



Short communication

Ultrathin proton-conducting sandwich membrane with low methanol permeability based on perfluorosulfonic acid polymer and phosphosilicate

Haibin Li^{a,*}, Minghuan Ai^a, Fengjing Jiang^{a,*}, Lijun Yu^a, Hengyong Tu^a, Qingchun Yu^a, Hong Wang^b

^a School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, China

^b Research Institute of Micro/Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history:

Received 8 October 2010

Received in revised form

13 December 2010

Accepted 20 January 2011

Available online 26 January 2011

Keywords:

Proton-conducting

Ultra-thin membrane

Methanol permeability

Fuel cell

ABSTRACT

An ultra-thin, free-standing proton-conductive membrane of Nafion[®]/Phosphosilicate/Nafion[®] (NPN) with a sandwich structure has been prepared. The NPN membrane of thickness 960 nm shows extremely low methanol permeability of $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and area specific resistance (ASR) smaller than $0.2 \Omega \text{ cm}^2$.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membranes, typically Nafion[®], are characterized by high proton conductivity and reasonable chemical stability, and are widely used in current low-temperature fuel cells (PEFCs and DMFCs). However, most of these membranes are susceptible to deformation due to the adsorption and desorption of water, and therefore, are permeable to fuel, especially methanol, which greatly lowers the fuel-cell efficiency. Proton-conducting inorganic membranes may offer very promising alternatives to polymeric membranes because of their low cost and high dimensional stability. Inorganic proton conductors, including sol-gel glasses (e.g., SiO₂, TiO₂, P₂O₅/SiO₂) [1–3], heteropolyacids (e.g., H₃PW₁₂O₄₀·29H₂O) [4,5], and solid acids (e.g., CsH₂PO₄) [6], have been reported. However, their membranes tend to be rather thick and inflexible, which results in large ohmic drops and poor processability in fuel-cell applications. Ultra-thin surfactant-templated porous glass films have been prepared as proton conductors, which have finely controllable pore sizes, a narrow pore distribution, and high surface area [7–9]. However, these films were not free-standing, and thus it was difficult to use them to construct a membrane electrode assembly (MEA) for application in a fuel cell. As a result, their wider use is hampered. Thus, the development of ultra-thin,

flexible, self-standing proton-conductive membranes is strongly desired.

Herein, we propose a strategy of organic/inorganic/organic sandwich structures for obtaining ultra-thin, flexible proton-conducting membrane. In such membrane, the middle inorganic layer is expected to suppress methanol permeation, while the bottom and upper organic layers are designed to provide sufficient mechanical strength and flexibility. Recently, we have reported the study on a proton-conducting glass membrane consisting of Nafion[®] and phosphosilicate [10]. It was found that Nafion[®] and phosphosilicate showed good compatibility and the hybrid membrane exhibited excellent proton conductivity which is comparable to Nafion[®]. Therefore, in this work, a perfluorosulfonic acid polymer (Nafion[®], DuPont) and phosphosilicate were chosen as the materials for the organic and inorganic layer of the membrane, respectively. The morphology, structure, proton conductivity and methanol permeability of the Nafion[®]/Phosphosilicate/Nafion[®] (NPN) membrane will be discussed in this work.

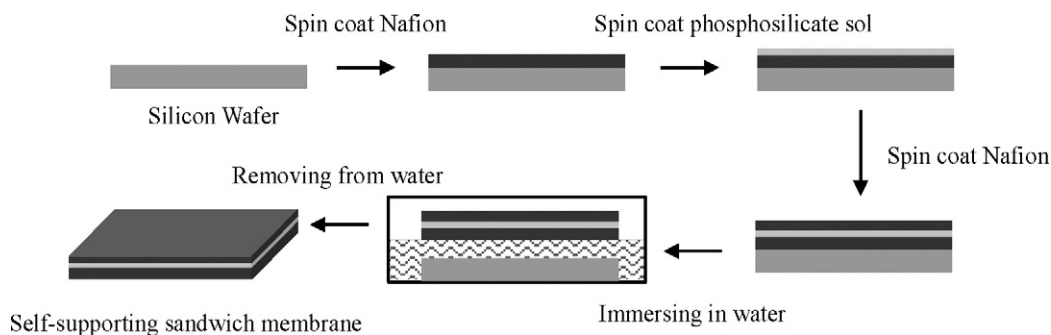
2. Experimental

2.1. Preparation of NPN the membranes

A 5 wt.% solution of Nafion[®] (Aldrich, 5 wt.% solution in a mixture of lower aliphatic alcohols and water) was firstly spin-coated onto a silicon wafer at 900 rpm for 1 min to form the bottom layer of the sandwich membrane. The obtained Nafion[®] thin film was then dried at 150 °C for 20 min. The inorganic layer (the phospho-

* Corresponding authors. Tel.: +86 21 34206249; fax: +86 21 34206249.

E-mail addresses: haibinli@sjtu.edu.cn (H. Li), fjzz@sjtu.edu.cn (F. Jiang).



Scheme 1. Process of preparing NPN sandwich membrane by spin-coating.

silicate thin film) was prepared by directly spin-coating a mixed solution of phosphoric acid and TEOS sol onto the obtained Nafion[®] thin film at 4000 rpm for 1 min and then dried at 100 °C for 30 min. First, 5.2 g of tetraethoxysilane (TEOS, Aldrich), 6 g of propanol and 0.45 ml (0.0045 N) of hydrochloric acid were mixed and stirred for 1 h at 60 °C. Then, 2 ml (0.1 N) of hydrochloric acid was added, and the resulting sol was stirred for additional 1 h at 70 °C. Then, 0.54 g phosphoric acid (85 wt.% aqueous solution, Sinopharm) was added while stirring the above prepared sol. The mixed solution was then stirred for 1 h at room temperature. In the final composition, the molar ratio of TEOS and H₃PO₄ is 84:16. For the preparation of the upper layer of Nafion[®] thin film, a 5 wt.% solution of Nafion[®] was spin-coated onto the phosphosilicate thin film at 4000 rpm for 1 min, and then the coated wafer was baked at 150 °C for 20 min. Finally, the NPN multilayer membrane was detached from the substrate by immersing in water. The membrane floating on the water surface could be cut with shears (Twin, Zwilling), and could be transferred onto various substrates, such as metal gasket, a carbon paper, an anodic alumina oxide (AAO), a slide glass, and an ITO plate.

2.2. Characterization

A membrane sample was photographed using a digital camera (DSC-W50, Sony). The tensile strength of the NPN membrane was tested using a Dynamic Mechanical Analysis (DMA Q800, TA Instruments). The morphology of the sandwiched membrane was observed by means of a field-emission scanning electron microscope (JSM-7401F, JEOL). Infrared spectra were recorded on an FTIR spectrometer (EQUINOX 55, Bruker). The proton conductivity of the sandwiched membrane was examined by means of an impedance analyzer (SI-1260, Solartron). The NPN membrane was transferred onto an ITO plate, such that the ITO glass served as the bottom electrode for the impedance measurement. An Au electrode of diameter 1 mm was sputtered on the top surface of the sample through a shadow mask. Electrical contacts to the ITO substrate and the top electrode were made with soldered Au wires. During the measurement, the samples were placed in an enclosed humid chamber. The conductivities of the samples were calculated from the following formula:

$$\sigma = \frac{L}{AR} \quad (1)$$

where R is determined from the semi-circle response on the real axis of the complex impedance plot, L represents the thickness of the sample film, and A is the area of the top Au electrode.

Methanol permeability of the membranes was determined by using a two-chamber method [13]. The membrane was clamped between the two chambers, the contents of which were stirred continuously during the experiments. One chamber contained pure deionized water (300 ml) and the other contained an 8 vol.% aque-

ous solution of methanol (300 ml). Samples were taken from the water chamber at intervals, and a gas chromatograph (GC-2010, SHIMADZU) was used to determine their methanol concentrations. The methanol permeability was calculated by the following equation:

$$C_B(t) = A \cdot DK \cdot C_A \cdot \frac{(t - t_0)}{V_B L} \quad (2)$$

where C_A and C_B are the methanol concentrations in the methanol chamber and in the water chamber; A and L are the effective area and the thickness of membrane; V_B is the volume of the water chamber; t is the permeation time; and D and K are the methanol diffusivity and partition coefficient. The product DK is the methanol permeability.

3. Results and discussion

3.1. Preparation of the NPN membranes

For obtaining ultra-thin free-standing films, a sacrificial layer is normally used for the purpose of detaching thin films from the substrates with no damage. This is usually done by dissolving the sacrificial layer in a proper solvent [11]. However, in this work, the obtained NPN membrane can be easily detached from the silicon wafer by immersing in water without using sacrificial layer. This is due to the weak adhesion force between the Nafion[®] film and the surface of silicon wafer. As a result, a crack-free sandwiched NPN membrane with an area larger than 16 cm² could be obtained. The process of preparing NPN sandwich membrane was schematically shown in Scheme 1. It is interesting to note that the membrane could be readily cut with shears to form any desired shape, such as the quadrangle shown in Fig. 1a and could be self-supporting (see Fig. 1b). The sandwich NPN membrane is uniform and transparent.

3.2. Mechanical property, morphology and chemical structure of the NPN membranes

Good mechanical strength is essential for a free-standing thin membrane. The NPN membrane has a tensile strength of 12.1 MPa, and a breaking elongation of 1.52%, which shows typical stress-strain behavior of brittle material (see Fig. 2). The tensile strength of NPN membrane is comparable to a recasted Nafion[®] film after annealing (~10 MPa) but smaller than that of a commercial Nafion[®] 117 (~32 MPa) [12].

SEM images of the NPN membrane supported by porous AAO support were shown in Fig. 3. The top-view image in Fig. 3a shows that the NPN membrane was crack-free, compact and smooth. Fig. 3b shows the cross-sectional view of the NPN membrane where the layered structure of NPN membrane can be observed. The average thickness of the NPN membrane is around 960 nm wherein the thickness of the bottom and upper Nafion[®] layer was about 590 nm

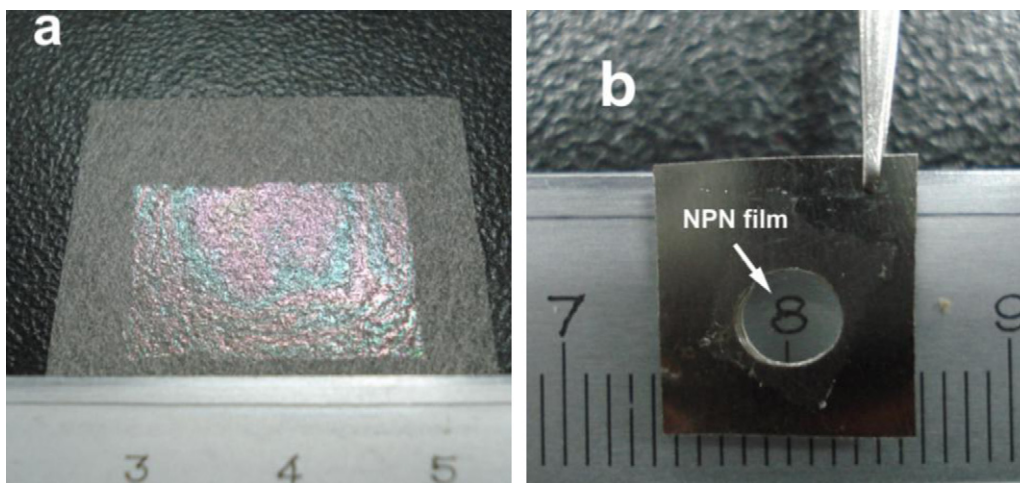


Fig. 1. Digital photos of the sandwiched NPN membrane, supported by carbon paper (a), self-supporting (b).

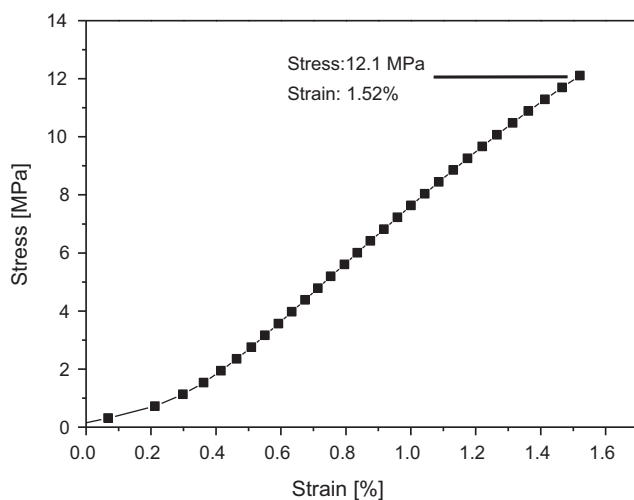


Fig. 2. Stress-strain curve for the NPN membrane at 25 °C.

and 110 nm, respectively, and the thickness of the middle phosphosilicate layer was around 260 nm. The thickness of each layer is mainly controlled by the spin speed.

In order to confirm the formation of the NPN membrane, FTIR spectra were recorded. IR spectra of the sandwiched NPN membrane are shown in Fig. 4. The peaks at 800 and 1080 cm^{-1} may

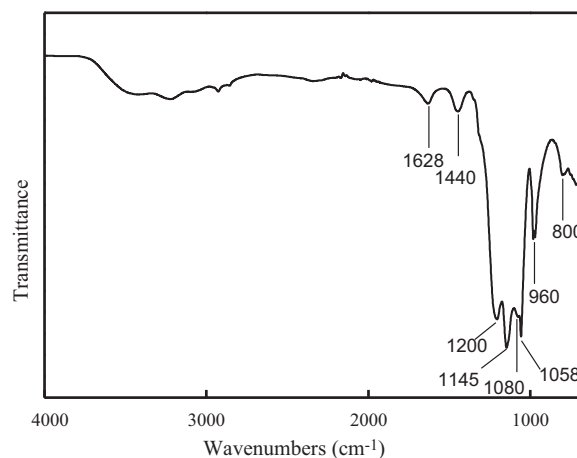


Fig. 4. IR spectra of a sandwiched NPN membrane.

be assigned as the characteristic peaks of Si–O–Si [13], which provide evidence for the formation of the Si–O–Si skeleton by the condensation reaction. An absorption shoulder at 960 cm^{-1} can be assigned to the Si–O stretch of silanol groups, Si–OH [9]. The band at 1628 cm^{-1} corresponds to the bending frequency of water [14]. It has been used as a measurement of water content by either its integrated absorbance or peak absorbance. Bands located between 4000 and 3000 cm^{-1} are relative to liquid water in the cluster. It

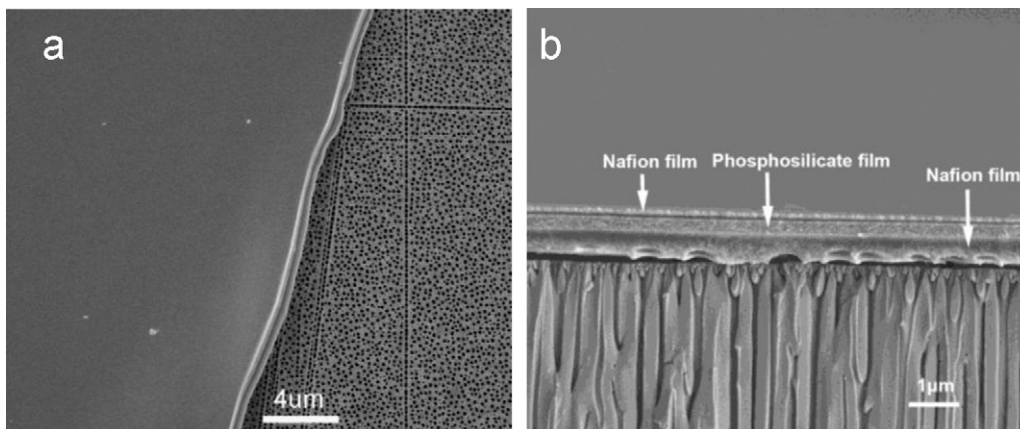


Fig. 3. SEM images of the sandwiched NPN membrane: (a) top view and (b) cross-sectional view.

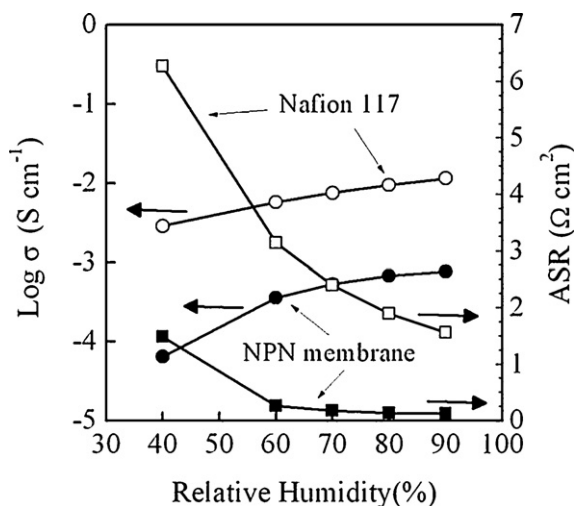


Fig. 5. Proton-conductivity of the sandwiched NPN membrane as a function of relative humidity (RH) at 50 °C.

consists of several sub-bands. A broad absorption band appearing at 3360 cm^{-1} can be attributed to the stretching vibrations of Si–O–H and P–O–H involved in hydrogen bonding with adsorbed water molecules, H–O–H [15]. The appearance of an infrared absorption bands at 1060 and 1440 cm^{-1} suggests the formation of sulfonic anhydride species [16]. Two peaks at 1216 and 1148 cm^{-1} were assigned to the C–F stretching modes [17].

3.3. Proton conductivity

The proton-conducting properties of the sandwiched NPN membrane were determined by AC impedance spectroscopy. Fig. 5 shows the humidity dependence of the proton conductivity of the membrane. The conductivity of the NPN membrane is seen to be sensitive to humidity, and with the increasing relative humidity (RH) it increases continuously up to about $7.6 \times 10^{-4}\text{ S cm}^{-1}$ at 50 °C under 95% RH. The proton conductivity of NPN membrane is almost 1–2 orders of magnitude lower than Nafion® 117 [18]. Due to the multilayered structure, the proton conductivity of the NPN membrane is controlled by the conductivity of each single layer and the influence of the interfaces. It is reported that the phosphosilicate glass was proton conductive where protons can migrate by jumping between the hydroxyl groups (Si–OH), the POH groups and the adsorbed water molecules [3]. The reported proton conductivity can reach as high as 10^{-2} S cm^{-1} [19]. Compared to those (10^{-2} S cm^{-1}) of both Nafion® 117 and phosphosilicate glass, the depressed proton conductivity ($\sim 10^{-3}\text{ S cm}^{-1}$) of the NPN membrane should be attributed to the effect of interfaces.

Area-specific resistance (ASR) of the proton exchange membrane (PEM) is more important than proton conductivity itself in evaluating the practical performance of fuel cells [20]. ASR value is given by L/σ , where L is the film thickness and σ is the conductivity. The conductivity of the NPN is not as high as that of Nafion® 117. However, the typical thickness of Nafion® 117 membrane as fuel cell electrolyte is about $180\text{ }\mu\text{m}$ and is almost 200 times thicker than that of our sandwiched NPN membrane. The ASR values of the NPN membrane under the humid condition of 70–90 RH are below $0.2\text{ }\Omega\text{ cm}^2$, and are significantly smaller than that of a commercially employed Nafion® 117 membrane. This is a big advantage for using an ultra-thin PEM in a fuel cell when the problem of fuel crossover can be suppressed.

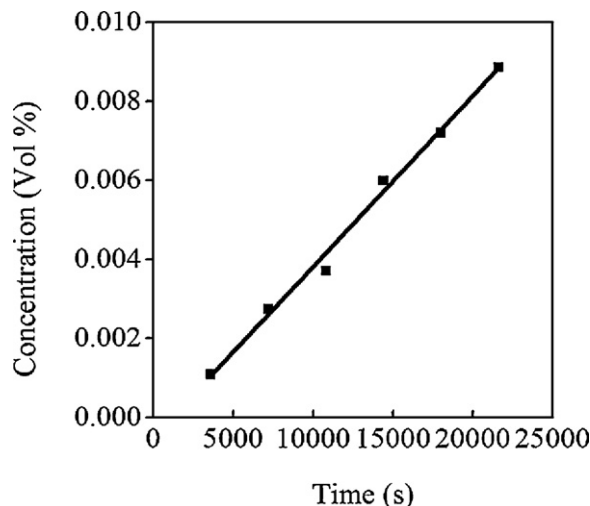


Fig. 6. Methanol concentration diffused through the sandwiched NPN membrane as a function of time.

3.4. Methanol permeation

The utmost requirement for a fuel-cell PEM is exclusive transport of protons, and the permeation of fuels, especially methanol (in the case of a direct methanol fuel cell, DMFC), should be suppressed. In the NPN membrane, the inorganic phosphosilicate layer was applied in order to enhance the mechanical property and more importantly, to reduce the crossover of fuel through the membrane, because the phosphosilicate film is more compact than the Nafion® film and is non-swelling in the presence of water. Fig. 6 shows the methanol concentration as a function of time. The increase of methanol concentration results from the permeation of methanol through the NPN membrane. The methanol permeability of the membrane was determined to be $1 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$. This value is two orders of magnitude lower than that of $2 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$ for a Nafion® membrane [21].

4. Conclusion

We have successfully prepared an ultra-thin, self-standing, proton-conducting NPN membrane. The NPN membrane has a sandwich structure with a phosphosilicate middle layer. The NPN membrane shows sufficient proton conductivity of $7.6 \times 10^{-4}\text{ S cm}^{-1}$ and extremely low methanol permeability of $1 \times 10^{-8}\text{ cm}^2\text{ s}^{-1}$. Due to the very small thickness of the membrane (960 nm), the ASR of the NPN membrane is significantly reduced as compared to that of Nafion® 117. An ultra-thin, self-standing membrane with sufficient proton conductivity is promising for the application in sensors, supercapacitors and especially, in fuel cells. For the application as PEM in fuel cells, an ultra-thin membrane has a notable advantage of low ASR, which may leads to much higher output power density. However, fuel permeation is a fatal shortage of an ultra-thin polymer film which can hardly be avoid. Preparing organic/inorganic/organic multilayered membrane might be an efficient approach to obtain ultra-thin PEM with low fuel crossover.

Acknowledgements

This work was supported by the National High-Tech R&D Program (863 Program) (grant 2009AA05Z113), Shanghai Pujiang Program (grant 08PJ1406500), the International Science & Technology Cooperation Program of Ministry of Science & Technology of China (grant 2008DFA51200), the National Natural Science Foundation of China (NSFC grant 50672058), the China Postdoctoral

Science Foundation and the Open Research Foundation of Shenyang Jianzhu University (JX-200914).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2011.01.056.

References

- [1] M. Nogami, R. Nagao, C. Wong, *J. Phys. Chem. B* 102 (1998) 5772–5775.
- [2] F.M. Vichi, M.T. Colomer, M.A. Anderson, *Electrochem. Solid State Lett.* 2 (1999) 313–316.
- [3] M. Nogami, R. Nagao, C. Wong, T. Kasuga, T. Hayakawa, *J. Phys. Chem. B* 103 (1999) 9468–9472.
- [4] O. Nakamura, T. Kodama, I. Ogino, Y. Miyake, *Chem. Lett.* 8 (1979) 17–18.
- [5] Y.I. Park, J.D. Kim, M. Nagai, *J. Mater. Sci. Lett.* 19 (2000) 2251–2253.
- [6] D.A. Boysen, T. Uda, C.R.I. Chisholm, S.M. Haile, *Science* 303 (2004) 68–70.
- [7] H. Li, M. Nogami, *Adv. Mater.* 14 (2002) 912–914.
- [8] H. Li, M. Nogami, *Chem. Commun.* 2 (2003) 236–237.
- [9] H. Li, T. Kunitake, *Microporous Mesoporous Mater.* 97 (2006) 42–48.
- [10] F. Jiang, Z. Di, H. Li, H. Tu, Q. Yu, *J. Power Sources* 196 (2011) 1048–1054.
- [11] M. Hashizume, T. Kunitake, *Soft Matter* 2 (2006) 135–140.
- [12] S. Werner, L. Joerissen, U. Heider, *Ionics* 2 (1996) 19–23.
- [13] P. Innocenzi, *J. Non-Cryst. Solids* 316 (2003) 309–319.
- [14] Y. Jin, S. Qiao, J.C.D. da Costa, B.J. Wood, B.R. Ladewig, G.Q. Lu, *Adv. Funct. Mater.* 17 (2007) 3304–3311.
- [15] A. Aronne, M. Turco, G. Bagnasco, P. Pernice, M. Di Serio, N.J. Clayden, E. Marenga, E. Fanelli, *Chem. Mater.* 17 (2005) 2081–2090.
- [16] F.M. Collette, C. Lorentz, G. Gebel, F. Thominet, *J. Membr. Sci.* 330 (2009) 21–29.
- [17] H. Lim, M. Yarmo, N. Huang, P. Khiew, W. Chiu, *J. Phys. Sci.* 20 (2009) 23–36.
- [18] M. Maréchal, J.L. Souquet, J. Guindet, J.Y. Sanchez, *Electrochem. Commun.* 9 (2007) 1023–1028.
- [19] A. Matsuda, T. Kanzaki, K. Tadanaga, M. Tatsumisago, T. Minami, *Solid State Ionics* 154–155 (2002) 687–692.
- [20] B.C.H. Steele, A. Heinzel, *Nature* 414 (2001) 345–352.
- [21] Y.A. Elabd, E. Napadensky, J.M. Sloan, D.M. Crawford, C.W. Walker, *J. Membr. Sci.* 217 (2003) 227–242.