Two-Cation Competition in Ionic-Liquid-Modified Electrolytes for Lithium Ion Batteries

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It is a common observation that when ionic liquids are added to electrolytes the performances of lithium ion cells become poor, while the thermal safeties of the electrolytes might be improved. In this study, this behavior is investigated based on the kinetics of ionic diffusion. As a model ionic liquid, we chose butyldimethylimidazolium hexafluorophosphate ($BDMIPF_6$). The common solvent was propylene carbonate (PC), and lithium hexafluorophosphate ($LiPF_6$) was selected as the lithium conducting salt. Ionic diffusion coefficients are estimated by using a pulsed field gradient NMR technique. From a basic study on the model electrolytes ($BDMIPF_6$ in PC, $LiPF_6$ in PC, and $BDMIPF_6 + LiPF_6$ in PC), it was found that the $BDMI^+$ from $BDMIPF_6$ shows larger diffusion coefficients than the Li^+ from $LiPF_6$. However, the anionic (PF_6^-) diffusion coefficients present little difference between the model electrolytes. The higher diffusion coefficient of $BDMI^+$ than that of Li^+ suggests that the poor C-rate performance of lithium ion cells containing ionic liquids as an electrolyte component can be attributed to the two-cation competition between Li^+ and $BDMI^+$.

1. Introduction

As energy densities and performances of lithium ion batteries are continually improving, the accompanying safety issues are considered to be a major concern. Volatile and flammable liquid electrolytes are believed to be a main cause for the safety problems. Among many efforts to improve the safety of lithium ion batteries, employing an ionic liquid (i.e., room-temperature molten salt) as an electrolyte component has been recommended as one of the promising candidates.[1−9] Nonflammability and negligible vapor pressure of ionic liquids are expected to mitigate violent thermal properties of lithium-salt-based liquid electrolytes. It has been often reported that while ionic-liquid-added electrolytes may have the possibility of improving thermal safeties of lithium ion batteries, they tend to worsen C-rate performances especially when combined with a carbon anode.[6−9] This problem is believed to be mainly due to the ionic liquid's reactivity with a carbon anode such as the cointercalation of cations and more facile reduction than the electrolyte solvents.[4−9] However, there has been no report for explaining the poor C-rate performances of ionic-liquid-modified electrolytes from the kinetic viewpoint of the ion transport mechanism.

The pulsed field gradient NMR (PFG-NMR) technique is known to give a direct measurement of translational self-diffusion coefficients with good accuracy and reliability.[10−13] In the PFG-NMR technique, all of the diffusing species such as the cation, anion, and solvent can be measured by choosing the appropriate nuclei for NMR experiments. Therefore, the PFG-NMR data can provide an insight for understanding the ion transport mechanism of ionic-liquid-modified electrolytes.

In this study, among various kinds of ionic liquids, $BDMIPF_6$ was chosen as a representative example of ionic liquids due to its good thermal stabilities against a charged $LiCoO_2$ cathode.[14] The chemical structure of $BDMIPF_6$ is shown schematically below.
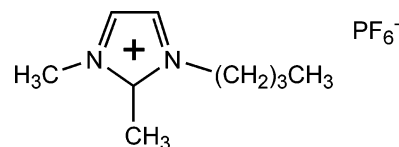
The C-rate performances of lithium ion cells employing the butyldimethylimidazolium hexafluorophosphate ($BDMIPF_6$)-added electrolyte (i.e., 10 wt % of $BDMIPF_6$ in 1 M lithium hexafluorophosphate ($LiPF_6$) in propylene carbonate (PC) solvents) were measured and discussed on the basis of the ion transport mechanism. To give a more fundamental basis to this investigation, a study on the model electrolytes, $BDMIPF_6$ in PC, $LiPF_6$ in PC, and $BDMIPF_6 + LiPF_6$ in PC, has been conducted.

2. Experimental Section

Fabrication and Characterization of Cells. One-stack laminated cells consisting of a $LiCoO_2$ cathode and a graphite carbon anode were assembled using the lithium ion polymer battery technology of LG Chem,[19] where 10 wt % of the $BDMIPF_6$ (purity > 99%, H_2O content < 30 ppm, C-Tri, South Korea) was added into conventional 1 M $LiPF_6$-based carbonate mixtures (Mitsubishi Chemical, Japan). The capacities and the C-rate performances of the cells were examined with discharge rates from 0.2 C (15.2 mA) to 2 C (152.0 mA) at a constant charge rate of 0.5 C (38.0 mA) between 3.0 and 4.2 V.

Preparation of Model Electrolytes. One-salt electrolytes ($BDMIPF_6$ in PC and $LiPF_6$ in PC) were prepared by dissolving $BDMIPF_6$ and $LiPF_6$ into PC, respectively, and stirring vigorously for several hours. The molar concentrations of $BDMIPF_6$ and $LiPF_6$ in PC are varied from 0.25 to 1.5 M. In addition to the one-salt electrolytes, the two-salt mixture electrolyte ($BDMIPF_6 + LiPF_6$ in PC) was also prepared. The molar ratio between $BDMIPF_6$ and $LiPF_6$ is 1.0 (0.5 mol/0.5 mol), and the molar concentration of total salts in PC is controlled at 1.0 M. All of the reagents were handled in a glovebox under argon atmosphere.

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Viscosity and Conductivity Measurements. The ionic conductivities of BDMIPF$_6$/PC and LiPF$_6$/PC were measured by a Metrohm 712 conductometer at 25 °C. The dynamic viscosities of BDMIPF$_6$/PC and LiPF$_6$/PC were measured using a vibration-type digital viscometer VM-100-L (Yamaichi Electronics Co., Ltd.) at 25 °C.

NMR Measurements. The self-diffusion coefficients of BDMI$^+$, PF$_6^-$, and Li$^+$ were obtained from the echo signal attenuation of the ^{1}H, ^{31}P, and ^{7}Li NMR spectra. The change in the echo signal intensity is described as follows[15,16]

$$I = I_0 \, e^{-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3 - \tau/2)} \tag{1}$$

where I is the observed intensity, I_0 the reference intensity without a field gradient, D the diffusion coefficient, γ the gyromagnetic ratio, g the gradient strength, δ the duration of the gradient pulse, Δ the time interval between the two gradient pulses, and τ the time interval between the bipolar gradients.

The PFG-NMR measurements were performed on Bruker DRX-600 spectrometer with the Bruker broad-band-inverse (BBI) probes equipped with a gradient coil. The sample cells were composed of two concentric glass tubes, i.e., a 5-mm tube and a Shigemi tube containing the sample solution and the acetone-d_6 for the signal locking. The gradient strength was calibrated to 6.95 G/(cm A), using the self-diffusion coefficient of H$_2$O.[16,17] The ^{1}H, ^{31}P, and ^{7}Li NMR spectra were acquired at 600.13, 242.90, and 233.23 MHz, respectively, using the stimulated echo pulse sequences with bipolar pulsed field gradients. The $\pi/2$ pulse widths were 11.5 μs for ^{1}H, 22 μs for ^{31}P, and 17.5 μs for ^{7}Li. Typical acquisition parameters were Δ = 100−200 ms for ^{1}H and 400−1000 ms for ^{31}P and ^{7}Li and δ = 1−4 ms for ^{1}H, ^{31}P, and ^{7}Li. In all cases, 8−32 transients were recorded with recycle delays of 4−5 s for the 16 different gradient strengths. All of the measurements were carried out at 25 °C.

3. Results and Discussion

The effect of 10 wt % BDMIPF$_6$-added electrolyte on the performances of lithium ion batteries is examined (Figure 1). In comparison to the pristine electrolyte (1 M LiPF$_6$ in the carbonate mixtures), a cell containing the BDMIPF$_6$ shows a poor initial capacity and a significant decrease in capacity as the charge/discharge rate increases. It is consistent with previous observations that ionic-liquid-modified electrolytes deteriorate C-rate performances of lithium ion batteries.[6−9]

As a first step to explain this interesting behavior, we investigated ion transport kinetics for two model electrolytes, BDMIPF$_6$ in PC and LiPF$_6$ in PC. The ionic conductivities of BDMIPF$_6$/PC and LiPF$_6$/PC are compared in Figure 2a. The LiPF$_6$/PC shows a maximum ionic conductivity around 1.0 M salt concentration. It is well-known that the existence of maximum ionic conductivity in LiPF$_6$/PC is attributed to the tradeoff effect between the increased number of solvated ions and their decreased mobility.[20] In contrast, the ionic conductivity of BDMIPF$_6$/PC exhibits a completely different behavior, an apparent proportionality to BDMIPF$_6$ concentration. Figure 2b shows that the viscosity of LiPF$_6$ solution in PC increases with salt concentration, which indicates the existence of a strong interaction between dissociated ions and PC molecules. The viscosities of BDMIPF$_6$/PC are lower than those of LiPF$_6$/PC over the examined concentration range and appear to remain constant. This indicates that the dissociated ions from BDMIPF$_6$ exhibit weaker interaction with PC molecules, which may in turn lead to poorer solvation of dissociated ions. This little
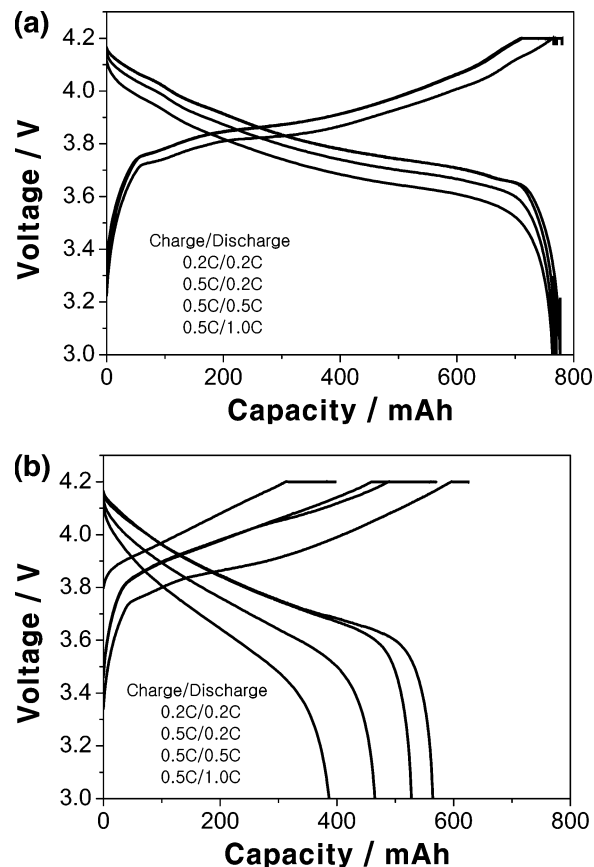
Figure 1. Charge/discharge profiles of (a) 1 M LiPF$_6$-based electrolytes (control) and (b) 1 M LiPF$_6$-based electrolytes containing 10 wt % of BDMIPF$_6$. The C-rate performances of the cells were examined with discharge rates from 0.2 C (15.2 mA) to 2 C (152.0 mA) at a constant charge rate of 0.5 C (38.0 mA) between 3.0 and 4.2 V.

change of viscosity with BDMIPF$_6$ concentration in the BDMIPF$_6$/PC suggests that the ionic conductivity of BDMIPF$_6$/PC may be affected predominantly by the number of dissociated ions rather than the viscosity, resulting in ionic conductivity being proportional to the BDMIPF$_6$ concentration.

The diffusion coefficients of each ion species in the BDMIPF$_6$/PC and the LiPF$_6$/PC were compared by using the PFG-NMR technique. Since the ionic conductivities of the electrolytes are known to depend on the number and the mobility of dissociated ions, it will be more reasonable to discuss diffusion coefficients as a function of the degree of dissociation rather than molar concentration of salt. The relative degree of dissociation ($\Lambda m/\Lambda m°$) is obtained by the following equation[21]

$$1/\Lambda m = 1/\Lambda m° + \Lambda m C/(K_a(\Lambda m°)^2) \tag{2}$$

where C is the salt concentration, $1/\Lambda m$ the molar ionic conductivity at different salt concentrations, $1/\Lambda m°$ the limiting molar ionic conductivity at an extremely dilute salt concentration ($C \rightarrow 0$), and K_a the ionization constant. From a plot of $1/\Lambda m$ as a function of $\Lambda m C$, the limiting molar ionic conductivity ($\Lambda m°$) can be obtained and thereby the relative degree of dissociation.

The diffusion coefficients for each ion species are plotted versus the relative degree of dissociation (Figure 3). It is interesting to note that the anion (PF$_6^-$) shows almost the same diffusion coefficients for both electrolyte salts over the complete range of dissociations. In contrast, the cations show quite a different behavior; the diffusion coefficients of BDMI$^+$ are much larger than those of Li$^+$ at comparable degrees of dissociation.

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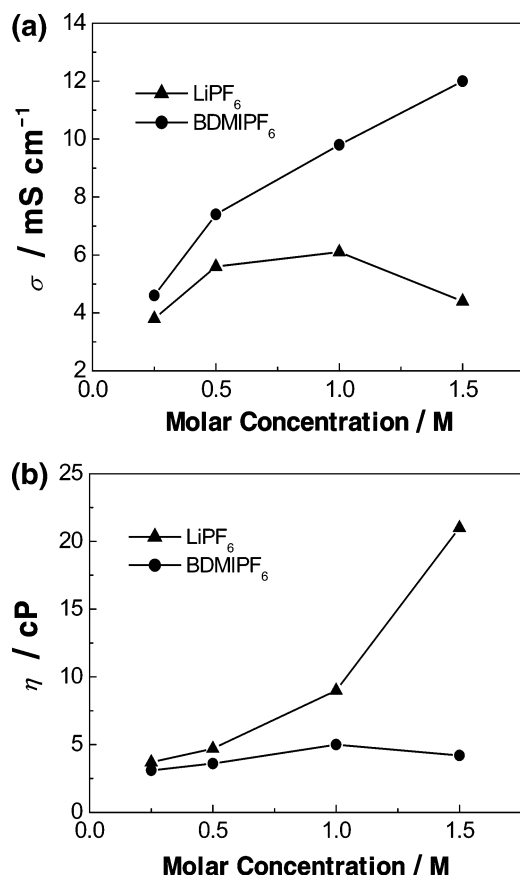
Figure 2. (a) Ionic conductivities and (b) viscosities of BDMIPF$_6$/PC and LiPF$_6$/PC as a function of molar concentration at 25 °C. The electrolytes were prepared by dissolving BDMIPF$_6$ and LiPF$_6$ into PC, respectively, and stirring vigorously for several hours. The molar concentrations of BDMIPF$_6$ and LiPF$_6$ in PC are varied from 0.25 to 1.5 M.

In view of the Stokes' law[11] that diffusion coefficients are inversely proportional to ion radii, the Li$^+$ is expected to show a larger diffusion coefficient than that of the BDMI$^+$ since the size of Li$^+$ (radius = 0.073 nm[10]) is much smaller than that of BDMI$^+$ (radius = 0.55 nm[22]). However, Li$^+$ is known to form a complex with polar solvents, resulting in an increase in the apparent size of its charge carrier. The lower diffusion coefficient of Li$^+$ than that of BDMI$^+$ indicates that the apparent charge carrier size of Li$^+$ is larger than that of BDMI$^+$, suggesting that the BDMI$^+$ is less solvated by the PC molecules than Li$^+$.

The cationic transference number ($t^+ = D^+/(D^+ + D^-)$) for both electrolytes was calculated (Figure 4). In the conventional lithium-salt-based electrolytes, the cationic transference number is reported to be less than 0.5, which means that the major contribution to current flow is from anionic transport.[13] Even though some deviation is observed with LiPF$_6$ concentration, the LiPF$_6$ appears to follow a traditional behavior. In contrast, the BDMIPF$_6$ exhibits a remarkably high cationic transference number (>0.8), which indicates that in the BDMIPF$_6$ the ion transport is mainly governed by the cation (BDMI$^+$) rather than the anion (PF$_6^-$).

As a next step, the cationic diffusion coefficients of the two-salt mixture electrolyte (0.5 mol BDMIPF$_6$ + 0.5 mol LiPF$_6$ in PC) were investigated and compared with those of the one-salt electrolytes (BDMIPF$_6$ in PC and LiPF$_6$ in PC). Figure 5a shows that in the two-salt mixture electrolyte the diffusion coefficient of BDMI$^+$ is much larger than that of Li$^+$ and the overall behavior of cationic diffusion seems to be consistent with the
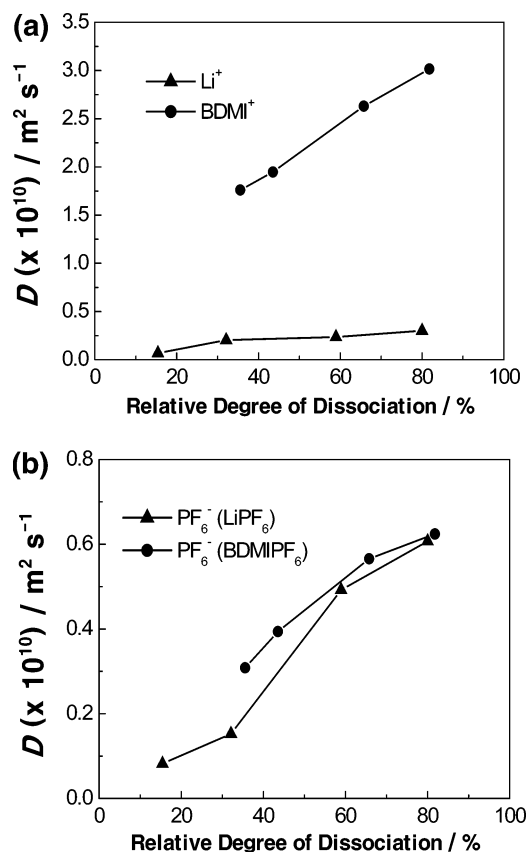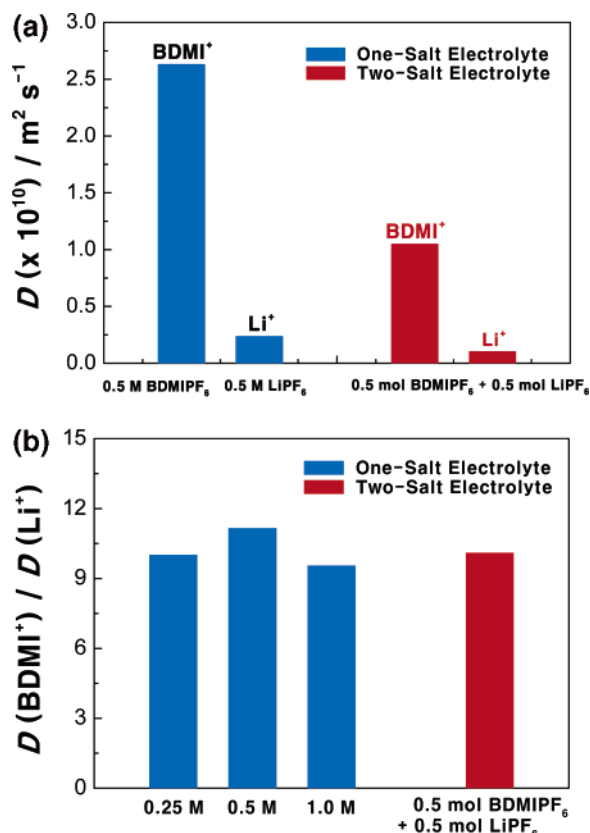

Figure 3. Diffusion coefficients of BDMIPF$_6$/PC and LiPF$_6$/PC as a function of the relative degrees of dissociation of the (a) cations and (b) anions. The self-diffusion coefficients of BDMI$^+$, PF$_6^-$, and Li$^+$ were obtained from the echo signal attenuation of the ^{1}H, ^{31}P, and ^{7}Li NMR spectra.
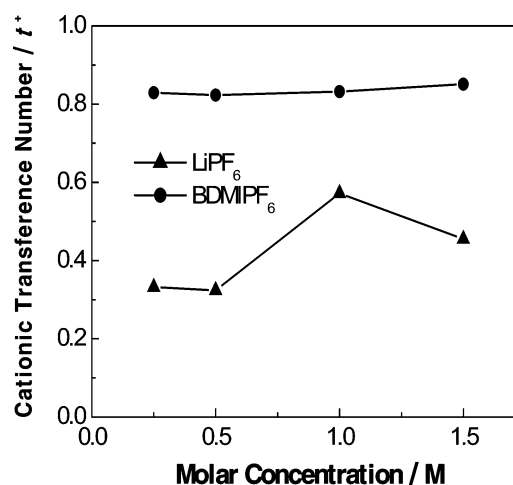
Figure 4. Cationic transference numbers ($t^+ = D^+/(D^+ + D^-)$) of BDMIPF$_6$/PC and LiPF$_6$/PC as a function of molar concentration.

one-salt electrolytes. To perform a quantitative analysis on the cationic transport phenomena, the ratios of cationic diffusion coefficients ($D(\text{BDMI}^+)/D(\text{Li}^+)$) for the one-salt electrolytes and the two-salt mixture electrolyte are compared in Figure 5b. For the one-salt electrolytes, the ratios of cationic diffusion coefficients are estimated to be around 10 and not change significantly with salt molar concentration. Similar to the one-salt electrolytes, the BDMI$^+$ in the two-salt mixture electrolyte is also observed to move about 10 times faster than the Li$^+$, which reflects the fact that the cationic (BDMI$^+$ and Li$^+$) transport is little influenced by the coexistence with other ions. This is

Figure 5. Comparison of cationic diffusion coefficients between one-salt electrolytes (BDMIPF$_6$ in PC and LiPF$_6$ in PC) and a two-salt mixture electrolyte (0.5 mol BDMIPF$_6$ + 0.5 mol LiPF$_6$ in PC): (a) cationic diffusion coefficient (D) one-salt electrolyte (salt concentration = 0.5 M) vs two-salt mixture electrolyte and (b) D(BDMI$^+$)/D(Li$^+$) one-salt electrolyte (salt concentrations = 0.25, 0.5, and 1.0 M) vs two-salt mixture electrolyte.

TABLE 1: Diffusion Coefficients of Each Ionic Species for 1 M LiPF$_6$-Based Electrolytes Containing 10 wt % of BDMIPF$_6$

D(Li$^+$) ($\times 10^{10}$, m^2 s^{-1})	D(BDMI$^+$) ($\times 10^{10}$, m^2 s^{-1})	D(PF$_6^-$) ($\times 10^{10}$, m^2 s^{-1})
0.16	2.11	0.38

[a] The self-diffusion coefficients of BDMI$^+$, PF$_6^-$, and Li$^+$ were obtained from the echo signal attenuation of the ^{1}H, ^{31}P, and ^{7}Li NMR spectra.

expected to provide fundamental information for interpreting the charge/discharge performances of lithium ion batteries containing BDMIPF$_6$.

On the basis of this study on the ion transport mechanism of model electrolytes such as the ionic-liquid-based electrolytes (BDMIPF$_6$ in PC), the lithium-salt-based electrolytes (LiPF$_6$ in PC), and the mixture electrolytes (BDMIPF$_6$ + LiPF$_6$ in PC), the poor C-rate performances (Figure 1) of lithium ion batteries employing the BDMIPF$_6$-added electrolyte are discussed in terms of diffusion coefficients for each ion species. Consistent with the observation on the model electrolytes, the diffusion coefficient of BDMI$^+$ in the electrolyte mixtures (i.e., 10 wt % of BDMIPF$_6$ in the 1M LiPF$_6$ in carbonate solvents) also turns out to be much larger than that of Li$^+$ (Table 1). Considering the faster movement of BDMI$^+$, we can reasonably understand that the BDMI$^+$ will arrive at the surface of the carbon anode much earlier than the highly solvated, thus sluggish, Li$^+$ (two-cation competition). The BDMI$^+$ forms an electric double layer around carbon anode (Scheme 1), which may then go through

SCHEME 1: Two-Cation Competition during the Charge Reaction of 1 M LiPF$_6$-Based Electrolytes Containing 10 wt % BDMIPF$_6$[a]

[a] The BDMI$^+$ may arrive at the surface of the carbon anode much earlier than the highly solvated, thus sluggish, Li$^+$ (two-cation competition).

reduction, possibly contributing to the thick SEI layer and the cointercalation into the carbon anode. This means that a kind of barrier layer against lithium ion transport may be formed, which is expected to give an unfavorable impact on the kinetics of the intercalation/deintercalation reaction of Li$^+$, resulting in the significant decrease in capacity.

4. Conclusion

Although ionic liquids possess interesting properties such as high ionic conductivity and nonflammability, their use as an electrolyte components in lithium ion batteries will be difficult. As we can tell from this work with the model electrolytes, BDMI$^+$ has a higher diffusion coefficient than that of the solvated Li$^+$. Therefore, the two cations compete with each other during the charge and discharge of lithium ion cells, and the facile BDMI$^+$ forms a blocking layer against lithium ion transport around the electrodes, resulting in very poor battery performance.

In this study, a new interpretation of the poor C-rate performances of lithium ion batteries employing ionic-liquid-added (BDMIPF$_6$) electrolytes was presented. A study on the ion transport mechanism of the model electrolytes (BDMIPF$_6$ in PC, LiPF$_6$ in PC, and BDMIPF$_6$ + LiPF$_6$ in PC) has provided the following explanation: Regardless of the salt type, the anion (PF$_6^-$) shows almost the same diffusion coefficients at all relative degrees of dissociation. However, the cations show quite a different behavior; the diffusion coefficients of BDMI$^+$ are found to be much larger than those of Li$^+$, indicating its poorer solvation in PC solvents. The faster movement of BDMI$^+$ than Li$^+$ in the BDMIPF$_6$-added electrolytes is suggested to be a main reason for developing a barrier layer for lithium ion transport, which leads to the deterioration of C-rate performances in lithium ion batteries. This is, to the best of our knowledge, the first report that has performed a quantitative investigation on the ion transport mechanism of ionic-liquid-modified electrolytes in lithium ion batteries.

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