Cellulose Triacetate-Based Polymer Gel Electrolytes

Jung Min Lee,[1,2] Dinh Quan Nguyen,[1] Seul Bee Lee,[1] Honggon Kim,[1] Byoung Sung Ahn,[1] Hyunjoo Lee,[1] Hoon Sik Kim[2]

[1]Energy and Environment Research Division, Korea Institute of Science and Technology, Seongbuk-gu, Seoul 136-791, Republic of Korea
[2]Department of Chemistry and Research Institute of Basic Sciences, Kyung Hee University, Dongdaemoon-gu, Seoul 130-701, Republic of Korea

ABSTRACT: New composite polymer gels were obtained from cellulose triacetate (CTA), N-methyl-N'-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr$_{1,3}$TFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Analysis by differential scanning calorimeter and scanning electron microscope showed that the ionic gel consisting of CTA, Pyr$_{1,3}$TFSI, and LiTFSI formed a completely homogeneous phase at the molar ratio of CTA/Pyr$_{1,3}$TFSI/LiTFSI = 1/3/1.5. The ionic conductivity of the polymer gel was significantly enhanced by the presence of LiTFSI. FTIR study strongly implies that the interaction of lithium ion with the carbonyl group of CTA could be responsible for the increase in conductivity. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 32–36, 2010

Key words: cellulose triacetate; gel electrolyte; ionic liquid; lithium conduction; lithium battery

INTRODUCTION

Current lithium ion rechargeable battery systems confront an inherent safety problem arising from the use of volatile and flammable organic carbonates as electrolyte solvents.[1,2] As alternatives to carbonate-based liquid electrolytes, solid polymer electrolytes (SPEs) have been extensively studied,[3–5] but their commercial application of SPEs has been restricted because of their poor ion conductivities at ambient temperature.[6–8] Accordingly, much effort has been made to improve the conductivities of SPEs and as a result some significant advance has been achieved by employing a concept of polymer gel electrolytes (PGEs).[9–12] PGEs are particularly attractive from a practical point of view because of their high conductivity, excellent chemical and thermal stability, and ease of preparation. In spite of these advantages of PGEs, there still exists an inherent safety problem by the presence of flammable organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), and N-methyl pyrrolidone (NMP), which is prerequisite for the preparation of gel electrolytes.[13,14]

Recently, many attempts have been made to use ionic liquids (ILs) to replace flammable organic chemicals because of their unique and favorable physical and electrochemical properties including nonflammability, high ion conductivity, and wide electrochemical window.[15,16] Especially, dialkyl-substituted cyclic quaternary ammonium-based ILs such as N-methyl-N'-propylpyrrolidinium bis(trifluoromethanesulfonyl) imide (Pyr$_{1,3}$TFSI) and N-methyl-N'-propylpiperidinum bis(trifluoromethanesulfonyl) imide (PP$_{1,3}$TFSI) have been used for this purpose.[17,18]

In previous papers, we reported that the lithium ion conduction in an IL-containing electrolyte can be improved to a certain extent by introducing an ester group on the cation of the IL, which is able to interact with lithium ion.[19,20] Being motivated by these results, we have investigated the effect of ester group on the property of PGEs. Cellulose triacetate (CTA), a biorenewable resource, was chosen as a polymer because it contains both ether and ester functional groups in the molecule that could interact with lithium ions. CTA is being used in diverse areas as optical film for displays, separation membranes, and thermoplastic materials because of its high melting point, high mechanical strength, and excellent film-forming properties,[21–23] but, to our knowledge, CTA has been scarcely considered as a candidate material for the gel polymer electrolyte.

Herein, we report on the preparation and physical and electrochemical properties of PGEs composed of CTA, Pyr$_{1,3}$TFSI, and LiTFSI.

EXPERIMENTAL

Materials

NMP (97%), CTA (acetyl content 43–49 wt %), 1-bromopropane (99%) were purchased from Aldrich Chemical (USA) and used as received. LiTFSI (98%) was obtained from TCI (Japan). Solvents were received from J.C. Baker (USA) and distilled before use. $Pyr_{13}TFSI$ was prepared according to the literature procedure.[24]

Preparation of gel electrolytes

A typical preparation of a PGE was as follows: LiTFSI (0.33 g, 1.15 mmol) dissolved in acetone (10 mL) was slowly added to a 100 mL flask containing a solution of CTA (0.22 g, 0.765 mmol) and $Pyr_{1,3}TFSI$ (1.25 g, 2.30 mmol) in CH_2Cl_2 (20 mL) and then stirred vigorously for 2 h until the solution became homogeneous. The total weight of three ingredients, LiTFSI, CTA, and $Pyr_{1,3}TFSI$, was set at 1.8 g to maintain the thickness of the resulting gel between 90 and 140 μm. The homogeneous solution was cast onto a mold made of polytetrafluoroethylene (PTFE). Slow evaporation of solvents in a nitrogen flow at room temperature produced a highly flexible and self-standing transparent film (thickness: 90–140 μm) (Fig. 1). Thus obtained film was further dried in vacuum oven and then stored in a glove box under an argon atmosphere. Other PGEs with different molar ratio of $CTA/Pyr_{1,3}TFSI/LiTFSI$ were similarly obtained.

Measurements

Thermal properties of the prepared gel electrolytes were determined by means of a TA Instruments Q10
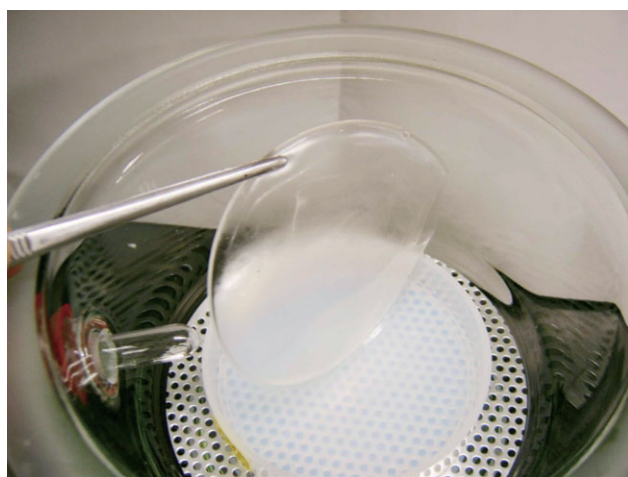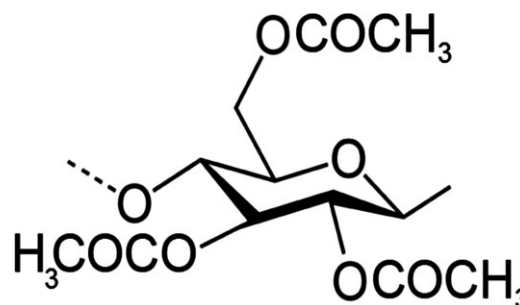

Figure 1 A photograph of the CTA-$Pyr_{1,3}$TFSI-LiTFSI gel (CTA : $Pyr_{1,3}$TFSI : LiTFSI = 1 : 3 : 1.5). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Scheme 1 A repeating unit of cellulose triacetate.

differential scanning calorimeter (DSC) in the range from −80 to 150°C at a scan rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was conducted using a Metter TGA 50 in a nitrogen atmosphere at a heating rate of 10°C/min. FTIR spectra were recorded on a Perkin-Elmer Spectrum GX spectrophotometer using a specially designed gas cell to avoid the contact with water and air.[25] The ionic conductivity data was obtained with a Solatron 1260A frequency response analyzer. The scanning electron micrograph (SEM) was performed on a XL-30 ESEM (FEI Company).

RESULTS AND DISCUSSION

The PGE films were fabricated by a casting method. The solution was prepared by mixing an acetone solution of LiTFSI with dichloromethane solution of CTA and Pyr_{13}TFSI because LiTFSI is sparingly soluble in dichloromethane. The molar ratio of $CTA/Pyr_{1,3}TFSI/LiTFSI$ was calculated by assuming that the repeating unit of CTA was glucose-based six-membered ring (Scheme 1). Table I shows the list of PGEs obtained at various molar ratios of $CTA/Pyr_{1,3}TFSI/LiTFSI$.

Each component of the three ingredients of a PGE seemed to play a crucial role in determining the thermal properties, flexibility, and mechanical

TABLE I
Gel Electrolytes Composed of CTA, $Pyr_{1,3}$TFSI, and LiTFSI

CTA : $Pyr_{1,3}$TFSI : LiTFSI (molar ratio)[a]	Conductivity (mS/cm, 30°C)	Remark
1 : 2 : 1	Not detected	Hard
1 : 3 : 0	Not detected	Flexible
1 : 3 : 0.75	0.923	Wet gel
1 : 3 : 1 (Gel A)	0.322	Flexible
1 : 3 : 1.25 (Gel B)	0.231	Flexible
1 : 3 : 1.5 (Gel C)	0.155	Flexible
1 : 4 : 0	Not detected	Flexible
1 : 4 : 1 (Gel D)	0.447	Flexible
1 : 4 : 2	n/a	Too soft to handle

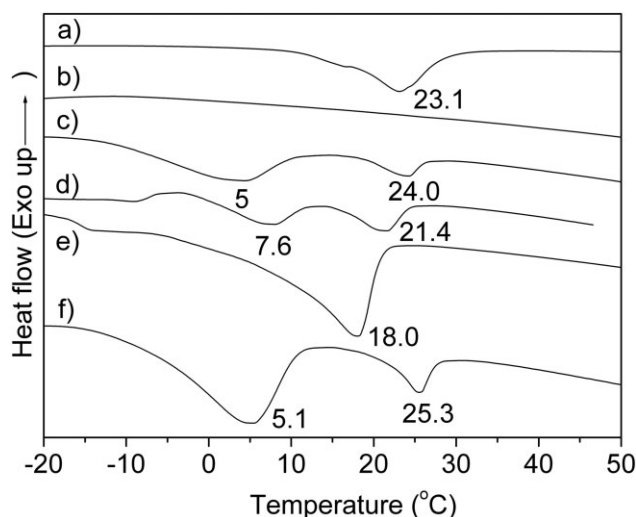[a] In the case of CTA, one repeating unit of 6-membered ring was regarded as a monomer.

Figure 2 DSC thermograms of (a) $Pyr_{1,3}TFSI$, (b) CTA : $Pyr_{1,3}TFSI$: LiTFSI = 1 : 3 : 0, (c) 1 : 3 : 1 (Gel A), (d) 1 : 3 : 1.25 (Gel B), (e) 1 : 3 : 1.5 (Gel C), and (f) 1 : 4 : 1 (Gel D).

strength of the resulting films. Of various PGEs prepared, Gel A–D was selected for further measurements.

Thermal properties of the gels were investigated using DSC and the results were shown in Figure 2. $Pyr_{1,3}TFSI$ exhibited a characteristic melting point at 23.1°C, whereas CTA only showed a T_g at around 125°C. In the absence of LiTFSI, the melting point of $Pyr_{1,3}TFSI$ was not detected for the gel composed of only CTA and $Pyr_{1,3}TFSI$ at the molar ratios of 1 to 3, suggesting CTA is compatible with $Pyr_{1,3}TFSI$. Interestingly, lithium salt-incorporated Gel A and Gel D exhibited an endothermic peak corresponding to the melting point of the free ionic liquid (23–25°C) together with a new peak centered in the vicinity of 5.3°C. The endothermic peak at 5.3°C and the melting point at 24.0°C for gel A (LiTFSI/CTA = 1) shifted to 7.6 and 21.4°C, respectively, for gel B (LiTFSI/CTA = 1.25). However, at the molar ratio of CTA/IL/LiTFSI = 1/3/1.5 (Gel C), only a single peak was detected at 18°C, indicating CTA, IL, and LiTFSI form a completely compatible gel at this composition.

The surfaces of the prepared PGEs were investigated by SEM (Fig. 3). The gels consisting of only CTA and $Pyr_{1,3}TFSI$ showed clean surface images at the SEM picture as shown in Figure 3(a,b). This is in good agreement with the results observed in the DSC experiments. In contrast, microscaled liquid droplets of $Pyr_{1,3}TFSI$ were observed at the surface of the Gels A, B, and D. The amounts of these liquid drops seemed to increase with the increasing contents of $Pyr_{1,3}TFSI$ and LiTFSI in the gel. As can be expected from the DSC study, the SEM picture of Gel C clearly demonstrates that the PGE with the molar ratio of CTA/$Pyr_{1,3}TFSI$/LiTFSI = 1/3/1.5

formed a completely compatible ternary system of a polymer, IL, and a lithium salt.

DSC and SEM experiments may imply that the structure of CTA changes with the incorporation of the lithium salt, possibly through an interaction of lithium ions with the carbonyl groups of CTA.

Such an interaction was supported by an IR experiment. The experiment was conducted in the absence of $Pyr_{1,3}TFSI$, because of the peak overlaps in the region of interest. As shown in Figure 4, the peak associated with the carbonyl group of CTA shifted to a lower frequency from 1751.1 to 1731.8 cm^{-1} upon interaction with one equivalent of LiTFSI. At the same time, the stretching frequency assigned to C—O single bond moved to a higher frequency from 1052 to 1064.5 cm^{-1}. However, at the molar ratio of LiTFSI/CTA = 2, the carbonyl stretching frequency remained unchanged, but C—O frequency shifted further to a higher frequency at 1070.5 cm^{-1}, possibly due to an increased resonance between the carbonyl group and C—O single bond as depicted in Scheme 2.
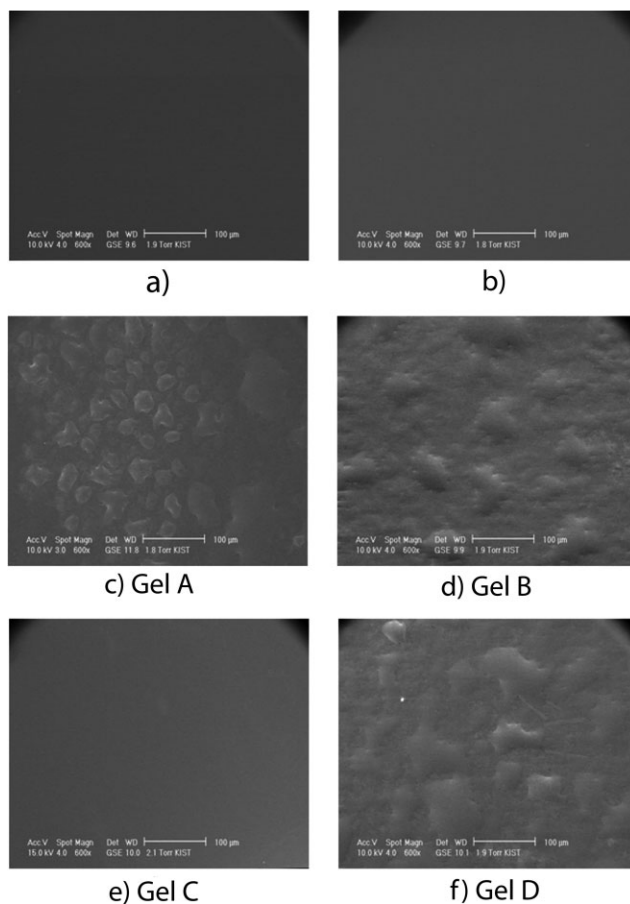

Figure 3 SEM images (×600) of the gels containing (a) CTA : $Pyr_{1,3}TFSI$: LiTFSI = 1 : 3 : 0, (b) 1 : 4 : 0, (c) 1 : 3 : 1 (Gel A), (d) 1 : 3 : 1.25 (Gel B), (e) 1 : 3 : 1.5 (Gel C), and (f) 1 : 4 : 1 (Gel D).
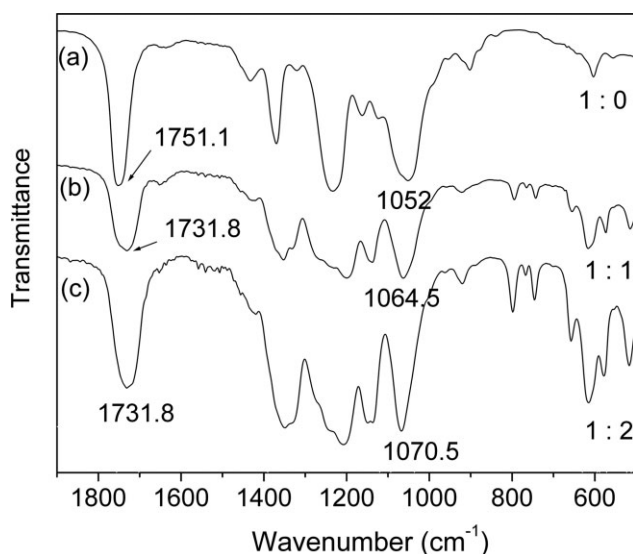
Figure 4 FTIR spectra showing the interaction of cellulose triacetate with LiTFSI: (a) CTA, (b) CTA : LiTFSI = 1 : 1, and (c) CTA : LiTFSI = 1 : 2.

The interaction between CTA and LiTFSI can be further supported from the TGA thermograms. As can be seen in Figure 5, all the gels exhibit two distinct decomposition temperatures at about 278°C and 451°C. The higher temperature is likely to be resulted from the decomposition of $Pyr_{1,3}TFSI$ and the lower one can be associated with the decomposition of CTA that decomposes at 366°C in the absence of a lithium salt. The lowering of the decomposition temperature of CTA from 366 to 278°C strongly indicates that thermal property of CTA was modified by the presence of LiTFSI and/or ionic liquid. To investigate the origin of the change in decomposition temperature of CTA, two different gels, CTA-LiTFSI (CTA/LiTFSI = 1/2) and CTA-$Pyr_{1,3}TFSI$ (CTA/$Pyr_{1,3}TFSI$ = 1/2) were prepared and their thermal stabilities were evaluated (see Supporting Information). The results on the thermal stability clearly revealed that the decomposition of CTA was affected only by LiTFSI, not by
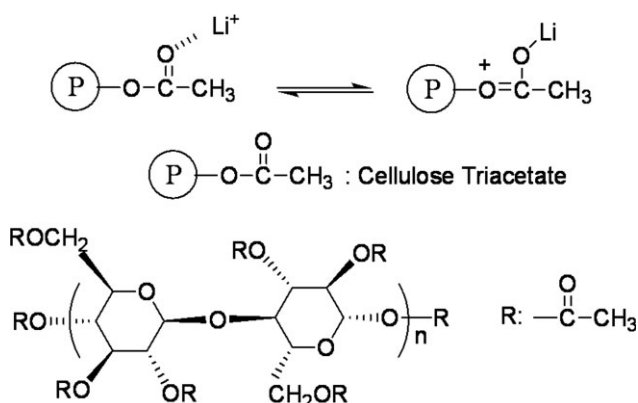
Scheme 2 Interaction between Li^+ and a carbonyl group on the backbone of CTA.
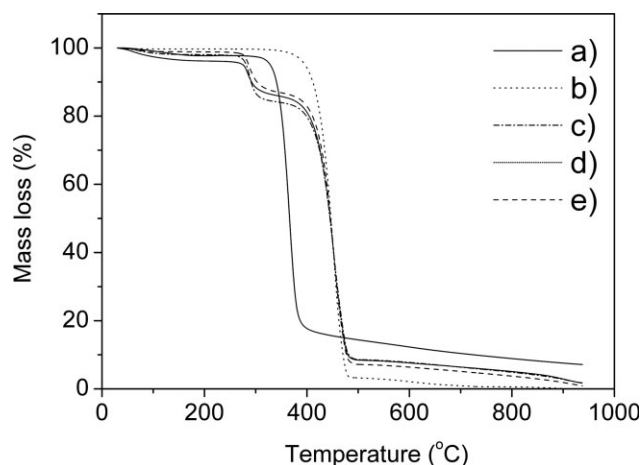

Figure 5 TGA data of (a) CTA, (b) $Pyr_{1,3}TFSI$, (c) CTA : $Pyr_{1,3}TFSI$: LiTFSI = 1 : 3 : 1 (Gel A), (d) 1 : 3 : 1.5 (Gel C), and (e) 1 : 4 : 1 (Gel D).

$Pyr_{1,3}TFSI$. The TGA experimental results also proved that PGEs consisting of CTA, $Pyr_{1,3}TFSI$, and LiTFSI are thermally stable enough.

The conductivities of the prepared PGEs were measured as a function of temperature using impedance analyzer (Fig. 6). All the PGEs prepared from CTA, $Pyr_{1,3}TFSI$, and LiTFSI showed relatively high ionic conductivities of 10^{-3}–10^{-4} S/cm. As expected, at the constant molar ratio of CTA/LiTFSI, the conductivity increased with the increasing content of $Pyr_{1,3}TFSI$, possibly due to the plasticizing effect of the ionic liquid. On the contrary, the increase of the lithium content decreased the conductivity of the gels. This could be attributed to the reduced concentration of the ionic liquid. The gels consisting of only CTA and LiTFSI showed negligible conductivity in the measured temperature range. The conductivities of the gels consisting of CTA and $Pyr_{1,3}TFSI$ were also
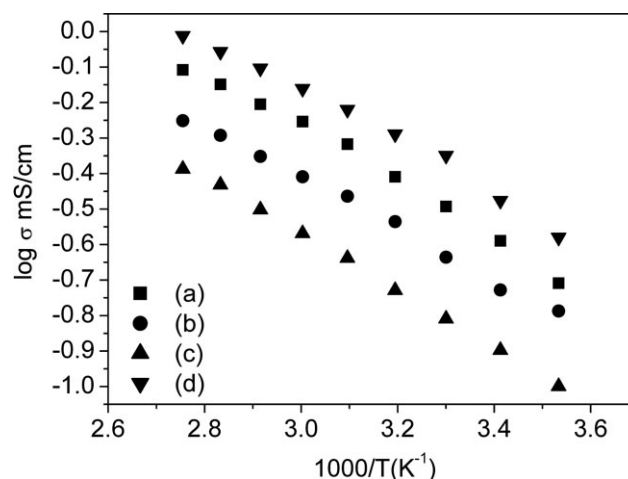

Figure 6 Conductivities of the gels containing (a) CTA : $Pyr_{1,3}TFSI$: LiTFSI = 1 : 3 : 1 (Gel A), (b) 1 : 3 : 1.25 (Gel B), (c) 1 : 3 : 1.5 (Gel C), and (d) 1 : 4 : 1 (Gel D).

too low to be detected even at 80°C in the absence of LiTFSI, even though $Pyr_{1,3}TFSI$ itself is known as an ion-conducting material.

From the IR experiments and conductivity measurements, it is likely that the conductivity of the gel is the result of the combined interactions among CTA, $Pyr_{1,3}TFSI$ and LiTFSI. The dissociation of LiTFSI into Li^+ and $TFSI^-$ is likely to be facilitated through the interactions with the carbonyl groups, and the mobility of dissociated lithium ions seems to be enhanced by the presence of $Pyr_{1,3}TFSI$.

The galvanostatic charge–discharge test was performed in one-stack laminated cell consisting of a $LiCoO_2$ cathode, a lithium foil anode, and CTA-$Pyr_{1,3}TFSI$-LiTFSI film (Gel C) as the electrolyte. However, the cell died soon after the operation at 0.5°C, possibly due to the decomposition of electrolyte on the cathode.

CONCLUSIONS

Cellulose triacetate-based polymer gels containing $Pyr_{1,3}TFSI$ and LiTFSI exhibit relatively high lithium ion conductivities and excellent mechanical strengths. An unique and homogeneous gel phase was obtained at the molar ratio of CTA/$Pyr_{1,3}TFSI$/LiTFSI = 1/3/1.5. From the experimental and FTIR results, it is concluded that the ester group of CTA is responsible for the dissociation of LiTFSI through the interactions with the carbonyl groups, and $Pyr_{1,3}TFSI$ is in charge of the mobility of dissociated lithium ions.

References

1. Xu, K. Chem Rev 2004, 104, 4303.
2. Lee, J. S.; Bae, J. Y.; Lee, H. J.; Quan, N. D.; Kim, H. S.; Kim, H. G. Ind Eng Chem 2004, 10, 1086.
3. Armand, M. Solid State Ionics 1994, 69, 309.
4. Johnson, P. L.; Kennedy, M. W.; Smith, C. M.; Truong, N.; Teeters, D. Electrochim Acta 2007, 53, 1490.
5. Kuila, T.; Acharya, H.; Srivastava, S. K.; Samantaray, B. K.; Kureti, S. Math Sci Eng B 2007, 137, 217.
6. Scrosati, B.; Croce, F.; Persi, L. J Electrochem Soc 2000, 147, 1718.
7. Watanabe, M.; Kanda, M.; Matsuda, H.; Tsumemi, K.; Tsuchida, E.; Shinohara, I. Makromol Chem Rapid Commun 1981, 2, 741.
8. Sutto, T. E. J Electrochem Soc 2007, 154, P101.
9. Meyer, W. H. Adv Mater 1998, 10, 439.
10. Bohnke, O.; Rousselot, C.; Gillet, P. A.; Truche, C. J. Electrochem Soc 1992, 139, 1862.
11. Lemaitre-Auger, F.; Prud'homme, J. Electrochim Acta 2000, 46, 1359.
12. Hayamizu, K.; Aihara, Y.; Arai, S.; Garcia-Martinez, C. J. Phys Chem 1999, 103, 519.
13. Mohamed, S. N.; Johari, N. A.; Ali, A. M. M.; Harun, M. K.; Yahya, M. Z. A. J Power Sources 2008, 183, 351.
14. Sato, T.; Marukane, S.; Narutomi, T.; Akao, T. J Power Sources 2007, 164, 390.
15. Galiński, M.; Lewandowski, A.; Stępniak, I. Electrochim Acta 2006, 51, 5567.
16. Diaw, M.; Chagnes, A.; Carré, B.; Willmann, P.; Lemordant, D. J Power Sources 2005, 146, 682.
17. Howlett, P. C.; McFarlane, D. R.; Hollenkamp, A. F. Electrochem Solid State Lett 2004, 7, A97.
18. Byrne, N.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. Adv Mater 2005, 17, 2497.
19. Stephan, A. M. Eur Polym Mater 2006, 42, 21.
20. Nguyen, D. Q.; Hwang, J.; Lee, J. S.; Kim, H.; Lee, H.; Cheong, M.; Lee, B.; Kim, H. S. Electrochem Commun 2007, 9, 109.
21. Lee, J. S.; Quan, N. D.; Hwang, J. M.; Bae, J. Y.; Kim, H.; Cho, B. W.; Kim, H. S.; Lee, H. Electrochem Commun 2006, 8, 460.
22. Kozlowski, C. A. Desal 2006, 198, 132.
23. Wallner, G. M.; Hausner, R.; Hegedys, H.; Schobermayr, H.; Lang, R. W. Sol Energy 2006, 80, 1410.
24. Sakaebe, H.; Matsumoto, H. Electrochem Commun 2003, 5, 594.
25. Quinn, H. W.; McIntyre, J. S.; Peterson, D. J. Can J Chem 1965, 43, 2896.