

Alkylated imidazolium salt electrolyte for lithium cells

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Abstract

The use of a nonflammable electrolyte in a lithium secondary battery will greatly improve battery safety. Therefore, we focused on the nonflammability of ionic liquids and investigated these liquids as possible electrolyte solvents. In this study, we synthesized 1,2-diethyl-3,4(5)-dimethyl imidazolium (DEDMI) cations with imido anions. DEDMI cations with bis(trifluoromethylsulfonyl)imido anions (DEDMI-TFSI) showed a lower solidification point of -35°C , and higher specific conductivity than DEDMI cations with BF_4^- . We prepared an electrolyte consisting of DEDMI-TFSI with LiTFSI, and applied it to a Li/LiCoO₂ cell. The cell was capable of charge–discharge cycling with LiCoO₂ cathode material showing a specific capacity of about 100 mAh g⁻¹.

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1. Introduction

High-energy density lithium ion batteries are expected to be employed in electric vehicles, load leveling and energy-storage devices. This application requires a large lithium ion battery with a high energy. However, it is generally difficult to ensure the safety of such batteries.

Organic solvents for lithium ion battery electrolytes have been widely marketed and include propylene carbonate, ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate, diethyl carbonate and γ -butyrolactone. Electrolytes with these organic solvents provide the following features: a wide temperature range in the liquid state between -20 and 60°C ; a high lithium salt solubility of more than 1.0 mol dm^{-3} ; high specific conductivity over a wide temperature range, a wide electrochemical window of 0 – 5.0 V versus Li/Li⁺; good chemical stability against both the cathode and anode [1].

Unfortunately, these organic solvents are flammable and volatile, which makes the batteries that employ them a safety risk. Therefore, various measures have been taken to make lithium ion batteries safe. However, the energy density increases year by year, and larger batteries are under devel-

opment. This raises serious concerns about the future safety of this type of battery.

One promising solution is to eliminate most of the flammable material from the battery. The development of a nonflammable, nonvolatile electrolyte is essential for this purpose. One candidate for a nonflammable electrolyte solvent is an ionic liquid. Ionic liquids consist of a cation and an anion, and the total charge of the compound is neutral. Ionic liquids generally have a number of features including nonflammability, nonvolatility, a high specific conductivity, and good chemical stability. There have been several studies of ionic liquids as lithium cell electrolyte solvent, but no electrolyte with ionic liquid exhibits enough performance with lithium secondary cells [2–6]. There are certain problems related to the use of ionic liquids as lithium ion battery electrolyte solvents. These include low specific conductivity, a narrow electrochemical window, a narrow temperature range in the liquid state, and high viscosity.

We found that alkylation of an imidazolium salt is extremely effective for lowering the reduction potential and 1,2-diethyl-3,4(5)-dimethyl imidazolium tetrafluoroborate (DEDMI-BF₄) exhibited very little decomposition at 0 V versus Li/Li⁺ and a wide electrochemical window up to 5 V versus Li/Li⁺ [7]. In this work, we synthesized two ionic liquids, 1,2-diethyl-3,4(5)-dimethyl imidazolium cations with

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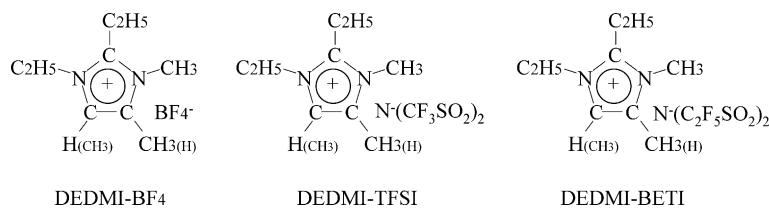


Fig. 1. Molecular structure of DEDMI-BF₄, DEDMI-TFSI and DEDMI-BETI.

two kinds of imido anions, bis(trifluoromethylsulfonyl)imido (TFSI), and bis(pentafluoroethylsulfonyl)imido (BETI), to improve the electrolyte performance of DEDMI-BF₄ as regards specific conductivity and solidification point. Moreover, we investigated the lithium cell performance with a Li/LiCoO₂ cell.

2. Experimental

1,2-Diethyl-3,4(5)-dimethylimidazolium bis(trifluoromethylsulfonyl)imido (DEDMI-TFSI) and 1,2-diethyl-3,4(5)-dimethylimidazolium bis(pentafluoroethylsulfonyl)imido (DEDMI-BETI) shown in Fig. 1 were obtained as follows. Fig. 2 shows the DEDMI-TFSI synthesis scheme. First, 2-ethyl-4(5)-methyl imidazole was reacted with an ethyl bromide, and then with a methyl iodide, and 1,2-diethyl-3,4(5)-dimethylimidazolium iodide (DEDMI-I) was obtained [7]. DEDMI-I was mixed with an equimolar amount of LiN(CF₃SO₂)₂ (LiTFSI) in water and the DEDMI-TFSI layer was separated from the water layer. The extracted DEDMI-TFSI was then washed with pure water several times, and dried in vacuo. DEDMI-BETI was also obtained with the same method but using LiN(C₂F₅SO₂)₂ (LiBETI) instead of LiTFSI. These ionic liquids were identified by using fluorescent X-ray spectrometry and ¹H NMR. We evaluated the nonflammability of a ionic liquids with reference to the UL-94 standard.

We measured the specific conductivity of each ionic liquid and electrolyte at 1 kHz by using an LCR bridge (GenRad, 1658 RLC digi-bridge) with a cell (Yanako, I-type cell) in

a thermostat (ESPEC, SU-240). The melting point of these solutions was determined by observation. We prepared an electrolyte consisting of DEDMI-TFSI and LiTFSI with respective concentrations of 0.4 and 0.8 mol dm⁻³. These electrolytes are denoted as 0.4 and 0.8 M LiTFSI/DEDMI-TFSI, respectively. We used a coin type cell with a LiCoO₂ pellet-type cathode and a lithium metal anode in a cell cycling test. The cells were cycled between 3.0 and 4.2 V with a constant current of 0.1 mA.

3. Results and discussion

Fig. 3 shows the fluorescent X-ray profile of DEDMI-I and DEDMI-TFSI. Peaks characterized as iodine in the DEDMI-I profile were absent from the DEDMI-TFSI profile. In contrast, a peak characterized as sulfur appeared in the DEDMI-TFSI profile, which did not appear in the DEDMI-I profile. The ¹H NMR spectra of DEDMI-TFSI are similar to that of DEDMI-I as shown in Fig. 4. This means the cation maintained the same structure before and after anion exchange. We confirmed that DEDMI-TFSI is nonflammable. DEDMI-BETI was also identified by the same method.

Fig. 5 shows the specific conductivity of DEDMI-TFSI, DEDMI-BETI, DEDMI-BF₄ at various temperatures. DEDMI-TFSI exhibits a higher specific conductivity than DEDMI-BF₄ at each temperature. The solidification point of DEDMI-TFSI is -35 °C, which is about 20° lower than that of DEDMI-BF₄. An ionic liquid with the TFSI anion tends to provide a lower solidification point and a wider temperature range in the liquid state than the others. As we expected,

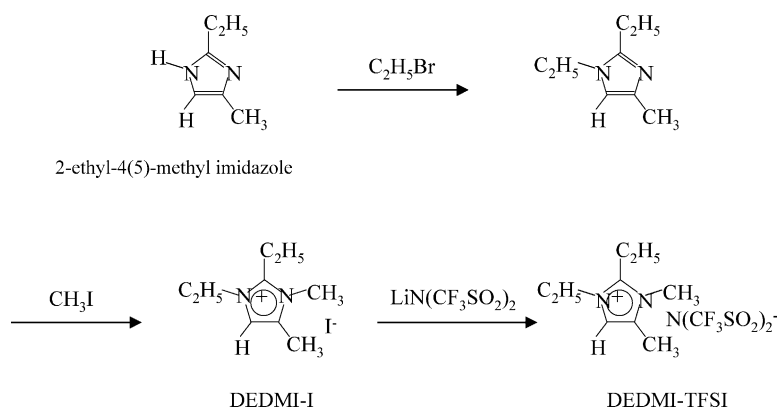


Fig. 2. DEDMI-TFSI synthesis scheme.

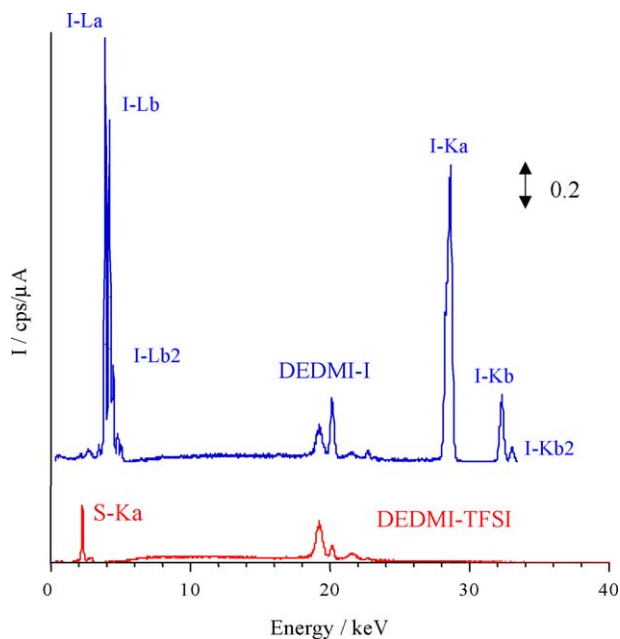


Fig. 3. The X-ray fluorescence profile of DEDMI-I and DEDMI-TFSI.

the performance of DEDMI-TFSI improved as regards both conductivity and temperature range in the liquid state. In contrast, DEDMI-BETI exhibits a lower specific conductivity than DEDMI-TFSI and a similar specific conductivity to DEDMI-BF4 at each temperature. The solidification point of DEDMI-BETI is about -5°C , which is higher than that of DEDMI-BF4 and DEDMI-TFSI. As regards ionic liquids with DEDMI⁺ cations, we found that using BETI⁻ is not effective in providing a better specific conductivity or solidification point than DEDMI-BF4. Table 1 shows the

Table 1
Physical properties of (1) DEDMI-TFSI and (2) DEDMI-BETI

	DEDMI-TFSI	DEDMI-BETI
Formula weight	433.38	533.40
Specific gravity (g ml^{-1})	1.40	1.50
Concentration (mol l^{-1})	3.24	2.80

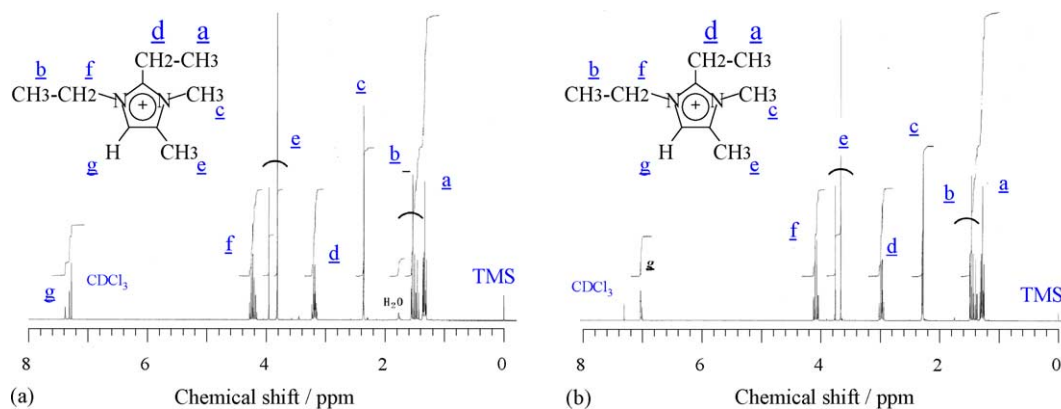


Fig. 4. ^1H NMR spectra of: (a) DEDMI-TFSI and (b) DEDMI-I.

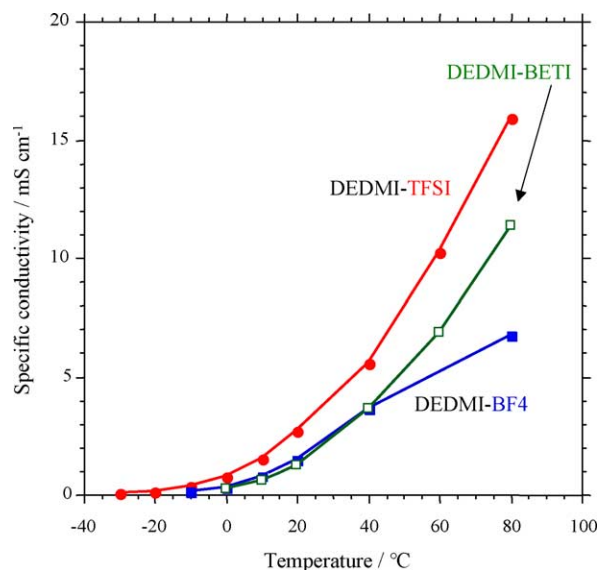


Fig. 5. Specific conductivity of each ionic liquid at various temperatures: (1) DEDMI-TFSI; (2) DEDMI-BETI; (3) DEDMI-BF4.

measured specific gravity at 25°C and the calculated concentration of each ionic liquid. The concentration of DEDMI-BETI is lower than that of DEDMI-TFSI, that is, there are fewer charge carriers in DEDMI-BETI than in DEDMI-TFSI. Moreover, the volume of BETI⁻ anions is larger than that of TFSI⁻ anions. Therefore, we think that TFSI⁻ anions can move faster than BETI⁻ anions. Overall, DEDMI-TFSI exhibited the best performance of the three materials as a lithium secondary cell electrolyte solvent.

Next, we prepared two electrolytes of 0.4 M LiTFSI/DEDMI-TFSI and 0.8 M LiTFSI/DEDMI-TFSI. The specific conductivities of 0.8 M LiTFSI/DEDMI-TFSI, 0.4 M LiTFSI/DEDMI-TFSI, and DEDMI-TFSI are shown in Fig. 6 and are 0.8, 1.4, and 2.7 mS cm^{-1} at 20°C , and 3.7, 6.1, and 10.2 mS cm^{-1} at 60°C , respectively. The order of increasing conductivity tends to be DEDMI-TFSI > 0.4 M LiTFSI/DEDMI-TFSI > 0.8 M LiTFSI/DEDMI-TFSI. This order coincides with that of low concentration of LiTFSI. This trend occurs mainly because dissolving Li salt in the

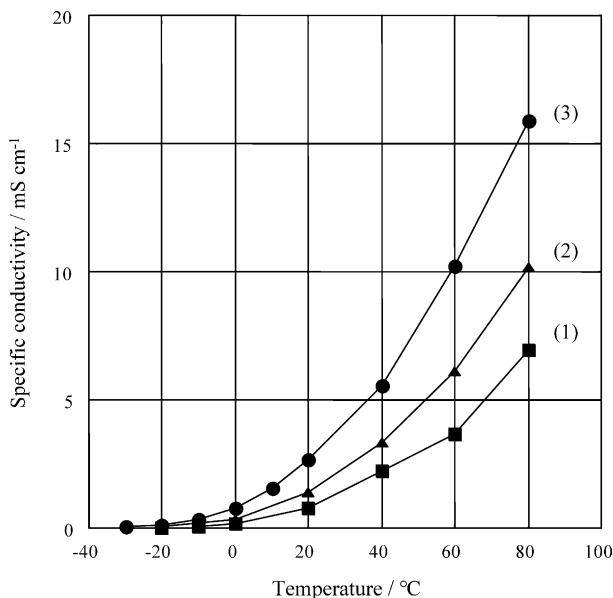


Fig. 6. Specific conductivity of each solution at various temperatures: (1) 0.8 M LiTFSI/DEDMI-TFSI; (2) 0.4 M LiTFSI/DEDMI-TFSI; (3) DEDMI-TFSI.

ionic liquid increases its viscosity. We think this phenomenon is unavoidable in this type of electrolyte system. Therefore, the reduction of the ionic liquid viscosity is a problem to be solved.

Fig. 7 shows the charge–discharge profiles of a Li/LiCoO₂ cell with 0.8 M LiTFSI/DEDMI-TFSI electrolyte. According

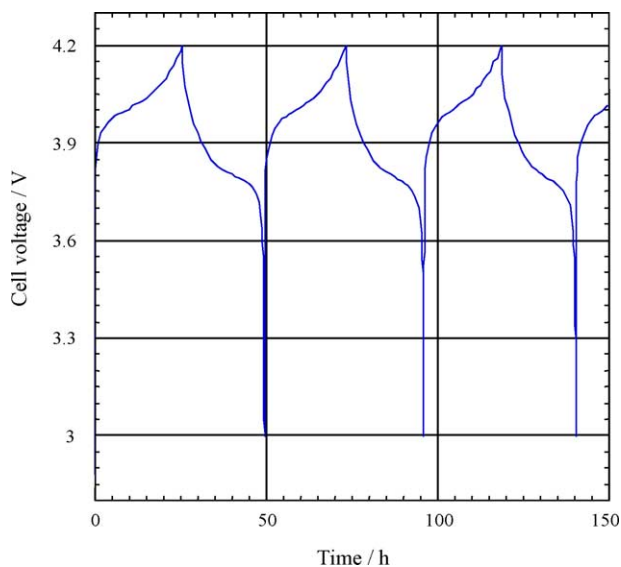


Fig. 7. Charge–discharge profiles of a Li/LiCoO₂ cell with 0.8 M LiTFSI/DEDMI-TFSI electrolyte.

to these cycling profiles, a LiCoO₂ cathode exhibits a lithium deinsertion and insertion reaction. The specific capacity of the cathode was about 100 mAh g⁻¹. We think the reason why the low specific capacity of the cathode is that low conductivity of lithium ion in this ionic liquid, and/or LiCoO₂ electrode was not sufficiently impregnated with the electrolyte. A typical ionic liquid with a 1-ethyl-3-methylimidazolium cation cannot usually be applied to a lithium cell electrolyte because of the reduction decomposition problem. However, the DEDMI-TFSI electrolyte system overcome this problem and a lithium cell with this electrolyte was capable of cell charging and discharging, although the overpotential was large.

4. Conclusions

We investigated an ionic liquid as a nonflammable and nonvolatile electrolyte solvent for lithium secondary cells. We improved the specific conductivity and expanded the temperature range in the liquid state of DEDMI-BF₄, which exhibits a wide electrochemical window, by exchanging BF₄ anions for TFSI anions. All electrolyte composed of DEDMI-TFSI with LiTFSI tends to have a lower specific conductivity than DEDMI-TFSI alone, as the LiTFSI concentration increases. However, 0.8 M LiTFSI/DEDMI-TFSI electrolyte provides good cell cycling with Li/LiCoO₂ and this electrolyte system shows considerable promise for use with lithium secondary cells.

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