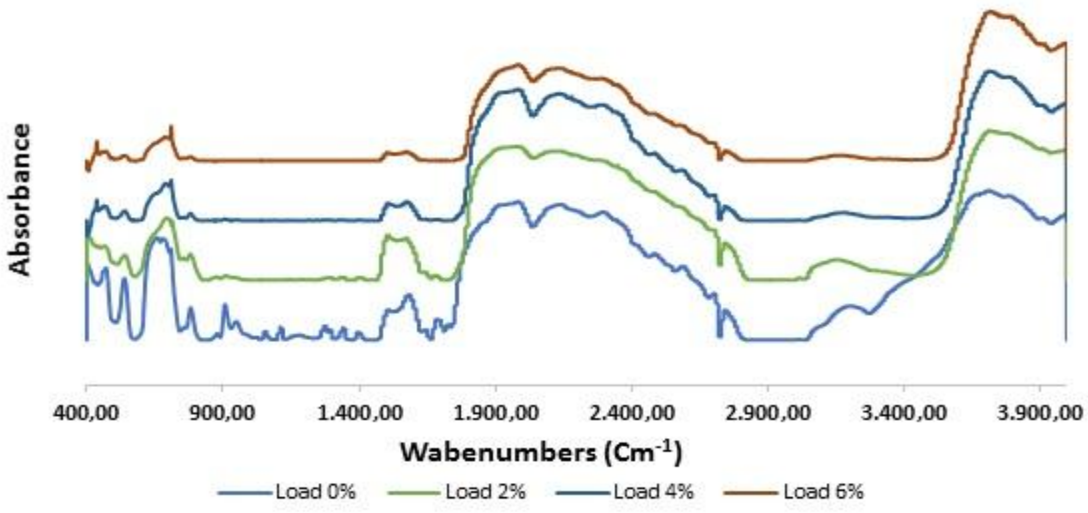

Figure 5. Fourier Transform Infrared Spectra

In the region attributed for water (2700 a 3500 cm^{-1}) it can see a peak widthclose to 3547 cm^{-1}attributed to O-H bond by the sulfonics groups interacting with the water, is more produced in sulfonated loaded membrane 2,4,6% due to the wet into these samples[31].

3.5. Mechanical Properties

Table shows mechanical properties for each membranes. Tensile stenchdecreases with increasing the loaded of vanadium pentoxide.The inorganic load improved the water uptake and the ionic Exchange capacity, however, the high oxidation power of the vanadium pentoxide affects the membrane matrix and this causes that the membranes become more fragile[32]. In addition, the water uptake reduces the tensilestretchdue to the water absorbed acts as a plasticizer thatdeteriorated the membrane[13].

Table 1. Mechanical Properties

Sample	Tensile Strech (N/mm^2)	Elongatión (%)
Sulfonated and loaded 0%	9,96	26,75
Sulfonated and loaded 2%	6,83	10,21
Sulfonated and loaded 4%	3,94	13,36
Sulfonated and loaded 6%	1,71	61,54

Elongation in the loaded membrane increases due to the accumulation of vanadium pentoxide in the membrane by giving an elastic property. In other investigations[32] were submitted elongation values for Nafion 117higher than reported in this research; however, other researches[33,34] have prepared the proton exchange membraneswith elongation and resistance values lower than reported in this work, and these membranes were used in fuel cell without problems of operation.

4. Conclusión

Synthesis of proton Exchange membrane was performed by usingsulfonated natural latex. Furthermore, membranes were modified with the addition of vanadium pentoxide. The water uptake of membrane is highest for loaded 2%; and the ion exchange conductivity increases with increasing the vanadium pentoxide load.The chemical stability is high due to the sulfonic groups that protect against oxidation of polymeric chains. According to the physicochemical properties, the prepared membranes have high potential for application in fuel cell.

Acknowledgment

The authors wish to thank University of Cartagena and COLCIENCIAS for providing the funding for the realization of this work.

References

1. Nayeemunisa S.M, Kiruthika S, Muthukumaran B. Electro-oxidation of Isopropanol in Membraneless Fuel Cells. International Journal of ChemTech Research., 2015, 7: 3057-3062.
2. Priyal M, Muthukumaran B. Enhanced Performance an Ethanol Membraneless Fuel Cell in Acidic Medium. International Journal of ChemTech Research., 2015, 7: 3026-3032.
3. Suneeta G, Chandra M, Kambila Vijay Kumar, Ashok M. Spectroscopic Characterization and Electrical study of Nano crystalline PEO based Conducting Polymer electrolyte system for low temperature Fuel cell applications. International Journal of ChemTech Research., 2011, 3: 1203-1212.
4. Realpe A, Nuñez D, Carbal I, Acevedo M. Preparation and characterization of titanium dioxide photoelectrodes for generation of hydrogen by photoelectrochemical wáter splitting. International Journal of Engineering and Technology., 2015, 7: 753-759.
5. Realpe A, Nuñez D, Carbal I, Acevedo M. Sensitization of TiO2 photoelectrodes using copper phthalocyanine for hydrogen production. International Journal of Engineering and Technology. 2015; 7: 1189-1193.
6. Realpe A, Nuñez D, Herrera A.Synthesis of Fe-TiO2 Nanoparticles for Photoelectrochemical Generation of Hydrogen. International Journal of ChemTech., 2016. Accepted for publication.
7. Realpe A, Salamanca A, Acevedo M.Effect Of Electrolyte Type On The Hydrogen Production Using A Plate Electrolyzer. International Journal of Applied Engineering Research., 2015, 10: 23871-23880
8. Realpe A, Salamanca A. Effect of spacing between electrodes on the hydrogen generation. national Journal of Applied Engineering Research., 2015, 10: 34262-34264.
9. Realpe A, Chamorro B, De Avila G.Modeling and Assessment of Wind Energy Potential in the Cartagena City. International Journal of ChemTech., 2016, 9: 614-623.
10. Kalaikathir S.P, Begila S. Synthesis and characterization of nanostructured carbonsupported Pt electrocatalysts for membraneless methanol fuel cells (MLMFC). International Journal of ChemTech., 2016, 9: 596-610.
11. Nguyen T, White R. A Water and Heat Management Model for Proton-Exchange-Membrane Fuel Cells. Journal of the electrochemical society.,1993, 140: 2178-2186.
12. Guo Q, Pintauro P, Tang H, Connor S. Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes. Journal Of Membrane Sience., 1998, 154: 175-181.
13. Realpe A, Méndez N, Toscano E, Acevedo M. Síntesis y caracterización fisicoquímica de una membrana carga con TiO2 preparada a partir de la sulfonación de un copolímero de Ester acrílico y estireno. Información tecnológica., 2015, 26: 97-104.

14. Realpe A, Pino Y, Acevedo M. Syntesis of a Proton Exchange Membranen from Natural Latex Modified with Vanadium Pentoxide For Application in a Fuel Cell. International Journal of Chem Tech Research., 2016, 9: 524-529.
15. Realpe A, Pino Y, Acevedo M. Synthesis of a Proton Exchange Membrane Obtained From SEBS Copolymer For Application In a Fuel Cell. International Journal of Applied Engineering Research., 2015, 10: 15905-15913.
16. Realpe A, Pino Y, Acevedo M. Effect of sulfonation of SEBS copolymer on the physicomechanical properties of proton Exchange membrane. International Journal of Engineering and Technology., 2015, 7: 1438-1442.
17. Realpe A, Romero K, Acevedo M. Síntesis de Membranas de Intercambio Protónico a Partir de Mezcla de Poliéster Insaturado y Látex Natural, para su uso en Celdas de Combustible. Información tecnológica., 2014, 26: 55-62.
18. Realpe A, Romero K, Acevedo M. Synthesis and characterization of proton Exchange membrane from Blend of unsaturated polyester resin and natural rubber. International Journal of Engineering and Technology., 2013, 4: 4005-4009.
19. Realpe A, Romero K, Santodomingo A. Synthesis of a Proton Exchange Membrane from Vinyl Acetate - Acrylic Ester Copolymer for Fuel Cells. International Journal of ChemTech Research., 2015, 8: 1319-1326.
20. Realpe A, Mendez N, Acevedo M. Proton Exchange Membrane from the Blend of Copolymers of Vinyl Acetate-Acrylic Ester and Styrene-Acrylic Ester for Power Generation Using Fuel Cell. International Journal of Engineering and Technology., 2014; 6: pp 2435-2440.
21. Elabd Y, Napadensky E. Sulfonation and characterization of poly (styrene-isobutylene-styrene) triblock copolymers at high ion-exchange capacities. Polymer., 2004, 45: 3037-3043.
22. Wang F, Hickner M, Kim Y, Zawodziski T, Mcgrath J. Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes. Journal of Membrane Science., 2001, 197: 231-242.
23. Balster J, Krupenko O, Pünt I, Stamatialis D, Wessling M. Preparation an Craracterisation of Monovalen Ion Selective Cation Exchange Membrane Based on Sulphonated Poly(Ether Ether Ketone). Journal of Membrane Science., 2005., 253: 137-145.
24. Kumar V, Agarwal A.K. Synthesis and Characterization of Isolongifoline Ketone. International Journal of ChemTech., 2013, 5: 2757-2768.
25. Wang L, Li K, Zhu G, Li J. Preparation and Properties of highly Branched Sulfonated poly (ether, ether ketone)s doped with antioxidant 1010 as proton exchange membranes. Journal Of Membrane Science., 2011, 379: 340-348.
26. Astiazaran J. Preparacion de Membranas de Intercambio Protonico apartir de Nafion modificadp con Silice Mesoporoso y Dendrimero Paman G4. Universidad Autónoma de Queretaro., 2011.
27. Dimitrova P, Friedrich K, Vogt B, Stimming U. Transport properties of ionomer composite membranes for direct methanol fuel cells. Journal of Electroanalytical Chemistry., 2002, 532: 75-83.
28. Kallitsis J, Goudorpi N. Proton Conducting Membranes Based on Polymer Blends for Use in High Temperature PEM Fuel Cells. Journal of new materials for electrochemical systems., 2003; 6: 217-222.
29. González D, Martínez L. Síntesis y caracterización de una membrana de Intercambio Aniónico con aplicación en Celdas de Combustible Alcalinas. Universidad Nacional., 2009.
30. Cáceres A. Estudio de caracterización Fisicoquímica de Látex Natural proveniente de Hevea Brasiliensis por medio de termogravimetría, Universidad Industrial de Santander., 2011.
31. Xing P, Robertson G, Guiver M, Mikhailenko S, Wang K, Kaliaguine S. Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. Journal of Membrane Science., 2004, 229: 95-106.
32. Palermo. V. Síntesis y caracterización de heteropoliácidos constituyendo materiales híbridos para su aplicación como catalizadores en la oxidación ecocompatible de sulfuros. Tesis doctoral, Universidad Nacional de la Plata., 2012.
33. Songjun Z, Lei Y, Sijia Y, Guoliang W, Yuanqin X, Weijian X. Amphibious hybrid nanostructured proton exchange membranes. Journal of Membrane Science., 2011, 367: 78–84.
34. Yang J, Li Q, Jensen J, Pan C, Cleemann L, Bjerrum N. He R Phosphoric acid doped imidazolium polysulfone membranes for high temperature proton exchange membrane fuel cells. Journal of Power Sources., 2012; 205: 114– 121.

*****