

Imidazolium-Organic Solvent–Alkali Metal Salt Mixtures as Nonflammable Electrolytes Incorporated into PVDF–PEG Polymer Electrolyte

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ABSTRACT: A mixture of flammable organic solvent, alkali metal salt, and nonflammable room temperature ionic liquid has been used as a new type of electrolyte. A novel microporous polymer electrolyte based on poly(vinylidene fluoride), i.e., PVDF, and poly(ethylene glycol), i.e., PEG, was prepared by a simple phase-inversion technique. The mixed electrolyte was observed to be nonflammable at ionic liquid contents of 60 vol % or greater. The viscosity

(range, 0.98–30.5 mPa s) and conductivity (range, 9.9 to 22.25 mS cm⁻¹) of the mixed electrolyte were discussed. The porosity, solution uptake, and conductivity mechanism of polymer membranes also were discussed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2492–2498, 2009

Key words: ionic liquid; polymer electrolyte; organic solvent; PVDF; PEG

INTRODUCTION

Electrolytes are of profound interest to chemists and engineers because of their application in electrochemical devices such as fuel cells, batteries, and sensors. The science of polymer electrolytes is a highly specialized interdisciplinary field that encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. The field has attracted ever-increasing interest both in academia and industry.^{1–3} At present, polymer electrolytes mainly include three types: solid-polymer electrolytes, gel-polymer electrolytes, and microporous-polymer electrolytes. Many microporous-polymer electrolytes comprising polymer matrices, plasticizing organic solvents, and alkali metal salts have been intensively studied for applications in rechargeable lithium batteries and other electrochemical devices.^{4,5}

Most microporous polymer electrolyte contains ethylencarbonate (EC), dimethylcarbonate (DMC), and diethylcarbonate (DEC) with lithium hexafluorophosphate as lithium salt.⁶ EC/DMC/DEC-based electrolytes permit numerous charging and discharg-

ing cycles without significant loss in capacity, but their thermal stability is a safety problem at high temperatures (60°C or greater) because of their volatility (DEC and DMC) and flammability.

Ionic liquids (ILs) are organic salts with unusually low melting points, well less than 100°C. These substances have been suggested as potentially “green” replacements for traditional molecular solvents because they are nonvolatile, nonflammable, thermally stable, and recyclable.⁷ Their unique properties favor applications in diverse fields, such as synthesis, catalysis, biocatalysis, separation technology, electrochemistry, analytical chemistry, and nanotechnology. The use of ILs may be an alternative to classical electrolytes for lithium batteries because of their low vapor pressure, their nonflammability, and their wide electrochemical window.⁸ Nonflammable liquid electrolytes that use room temperature ILs (RTILs) have been developed, and the performance of cells that use RTIL has been investigated. The electrochemical stability of the RTIL was found to be sufficient for lithium cells. However, some limitations still remain for application to cells for high-power use, for example hybrid electric vehicles and fuel cell electric vehicles, because of the high viscosity and low ionic conductivity of the electrolyte.⁹

Recently, the use of mixed electrolytes of organic solvents and RTILs has been investigated to improve the safety of lithium-ion cells that incorporate flammable organic solvents.^{10,11} Butyrolactone has been

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mixed with RTIL 1-butyl 3-methyl-imidazolium tetrafluoroborate (BMIBF₄) (ratio 3 : 2, v/v) in the presence of lithium tetrafluoroborate (LiBF₄) for use as an electrolyte in lithium-ion batteries. The cycling ability of this electrolyte has been investigated as a graphite, a titanate oxide (Li₄Ti₅O₁₂), and a cobalt oxide (Li_xCoO₂) electrodes.¹⁰ It is reasonable to think that the RTIL can function as a flame-retardant additive.

In the present work, we report the preparation and characterization of microporous poly(vinylidene fluoride)-poly(ethylene glycol) (PVDF-PEG) polymer electrolytes with imidazolium-organic solvent mixtures. The viscous, conductivity, and flammability of the imidazolium-organic solvent-alkali metal salt mixtures were discussed. The porosity, weight uptake, and ionic conductivity of PVDF-PEG electrolytes also were discussed.

EXPERIMENTAL

Materials

Methylimidazole was purchased from KaiLe Chemical Company (Zhejiang, China) and distilled under reduced pressure before use. PVDF ($M_w = 900,000$) was obtained from Shanghai 3F New Material (Shanghai City, China) and dried in a vacuum oven at 100°C for 48 h before use. PEG ($M_w = 10,000$) was purchased from Shanghai Pudong Yamei Chemical Company (Shanghai, China). The ES-002 electrolyte solution (EC/DMC/EMC: 1 : 1 : 1/1 v/v/v 1M LiPF₆) was purchased from Shanghai Tuer Industry Development (Shanghai, China). The conductivity of this electrolyte is 9.9 mS cm⁻¹. 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄) was synthesized in our laboratory.¹² Other chemicals were obtained from commercial suppliers and used without further purification.

Preparation of the mixed electrolyte

The mixed electrolyte was prepared by adding predetermined amounts of EMImBF₄ to the organic solvent mixture (EC/DMC/EMC 1 : 1 : 1/1 v/v/v 1M LiPF₆). The mixed electrolyte was a homogeneous liquid over the entire composition.

Flammability of the mixed electrolyte

To confirm the safety of the mixed electrolyte, the flammability of the mixture was examined.¹¹ A glass filter was soaked with the electrolyte, and the flame of an alcohol lamp was then brought close to the filter. The interval between the glass filter and the wick of alcohol lamp was kept at 100 mm. After 10 s, the alcohol lamp was removed from under the

glass filter. The electrolyte was judged to be non-flammable if the electrolyte never ignited during the testing or if the ignition of electrolyte ceased when the flame was removed. Each electrolyte was tested three times.

Preparation of PVDF-PEG polymer membrane

The PVDF-PEG microporous membranes were prepared by a phase inversion method.⁴ Desired amounts of PVDF and PEG were dissolved in a mixture of DMF (solvent) and glycerin (nonsolvent) (v/v = 10/1). After stirring for 4 h at 80°C, the resulting homogeneous solutions were cast onto a glass plate and then placed in an oven at 120°C for 36 h. This procedure yielded mechanically stable, free-standing films of thickness ranging from 100 to 300 μm. TG analysis confirmed that both solvent and nonsolvent evaporated completely during the aforementioned preparation process. In this experiment, the weight ratio of PVDF to PEG is 1.

Characterization

Viscosity measurements were performed with a Rotating viscometer (NDS-8S). Conductivity measurements were conducted with a PM6303 impedance analyzer operating at 1000 Hz and a conductivity cell equipped with platinum electrodes.

Pore distribution and pore structure in the surface and bulk of PVDF-PEG microporous membranes were studied by scanning electron microscopy (SEM) with a field emission scanning electron microscope (JSM-6701F) with gold sputtered coated films. To observe the cross section of the samples, the membranes were broken in liquid nitrogen.

The porosity was measured by immersing the membrane into 1-butanol for 2 h, after which the membrane surface was dried by filter paper. The membrane was weighed before and after absorption of 1-butanol. The porosity was calculated by the use of eq. (1):

$$\text{Porosity (\%)} = 100 \times (w_t - w_0) / \rho V \quad (1)$$

where w_t and w_0 are the weight of the wet and dry membrane, respectively. V is the apparent volume of the membrane. ρ is the density of 1-butanol.

The liquid electrolyte uptake of PVDF-PEG microporous membranes was measured in a simple glove box. The electrolyte membrane was cut into a disk with a diameter of 1 cm. After the mass (w_0) of the membrane disk was measured, it was soaked in mixed electrolyte for 48 h to obtain the wetted polymer electrolyte. After the remaining solution at the surface of the wetted polymer electrolyte membrane was absorbed with filter paper, the membrane was

weighed (w_t). In this study, the mixed electrolyte solution uptake was calculated by the following eq. (2):

$$\text{Weight uptake (\%)} = 100 \times (w_t - w_0)/w_0 \quad (2)$$

where w_t and w_0 are the weight of the wet and dry membrane, respectively.

The ionic conductivity of the polymer electrolyte was determined by AC impedance spectroscopy at room temperature. The samples were sandwiched between stainless steel blocking electrodes. The impedance measurements were carried out on an Automatic Component Analyzer (TH2818) with a frequency range of 20 Hz to 300 kHz.

RESULTS AND DISCUSSION

Flammability of the mixed electrolyte

Table I shows the results of flammability testing on mixed electrolyte containing EMImBF₄ and ES-002 electrolyte. It is reported that the flash point of linear-chained carbonates is near ambient temperature (for example, the flash point of DMC is 16°C, and that of EMC is 24°C), and they are easily ignited.¹¹ In this work, the conventional ES-002 electrolyte (0 vol % ratio of EMImBF₄) ignited and continued burning for 10 s every time, since the organic solvent is flammable at the ambient temperature. To add EMImBF₄ in the mixed electrolyte, the content of the organic solvent is decreased. At a 60 vol % ratio of EMImBF₄, the mixed electrolyte appeared to be non-flammable, even though it contained 40 vol % flammable organic solvent.

This result can be explained because the partial pressure of the flammable gas (ie, the organic solvent vapor) around the test flame was decreased by the addition of nonflammable EMImBF₄, and was brought under the range of flammability.¹¹ Therefore, it is concluded that EMImBF₄ may be applicable as flame-retardant additives to improve the safety of cells incorporating organic electrolytes.

TABLE I
Results of Flammability Testing of Mixed Electrolyte Containing the Mixed Electrolyte

Content of EMImBF ₄ (vol %)	Occurrence of ignition
0	3/3
20	3/3
40	2/3
60	0/3
80	0/3
100	0/3

Each sample was tested three times.

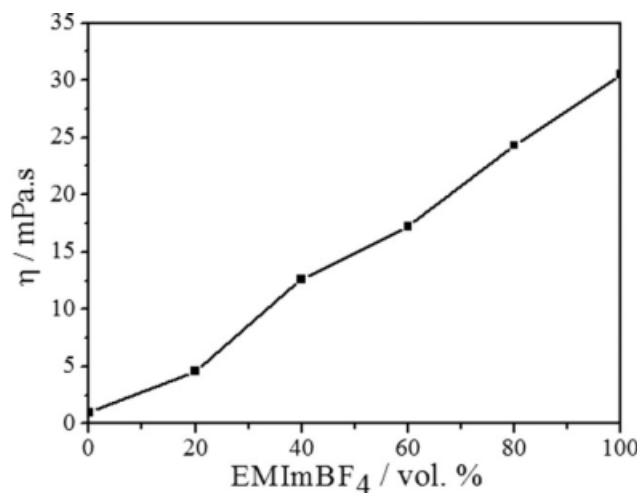


Figure 1 Viscosity of the mixed electrolyte vs. vol % (EMImBF₄).

Viscosities and conductivities

Viscosity studies provide a useful insight on the mobility of ions in liquid or gel electrolytes. Pure ILs are highly viscous and exhibit relatively low conductivities. The viscosity of an IL depends on hydrogen bonding and the van der Waals force, but mainly on hydrogen bonding.¹³ ILs that contain the hexafluorophosphate anion are more viscous than ILs that contain the tetrafluoroborate anion, as the result of stronger interactions in solution. Conductivity of the IL is related to the molecular weight, density, size of ions, and especially viscosity. The viscosity of IL may be decreased by adding some organic solvents.

Figures 1 and 2 display the results of viscosity and conductivity of the mixed electrolyte as a function of EMImBF₄ content, respectively. The addition

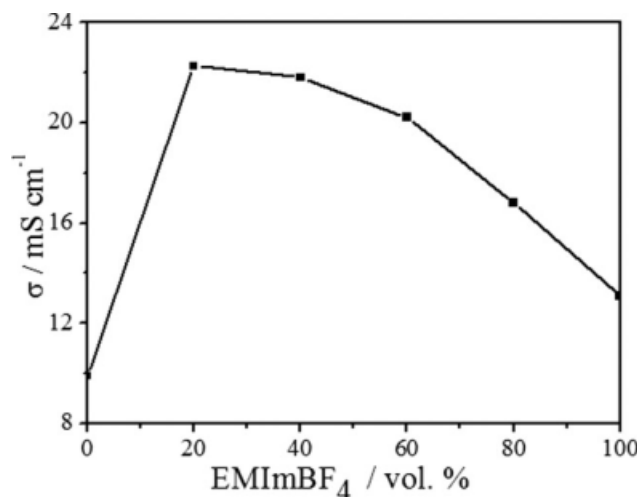


Figure 2 Conductivity of the mixed electrolyte vs. vol % (EMImBF₄).

of an organic solvent to these ILs results in a lower viscosity and an enhanced ionic conductivity. To increase the permittivity of the electrolyte and hence to improve ion dissociation, ES-002 solution was used as cosolvent. It is worth noting that with the increasing amount of EMImBF₄, the viscosity of the mixed electrolyte can be increased to 30.5 mPa s. For example, the addition of ES-002 electrolyte solution to EMIBF₄ decreases drastically the viscosity from 30.5 mPa s for EMIBF₄ to 4.6 mPa s for the mixed electrolyte (vol % (EMIBF₄) = 20) at 25°C. Simultaneously, the conductivity increases from 13.1 mS cm⁻¹ for EMIBF₄ to 22.25 mS cm⁻¹ for the mixed electrolyte (vol % (EMIBF₄) = 20) at 25°C.

In this experiment, considering the results of non-flammability, viscosities and conductivities, we fixed the optimal composition of the mixed electrolyte is obtained when 60 vol % EMImBF₄ added to 40 vol % ES-002 electrolyte solution.

Scanning electron microscopy

It has been reported that morphology of the film cast from solution is influenced by polymer-solvent complex formation, solution preparation temperature, sol-

vating power, solvent evaporation temperature, and solvent evaporation rate.¹⁴⁻¹⁶ The pore structure usually is controlled by the phase inversion process and is discussed in terms of the liquid-liquid phase separation such as nucleation-growth and spinodal decomposition.¹⁷⁻¹⁹ The morphology of the membrane plays a fundamental role in the transport of ions through the porous matrix and, therefore, in conductivity behavior. The porous membranes were prepared by the phase-inversion method. This process creates a polymer-rich phase that forms the solid membrane structure and a polymer-poor phase that forms the liquid-filled pores of the membrane.²⁰

It is well known that during coating process, there is always one surface of the membrane facing the air whereas the other one faces the substrate. Thus, these two surfaces may differ in morphology to some extent. Usually, the surface facing the air looks rough, whereas the surface facing the substrate appears smoother, as shown in Figure 3(a). Figure 3(b) presents SEM images of the top surface of PVDF-PEG membranes. It can be seen that the formed membrane exhibits an asymmetric morphology. Those cellular pores are largely independent and are embedded in a continuous polymer matrix. Figure 3(c) shows the cross-section SEM

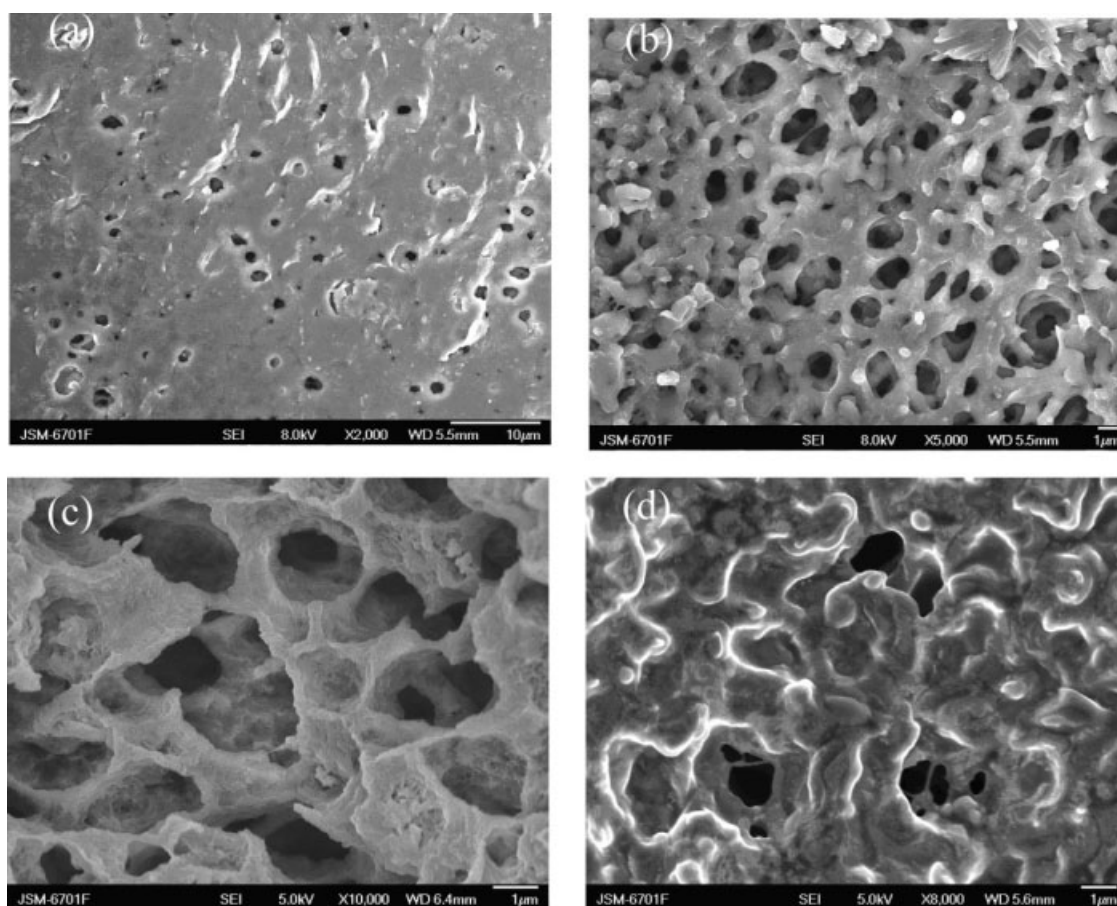


Figure 3 SEM images of polymer membrane and the gels after immersion in the mixed electrolyte: (a) bottom surface; (b) top surface; (c) cross-section; (d) gel of polymer membrane.

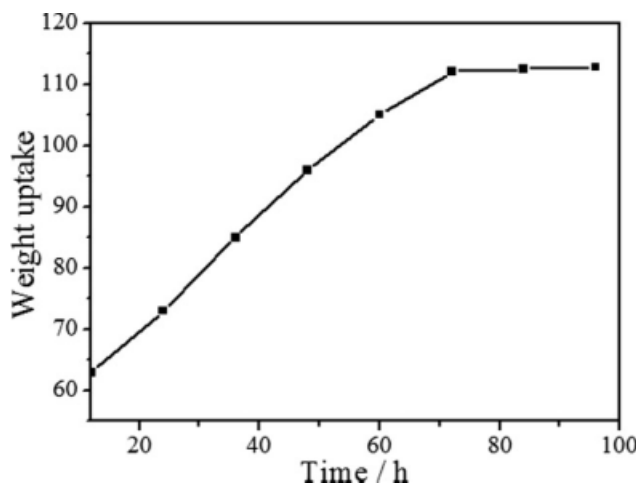


Figure 4 Weight uptake of the mixed electrolyte vs. time.

micrographs of polymer films. It is worth noting that the honeycomb structure is different from the finger-like structure, in which channels of different sizes are separated by layers of discrete polymer globules.²¹ Figure 3(d) shows the surface morphology of the polymer membrane after immersion. It is worth to note that many small pores disappear as compared to Figure 3(b). This result may contribute to the swelling of polymer. Swelling is the process of dissolution of a polymer in a defined solvent. At first, the solvent molecules slowly diffuse into the polymer to produce a swollen gel. If the polymer–polymer intermolecular forces are high, thanks to crosslinking, crystallinity, or strong hydrogen bonding, this is all what happens. However, if these forces are overcome by the introduction of strong polymer–solvent interactions, a second stage, the dissolution of the polymer, can take place. The process of swelling results actually from the balance between repulsive and attractive phenomena. Overall, polymer–solvent systems tend to reach the minimum of the Gibbs energy of mixing, G_{mix} , which is the driving force of the process.

In this experiment, the solvent DMF has a C=O functional group, which is the main factor for polymer solvent interaction via the interaction of the C=O dipole with the CH_2CF_2 dipole or by limited hydrogen bond. Apart from the pure geometrical effect of confinement, the properties of ILs might also be influenced interaction with the polymer matrix. Detailed mechanism for the swell of PVDF and PEG in the mixed electrolyte containing EMImBF₄ and ES-002 electrolyte solution is beyond the scope of the current work.

Porosity and solution uptake

Ionic conductivity in the conventional battery separator is achieved by continuous pathways formed by

the absorbed liquid electrolyte within the interconnected pores of the separator. Thus pore structure is an important factor that determines the ionic transport of polymer membranes. The porosity (48.6%) of the membrane formed by phase inversion was determined by eq. (1). Figure 4 displays the weight uptake at different immersing time. It can be seen that the weight uptake increases with the increasing immersing time and then reach to equilibrium state. It is worth to note that the maximum weight uptake is obtained after a 72-h gelation period. This immersing time is longer than the conventional organic electrolyte. This result may be attributed to the fact the mixed electrolyte shows higher viscosity (17.2 mPa s) than conventional organic electrolyte (0.98 mPa s).

Ionic conductivities

The ionic conductivity (σ) was then calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and the electrode area (A) according to the equation $\sigma = l/AR_b$.

Impedance data are presented in the form of imaginary, Z'' (capacitive) against real, Z' (resistive). Figure 5 displays the typical impedance plots (Z' vs. Z''). It can be seen that the entire semicircular portion in the complex impedance representation measured at room impedance plots was disappeared, leading to a conclusion that the total conductivity is mainly the result of ion conduction. This phenomenon is quite reasonable because the facile mobility in liquid- and gel-type electrolyte systems, when compared with solid-polymer electrolytes, indicates that ions possess dielectric relaxation times and, hence, the inconsequential capacitive effect of the bulk electrolyte in the spectrum.²²

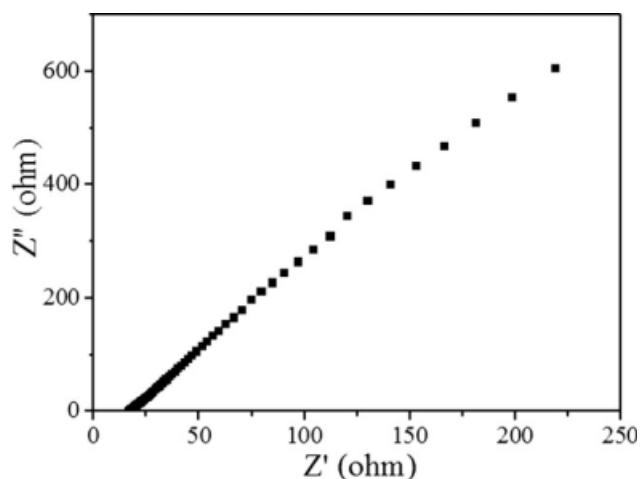


Figure 5 Room temperature (25°C) impedance plots of PVDF-PEG polymer membrane (soaking with the mixed electrolyte).

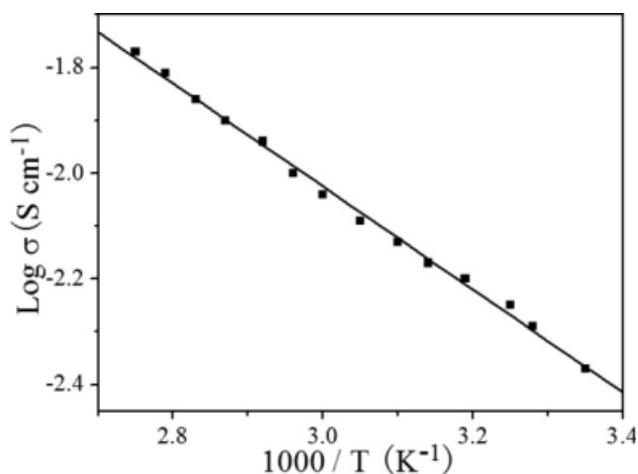


Figure 6 Arrhenius plots of PVDF-PEG polymer electrolyte.

In this experiment, the maximum conductivity (4.2 mS cm⁻¹) was obtained after a 72-h immersion in the mixed electrolyte.

Carrier migration in the porous structure can be restricted because of the convoluted transport pathways that comprise interconnected pores. The restricted condition in migration is affected by pore size, porosity, pore linking condition, and chemical effect of the porous medium on the carriers.²³ It is reported that the confinement of the IL into the polymer matrix affects the basic physical properties and in this way is a factor in the overall decrease of the conductivity. The origin of the decrease in conductivity is to be sought both in the morphology of the membrane and in possible interactions between the conducting IL and the polymer matrix.²⁴

It is reported that the interaction between the salt (and/or ion) and the polymer in the gel dominates the mobility and concentration of the carrier in the PVDF type gel.^{25,26} The conduction properties of the PEO type polymer electrolyte without solvent have been studied previously in detail.²⁷ It was confirmed that the cations were solvated by coordination to the ether oxygen on the polymer chains. As a result, the motion of the cation is strongly correlated with the segmental motion of the polymer chain. In this experiment, it is reasonable to think that the interaction between the polymer and the salt influences carrier migration even in a gel composed of PEG. The dissociated Li ions interact with the polymer through Coulombic force. The Li⁺ would be effectively trapped at the oxygen sites on the polymer chains. As a result, the Li⁺ tends to hop on the sites along the chains supported by the segmental motion of the chain rather than migrates randomly in the liquid. The increasing conductivity may also partly be explained in terms of a hopping mechanism between coordinating sites, local structural relaxa-

tions, and segmental motions of PEG. It is necessary to note that PVDF is polymorphic polymer, and it can be crystallized in polar form. However, although it is crystallized in nonpolar form at the formation of porous structure, the ties between crystallites may be stressed and have TTTT-conformations. These factors may strongly influence on ionic conductivity and interphase polarization in PVDF (the processes take place in polymer material between pores).²⁸

Figure 6 shows an Arrhenius plot of PVDF-PEG polymer electrolyte. It is quite obvious from the figure that the ionic conductivity of PVDF-PEG polymer electrolyte increases with increase in temperature. Nevertheless, the ionic conduction mainly depends on the entrapped liquid phase in a fully interconnected pore structure and the gel phase. The fact that the conductivity perfectly follows a VTF behavior implies that the motion of the charged species, anions and cations, is controlled by the viscous properties of the mixed electrolyte. These curves appear linear, so the apparent activation energy for the ions transport (E_a) are obtained using the Arrhenius model $\sigma = \sigma^0 \exp(-E_a/RT)$, where R , T , σ , and σ^0 are gas constant, temperature, the ionic conductivity of PVDF-PEG polymer electrolyte, and the preexponential factor, respectively. According to this equation, the activation energy (19.16 kJ mol⁻¹) for the ions transport can be calculated from the slope of imitated straight line. The activation energy for the conduction of PVDF-based electrolytes (19.16 kJ mol⁻¹) is still larger than that of their neat electrolytes (<8.0 kJ mol⁻¹), which may imply that the influence of PVDF upon ionic mobility still exists even if they have been made nanoporous.²²

CONCLUSIONS

EMImBF₄ mixed with conventional organic electrolyte was prepared as a new concept nonflammable electrolyte. Flammability testing results indicate that EMImBF₄ has potential as a flame-retardant additive for the organic electrolytes, which can improve the safety of battery. The morphology, porosity, weight uptake, and ionic conductivity of PVDF-PEG polymer electrolyte also were discussed. The maximum conductivity 4.2 mS cm⁻¹ can be obtained, which is sufficient for the application. This new concept nonflammable electrolyte may have potential use in polymer electrolyte.

References

- Li, Z. H.; Zhang, P.; Zhang, H. P.; Wu, Y. P.; Zhou, X. D. *Electrochem Commun* 2008, 10, 791.
- Rajendran, S.; Ramesh Prabhu, M.; Usha Rani, M. *J Appl Polym Sci* 2008, 110, 1945.

3. Zhang, H.; Zhou, Z. *J Appl Polym Sci* 2008, 110, 1756.
4. Xi, J.; Qiu, X.; Li, J.; Tang, X.; Zhu, W.; Chen, L. *J Power Sources* 2006, 157, 501.
5. Wang, Y.-P.; Gao, X.-H.; Wang, R.-M.; Liu, H.-G.; Yang, C.; Xiong, Y.-B. *React Funct Polym* 2008, 68, 1170.
6. Geoffroy, I.; Willmann, P.; Mesfar, K.; Carré, B.; Lemordant, D. *Electrochim Acta* 2000, 45, 2019.
7. Weingärtner, H. *Angew Chem Int Ed* 2008, 47, 654.
8. Hu, Y.; Li, H.; Huang, X.; Chen, L. *Electrochem Commun* 2004, 6, 28.
9. Sakaebe, H.; Matsumoto, H.; Tatsumi, K. *J Power Sources* 2005, 146, 693.
10. Chagnes, A.; Diaw, M.; Carré, B.; Willmann, P.; Lemordant, D. *J Power Sources* 2005, 145, 82.
11. Nakagawa, H.; Fujino, Y.; Kozono, S.; Katayama, Y.; Nukuda, T.; Sakaebe, H.; Matsumoto, H.; Tatsumi, K. *J Power Sources* 2007, 174, 1021.
12. Lewandowski, A.; Widerska, A. *Solid State Ionics* 2004, 169, 21.
13. Bonhote, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg Chem* 1996, 35, 1168.
14. Benz, M.; Euler, W. B.; Gregory, O. J. *Langmuir* 2001, 17, 239.
15. Barnes, M. D.; Ng, K. C.; Fukui, K.; Sumpter, B. G.; Noid, D. W. *Macromolecules* 1999, 32, 7183.
16. Young, T. H.; Huang, J.-H.; Chuang, W.-Y. *Eur Polym J* 2002, 38, 63.
17. Young, T. H.; Lin, D.-T.; Chen, L.-Y.; Huang, Y.-H.; Chiu, W.-Y. *Polymer* 1999, 40, 5257.
18. Young, T. H.; Lai, J.-Y.; You, W.-M.; Cheng, L.-P. *J Membr Sci* 1997, 128, 55.
19. Boom, R. M.; Wienk, I. M.; van den Boomgaard, T.; Smolders, C. A. *J Membr Sci* 1992, 73, 277.
20. Kimmerle, K.; Strathmann, H. *Desalination* 1990, 79, 283.
21. Quartarone, E.; Mustarelli, P.; Magistris, A. *J Phys Chem B* 2002, 106, 10828.
22. Song, J. Y.; Wang, Y. Y.; Wan, C. C. *J Electrochem Soc* 2000, 147, 3219.
23. Saito, Y.; Hirai, K.; Emori, H.; Murata, S.; Uetani, Y.; Kii, K. *J Phys Chem B* 2004, 108, 1137.
24. Martinelli, A.; Matic, A.; Jacobsson, P.; Borjesson, L.; Fericola, A.; Panero, S.; Scrosati, B.; Ohno, H. *J Phys Chem B* 2007, 111, 12462.
25. Saito, Y.; Kataoka, H.; Capiglia, C.; Yamamoto, H. *J Phys Chem B* 2000, 104, 2189.
26. Saito, Y.; Kataoka, H.; Stephan, A. M. *Macromolecules* 2001, 34, 6955.
27. Meyer, W. H. *Adv Mater* 1998, 10, 439.
28. Gregorio, R.; Ueno, E. M. *J Mater Sci* 1999, 34, 4489.