Taylor & Francis
Taylor & Francis Group

Sulfonated Poly (Ether Ether Ketone)-Based Composite Proton-Exchange Membrane for Energy Production

S. Seetharaman, G. Sozhan, S. Ravichandran, S. Vasudevan, and J. Davidson

Electro-Inorganic Chemicals Division, Central Electrochemical Research Institute, Karaikudi, India

The preparation of a proton-conducting membrane from Sulponated Poly Ether Ether Ketone (SPEEK), tungsto phosphoric acid (TPA), and inorganic fillers such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), and zirconium dioxide (ZrO_2) was prepared and the electrochemical and mechanical properties were investigated with regards to its application in energy production. The role of tungsto phosphoric acid is to minimize water assistance at elevated temperatures, which led to a decrease in mechanical strength. The fabricated membranes were characterized by FT-IR, TGA, DSC, and SEM techniques. This work may efficiently serve as a basis for new projects as many aspects need to be investigated further. First, it would be interesting to devote a study to the direct comparison of the different fillers of side-chain poly ether ether ketone in order to elucidate the exact morphological features of these membranes, especially in the swollen state.

Keywords   composite proton exchange membrane, polymer electrolyte membrane, SPEEK, TPA

INTRODUCTION

In view of the increasing financial and environmental disadvantages of fossil fuels, hydrogen and methanol fuel cells are an interesting aspect. The basic unit of a fuel cell consists of a cathode and an anode, separated by a proton-conducting polymer membrane.

A substantial research effort around the world has been focused on solving the inherent problems associated with operating the commercially available perfluorinated ionomer membranes at elevated temperatures ($>100°C$). Specifically, maintaining high ionic conductivity and high mechanical strength, resisting dehydration and fuel impermeability remain problematic, especially at elevated operating temperatures.

The most advanced fuel cell systems are fuelled with hydrogen and are based on perfluorinated sulfonic acid solid polymer electrolytes. These solid electrolytes offer numerous advantages over classical liquid electrolytes, such as sulphuric acid, including higher power densities, reduced fuel crossover and, more obviously, improved handling. The motivation for the work described in this paper is to find an alternative membrane to Nafion membranes for fuel cell applications with low production cost and better processability. Nafion membranes are expensive; they tend to lose their proton conductivity at temperatures $>80°C$, due to their inability to remain fully hydrated at elevated temperatures, when they are most efficient, and the modification of the state-of-the-art membrane to reach the desired characteristics.

Because of the challenges that conventional Nafion membranes face, significant research recently has been devoted to the development of more nonfluorinated polymers. Sulphoned Poly (Ether Ether Ketone) (SPEEK) [1–4], Poly (Benzimidazole) (PBI), Sulponated Poly (Ether Ketone) (SPEK), Poly (Ether Sulfone) (PES), poly(arylene ethers), polyimides, and polyphosphazene [5–8], etc., have excellent chemical mechanical and thermooxidative stability and are low cost. Among these, membranes based on aromatic poly ether ether ketone (PEEK) were shown to be very promising performance thermo stable engineering polymers with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether ($-O-$) and carbonyl ($-CO-$) linkages. The PEEK can be functionalized by sulfonation and the degree of sulfonation (DS) can be controlled by reaction time and temperature since they possess good mechanical properties on degree of sulfonation.

The main problem with PEEK, however, is the high degree of sulfonation that is required to achieve sufficient proton conductivity; this causes PEEK polymers to become excessively water-swollen or water-soluble, thereby destroying their mechanical properties with a deleterious effect on the cell performance. For all these reasons, great interest has been focused on the development of alternative membranes for nafion. Designing these inorganic organic composite membranes [9–11] has attracted attention, because such

composites show controllable physical properties, such as electrical, thermal, and mechanical behavior, by combining the properties of both organic polymers and inorganic compounds.

Heteropolyacids (HPA) have the dual role of being both hydrophilic and proton conducting. However, HPAs are generally water-soluble; the degree of solubilities is reduced in composite HPAs while maintaining their high proton conductivity. A composite matrix reduces the leaching of HPA. The objective of this research is to develop a new type of composite membrane by incorporating heteropolyacids [12–14] such as tungstophopsphoric acid (TPA) and inorganic fillers [15,16] such as titanium dioxide (TiO_2), silicon dioxide (SiO_2), and zirconium dioxide (ZrO_2) into partially sulfonated poly-ether ether ketone (PEEK) polymer matrices, giving a significant influence on Polymer Electrolyte Membrane performance (PEM), PEM having high proton conductivity and optimized membrane properties.

Although several studies on SPEEK as a fuel cell PEM were previously conducted, these studies were not citied.

EXPERIMENTAL

Materials

Poly (ether ether ketone) (PEEK) was obtained from Victrex® US, Inc. (450 PF); 1-methyl-2-pyrrolidinone (NMP) was obtained from Merck; titanium dioxide (TiO_2), silicon dioxide (SiO_2), zirconium dioxide (ZrO_2), and phospho-tungstic acid (PWA) were obtained from Himedia and were used as received.

Synthesis of SPEEK

PEEK was sulfonated as described in the previous studies [17]. PEEK was first dried at $120°C$ in a vacuum oven for 6–8 h. Then, 20 g of the polymer was dissolved in one liter of concentrated (98%) sulfuric acid (Merck) and vigor-ously stirred at room temperature for different lengths of reaction times (from 24 h to 110 h). The polymer solution was gradually precipitated over ice-cold water under continuous mechanical agitation and left to settle overnight. The precipitate was filtered and washed with distilled water. It was then dried under vacuum for 8–10 h at $100°C$. The final product is the sulfonic acid form of PEEK (SPEEK).

Preparation of SPEEK Composite Membranes

SPEEK membranes were prepared by dissolving the SPEEK sample in NMP solvent under constant stirring to form a homogenous solution at $70°C$ to which 10 wt% phosphotungstic acid and 10 wt% $TiO_2/SiO_2/ZrO_2$ were added, respectively, and then refluxed $80°C$ for 6 h to obtain a clear viscous

gel. The film was cast on a clean glass plate with the desired thickness and dried at $80°C$ for 12 h. The thickness of the wet composite polymer membrane was between 0.20 and 0.30 mm. Then the composite membranes were detached from the glass tray by adding de-ionized water. In order to enhance the mechanical properties, the membranes were hot pressed between two Teflon films at $80°C$ for 3 min. Finally, the membranes were purified by heating at $70°C$ in 3% H_2O_2, 15% H_2SO_4, and in de-ionized water for 1 h, respectively.

MEASUREMENTS

Ionic Conductivity and Transport Property Measurements

Conductivity measurements were made for composite membrane by two-probe impedance technique under potentiostatic conditions using 5-mV/sec in 1 Hz to 1 MHz excitation signal. Prior to the conductivity measurements, membranes were immersed in deionized water for 24 hrs to attain hydration equilibrium. During the measurement, each membrane was sandwiched between stainless-steel plates and ion blocking electrodes; the cross-sectional area of the membranes was $0.502\,cm^2$. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = L/RA$, where A is the Area of the electrodes, L and R are the thickness and bulk resistance of the films, respectively. The R was derived from the high frequency x-axis intercept of the complex impedance plot.

Swelling

The membrane swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 4 hrs. The swelling ratio was calculated by the following equation:

$$\text{Swelling } (\%) = \frac{S_{wet} - S_{dry}}{S_{dry}} \times 100$$

where S_{dry} and S_{wet} are the area of dry and wet samples, respectively.

Water Uptake

Water uptake (W_{wd}) after two hours of immersion was determined as the difference in weight (W) between the dried and the swollen membranes.

$$W_{wd} \ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100$$

where W_{dry} and W_{wet} are the mass of the dry and wet membranes.

Ion Exchange Capacity

The ion exchange capacity of the membranes was determined using the titration procedure [18]. The dry composite membrane was immersed in 100 ml of 0.1 M sodium chloride aqueous solution for 48 hrs to change it into H^+ form. The samples were washed with distilled water to remove excess HCl, and then titrated with a saturated sodium hydroxide solution using phenolphthalein as an indicator.

The ion exchange capacity (IEC) was calculated using the following equation.

$$IEC = \frac{V \times M}{W_{dry}}$$

where IEC is the ion exchange capacity (mequiv. g^{-1}), V the added titrant volume at the equivalent point (ml), M the molar concentration of the titrant, and W_{dry} is the dry mass of the sample (g).

It was necessary at this stage to reflect on the possible utility of these composite membranes in comparison with the conventional Nafion membrane and the other composite membrane such as SPEEK/TPA/TiO$_2$, SPEEK/TPA/SiO$_2$, and SPEEK/TPA/ZrO$_2$ membranes.

Characterization

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-3000 H electron microscope. The Fourier transform infrared (FTIR) spectra were recorded on a thermo electron Corporation Nexus 670 System FTIR spectrophotometer that ranged from 4,000–400 cm^{-1}. The thermo gravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were obtained with TA Instruments SDT Q600 V8.3 operated at a heating rate of 10°C in presence of nitrogen atmosphere. The mechanical properties of the dried membranes were measured with a tension tester AGS – J 10 KN (Shimadzu, Autograph) at room temperature.

^{1}H NMR Measurements

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer.

^{1}H NMR spectroscopy was used to identify the incorporation of the sulfonate group into the SPEEK structure. The degree of sulfonation of polymers was determined by ^{1}H NMR.

RESULTS AND DISCUSSION

^{1}H NMR Analysis

The spectra are shown in Figure 1 where spectra were measured in d_6-DMSO solutions. A significant low-field shift of the H_5 resonance is observed in the ^{1}H NMR spectra because of the incorporation of the sulfonic acid group into the SPEEK polymer chain. The H_5 resonance signal appears at a low field ($\delta = 7.8$ ppm) due to the electronic shielding from the sulfonate and carbonyl groups. The degree of sulfonation was determined quantitatively by ^{1}H NMR following the technique described in the literature [19]. The degree of sulfonation of polymers determined by ^{1}H NMR is in good agreement with the amount of the sulfonic acid material. These results again confirm that the sulfonate groups are incorporated into the SPEEK polymer chain.

FT-IR Analysis

The FT-IR spectra obtained for the membrane are shown in Figure 2. The FT-IR spectrum of hybrid membranes showed bands around 1025, 1075, and 1240 cm^{-1}, representing symmetric and asymmetric stretching vibrations of the sulfonic acid group in SPEEK [20]. A new absorption band at 1080 cm^{-1}, which appeared upon sulfonation, was assigned to sulfur-oxygen symmetric vibration O=S=O. The positions of vibration modes of all types of M−O bonds were strongly influenced by interaction of phosphotungstic acid with the
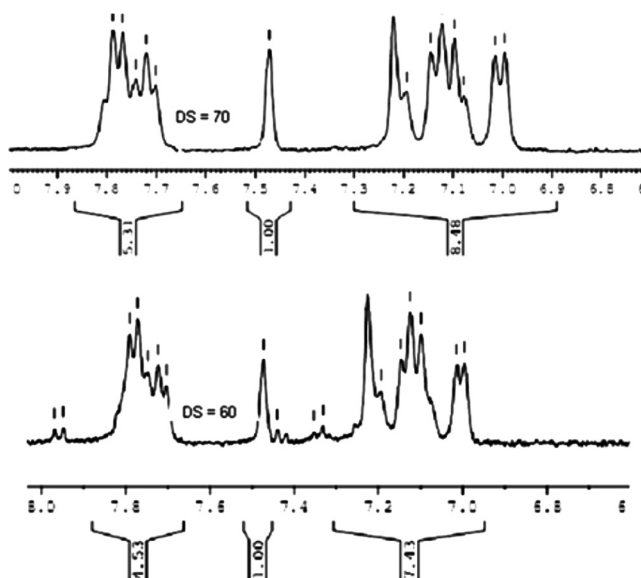

Figure 1: ^{1}H NMR spectra of pure SPEEK polymer dissolved directly in DMSO-d$_6$.
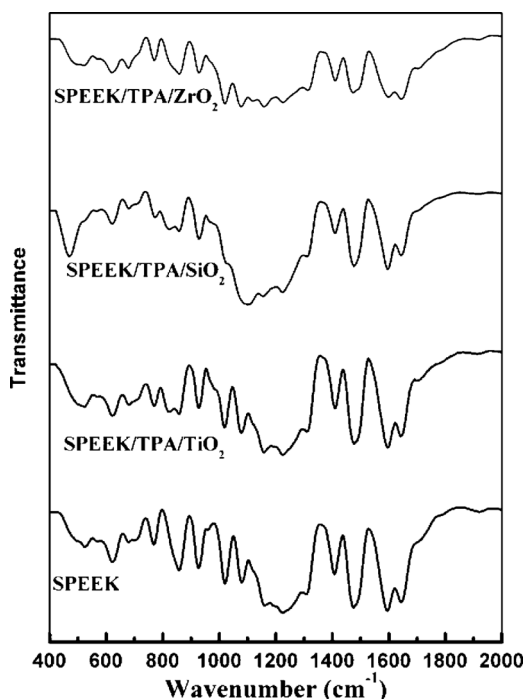
Figure 2: FT-IR spectra of composite membrane and its components.

polymer and fillers. In SPEEK spectra, the band around $3400\,cm^{-1}$ was very broad, due to the υOH hydration water molecule. In subsequent spectra this peak was sharper, due to the removal of the water molecule. The bands around $550\,cm^{-1}$ were due to Ti-O asymmetric stretching. The bands around $1100\,cm^{-1}$ were due to Si-O stretching vibration. The heteropolyacids have been successfully incorporated in the hybrid matrix. Also, new Zr–O vibration appeared at 530–$560\,cm^{-1}$. The symmetric stretching bands of terminal oxygen (W–O_t–W) have a red shift from 980 to $910\,cm^{-1}$ and the symmetric stretching bands of bridged oxygen (W–O_b–W) have a blue shift from 765 to around $792\,cm^{-1}$. This was due to the columbic interaction between the hydroxyl group of the PEEK donor and the salt of TPA in the composite membrane. The FTIR spectral data thus confirmed that sulfonation of PEEK in sulfuric acid only takes place at the para position of the terminal phenoxy group.

Thermal Study

The TGA data are shown in Figure 3(a). This illustrates the TGA obtained for the membranes. All experiments were run up to $900°C$ at a heating rate of $10°C/min$ under flowing nitrogen. They show three stages of degradation with
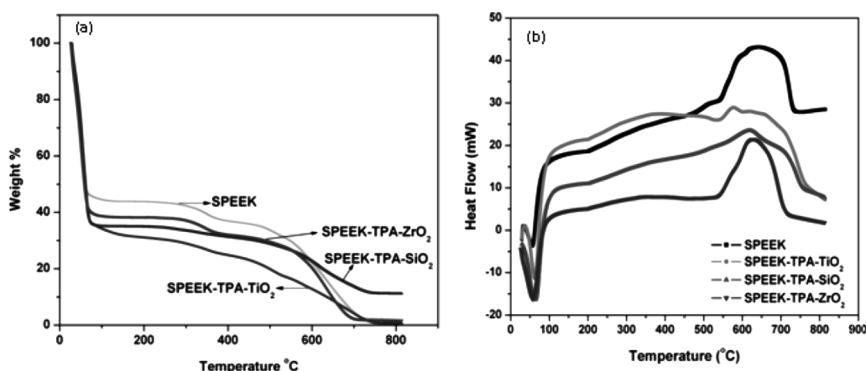
Figure 3: (a) TGA analysis of composite membranes; (b) DSC thermograms of composite membranes.

the increase in temperature. First weight loss occurred around 100°C due to loss of absorbed water molecule. Second weight loss in the temperature region 310°C was due to the de-sulfonation process. Third weight loss in the temperature region 400°C was due to the decomposition of the polymer matrix (Figure 3(b)). In showing the DSC obtained for all the membranes, it was found that the degree of crystallinity decreased as the fillers were added to SPEEK polymer matrix. The function of the filler was to retard or inhibit the recrystallization of the SPEEK polymer, increasing the domain of the amorphous phase and creating more free volume for the mobility of the ion. In the TGA curves, no difference was found between the composite membranes. In general, the sulfonic acid group acts as an initiator for the degradation of SPEEK membranes.

The thermal properties of the composite membrane are satisfactory for the operating requirement of the PEM water electrolysis cell.

Surface Study

The distribution of inorganic fillers was relatively uniform in the organic matrix. It is evident that the pure SPEEK polymer is nonporous. Encapsulating the heteropolyacids into the polymer matrix had a profound influence on the polymer structure. Figure 4(a) shows a highly porous composite membrane with pore diameter in the range 2–6 μm. The pore formation in the composite membranes could also be responsible for the increase in the conduction activation energy compared to pure SPEEK membranes. The addition of fillers resulted in a modification of the composite membranes; the surface homogeneity was reduced and an extended porosity was clearly revealed with no evidence of agglomeration. Figure 4(b) shows that the pure SPEEK membrane is homogeneous.
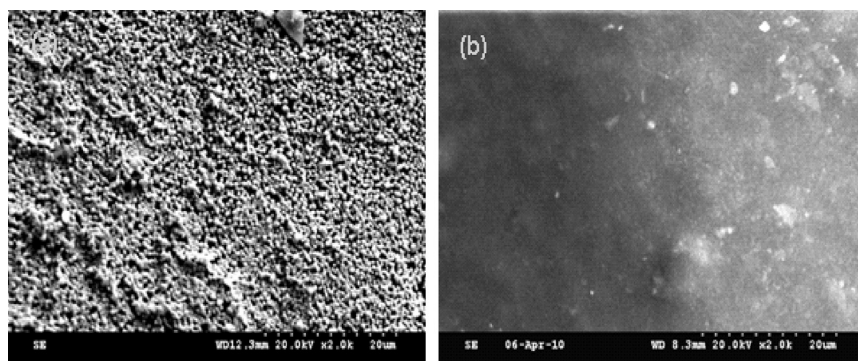
Figure 4: Scanning electron microscopy image of the composite membranes: (a) SPEEK-TPA-ZrO$_2$ composite membrane; (b) SPEEK membrane.

IEC Study

The water uptake and ion exchange capacity (IEC) play a vital role in membrane conductivity. At higher IEC values, the water uptake increased sharply at a proportional rate larger than that observed for lower IEC values, due to the hydration regions near the ions overlapping and the decreased volume fraction of the unfunctionalized phase. The data on water uptake, extent of swelling, and IEC data for the membranes are given in Table 1. It is observed that the SPEEK composite membranes exhibit lower water uptake when compared to pure SPEEK, although the additives are hydrophilic. Excessively high levels of water uptake can result in membrane dimensional change leading to failures in mechanical properties. Hence the relationship between IEC and water uptake (%) plays a crucial role in membrane morphology.

However, the pure SPEEK membrane became structurally unstable at 80°C due to excess of water uptake and swelling. SPEEK-TPA-ZrO$_2$ composite membrane showed near comparable performance to Nafion® 117 due to high proton conductivity as well as on IEC values. Furthermore, the addition of

Table 1: Thickness, water uptake, swelling, and IEC values for different composition.

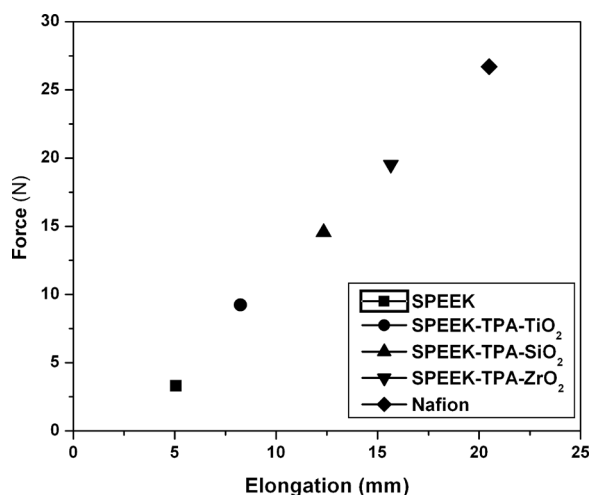| Membranes	Thickness (μm)	Water uptake (%)	Swelling (%)	IEC (mequiv.g^{-1})	Conductivity S/cm
SPEEK	244	78	31.12	0.75	2.5×10^{-2}
SPEEK-PWA-TiO$_2$	246	22.45	26.68	1.44	3.3×10^{-2}
SPEEK-PWA-SiO$_2$	255	29.17	23.25	1.53	6.4×10^{-2}
SPEEK-PWA-ZrO$_2$	220	32.54	20.16	1.72	1.1×10^{-2}
Nafion-117	175	34	15	0.92	7.6×10^{-1}

Figure 5: Tensile strength of the membranes.

tungstophosphoric acid and zirconium oxide in the sPEEK polymer organic matrix enabled the preparation of composite membranes with a wide range of properties concerning proton conductivity, water uptake, and IEC values. Therefore, these membranes can be used in the future to make a critical evaluation of the relationship between the proton electrolyte membrane properties and the cell performance.

Mechanical Properties

Figure 5 shows the mechanical strength of SPEEK and SPEEK composite matrix of 60% sulfonation degree (SD) on the tensile strength–elongation. Tests were carried out at room temperature. It is observed that the SPEEK composite membranes exhibit near comparable mechanical strength when compared to Nafion membranes.

CONCLUSIONS

A new route for preparing sulfonated PEEK proton exchange membrane has been initiated in the work presented here. The membranes were prepared from poly ether ether ketone as organic matrix and inorganic fillers such as titanium dioxide, silicon dioxide, zirconium dioxide, and high proton conductivity of phosphotungstic acid. The composite membranes were prepared by a straightforward sol-gel method. The electrochemical properties, tensile strength, swelling, and dimensional stability were found to improve with

the addition of fillers and blended with TPA to avoid excessive water swelling and to reinforce their mechanical properties. This afforded excellent proton conductivity at controlled levels of water uptake in contrast to schematic sulfonated aromatic polymers. In addition, it was found that a certain level of flexibility of the side chains is necessary for the formation of an efficient percolating network. Increasing the local concentration of sulfonic acid units as well as separating the hydrophilic moieties from the hydrophobic polymer main chain enabled the stabilization of the morphology of the water-swollen membranes and a promotion of the proton conduction. The SPEEK/TPA10/$ZrO_2$10 exhibits better membrane property values as follows: proton conductivity of 0.011 S/cm at 35°C; water uptake of 22.54%; ion-exchange capacity of 1.72 mequiv.g^{-1}. These performances reveal the best performance for the five membranes mentioned above are in the order of Nafion 117, >SPEEK-TPA-ZrO_2>, SPEEK-TPA-SiO_2 > SPEEK-TPA-TiO_2 > SPEEK. From the economic and application points of view, the SPEEK composite membranes can be easily prepared for mass production and a unique set of properties make them interesting for testing in PEM environments.

REFERENCES

[1] Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. *J. Membr. Sci.* **2001**, *185*, 73.

[2] Jorissen, L.; Gogel, V.; Kerres, J.; Garche, J. *J. Power Sources* **2002**, *105*, 267.

[3] Sangeetha, D. *Int. J. Polmeric Materials* **2007**, *56*, 535.

[4] Shashidhara, G.M.; Naveen Kumar, K. *Polymer-Plastics Technology and Engineering* **2010**, *49*, 796.

[5] Samuns, S.R.; Wasmus, S.; Savinell, R.F. *J. Electrochem. Soc.* **1996**, *143*, 1225.

[6] Xing, P.; Robertson, G.P.; Guiver, M.D.; Mikhailenko, S.D.; Kaliaguine, S. *J. Polymer* **2005**, *46*, 3257.

[7] Einsla, B.R.; Hong, Y.T.; Kim, Y.S.; Wang, F.; Gunduz, N.; McGrath, J.E. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 862.

[8] Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 359.

[9] Vernon, D.R.; Meng, F.; Dec, S.F.; Williamson, D.L.; Turner, J.A.; Herring, A.M. *J. Power Sources* **2005**, *139*, 141.

[10] Ruffmann, B.; Silva, H.; Schulte, B.; Nunes, S.P. *Solid State Ionics* **2003**, *162*, 269.

[11] Li, S.; Zhou, Z.; Liu, M.; Li, W.; Ukai, J.; Hase, K.; Nakanishi, M. *Electrochim. Acta* **2006**, *51*, 1351.

[12] Giordano, N.; Staiti, P.; Hocevar, S.; Arico, A.S. *Electrochim. Acta* **1996**, *41*, 397.

[13] Nakamura, O.; Kodama, T.; Ogino, I.; Miyake, Y. *Chem. Lett.* **1979**, *1*, 17.

[14] Guhan, S.; Sangeetha, D. *Int. J. Polmeric Materials* **2009**, *58*, 87.

[15] Silva, V.S.; Ruffmann, B.; Silva, H.; Gallego, Y.A.; Mendes, A.; Madeirab, L.M.; Nunesa, S.P. *J. Power Sources* **2005**, *140*, 34.

[16] Watanabe, M.; Uchida, H.; Emori, M. *J. Electrochem. Soc.* **1998**, *145*, 1137.

[17] Li, L.; Zhang, J.; Wang, Y. *J. Membr. Sci.* **2003**, *226*, 159.

[18] Sambandam, S.; Ramani, V. *J. Power Sources* **2007**, *170*, 259.

[19] Robertson, G.P.; Mikhailenko, S.D.; Wang, K.; Xing, P.; Guiver, M.D.; Kaliaguine, S. *J. Membr. Sci.* **2003**, *219*, 113.

[20] Zaidi, S.M.J. *The Arabian Journal for Science and Engineering* **2003**, *28*, 183.