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Sulfonated poly(ether ether ketone) membranes for electric double layer capacitors

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Abstract

Sulfonated poly(ether ether ketone) (S-PEEK) with different degree of sulfonation (DS) has been prepared and evaluated as a proton conducting membrane for electric double layer capacitor (EDLC). The polymer electrolytes prepared with S-PEEK membrane exhibited ionic conductivities about 1.2×10^{-3}–4.5×10^{-3} S cm^{-1} at room temperature, which depended on both soaking solvent and degree of sulfonation. The quasi-solid-state EDLCs consisted of activated carbon electrodes and S-PEEK membrane were assembled, and their electrochemical characteristics were studied by cyclic voltammetry and charge–discharge cycle tests. The effect of DS on the electrochemical performances of EDLCs has been investigated.

Keywords: Degree of sulfonation; Electric double layer capacitor; Polymer electrolyte; Proton conducting membrane; Sulfonated poly(ether ether ketone)

1. Introduction

Electric double layer capacitors (EDLCs) have been considered to be one of the most important power sources in several devices such as memory back-ups, digital communications and electric vehicles, because they have the characteristics such as high power density and long cycle life. Such EDLCs are composed of a pair of activated carbon electrodes and an electrolyte. Liquid electrolytes like aqueous electrolyte solution and organic electrolyte solution have been usually used as an electrolyte in EDLCs. By replacing the liquid electrolyte with polymer electrolyte, the reliability of the capacitors could be improved from practical viewpoints. Therefore, many efforts have been made to develop the EDLCs using polymer electrolytes. [1–13] A proton exchange membrane is one of the polymer materials which can be applied in EDLCs as well as fuel cells. By some authors, the solid-state EDLCs based on Nafion have been investigated [11–13]. Nafion has excellent mechanical properties, chemical stability and high proton conductivity in the hydrated state [14,15], but the high cost of the material is one of the barriers against practical application. An alternative polymer material to be used as a proton conducting membrane is sulfonated poly(ether ether ketone)(S-PEEK), as it possesses good thermal stability and mechanical properties, and the concentration of sulfonic acid group can be easily varied by changing degree of sulfonation. However, the previous studies to date have focused mainly on the performances as a polymer electrolyte in fuel cells [16–19]. Recently, we have demonstrated that S-PEEK could be an appropriate polymer membrane for the realization of quasi-solid-state EDLCs [20]. The remaining work in this material was an optimization of degree of sulfonation (DS) for obtaining good performances of EDLCs. In the present work, S-PEEKs with different DS have been synthesized and characterized. Polymer electrolytes were prepared by immersing the S-PEEK membranes with different DS in water or dilute sulfuric acid solution. The quasi-solid-state EDLCs with activated carbon electrodes and S-PEEK membrane were prepared, and their electrochemical characteristics were studied. The effect of DS on electrochemical performances of the EDLCs has been investigated.

2. Experimental

2.1. Synthesis of S-PEEK

S-PEEK has been synthesized as previously described [18,20]. PEEK (450G extruded grade, Vitrex$^{®}$) was dried in a vacuum oven at 100 °C overnight. Thereafter, it was gradually added into vigorously stirred sulfuric acid (95–98%) in a glass

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reactor under argon atmosphere. The sulfonation was carried out at 35 °C for 12, 24, 36 and 48 h, respectively, in order to control the degree of sulfonation. After a predescribed time, the sulfonated polymer was recovered by precipitating the polymer solution into a large excess of ice-cold water under mechanical agitation. The polymer precipitate was isolated by filtration and washed successively with deionized water until the pH of rinse water was neutral. The obtained S-PEEK was then dried in a vacuum oven at 80 °C for 24 h. ^{1}H NMR spectra were obtained to determine the DS value of S-PEEK in DMSO-d_6 solvent on a Bruker-DRX-300 NMR spectrometer.

2.2. *Preparation of membrane and polymer electrolyte*

Dried S-PEEK was dissolved at a concentration of 20 wt.% in *N*,*N*-dimethylacetamide (DMAc). The resulting polymer solution was cast with a doctor blade onto a glass plate, and left to allow the solvent to evaporate slowly at room temperature for 24 h. The glass plate was put in water bath in order to promote the release of the polymer membrane, and the resulting membrane was finally dried in a vacuum oven at 60 °C for 24 h. The thickness of the dried membranes was in the range of 60–80 μm. The dried membrane was immersed in deionized water or 0.25 M H_2SO_4 solution. The liquid on the surface of wetted membrane was removed using tissue paper. The wetted S-PEEK membrane was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The ac impedance measurements were performed using an impedance analyzer (CH instruments, model 604A) over the frequency range 10 Hz–100 kHz. The ionic conductivity (σ) was calculated from the impedance data, using the relation $\sigma = t/RA$, where t and A are thickness and area of the polymer electrolyte film, respectively, and R was bulk resistance derived from the intersect on a complex impedance plane with the real axis.

2.3. *Cell assembly and electrochemical characterization*

Carbon electrode was prepared by coating on a titanium foil slurry containing activated carbon powder (MSC-30, Kansai Coke)(85 wt.%), super-P carbon (10 wt.%), carboxy methyl cellulose (CMC) (3 wt.%) and styrene–butadiene rubber (SBR) (2 wt.%) in aqueous medium. The electrode was roll-pressed to enhance particulate contact and adhesion to current collector. The thickness of electrodes was about 40 μm after roll-pressing, and their active area was 4 cm^2. EDLC was assembled by sandwiching the S-PEEK membrane soaked with sulfuric acid between two carbon electrodes. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. Cyclic voltammetry (CV) measurements were carried out in the potential range of 0–0.9 V. The scanning rates for CV were 5, 10, 20 and 50 mV s^{-1}. The charge and discharge cycling tests of EDLCs were conducted over a voltage range of 0–0.9 V with Toyo battery test equipment (TOSCAT-3000U) at room temperature.

3. Results and discussion

In order to determine DS of S-PEEKs obtained by varying reaction time, we tried to analyze ^{1}H NMR spectra of S-PEEKs. A typical ^{1}H NMR spectrum of S-PEEK in DMSO-d_6 is shown in Fig. 1. DS could be calculated from the relative integration of peak for hydrogen adjacent to sulfonic acid in hydroqunone segment of the polymer chain, as reported in details previously [16,18]. The aromatic hydrogen is significantly down-field shifted in the presence of a sulfonic acid group and the corresponding peak is distinctly observed at $\sigma = 7.51$ ppm. The DS value calculated from the ^{1}H NMR spectrum in Fig. 1 is 0.70. Here, DS is defined as the ratio of the sulfonated PEEK repeat unit to the total initial repeat unit of PEEK. DS values of S-PEEKs as a function of reaction time are summarized in Table 1. It can be seen that the sulfonation of PEEK increases with reaction time rapidly initially and progressed slowly thereafter, which is consistent with the kinetic behavior for sulfonation of PEEK [18,21,22]. At reaction time of 48 h, DS of 0.83 has been achieved. In this study, the four different S-PEEKs obtained will be designated according to their DS values as S-PEEK(58), S-PEEK(70), S-PEEK(78) and S-PEEK(83), respectively. We tested the solubility of S-PEEKs in water at room temperature; the results are also summarized in Table 1. It is found the solubility of S-PEEK in water increases with DS. This result is due to the fact that sulfonation not only increases the hydrophilicity but also reduces the crystallinity of the polymer. In the present work, DS has been limited to 0.83, in order to avoid mechanical deterioration of the polymer membrane due to its solubility in water. Moreover, the dry polymer membrane with higher DS than 0.83 was found to be brittle, which makes the sulfonated polymer not be suitable to prepare the mechanically stable membrane.

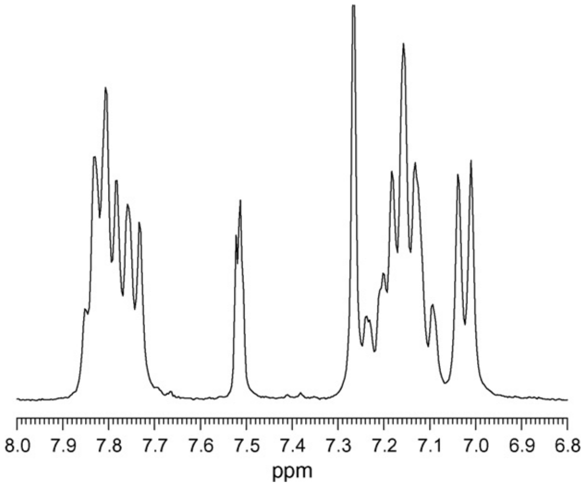

Fig. 1. ^{1}H NMR spectrum of S-PEEK(70) in DMSO-d_6.

Activated carbons of high specific surface area are very porous materials, and the radius of active pores is within

Table 1
DS and solubility of S-PEEKs with reaction time

Polymer designation	Reaction time (h)	DS	Solubility in water
S-PEEK(58)	12	0.58	Insoluble
S-PEEK(70)	24	0.70	Insoluble
S-PEEK(78)	36	0.78	Swelled
S-PEEK(83)	48	0.83	Partially soluble

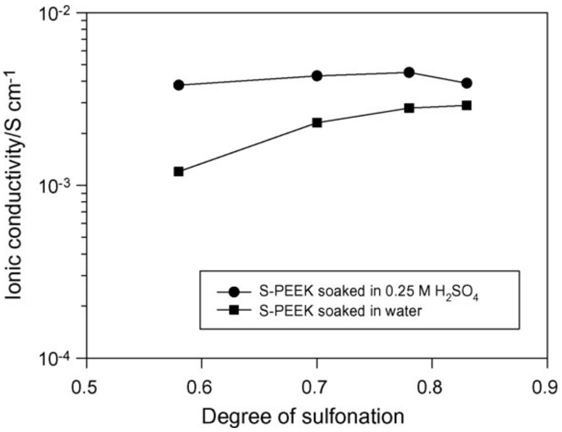

Fig. 2. Ionic conductivities of polymer electrolytes prepared with S-PEEK as a function of DS.

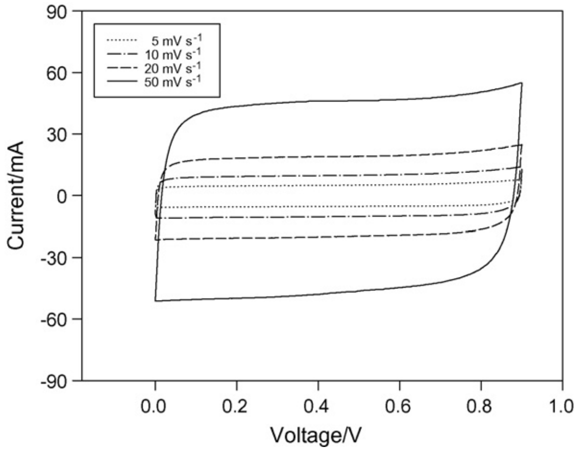

Fig. 3. Cyclic voltammograms of the EDLC assembled with S-PEEK(70) membrane.

nanometers. In the result, the polymer membrane must be filled with a liquid electrolyte, which forms the double layer at carbon electrodes. Thus, the S-PEEK membranes were immersed in deionized water or 0.25 M H_2SO_4 solution. Ionic conductivities of the polymer electrolytes prepared with S-PEEK membranes are shown in Fig. 2. Soaking solutions are observed to be well encapsulated in the polymer electrolyte due to their high affinity for S-PEEK. The polymer electrolytes prepared with H_2SO_4 solution exhibit higher ionic conductivity than those prepared with water. The higher values of ionic conductivities for the S-PEEK membranes soaked by H_2SO_4 solution can be attributed to the high concentration of ions dissociated in the sulfuric acid solution. It should be noted that the conductivity behavior with increasing the DS of S-PEEK is different for two systems. When soaked in water, the ionic conductivities are found to be increased with DS of S-PEEK. Since the number of available sulfonic acid groups in the polymer chain increases with DS, and water molecules can dissociate them and facilitate proton transport, the ionic conductivities increase with DS. On the other hand, the maximum conductivity is observed at DS of 0.78, when soaked in dilute H_2SO_4 solution. In case of soaking the S-PEEK membrane in H_2SO_4 solution, the number of mobile ions is so high that the effect of the number of sulfonic acid in the S-PEEK to affect the ionic conductivity may be negligible. The fall in ionic conductivity over 0.78 may be associated with a decrease of ionic mobility, which due to the increase of interactions among the polar $-SO_3H$ groups in the polymer chain. These results are important considering that the electrochemical performances of EDLC may be correlated to the ionic conductivity of the polymer electrolyte.

Cyclic voltammograms for EDLC assembled with S-PEEK are presented in Fig. 3, which are obtained at different scan rates. In this cell, the polymer electrolyte was prepared by soaking the S-PEEK(70) membrane in 0.25 M sulfuric acid. Unlike the fuel cell applications, EDLC needs both cations and anions to be adsorbed in electric double layer of the cell. So, the sulfuric acid was used as a soaking solution instead of water, when preparing the polymer electrolyte for application in EDLC. The almost rectangular shape of the curves shown in Fig. 3 suggests a nearly ideal behavior for the EDLC. Current value is found to increase with increasing scan rate, which is generally expected for EDLC, according to $I = C\mathrm{d}V/\mathrm{d}t$. The currents are very stable and unchanged through cycling, which indicates excellent reversibility of the electrochemical reaction. Cyclic voltammograms for EDLCs assembled with S-PEEK of different DS are presented in Fig. 4, which are obtained at scan rate of 10 mV s^{-1}. The almost similar CVs are observed, which indicates that the DS value of S-PEEK does not affect substantially the capacitive behavior of the EDLC, at a scan rate tested.

The EDLC assembled with S-PEEK(70) was subjected to charge/discharge cycling in voltage range of 0–0.9 V at a constant current density of 5 mA cm^{-2}, and its typical charge/discharge curves during the cycles (from 501 to 506th cycle) are given in Fig. 5. Almost linear charge and discharge curves are observed, which corresponds to those of the ideal EDLC. These curves are also in good agreement with those from the cyclic voltammograms shown in Fig. 3. The specific capacitance estimated from the curves was about 161 F g^{-1} based on weight of the activated carbon powder, and the value was maintained to be constant through cycling. Lufrano and Staiti [13] have reported the specific capacitance of EDLC with activated carbon having surface area of 1500 m^2 g^{-1} and Nafion

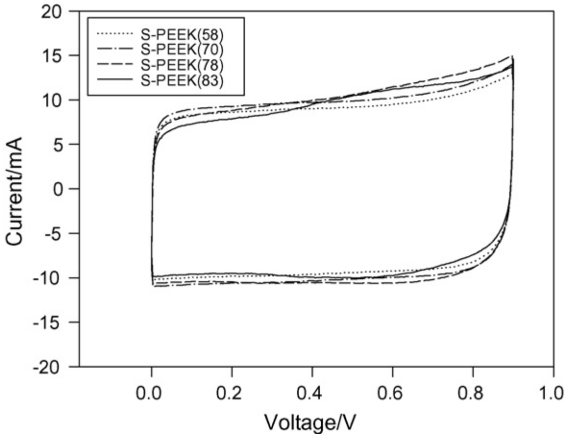

Fig. 4. Cyclic voltammograms of the EDLCs assembled with S-PEEK membranes of different DS. Scan rate is 10 mV s^{-1}.

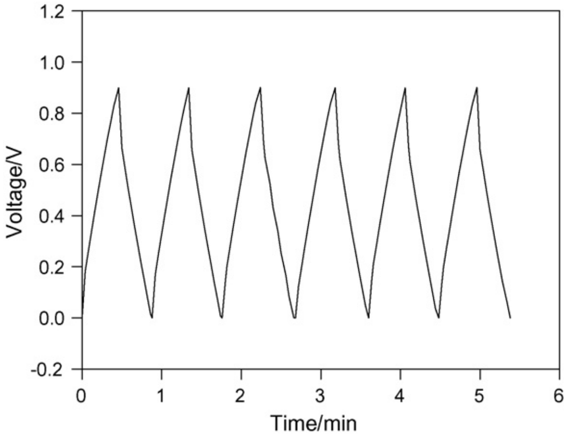

Fig. 5. Charge and discharge curves of EDLC at a current density of 5 mA cm^{-2} (501–506th cycles). The polymer electrolyte was prepared by soaking the S-PEEK(70) membrane with 0.25 M H_2SO_4 solution.

membrane as 132 F g^{-1} at same current rate. Higher specific capacitance obtained in our study may be ascribed to the higher surface area of activated carbon. The BET surface area of activated carbon (MSC-30) used in this work was measured to be about (3000 m^2 g^{-1}).

Fig. 6 shows the specific capacitance of EDLCs assembled with S-PEEK of different DS, as a function of cycle number, which are obtained at 5 mA cm^{-2}. It can be seen that the cycling performances of EDLCs are dependent on DS of S-PEEK. Initial capacitance of EDLC are almost the same, except for EDLC with S-PEEK(58). The cell assembled with S-PEEK(58) exhibited the lowest initial capacitance of 157 F g^{-1}. It is probable that sulfuric acid of the membrane distributes into the electrodes after cell assembling. We measured the content of sulfuric acid in the membrane and electrodes after cell assembling, and the results are summarized in Table 2. It is clearly seen that the cell assembled with S-PEEK(58) has the lowest acid content in both membrane and electrodes. Thus, the lower capacitance of EDLC prepared with S-PEEK(58) can be attributed to the low concentration of ions at the interface between electrode and electrolyte. In consideration of capacitance retention, the EDLC assembled with S-PEEK(70) showed the best cycle life among those studied in this work. This result suggests that the polymer electrolyte prepared with S-PEEK(70) is the most stable under charge–discharge cycles and keeping good interfacial contact with the activated carbon electrodes. Use of S-PEEK(58) is thought to be less effective for preventing the leakage of the sulfuric acid, due to the low capacity of the membrane to retain solution, thus could not maintain both the initial high ionic conductivity and the initial good contact between polymer electrolyte and carbon electrode. The large capacitance decline of EDLC assembled with S-PEEK of high DS can be ascribed the membrane degradation during cell operation. During prolonged cycle, the dimensional change of the S-PEEK membrane with high DS may occur due to its solubility in sulfuric acid, leading to deterioration of the interfacial contact between electrolyte and electrode.

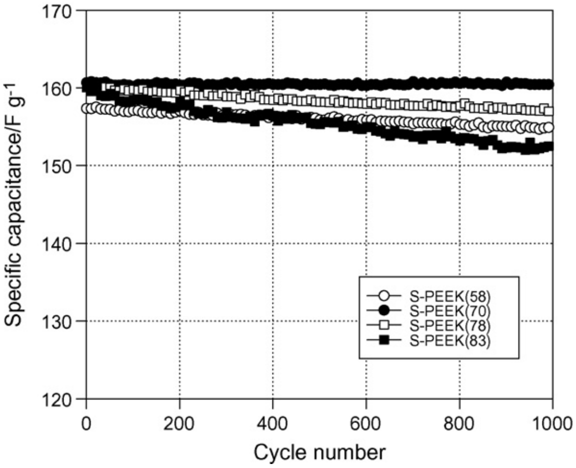

Fig. 6. Specific discharge capacitance as a function of cycle number for the EDLCs assembled with S-PEEK of different DS, which are obtained at a current density of 5 mA cm^{-2}.

Table 2
Sulfuric acid content in the membrane and electrodes after cell assembly

Membrane in the capacitor	Membrane (%)	Electrodes (%)
S-PEEK(58)	39.0	37.2
S-PEEK(70)	47.7	44.6
S-PEEK(78)	54.9	49.8
S-PEEK(83)	61.2	53.1

Rate capabilities of EDLCs assembled with S-PEEK were evaluated. The charge and discharge curves of EDLC prepared with S-PEEK(70) at different current rates are given in Fig. 7. The capacitance of the cell decreased slightly with increasing current density. At a current density of 20 mA cm^{-2}, the cell gave a specific capacitance of 157 F g^{-1}, which corresponds to 90% of the capacitance obtained at 1 mA cm^{-2}. Good performance at high current rate can be ascribed high ionic conductivity of polymer electrolyte and good electrolyte/electrode interface. Fig. 8 represents the specific capacitance of EDLCs assembled with S-PEEK of different DS, which are obtained at different current densities, ranging from 1 to 20 mA cm^{-2}. As shown in the figure, the cell with S-PEEK(78) has the highest capacitance at

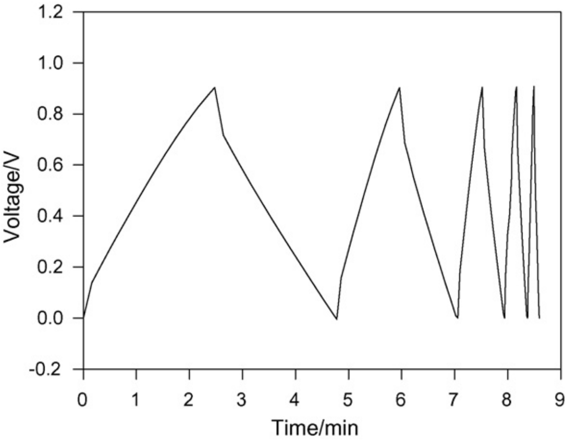

Fig. 7. Charge and discharge curves of EDLC prepared with S-PEEK(70), which are obtained at different current rates. Current density increases in order of 1, 2, 5, 10, 20 mA cm^{-2}.

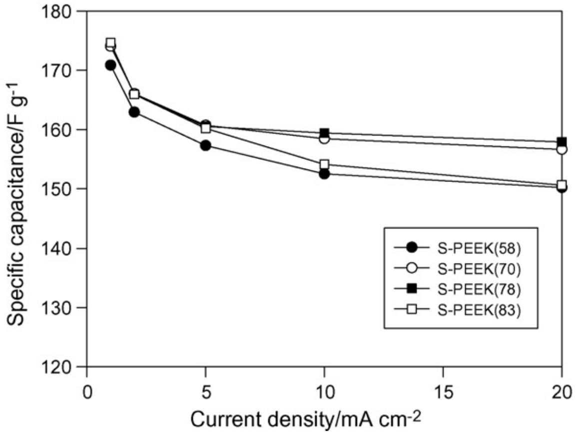

Fig. 8. Specific capacitance as a function of current density for the EDLCs assembled with S-PEEK of different DS.

high current rate. It is plausible that S-PEEK(83) membrane has a higher mass transport limitation than S-PEEK(78), due to the interactions among the polar $-SO_3H$ groups, as explained previously in Fig. 2. On the other hand, the low capacitance value of the EDLC with S-PEEK(58) at high current rate may be related to the higher resistance of the cell due to the lower uptake of sulfuric acid. From the results, it can be said that the use of S-PEEK with proper DS is effective in achieving high solution-holding capacity and maintaining fast ionic motion, which can result in good high rate performances.

4. Conclusions

Sulfonation of PEEK has been performed using sulfuric acid, and its degree of sulfonation was varied from 0.58 to 0.83. The S-PEEK membrane with sulfuric acid was used to prepare polymer electrolyte for EDLC application. The polymer electrolytes prepared with S-PEEK showed ionic conductivities exceeding $10^{-3}\,\mathrm{S\,cm^{-1}}$ and up to a maximum of $4.5 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at DS of 0.78. The quasi-solid-state EDLCs with activated carbon electrodes and S-PEEK membrane were prepared, and their electrochemical characteristics were studied. In consideration of cycle life and high rate performance, the S-PEEK with DS of 0.70 was most suitable for EDLC application. The lower performances of EDLCs prepared with lower and higher DS membranes could be explained with an insufficient acid content in the membrane and electrodes with the first membrane, and with the no-optimal mechanical property with the second membrane. The cell assembled with S-PEEK(70) showed an initial specific capacitance of $161\,\mathrm{F\,g^{-1}}$ with good capacitance retention and acceptable high rate performance. It is concluded that the S-PEEK membrane with proper DS can be a promising material to the development of the reliable and flexible EDLC with leakage-free, from practical point of view.

References

[1] A. Matsuda, H. Honjo, M. Tatsumisago, T. Minami, Solid State Ionics 113 (1998) 97.
[2] Y. Matsuda, K. Inoue, H. Takeuchi, Y. Okuhama, Solid State Ionics 113 (1998) 103.
[3] T. Osaka, X. Liu, M. Nojima, T. Momma, J. Electrochem. Soc. 146 (1999) 1724.
[4] H.B. Gu, J.U. Kim, H.W. Song, G.C. Park, B.K. Park, Electrochim. Acta 45 (2000) 1533.
[5] A. Lewandowski, M. Zajder, E. Frackowiak, F. Beguin, Electrochim. Acta 46 (2001) 2777.
[6] A. Lewandowski, A. Swiderska, Solid State Ionics 161 (2003) 243.
[7] P. Sivaraman, V.R. Hande, V.S. Mishra, C.S. Rao, A.B. Samui, J. Power Sources 124 (2003) 351.
[8] M. Morita, J.L. Qiao, N. Yoshimoto, M. Ishikawa, Electrochim. Acta 50 (2004) 837.
[9] H. Wada, S. Nohara, N. Furukawa, H. Inoue, N. Sugoh, H. Iwasaki, M. Morita, C. Iwakura, Electrochim. Acta 49 (2004) 4871.
[10] S.K. Tripathi, A. Kumar, S.A. Hashimi, Solid State Ionics 177 (2006) 2979.
[11] K.W. Park, H.J. Ahn, Y.E. Sung, J. Power Sources 109 (2002) 500.
[12] P. Staiti, M. Minutoli, F. Lufrano, Electrochim. Acta 47 (2002) 2795.
[13] F. Lufrano, P. Staiti, Electrochim. Acta 49 (2004) 2683.
[14] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29.
[15] G. Alberti, M. Casciola, Solid State Ionics 145 (2001) 3.
[16] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 173 (2000) 17.
[17] B. Yang, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A229.
[18] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, J. Membr. Sci. 229 (2004) 95.
[19] A. Basile, L. Paturzo, A. Iulianelli, I. Gatto, E. Passalacqua, J. Membr. Sci. 281 (2006) 377.
[20] D.W. Kim, J.M. Ko, W.J. Kim, J.H. Kim, J. Power Sources 163 (2006) 300.
[21] N. Shibuya, R.S. Porter, Polymer 35 (1994) 3237.
[22] R.Y.M. Huang, P. Shao, C.M. Burns, X. Feng, J. Appl. Polym. Sci. 82 (2001) 2651.