

Ionic Liquids for Lithium Secondary Batteries

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Abstract

We focused on the nonflammability of imidazolium salts and investigated these salts as electrolyte solvents for lithium secondary cells. An imidazolium salt, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄), has been reported to exhibit a high reduction potential of about 1 V vs. Li/Li⁺, which is insufficient for the electrolyte of a lithium secondary cell. Therefore, we attempted to lower its reduction potential by modifying its molecular structure. We synthesized two types of alkylated EMI-BF₄: 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate (ETMI-BF₄) and 1,2-diethyl-3,4(5)-dimethylimidazolium tetrafluoroborate (DEDMI-BF₄). Both salts exhibited very little decomposition at 0 V vs. Li/Li⁺ and a wide electrochemical window up to 5 V vs. Li/Li⁺. Moreover, DEDMI-BF₄ had a relatively low melting point of about 20°C and a good specific conductivity of 1.44 mS cm⁻¹ at 20°C.

1. Introduction

High-energy-density lithium ion batteries are expected to be employed as energy storage devices for uninterruptible power supplies for telecommunications, load leveling equipment, and electric vehicles. This application requires a large lithium ion battery with a high energy. However, it is generally difficult to ensure the safety of such batteries, which must not catch fire or burst when the battery experiences problems such as a short circuit, overcharging, a high temperature, or a crushing force.

Various organic solvent-based solutions have been widely marketed for use as lithium ion battery electrolytes, including propylene carbonate, ethylene carbonate, dimethyl carbonate, ethylmethyl carbonate, diethyl carbonate, and γ -butyrolactone as the solvent. Electrolytes with these organic solvents provide the following features: a high lithium salt solubility of

1.0 to 3.0 mol dm⁻³, high specific conductivity over a wide temperature range such as -20 to 60°C, a wide electrochemical window of 0 to over 5.0 V vs. Li/Li⁺, and good chemical stability against both the cathode and anode.

However, 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, year by year the energy density has increased, and larger batteries are being developed. This raises serious concerns about the future safety of this type of battery.

One promising solution is to use a nonflammable, nonvolatile electrolyte since this would eliminate most of the flammable material from the battery. This nonflammability is effective in preventing batteries from catching fire, and a nonvolatile electrolyte prevents batteries from bursting. One candidate for a nonflammable electrolyte solvent is a room-temperature molten salt (ionic liquid).

Ionic liquids consist of a cation and an anion, and the total charge of the compound is neutral. They generally have a number of features including nonflam-

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mability, nonvolatility, a relatively wide electrochemical window, a high specific conductivity, and good chemical stability. Moreover, they are liquid at about room temperature. Therefore, ionic liquids are promising materials for both battery electrolytes and other chemical devices.

Figure 1 shows examples of cations and anions for ionic liquids. Butyl pyridinium (BP) cations are suitable cations for molten salts, but they are not very stable and have a narrow electrochemical window. Trimethylpropylammonium (TMPA) cations and N-methylpiperidinium (PP13) cations are stable and can be used as the electrolyte of lithium ion batteries [1]. However, their specific conductivity is not very high and only a limited number of counter anions can be used with them to form ionic liquids. 1-ethyl-3-methylimidazolium cations (EMI⁺) are compact and very stable and have a structure that can be modified. Cl⁻ with AlCl₃, BF₄⁻, PF₆⁻, CF₃SO₃⁻ and N(CF₃SO₂)₂⁻ are examples of anions for ionic liquids.

Initially, ionic liquids with imidazolium and pyridinium cations were widely studied. For example, 1-ethyl-3-methylimidazolium chloride (EMI-Cl) with AlCl₃ provides high specific conductivity, relatively low viscosity, and a relatively wide electrochemical window [2]. However, this salt is sensitive to air and moisture, so it must be handled carefully.

Then it was reported that EMI⁺ with other anions

(PF₆⁻, CF₃SO₃⁻, and BF₄⁻) shows good stability against air and moisture [3]. However, the reduction potential of these EMI salts is about 1 V vs. Li/Li⁺, which is insufficient for lithium ion battery applications. It is thought that the reduction potential of these salts depends mainly on EMI⁺ [4]. There have been some reports of lithium cell applications using imidazolium salts with high potential anodes [5]-[8] or electrolyte additives [9], [10]. If we can obtain an imidazolium salt with no decomposition within the potential range of a lithium ion cell, we believe that an electrolyte with this salt could enhance the safety of high-energy lithium ion cells.

In this study, we modified the cation structure of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) to lower its reduction potential for use in lithium ion batteries.

2. Experimental

EMI-BF₄ (Aldrich) was used as received. EMI-BF₄ and other imidazolium salts were dried *in vacuo* at 80°C for 24 hrs. All salt preparation was performed in an argon-filled glove box. 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate (ETMI-BF₄) and 1,2-diethyl-3,4(5)-dimethylimidazolium tetrafluoroborate (DEDMI-BF₄), which were synthesized in this study for the first time, were identified by H¹-NMR (JEOL JNM-ECX400), mass spectroscopy

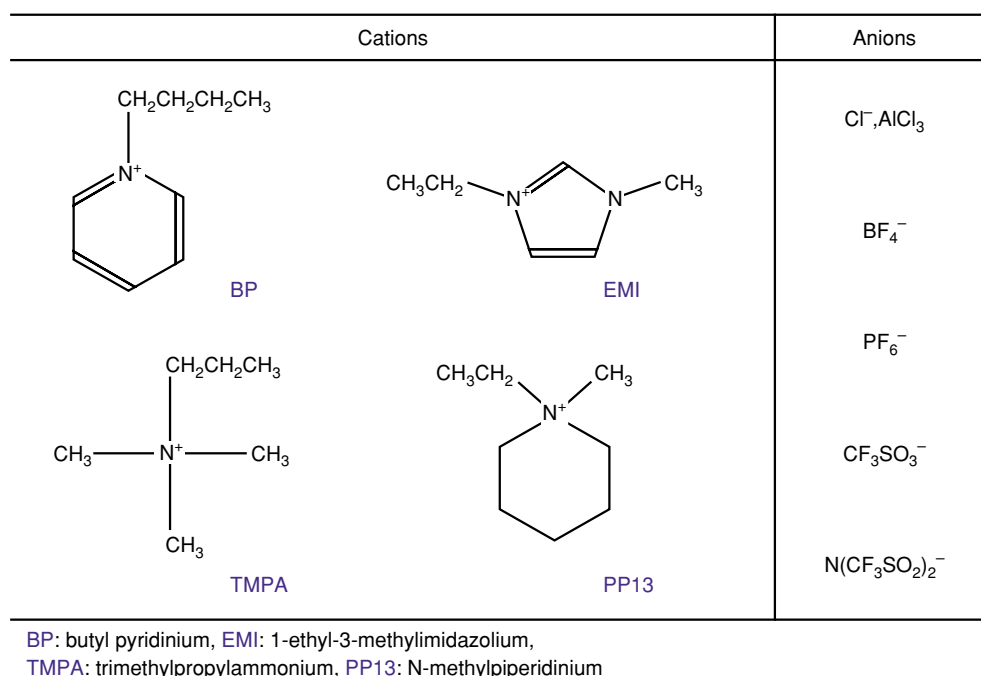


Fig. 1. Cations and anions for ionic liquids.

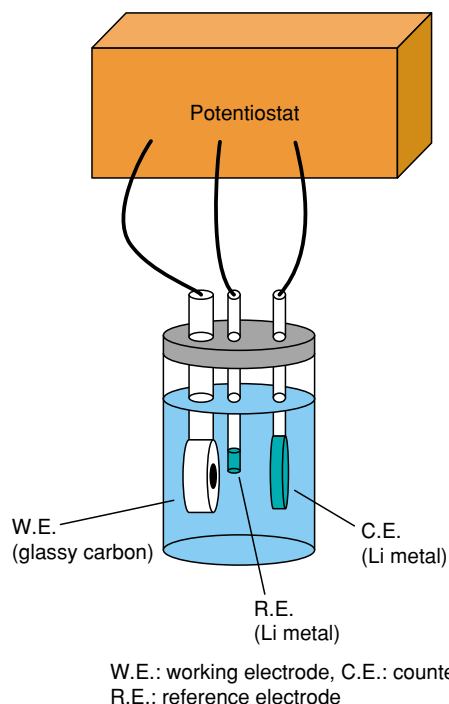


Fig. 2. Electrochemical cell for electrochemical window evaluation.

(JEOL JMS-700), high-throughput liquid chromatography, HPLC (Shimadzu LC-2010), and elemental analysis. The melting points of these salts were determined by observation.

The cell we used for the potential measurement (**Fig. 2**) had three electrodes: a glassy carbon working electrode, a lithium metal reference electrode, and a lithium metal counter electrode. Measurements were carried out using the linear potential sweep method with a potentiostat (BioLogic, Macpile II) at 80°C. The voltage range with respect to Li/Li⁺ was from 0 to 5 V, and the sweep speed was 0.1 mV s⁻¹.

We measured the specific conductivity of each electrolyte at 1 kHz by using an LCR bridge (GenRad, 1658 RLC digibridge) with a cell (Yanako, I-type cell) in a thermostat (ESPEC, SU-240) (**Fig. 3**).

3. Results and discussion

3.1 Drawback of EMI-BF₄ and improvement strategy

The potential-current profile of EMI-BF₄ with a three-electrode cell is shown in **Fig. 4**. The reduction current of EMI-BF₄ appeared at around 1 V vs. Li/Li⁺, which is the same as that in a previous report [4]. This reduction decomposition of EMI-BF₄ was due to imidazolium cations (EMI⁺) [4], and it implies

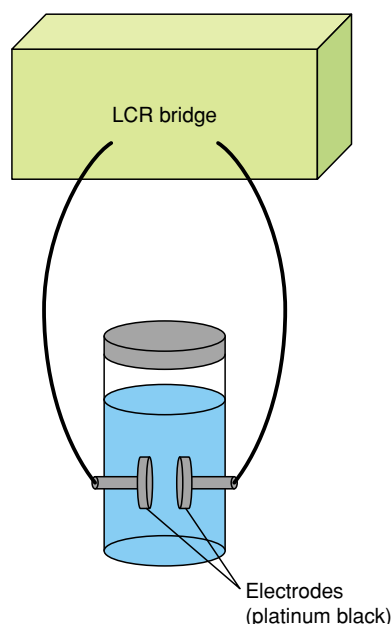


Fig. 3. Electrochemical cell for specific conductivity measurement.

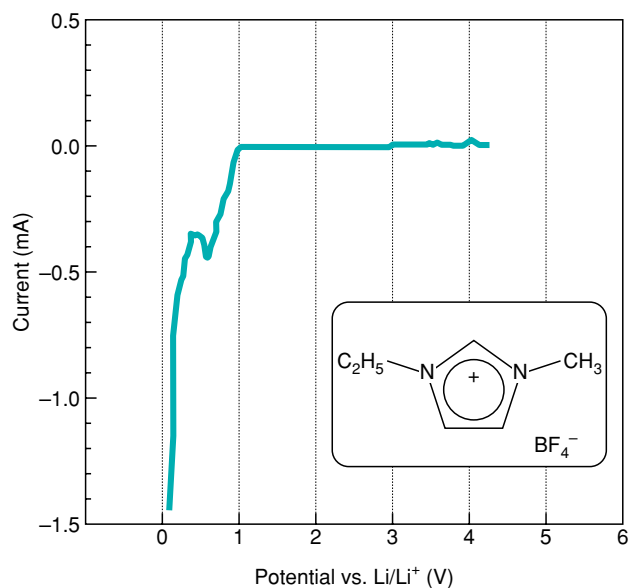


Fig. 4. Potential-current curve of EMI-BF₄.

that we cannot use conventional graphite anode material with a redox potential close to 0 V vs. Li/Li⁺ in this salt. We believe this high reduction potential is caused by the high charge density of the cations and that reducing this charge density will lead to a low reduction potential.

The imidazolium cation itself has one positive charge, and the position of the highest charge density

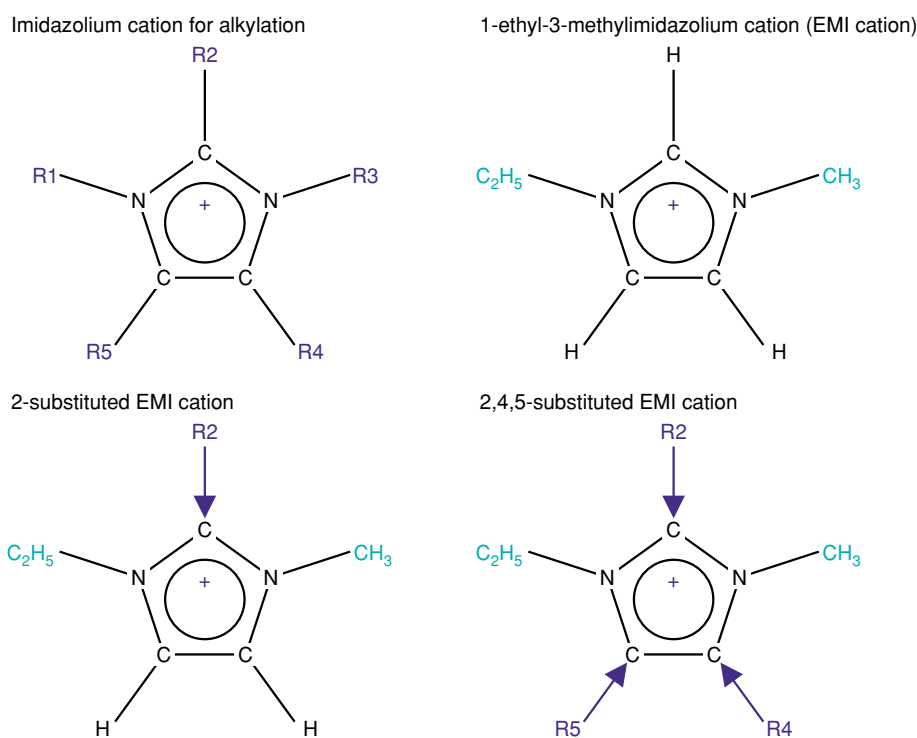
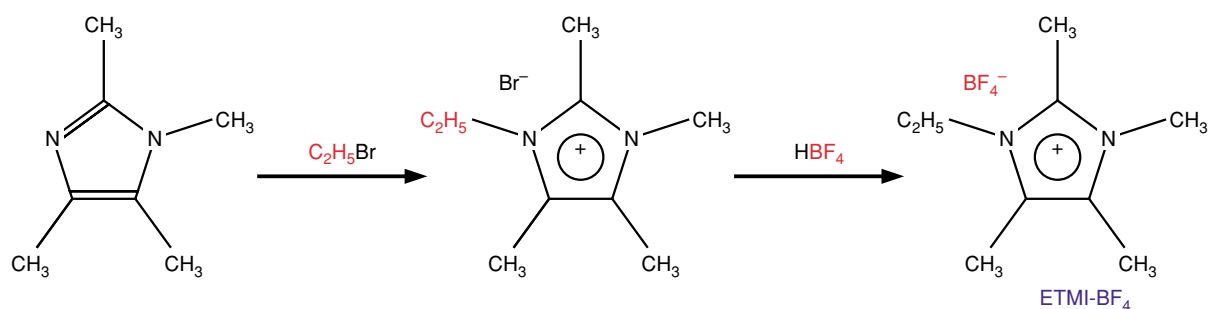


Fig. 5. Structure of modified EMI cations.

ETMI-BF₄: 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborateFig. 6. Synthesis scheme of ETMI-BF₄.

is believed to be between two nitrogens. **Figure 5** shows the structures of modified imidazolium cations designed by using the above hypothesis. Here EMI⁺ is at R1=C₂H₅, R3=CH₃, R2=R4=R5=H. We substituted the electron donor R2 at the 2nd carbon. We also substituted the electron donors R4 and R5 at the 4th and 5th carbons. These substitutions were expected to reduce the peak positive charge density and also to lessen the reactivity of EMI⁺ with electrons due to steric hindrance. We selected an alkyl group as an electron donor substituent.

3.2 Modified imidazolium salt I, ETMI-BF₄

We examined the possibility of synthesizing alky-

lated EMI⁺ and selected a methyl group, in this case the smallest alkyl group, for the electron donors R2, R4, and R5. We then synthesized 1-ethyl-2,3,4,5-tetramethylimidazolium tetrafluoroborate (ETMI-BF₄). **Figure 6** shows the ETMI-BF₄ synthesis scheme. Ethyl bromide was reacted with 1,2,4,5-tetramethylimidazole and the anion was changed from Br⁻ to BF₄⁻. ETMI-BF₄ was identified by ¹H-NMR spectrometry, mass spectrometry, elemental analysis, and HPLC.

Table 1 shows the physical properties of various imidazolium salts. The melting point of ETMI-BF₄ was observed to be 78–80°C. This is higher than that of EMI-BF₄ and similar to that of EMI-Cl. ETMI-BF₄

and EMI-BF₄ show almost the same symmetry, so this trend is mainly caused by the volume of ETMI-BF₄ being larger than that of EMI-BF₄.

Figure 7 shows the electrochemical profile of the current and potential for ETMI-BF₄ at 80°C. The current around 1 V vs. Li/Li⁺, which was observed in EMI-BF₄ (Fig. 4), was not present in ETMI-BF₄. In addition, there was no decomposition of ETMI-BF₄ from 0 to 5 V vs. Li/Li⁺; that is, ETMI-BF₄ is stable within the electrochemical potential range of lithium ion batteries. Consequently, as we expected, alkylating EMI⁺ gave it a much lower electrochemical reduction potential than EMI⁺.

The specific conductivities of ETMI-BF₄ and EMI-BF₄ are shown in **Fig. 8**. The specific conductivity of ETMI-BF₄ at 20°C was 0.12 mS cm⁻¹ and this value is much lower than that of EMI-BF₄. Although ETMI-BF₄ has a high melting point of 78–80°C, ETMI-BF₄ is liquid down to 10°C as a result of supercooling. A similar phenomenon was observed for EMI-BF₄: the melting point is 15°C and the liquid state was maintained down to –30°C as a result of

Table 1. Physical properties of imidazolium salts.

Abbreviation	Anion	Formula weight	Melting point (°C)
ETMI-BF ₄	BF ₄ ⁻	240.05	78-80
DEDMI-BF ₄	BF ₄ ⁻	240.05	19-20
EMI-BF ₄	BF ₄ ⁻	197.97	15
EMI-Cl	Cl ⁻	146.62	77-79
EMI-PF ₆	PF ₆ ⁻	256.13	58-62

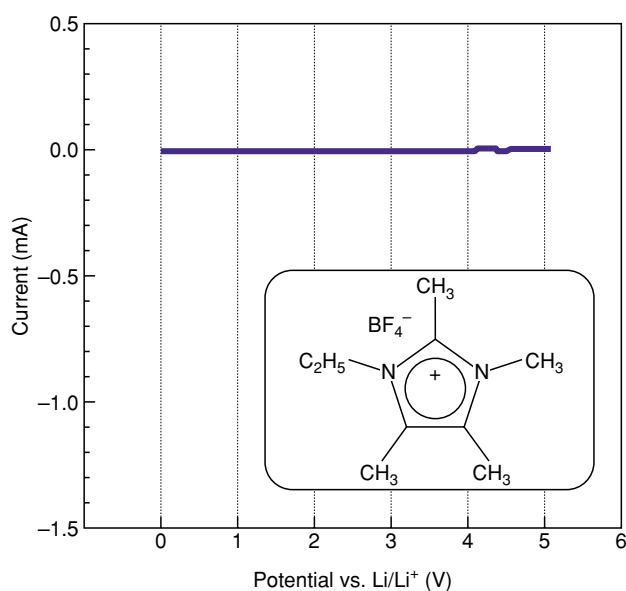


Fig. 7. Potential-current curve of ETMI-BF₄ at 80°C.

supercooling.

Thus, our investigation of the alkylation of imidazolium salts as a way of boosting the performance of EMI-BF₄ showed that alkylation of the cations improves the stability when the electrochemical potential is low and provides a wide enough electrochemical window for use in Li-ion batteries. However, ETMI-BF₄ exhibits a high melting point and a low specific conductivity, so both these characteristics must be improved before it can be used as a lithium ion battery electrolyte solvent.

3.3 Modified imidazolium salt II, DEDMI-BF₄

We redesigned the structure of the imidazolium cations and investigated 1,2-diethyl-3,4(5)-dimethylimidazolium tetrafluoroborate (DEDMI-BF₄). DEDMI-BF₄ is less symmetrical than ETMI-BF₄ and is a mixture of 4- and 5-methyl isomers. Asymmetric molecules tend to have a lower melting point than symmetric compounds with the same formula weight. Moreover, the solidification point of the mixture is lower than that of any of the original components. Therefore, we expected the melting point to be lower than that of ETMI-BF₄.

Figure 9 shows the DEDMI-BF₄ synthesis scheme. 2-ethyl-4(5)-dimethyl imidazole was reacted with ethyl bromide and then reacted with methyl iodide. Finally, I⁻ was replaced by BF₄⁻. DEDMI-BF₄ was identified by H¹-NMR spectrometry, mass spectrometry, elemental analysis, and HPLC.

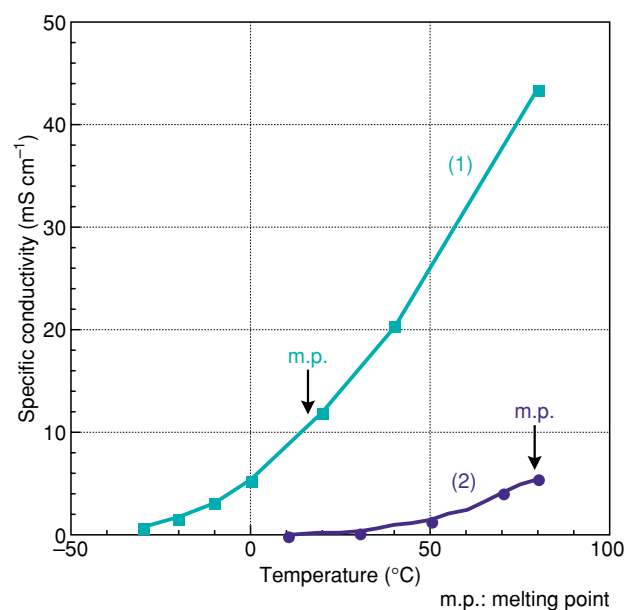
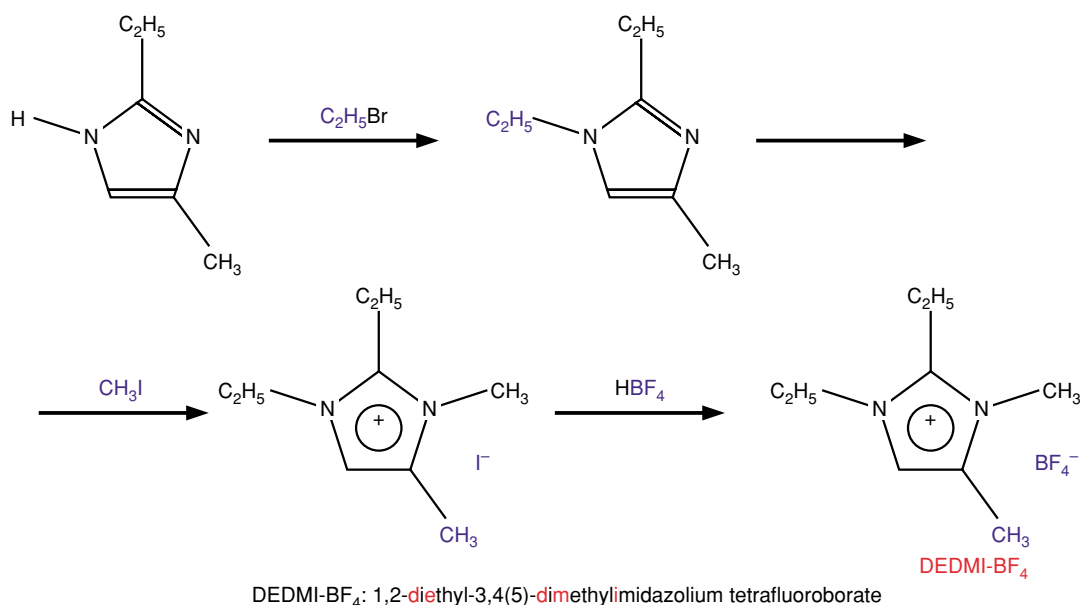
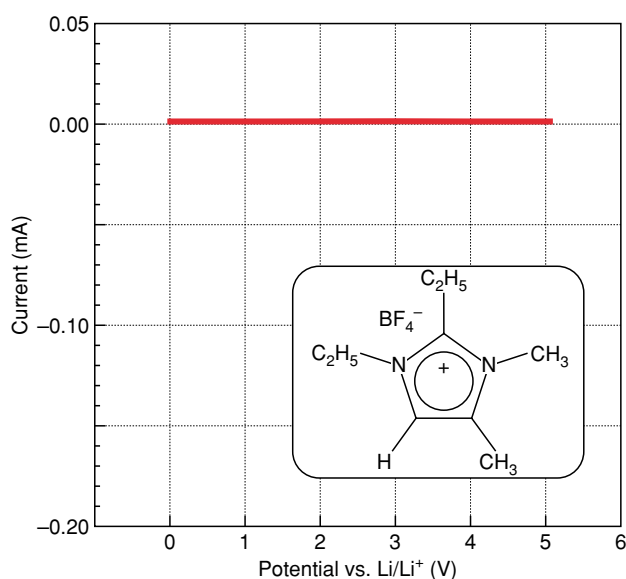
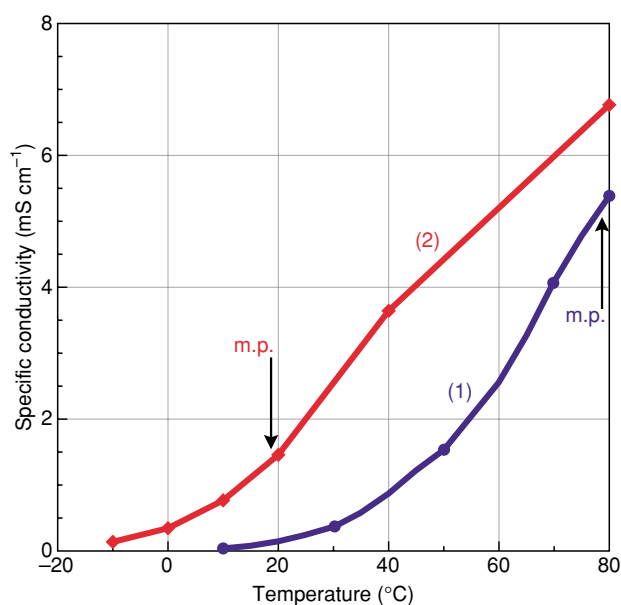


Fig. 8. Temperature dependence of specific conductivity of each salt. (1) EMI-BF₄ and (2) ETMI-BF₄.

Fig. 9. Synthesis scheme for DEDMI-BF₄.Fig. 10. Potential-current curve of DEDMI-BF₄ at 80°C.

The melting point of DEDMI-BF₄ was observed to be 19–20°C, as shown in Table 1. As we expected, this is much lower than that of ETMI-BF₄ and close to that of EMI-BF₄. Therefore, we succeeded in obtaining an imidazolium salt with a room-temperature melting point.

The electrochemical profile of the current and potential for DEDMI-BF₄ at 80°C is shown in Fig. 10. The profile is almost flat, similar to that for ETMI-BF₄ (Fig. 7). There was no decomposition when the potential was between 0 and 5 V. Therefore,

Fig. 11. Temperature dependence of specific conductivity of each salt. (1) ETMI-BF₄ and (2) DEDMI-BF₄.

DEDMI-BF₄ provides a sufficiently wide electrochemical window for use in Li-ion batteries.

Figure 11 shows how the specific conductivity varied with temperature. DEDMI-BF₄ had a higher specific conductivity of 1.44 mS cm⁻¹ at 20°C than ETMI-BF₄. DEDMI-BF₄ was in the liquid state, even below the melting point. It also exhibited supercooling, with the limit being –10°C.

DEDMI-BF₄ still does not meet the requirements

for a lithium ion cell electrolyte solvent. We should expand the temperature range of its liquid state to at least below -20°C , select a suitable lithium salt and electrolyte composition, and then evaluate the lithium cell performance and cell safety with this type of electrolyte.

4. Conclusion

We found that alkylating EMI^+ is an effective way to improve its stability when the electrochemical potential is low. It also provides a sufficiently wide electrochemical window for use in Li-ion batteries. DEDMI- BF_4 retained its liquid state down to -10°C and has a good specific conductivity at room temperature. However, we must further improve the performance of DEDMI- BF_4 for use in lithium ion cells. We firmly believe that ionic liquid electrolytes will be used as nonflammable electrolytes for lithium ion cells, which will greatly improve their safety.

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