



## Short Communication

Surface-modified Nafion membranes with mesoporous SiO<sub>2</sub> layers via a facile dip-coating approach for direct methanol fuel cellsYuhan Lin<sup>a</sup>, Haidong Li<sup>a</sup>, Changpeng Liu<sup>b</sup>, Wei Xing<sup>b,\*</sup>, Xiangling Ji<sup>a,\*</sup><sup>a</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Graduate School of the Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China<sup>b</sup> Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Science, 5625 Renmin Street, Changchun 130022, PR China

## ARTICLE INFO

## Article history:

Received 8 July 2008

Accepted 20 August 2008

Available online 30 August 2008

## Keywords:

Nafion

Mesoporous silica

Surface-modified

Proton conductivity

Methanol permeability

## ABSTRACT

In this study, Nafion® 117 membrane is surface-modified with mesoporous silica layers through in situ surfactant-templated sol–gel reaction. The reaction makes use of tetraethyl orthosilicate (TEOS) under acidic condition via dip-coating technique on both sides. Scanning electron microscopy (SEM), Fourier transformation infrared (FTIR), and thermogravimetric analysis (TGA) are employed to characterize the resultant membranes. Proton conductivity and methanol permeability of the membranes are also studied. It is determined that the aging time, along with the number of the silicon dioxide (SiO<sub>2</sub>) layer, influence both proton conductivity and methanol permeability. Specifically, double-side modified membrane with 5 min interval of the second layer (S (5)) exhibits optimal properties on the combined criterion of conductivity and permeability. However, the application of mesoporous silica layer in modifying commercial Nafion membranes through dip-coating is proven to be a facile route in improving the said criteria simultaneously.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Growing concern over the environmental impact of exhaust emissions has led to widespread attempts to reduce long-term dependence on oil and other fossil fuels. In turn, this rippled towards the emergence of clear energy efforts and continued development of fuel cells that can provide both ultra-low emissions and high efficiencies. Among the different types of fuel cells, the direct methanol fuel cell (DMFC) is one of the most promising power sources for vehicular and portable applications. DMFC is a polymer electrolyte fuel cell (PEFC).

In the development of DMFC, the proton conducting membrane is a key issue. It offers vessels for hydrogen ions while separating the gases on the different electrode surfaces during the electrochemical reaction. It likewise poses great influence on the performance and the efficiency of fuel cells. So far, Nafion® membranes have been commonly used as polymer electrolytes in DMFCs, owing to their good chemical stability, strong thermal resistance, and relative ideal conductivity. However, the use of the Nafion membranes as polymer electrolytes is affected by certain drawbacks. For example, its poor methanol barriers cause overpotential losses

at the negative electrode of the fuel cell. Also, the membranes cannot sustain a long-term operation when temperatures are elevated. Definitely, it will limit the commercial applications of Nafion membranes [1].

Due to these problems, modification of Nafion has attracted research attention in recent years. Much of the aims of the studies has been to diminish methanol crossover and increase the efficiency of DMFCs. Numerous efforts have been done on the preparation of Nafion/silica-based composite membranes [2]. Kim et al. [3] employed the plasma enhanced chemical vapor deposition technique to deposit nano-scaled films of silica on Nafion membrane. It was found that the composite membrane is a viable candidate for DMFC. Tang et al. [4] developed a self-assembly process to synthesize Nafion–SiO<sub>2</sub> nanoparticles. These were used to modify the Nafion/silica nanocomposite membrane. The novel membrane exhibited significantly high durability under the tests. The said result was explained as the excellent interface between the Nafion polymeric matrix and the self-assembled Nafion–SiO<sub>2</sub> nanoparticles. On the other hand, research on the preparation of composite membranes by sol–gel route has been reported [5–12]. Dimitrova et al. [8] recast the mixture of Nafion ionomer and silica solution. In their study, the composite membrane showed higher conductivity than pristine Nafion. Meanwhile, infiltration of Nafion with sol–gel solutions has also generated some promising results [13–16]. To illustrate, Miyake et al. [5,6] reported that hybrid mem-

\* Corresponding authors. Tel.: +86 431 8526 2223/2876; fax: +86 431 8526 5653.  
E-mail addresses: [xingwei@ciac.jl.cn](mailto:xingwei@ciac.jl.cn) (W. Xing), [xlji@ciac.jl.cn](mailto:xlji@ciac.jl.cn) (X. Ji).

branes with silica content of 10–20 wt% decreased methanol uptake from the liquid phase. However, the proton conductivities of the membranes were revealed to be lower than or equal to that of pristine Nafion membranes.

In this study, a series of Nafion/SiO<sub>2</sub> composite membranes were prepared via dip-coating surfactant-templated mesostructured silica on both sides of the Nafion® 117. The aim is to improve the performance of commercial Nafion membranes by making full use of mesoporous silica thin films. Finally, the methanol permeability and proton conductivity are considered as a combined criterion for all the specimens.

## 2. Experimental

### 2.1. Membrane preparation

The Pluronic® P123 surfactant (PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>, where PEO is poly(ethylene oxide) and PPO is poly(propylene oxide)) was purchased from BASF. Tetraethyl orthosilicate (TEOS) (Beijing, China) and ethanol from the Beijing Chemical Factory were utilized as prepared. Methanol was distilled prior to use. The commercial Nafion® 117 (denoted as N117 in the paper) has 1100 equiv. weight ( $M_W$  per sulfonic acid group of Nafion 117) and 175  $\mu\text{m}$  thickness. It was pre-treated before use according to previously published literature [17]. The mesoporous SiO<sub>2</sub> films on each side of Nafion membrane were prepared by dip-coating silicate/surfactant sols on the membrane. The triblock copolymer surfactant P123 was used to template the pore structure of SiO<sub>2</sub> layer. Typically, the sols were prepared by mixing TEOS, P123, HCl, H<sub>2</sub>O, and ethanol in a molar ratio at approximately 1:0.0097:0.0087:5:20. This process was adapted from the one suggested by Wang et al. [18], with slight modifications.

The sample was designated as S (min) relative to Nafion® 117. For example, S (0) represents the sample of the second layer which was coated immediately. Meanwhile, S (5) pertains to the second layer coated 5 min after the formation of the first layer. In addition, NS means the sample with only one coated layer. Dip-coating

was carried out at a speed of 50 mm min<sup>-1</sup> and a typical route is as follows. The membranes were immersed in the sol and were subsequently pulled out. For the second layer, the above process was repeated after 5 min. The prepared membranes were laid in a petri dish and aged for 4–6 h. Afterwards, they were eluted with ethanol and deionized water to remove the surfactant completely. Membrane composition and symbols are presented in Table 1. All the samples were soaked in deionized water prior to taking the different measurements.

### 2.2. Analysis

Thermogravimetric analysis (TGA) was performed with TGA-51H, Shimadzu at a heating rate of 2 °C min<sup>-1</sup> under N<sub>2</sub> in the range of 20–140 °C. Scanning electron microscopy (SEM) images were taken using a Philips XL 30 ESEM FEG scanning electron microscope. Similarly, transmission electron microscopy (TEM) images were taken with a JEOL JEM-2010 transmission electron microscope, with an accelerating voltage of 200 kV. Samples were then scraped from the surface of modified membrane, and the result was shown in the supporting information. Fourier transform infrared spectroscopy (FTIR) spectra of the composites were recorded on a Bruker Vertex 70 FTIR spectrometer in Attenuated Total Reflection (ATR) mode from 4000 to 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The water uptake experiment was carried out by drying the membranes in a vacuum oven at 80 °C for 4 h and weighed subsequently. Afterwards, the membranes were immersed in distilled water and isothermally oscillated at 60 °C for 2 h, and after drying with filter paper, the wet membrane was weighed. The water uptake in Table 1 was calculated using the following equation: water uptake (%) =  $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}$ ; where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  represent the weights of the wet and dry membrane, respectively. Next, the dimension of wet membranes was measured.

Proton conductivity  $\sigma$  (S cm<sup>-1</sup>), was measured by the alternating current (AC) impedance method using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detec-

**Table 1**  
Water uptake for N117 and modified membranes

Sample name	Preparation conditions	Number of SiO <sub>2</sub> layers on one side of N117	Thickness <sup>a</sup> ( $\mu\text{m}$ )	Water uptake (%)	Dimensional change <sup>b</sup> (%)
N117	Nafion® 117 membrane	0	210	18.8	11.9
NS	One SiO <sub>2</sub> layer coated on N117	1	210	33.2	2.1
S (0)	The second SiO <sub>2</sub> layer was coated immediately on NS	2	220	28.5	1.6
S (5)	The second SiO <sub>2</sub> layer was coated at 5 min later on NS	2	230	36.9	1.5
S (7)	The second SiO <sub>2</sub> layer was coated at 7 min later on NS	2	220	31.6	1.5
S (10)	The second SiO <sub>2</sub> layer was coated at 10 min later on NS	2	220	27.3	1.5
S (15)	The second SiO <sub>2</sub> layer was coated at 15 min later on NS	2	220	36.8	1.5
S (20)	The second SiO <sub>2</sub> layer was coated at 20 min later on NS	2	220	30.3	1.4
S (25)	The second SiO <sub>2</sub> layer was coated at 25 min later on NS	2	220	27.6	1.4
S (30)	The second SiO <sub>2</sub> layer was coated at 30 min later on NS	2	230	36.0	1.4
S (45)	The second SiO <sub>2</sub> layer was coated at 45 min later on NS	2	230	29.6	1.4
S (5)-3	The third SiO <sub>2</sub> layer was coated at 5 min later on S (5)	3	230	29.0	1.4
S (5)-4	The fourth SiO <sub>2</sub> layer was coated at 5 min later on S (5)-3	4	220	31.2	1.3
S (5)-5	The fourth SiO <sub>2</sub> layer was coated at 5 min later on S (5)-4	5	230	25.1	1.1

<sup>a</sup> In hydrated state.

<sup>b</sup> Dimensional change in length in both hydrated and dry state,  $\Delta L/L$  (%).

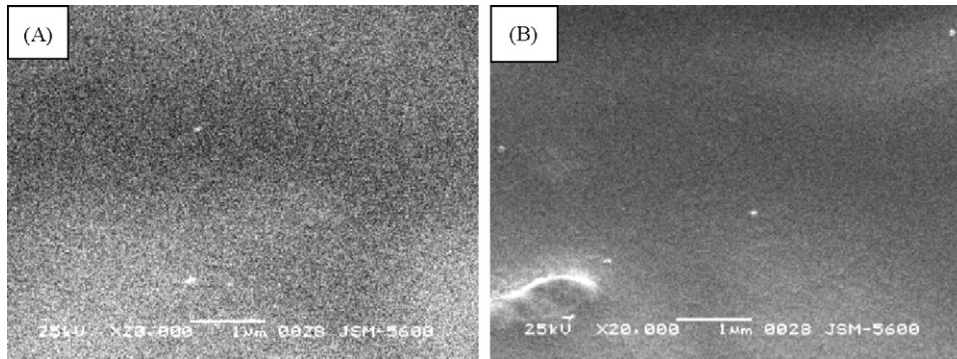


Fig. 1. SEM images of (a) N117 and (b) NS.

tor, EG&G PARC, Princeton, NJ) from 10 Hz to 1 MHz with 10 mV AC perturbation and 0.0 V DC rest voltage. Here, the composite membrane was fixed in a four-point probe conductivity measuring cell. The conductivity was measured in a longitudinal direction [21] and was calculated using the following equation:  $\sigma = RA/L$ , where  $L$  is the distance between reference electrodes,  $A$  is the cross-sectional area, and  $R$  is the resistance.

Methanol permeability of the composite membranes was determined by the diffusion coefficient,  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) using an electrochemical monitoring technique with two connected compartment cells [19,20]. During measurement, the membrane was supported by a platinum mesh which served as a current collector for the working electrode. In this regard, an Ag/AgCl electrode was used as a reference electrode while a platinum foil was used as a counter electrode. The working electrode's potential was kept at a constant value of 0.7 V where the complete methanol oxidation is controlled by the methanol through membrane transport.

### 3. Results and discussion

Since, all as-prepared samples are transparent, flexible, and homogeneous, these indicate a good miscibility between  $\text{SiO}_2$  layer and Nafion membrane. In fact, the SEM image in Fig. 1 displays a very smooth and homogeneous surface for both the Nafion and modified Nafion membranes. Actually, the  $\text{SiO}_2$  gel network was formed within the presence of the surfactant during the dip-coating procedure. In Fig. 2, the FTIR spectra exhibit the structural

change for different composite membranes. The peak of  $1057 \text{ cm}^{-1}$  is attributed to the symmetric stretch vibration of  $\text{SO}_3^-$  ions. Generally, the Si–O–Si asymmetric stretching vibration appears approximately at  $1080 \text{ cm}^{-1}$  with a strong band. However, since the mesoporous silica film is very thin at about 200 nm, it is difficult to detect its existence. On the other hand, the stretch vibration of  $\text{SO}_3^-$  ions somewhat overlaps with Si–O–Si vibration. Noticeably, a small band at  $1083 \text{ cm}^{-1}$  for sample S (45) was assigned to be the vibration of Si–O–Si. Water uptake data and dimensional change are summarized in Table 1. Obviously, all the  $\text{SiO}_2$  mod-

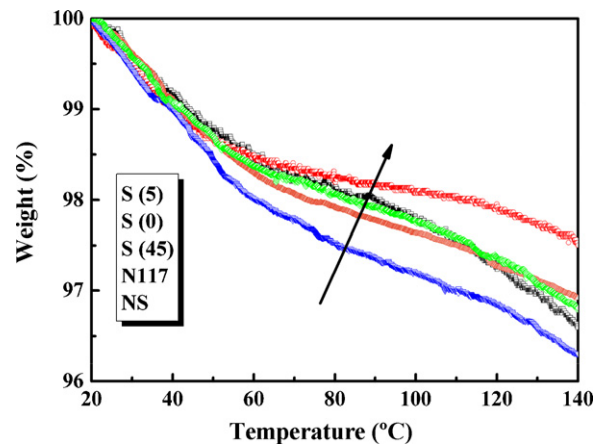


Fig. 3. TGA curves of N117 and the modified membranes.

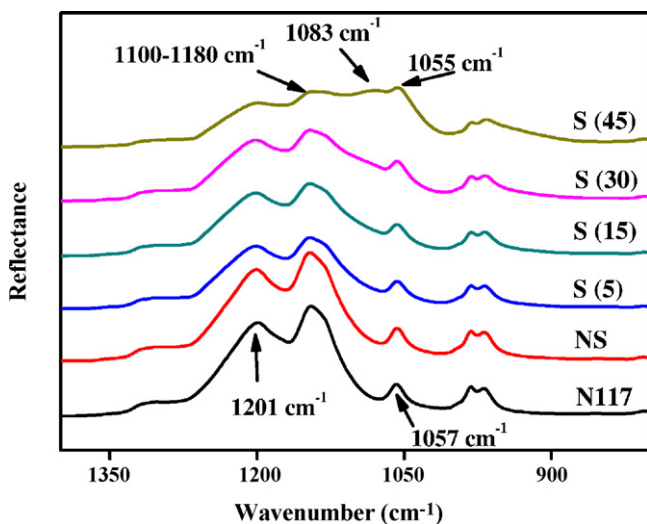


Fig. 2. FTIR spectra of N117 and the modified membranes.

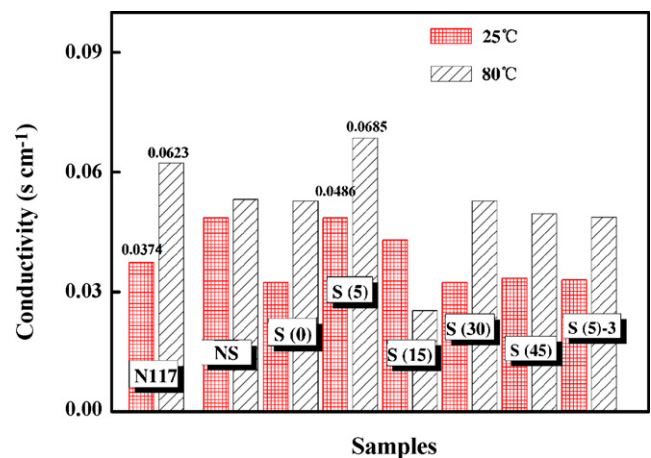


Fig. 4. Proton conductivity of the samples at 25 and 80 °C.

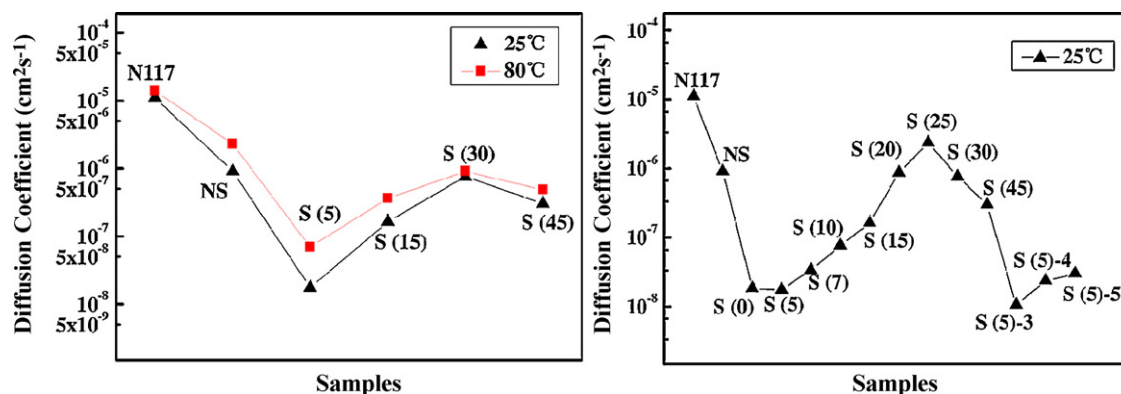


Fig. 5. Methanol permeability of the samples at 25 and 80 °C.

ified samples have a higher water uptake value than that of the pristine membrane. In spite of sample S (3) which has the lowest water uptake of 25.7%, it is much higher than that of N117 by 12.8%. Interestingly, the sample S (5) (with the 2nd coating followed by a 5-min-interval) has a remarkably elevated water uptake, as high as 36.9%, which was almost 2.8 times that of a pristine N117 membrane. Such uptakes for most modified membranes show an increase in the number of SiO<sub>2</sub> coatings. NS possesses a water uptake of 33.2% while S (15) has 36.8%. Moreover, the interval of the 2nd coating layer influences water uptake. For example, the water uptake of S (7), S (20), and S (30) are 31.6%, 30.3%, and 36.0%, while S (10), S (25), and S (45) have 27.3%, 27.6%, and 29.6%, respectively. However, the amount of water uptake in the Nafion/mesoporous silica hybrid membrane was increased [14]. As for the dimensional change before and after uptake, all composite membranes show a slight increase in length below 2.2% in a hydrated state. In contrast, N117 has a significant increase of 11.9% as shown in Table 1. Obviously, the modified membranes have more dimensional stability than N117. Furthermore, since mesoporous silica network is a rigid framework which adheres to the surface of N117, it finally facilitates the decrease of membrane swelling in the solvent.

Thermalgravimetric analysis is exploited to investigate the dehydration in membranes. In Fig. 3, the sample NS shows more weight loss from room temperature to 140 °C compared to pristine N117. This indicates that more water molecules are liberated in NS during heating. However, in the case of S (5), S (40), and S (0), the modified membranes show less weight loss compared to N117. Interestingly, two-layer modified membranes improve the thermal stability to some extent, which is possibly due to a slightly thicker SiO<sub>2</sub> layer in S (0, 5, 40) despite a total of only a few hundred nanometers in thickness.

Fig. 4 shows the proton conductivity of membranes at 25 and 80 °C, respectively. It is well known that raising the temperature will lead to a higher conductivity for the same membrane. When mesoporous SiO<sub>2</sub> is coated on both sides of a N117 membrane, the conductivity increases to some extent. Meanwhile, the samples NS and S (5) almost have the same proton conductivity of 0.0486 S cm<sup>-1</sup> at 25 °C, which is about 30% higher than that of N117. The elevated proton conductivity of S (5) is attributed to the hydrophilic mesoporous silica layer, which can absorb more water and form proton tunnels to facilitate proton mobilization better than other multi-layer samples. Unfortunately, other samples show low proton conductivity, possibly due to the poor inter-connectivity of pore channels in silica layers.

Fig. 5 shows the methanol permeability of the modified membranes which was depicted as effectively reduced. All the modified membranes have a lower methanol diffusion coefficient than N117. It is worth mentioning that the sample S (5)-3 exhibits the low-

est methanol crossover of  $1.06 \times 10^{-8}$  at 25 °C. Among the samples with less than two layers of mesoporous SiO<sub>2</sub>, S (5) possesses the lowest methanol crossover at both 25 and 80 °C, and its diffusion coefficient is  $1.75 \times 10^{-8}$  and  $6.95 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, respectively. Methanol permeability is a crucial factor in DMFC. Nevertheless, there remains a debate on how methanol permeates ionomer membranes and whether it passes through the same pathway where protons are transported [22]. It is believed that the membranes with multi-layer mesoporous SiO<sub>2</sub> on the surface of N117 restrained the passage of methanol molecules. In addition, the membranes will swell in both methanol and water during the testing and in the practical fuel cells. Thus, the competition between water and methanol uptake is related to ultimate methanol permeability. Moreover, the different swelling behavior of the composite in water and methanol may be attributed to the different dielectric constants of the electrolytes. The dielectric constant of methanol is only 33 while water has as high as 80 [23]. In this case, if the dielectric constant is lower, the dissociation of the acid–base interaction is weaker and less liquid absorption can be anticipated as a consequence. Owing to the hydrophilicity of the SiO<sub>2</sub> layers, water absorption in hybrid membranes predominate which means less absorption for methanol. Therefore, the methanol permeability is lower for the modified membranes.

#### 4. Conclusions

In summary, mesoporous SiO<sub>2</sub> layers were exploited to modify the surface of Nafion® 117 membrane via a simple dip-coating technique. Only adjusting coating conditions, such as layers aging internally and improved membranes are available. Among these, sample S (5) which is a second SiO<sub>2</sub> layer coated on NS after 5 min, exhibits the best performance, for instance, through an elevated proton conductivity of 0.0486 and 0.0685 S cm<sup>-1</sup> at 25 and 80 °C while possessing the lowest methanol crossover at both temperatures. Also, the diffusion coefficient is  $1.75 \times 10^{-8}$  and  $6.95 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, which almost was decreased by about three orders compared with Nafion 117 membrane at the same condition. However, this provides a superficial pathway in improving the performance of current commercial Nafion membranes in DMFC in the future.

#### Acknowledgements

We are grateful for the support for this study provided by the National Natural Science Foundation of China (Creative Research Group: 50621302), “863” Project (2006AA03Z224), the Distinguished Young Fund of Jilin Province (20050104), the Inter-

national Collaboration Project (20050702-2) from Jilin Province, China.

## References

- [1] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, *J. Electroanal. Chem.* 532 (2002) 75.
- [2] R.B. Moore, K.A. Mauritz, R.V. Gummaraju, *J. Polym. Sci., Part B: Polym. Phys.* 34 (1996) 2383.
- [3] D.J. Kim, M.A. Scibioh, S. Kwak, I.H. Oh, H.Y. Ha, *Electrochem. Commun.* 6 (2004) 1069.
- [4] H. Tang, Z. Wan, M. Pan, S.P. Jiang, *Electrochem. Commun.* 9 (2007) 2003.
- [5] N. Miyake, J.S. Wainright, R.F. Savinell, *J. Electrochem. Soc.* 148 (2001) A905.
- [6] N. Miyake, J.S. Wainright, R.F. Savinell, *J. Electrochem. Soc.* 148 (2001) A898.
- [7] P.L. Antonucci, A.S. Arico, P. Creti, E. Ramunni, V. Antonucci, *Solid State Ionics* 125 (1999) 431.
- [8] P. Dimitrova, K.A. Friedrich, U. Stimming, B. Vogt, *Solid State Ionics* 150 (2002) 115.
- [9] R.A. Zoppi, I.V.P. Yoshida, S.P. Nunes, *Polymer* 39 (1998) 1309.
- [10] R.A. Zoppi, S.P. Nunes, *J. Electroanal. Chem.* 445 (1998) 39.
- [11] K.T. Adjemian, S.J. Lee, S. Srinivasan, J. Benziger, A.B. Bocarsly, *J. Electrochem. Soc.* 149 (2002) A256.
- [12] A.S. Arico, V. Baglio, V. Antonucci, I. Nicotera, C. Oliviero, L. Coppola, P.L. Antonucci, *J. Membr. Sci.* 270 (2006) 221.
- [13] Q. Deng, Y. Hu, R.B. Moore, C.L. McCormick, K.A. Mauritz, *Chem. Mater.* 9 (1997) 36.
- [14] D.H. Jung, S.Y. Cho, D.H. Peck, D.R. Shin, J.S. Kim, *J. Power Sources* 106 (2002) 173.
- [15] K.A. Mauritz, R.M. Warren, *Macromolecules* 22 (1989) 1730.
- [16] I.D. Stefnithis, K.A. Mauritz, *Macromolecules* 23 (1990) 2397.
- [17] B. Baradie, J.P. Dodelet, D. Guay, *J. Electroanal. Chem.* 489 (2000) 101.
- [18] D.H. Wang, W.L. Zhou, B.F. McCaughey, J.E. Hampsey, X.L. Ji, Y.B. Jiang, H.F. Xu, J.K. Tang, R.H. Schmehl, C. O'Connor, C.J. Brinker, Y.F. Lu, *Adv. Mater.* 15 (2003) 130.
- [19] W.L. Xu, T.H. Lu, C.P. Liu, W. Xing, *Electrochim. Acta* 50 (2005) 3280.
- [20] W.L. Xu, C.P. Liu, X.Z. Xue, Y. Su, Y. Lv, W. Xing, T.H. Lu, *Solid State Ionics* 171 (2004) 121.
- [21] Y. Sone, P. Ekdunge, D. Simonsson, *J. Electrochem. Soc.* 143 (1996) 1254.
- [22] K.A. Mauritz, R.B. Moore, *Chem. Rev.* 104 (2004) 4535.
- [23] H.L. Wu, C.C.M. Ma, H.C. Kuan, C.H. Wang, C.Y. Chen, C.L. Chiang, *J. Polym. Sci., Part B: Polym. Phys.* 44 (2006) 565.