

Ionic liquids containing carbonate solvent as electrolytes for lithium ion cells

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Abstract

A novel aliphatic quaternary ammonium type ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI), is a practical and useful ionic liquid as an electrolyte for electrochemical devices. Its desirable properties include non-flammability, a quite wide potential window (5.4 V), and a high ionic conductivity (4.0 mS cm^{-1} at 30°C). We attempted to utilize Li-binary ionic liquids composed of LiTFSI and DEME-TFSI as an electrolyte in a lithium deposition and dissolution media. However, although DEME-TFSI had a relatively large potential window among recently reported ionic liquid species, it decomposed on the negative electrode at a positive potential relative to that of the Li/Li^+ . To provide a solid electrolyte interface that would overcome the reductive decomposition of the electrolyte, we added two kinds of organic solvent to the Li-binary ionic liquids. The selected additives, vinylene carbonate (VC) and ethylene carbonate (EC) effectively prevented the decomposition and improved the reversible lithium deposition/dissolution. To evaluate the potential of these liquids with additives as electrolytes for lithium ion batteries, we prepared demonstration cells composed of a graphite/Li-DEME-TFSI containing 10 wt.% of VC/LiCoO₂ and investigated its cell performance. This is the first report of our knowledge that a lithium ion cell with an ionic liquid electrolyte performed, in terms of cell performance and cycle durability, at a level of practical utility. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ionic liquid; Lithium ion cell; Safety; Cycle durability; Solid electrolyte interface

1. Introduction

Commercialized lithium ion batteries, consisting of graphite-based anodes and organic solvent electrolytes, have several advantages, such as a high operating voltage, a high energy density, and good cycle durability [1]. However, the applications of lithium ion cells presently include only those for which a small capacity cell suffices, since their flammable electrolytes still raise safety concerns. To develop a truly safe large size lithium ion cell suitable for electric or hybrid vehicles, a new kind of non-flammable electrolyte is necessary.

Ionic liquids are known to be non-volatile, non-flammable, and highly conductive. Recently, therefore, interest has increased in the possible use of this type of liquid (or room

temperature molten salt) in energy storage devices, for example, a lithium rechargeable battery [2–8] and an electric double layer capacitor [9–13]. In particular, researchers have focused on imidazolium derivatives that have a relatively low viscosity and high ionic conductivity [2–6]. Fung and Zhou [3] discussed the performance of a rechargeable battery using ionic liquids as an electrolyte: Li-Al/LiCl + 1-ethyl-3-methylimidazolium chloride (EMI-Cl) + AlCl₃/LiCoO₂ system. In an attempt to use chloride-free ionic liquids such as EMI-tetrafluoroborate (BF₄) for a lithium ion cell, Nakagawa et al. [6] chose Li[Li_{1/3}Ti_{5/3}]O₄ as the anode active material, to avoid the cathodic decomposition of the liquid during the charge–discharge cycles. Sakaebe and Matsumoto [7] reported on the performances of cells using aliphatic quaternary ammonium-based ionic liquids that have a higher cathodic stability than the aromatic type ionic liquids. This type of half-cell consisted of a Li metal anode, a

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LiCoO₂-based cathode, and an ionic liquid system using the cyclic alkyl ammonium cation *N*-methyl-*N*-propylpiperidinium bis(trifluoromethylsulfonyl)imide (PP-13); it demonstrated good coulombic efficiency and charge–discharge cycle durability. Unfortunately, however, other cells using different alkyl type ammonium cation-based ionic liquids performed rather poorly in cycle durability when compared to those using PP-13.

As is well known, an elegant way to overcome the cathodic decomposition of an organic electrolyte on the charged negative electrode is to form a solid electrolyte interface (SEI) on the negative electrode's active material surface by the addition of small amounts of additives, which prevents further decomposition [17–22]. Although there have been a few electrochemical investigations into the effect of additives on lithium ion batteries based on 1-ethyl-3-methylimidazolium (EMI)-type ionic liquids [14,15], to our knowledge, there has been no report on an ordinary lithium ion cell, composed of a graphite/LiCoO₂ system with additives added to aliphatic quaternary ammonium-based ionic liquids as the electrolyte.

In this paper, therefore, we present the results of our investigation into the physicochemical properties of a Li-binary, aliphatic, quaternary-type *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium (DEME)-based ionic liquid, and the effects of organic additives on the ionic liquids electrolyte system of a graphite/LiCoO₂ rechargeable lithium ion cell.

2. Experimental

2.1. Materials

We synthesized *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate (DEME–BF₄) and *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide (DEME–TFSI) by the procedures described in our patent application [16] and paper [13]. First, we dried all of the ionic liquids used as an electrolyte to a moisture content (w/w) of less than 20 ppm and purified them to a concentration of less than 10 ppm of metal and halogen ion impurities. To prepare the Li-binary ionic liquids, we dissolved weighed quantities of LiBF₄ into DEME–BF₄ (i.e. Li–DEME–BF₄) and LiTFSI into DEME–TFSI (i.e. Li–DEME–TFSI), respectively. Electrochemical device grade vinylene carbonate (VC), ethylene carbonate (EC), and other chemicals, were purchased from Kishida Chemical Co. and used without further purification.

2.2. Fabrication of lithium ion cells

In order to prepare the anode, we first spread on a copper foil an ink suspension of synthetic graphite (MCMB #6–28; Osaka Gas Chemical Co. Ltd.) suspended in a solution of poly(vinylidene)fluoride (PVDF; average Mw ca.

71000, purchased from Sigma-Aldrich Fine Chemicals Co. Ltd.) in 1-methyl-2-pyrrolidinone (NMP) by use of a knife blade designed to maintain a fixed distance from the copper foil. We then dried the foil at 140 °C for 72 h in vacuum to remove NMP and moisture, pressed it with a roll press at 30 MPa and dried it again at 120 °C in vacuum for 15 h. The electrode thus obtained, which was composed of 88 wt.% of graphite and 12 wt.% of PVDF, was 76 μm thick. We prepared the cathode in the same manner, except that, instead of copper foil, we used aluminum foil as a current collector. The cathode, composed of 91 wt.% of LiCoO₂ (Honjyo Chemical Corp.), 3 wt.% of acetylene black (Denka) as an electrically conductive material and 6 wt.% of PVDF, was 115 μm thick. We then electrically welded a nickel tab onto the electrode and arranged them all with a paper separator (35 μm thick) sandwiched between them. After pressing the resultant stack of electrodes and fixing them onto a tape, we inserted the electrode assembly into a bag made of thermoplastic film laminated to an aluminum sheet. We allowed the Li-binary ionic liquid (*c*: 0.9, 1.2, and 1.35 M LiTFSI) to penetrate the electrode assembly in the bag by keeping them under reduced pressure for 8 h; afterward, we sealed the bag by hot pressing under reduced pressure. For a half-cell preparation, we used a lithium metal foil instead of a LiCoO₂ electrode. We performed all of this fabrication process in a dry atmosphere (dew point of air <–80 °C).

2.3. Solid electrolyte interface formation and charge–discharge operation

To form a SEI on the electrodes, we used the following procedure. First, we charged the assembled cell at a quite small constant current, *I* = 0.11 and 1.1 mA to 3.2 and 4.0 V, respectively and discharged the cell to 3.0 V at 1.1 mA. Then, we charged it a second time to 4.2 V at 1.1 mA, and discharged it to 2.7 V at the same current at 25 °C.

The nominal operating voltage of the cells ranged from 2.7 to 4.2 V. To carry out the cell testing, we used a Charge–Discharging System (Hokuto Denko Co. Ltd.). The charge–discharge current of 1.1 mA (current density of 78.5 μA cm^{–2}) corresponds to approximately 0.1 C. We calculated the specific capacity of the cell from the result of the 0.1 C charge–discharge process and found the specific capacity of the cell per LiCoO₂ weight unit by dividing the cell capacity value by the total weight of the LiCoO₂ in the cathode. The cells cycled through the 0.1 C charge–discharge cycles at 25 °C; the cut-off limit voltages were 4.2 V for the charge and 2.7 V for the discharge.

2.4. Measurements

To carry out the ionic conductivity measurement, the voltammetry, the thermal gravimetric analysis (TGA) and the dynamic viscosity measurements of the ionic liquids and Li-binary ionic liquids, we used the methods described in our previous paper [13].

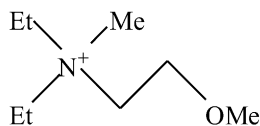


Fig. 1. Schematic illustration of the molecular structure of the DEME cation.

3. Results and discussion

3.1. Electrochemical properties of Li-binary ionic liquid

Generally, small-sized aliphatic quaternary ammonium cations cannot easily form an ionic liquid; however, by attaching a methoxyethyl group to the nitrogen atom, many aliphatic quaternary ammonium salts can form ionic liquids with BF_4^- and TFSI anions. For instance, DEME- BF_4 and DEME-TFSI are novel ionic liquids whose liquid state covers a wide temperature range [13]. Since the electron-donating feature of an oxygen atom in a methoxyethyl group weakens the cation's positive charge, the electrostatic binding between the ammonium cation and anion weakens, and an ionic liquid forms (Fig. 1).

Notably, DEME-TFSI has a relatively low viscosity and a high conductivity, $4.0 \times 10^{-3} \text{ S cm}^{-1}$ at 30°C , a remarkably wider potential window (5.4 V) than the other aromatic type ionic liquids. In Figs. 2 and 3, we show the values of the dynamic viscosity (η) and the ionic conductivity (σ) for the ionic liquids and the Li-binary ionic liquids at various temperatures.

The dynamic viscosity values of the Li-binary ionic liquids (c ; 0.9 M) are approximately 2.5–2.8 times higher than that of the pure ionic liquids. The ionic conductivities at 30°C of Li-DEME-TFSI and Li-DEME- BF_4 were, respectively,

0.37 and 0.34 mS cm^{-1} , values which were about one order of magnitude lower than those of the pure ionic liquids. As in the Li-EMI- BF_4 system, Walden's rule ($\lambda\eta = \text{const}$; where λ is the equivalent conductivity and η is the viscosity) does not hold here [6]. However, we should note that the conductivity values of the Li-DEME-TFSI and Li-DEME- BF_4 are almost identical, although the viscosities differ greatly. The viscosities were 300 and 3450 mPa s for the Li-DEME-TFSI and Li-DEME- BF_4 , respectively. The Arrhenius activation energies for conduction ($\kappa = A e^{-E_a/RT}$) in the region from 0 to 80°C are also almost the same: 33.8 and 35.1 kJ mol^{-1} for the Li-DEME-TFSI and Li-DEME- BF_4 , respectively, though the k values case of the pure ionic liquids were 19.9 kJ mol^{-1} for the DEME-TFSI and 40.1 kJ mol^{-1} for the DEME- BF_4 . Probably, in the Li-binary ionic liquids system, the Li cation is the main carrier of the ionic conduction.

Fig. 4 illustrates the limiting reduction potentials (E_{red}) on platinum of the ionic liquids as measured by cyclic voltammetry at room temperature, as well as a voltamogram of an ordinary organic electrolyte Li-TFSI in ethylene carbonate/diethylene carbonate (EC/DEC = vol. 1/1). The sharp peaks around -3.2 V are probably due to the deposition and dissolution of Li metal since a current loop appears there. The E_{red} and E_{oxd} were defined as the potential where the limiting current density reached 1 mA cm^{-2} . The E_{red} of the DEME-based ionic liquids was merely somewhat positive against the Li/Li $^+$. Therefore, we realized that, from the viewpoint of cycle durability, the Li-binary DEME-based ionic liquid was not useful as an electrolyte for a lithium ion cell without a solid electrolyte interface that could protect against a reductive decomposition of the electrolyte on the negative electrode's active material surface. On the other hand, the DEME-based ionic liquids a higher anodic stability than do the conventional organic electrolytes such as EC/DEC.

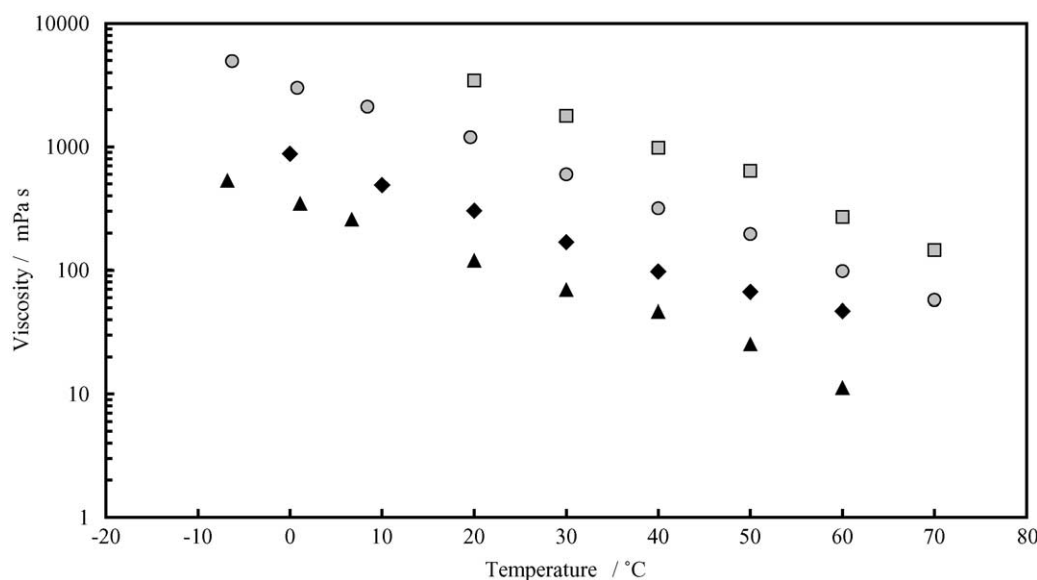


Fig. 2. Dynamic viscosity (η) as a function of temperature for the ionic liquids and the Li-binary ionic liquids. (▲): DEME-TFSI, (◆): Li-DEME-TFSI, c : 0.9 M of LiTFSI, (○): DEME- BF_4 , (□): Li-DEME- BF_4 , c : 0.9 M of Li- BF_4 .

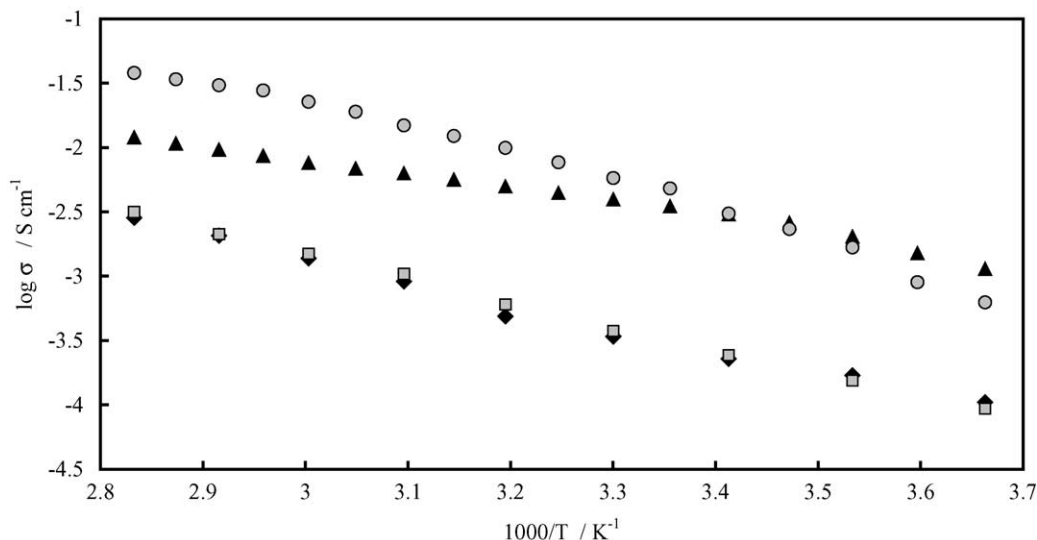


Fig. 3. Arrhenius plot of specific conductivity (σ) for the ionic liquids and the Li-binary ionic liquids. (▲): DEME-TFSI, (◆): Li-DEME-TFSI, c : 0.9 M of LiTFSI, (○): DEME-BF₄, (□): Li-DEME-BF₄, c : 0.9 M of Li-BF₄.

3.2. Solid electrolyte interface formation and lithium ion cell performance

In this part of our study, we added VC and EC to the Li-binary DEME-based ionic liquid system to provide a protective SEI.

Fig. 5 shows the discharge curves for an electrode composed of graphite of a half-cell system Li-metal/Li-DEME-TFSI, containing 10 wt.% of VC/graphite. For the cell's electrolyte, we used LiTFSI at a concentration of 0.9 M. In the first discharge curve, we noted two plateaus at 1.5–1.0 and 1.0–0.25 V, apparently due to some electrochemical reactions as well as plateaus at 0.25–0 V that indicated a lithium intercalation into graphite. The second and third discharge

curves were very similar, and we observed only one plateau due to the lithium intercalation. The capacity of the graphite was 290 mA h g⁻¹ at 0 V with respect to the Li/Li⁺ potential, a level which was similar to that observed in a conventional electrolyte, 0.9 M LiTFSI-EC/DEC vol. 1/1 solution. A protective SEI successfully formed on the graphite surface, presumably as a result of the reductive reaction between the VC, the ionic liquid, and the graphite in the plateau regions (1.5–0.25 V) in the initial discharge. Where the VC was absent a SEI apparently did not form because a plateau covering a wide voltage range appeared not only upon the first discharging but also after continuous discharging. Furthermore, the smaller charge capacity of the graphite electrode lacking the VC is probably due to the decomposition of the

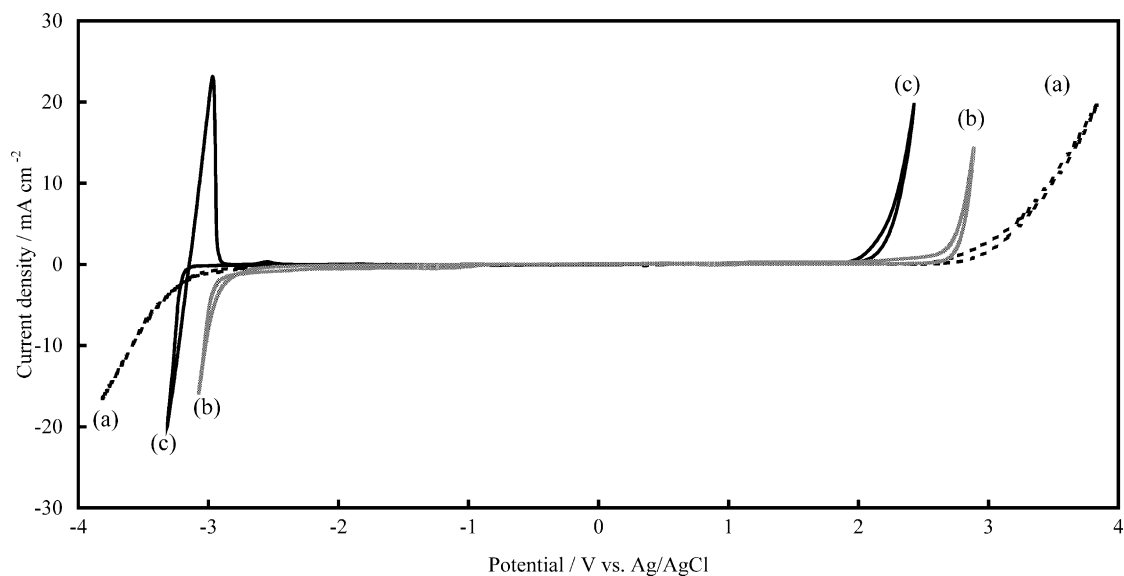


Fig. 4. Cyclic voltammogram of the ionic liquids and an organic electrolyte at 25 °C. Scan rate: 1.0 mV s⁻¹; platinum working and counter electrodes; Ag/AgCl reference electrode. (a) DEME-BF₄, (b) DEME-TFSI, (c) 0.9 M LiTFSI in EC/DEC (vol. 1/1) solution.

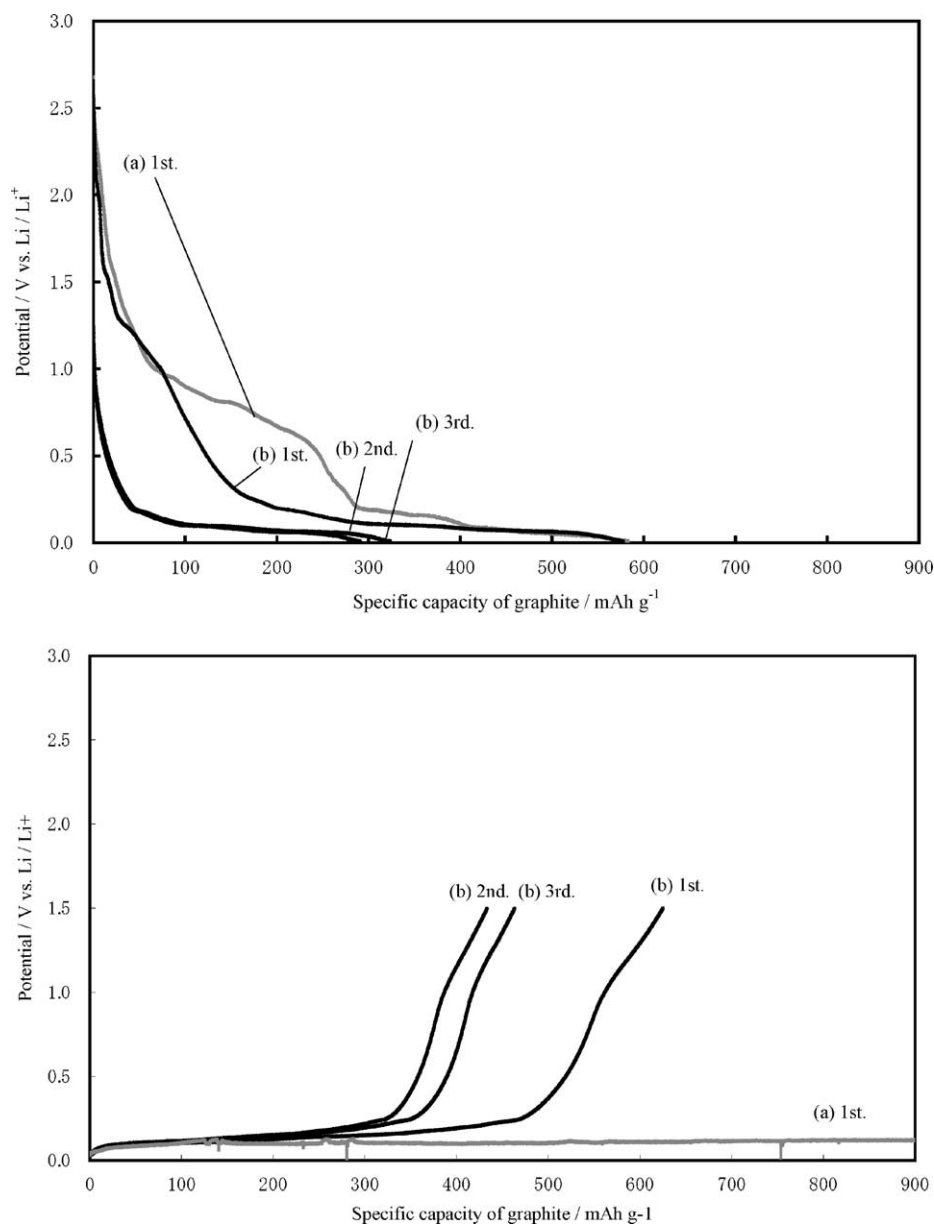


Fig. 5. The discharge and charge curves of the half-cells Li-metal/electrolyte/graphite system at 25 °C. Discharge and charge current density: $78.6 \mu\text{A cm}^{-2}$ (0.1 C), electrolyte; (a) Li-DEME-TFSI, c : 0.9 M of LiTFSI, (b) Li-DEME-TFSI containing 10 wt.% of VC, c : 0.9 M of LiTFSI.

DEME-TFSI. The Li-DEME-BF₄ containing 10 wt.% of VC yielded quite a low coulombic efficiency, although we ensured that the current density was quite small in each cycle; no doubt the formation of the SEI was inadequate.

In Fig. 6, we show the charge–discharge potential curves at 25 °C of the demonstration cells, comprising graphite/Li-DEME-TFSI containing 10 wt.% of VC/LiCoO₂, at the first, second, 10th, and 100th cycles. About 25% of the charged capacity was lost as irreversible capacity at the first cycle; however, an SEI formation presumably occurred on the graphite surface during this time. Therefore, after several initial charge–discharge cycles, the coulombic efficiency was over 99%. This result indicated that the DEME-TFSI no longer decomposed during the charging

process. The cell voltage plateaued from 4.2 to 3.0 V and dropped abruptly from 3.0 V to the end of the discharge. This plateau region indicated that a smooth electrochemical reaction of Li ion intercalation/de-intercalation occurred between the LiCoO₂ cathode and the graphite anode. This charge–discharge profile was similar to that observed in the graphite/LiCoO₂ system using a conventional electrolyte such as LiTFSI-EC/DEC. Superfluous ions, such as the DEME⁺ and TFSI⁻, evidently participated little, if at all, in the charge–discharge process.

The rate capability of the Li-DEME-TFSI cell at 25 °C appears in Fig. 7. As the discharge current increased, the discharge capacity of this cell decreased significantly faster than that of the cell using the conventional. The capacity at 1 C

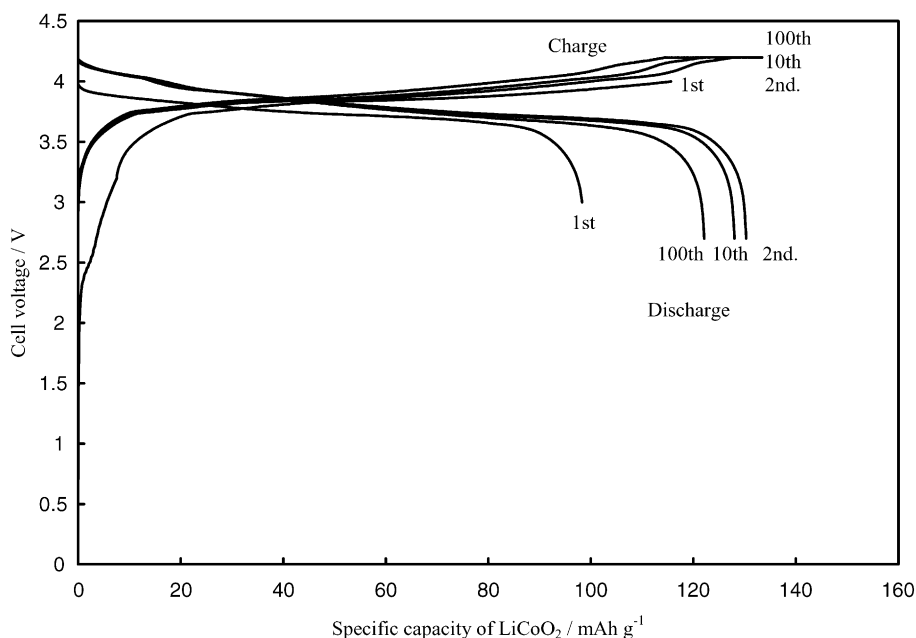


Fig. 6. The charge and discharge curves of the cell at 25 °C; graphite/electrolyte/LiCoO₂, composition, where the electrolyte was Li–DEME–TFSI containing 10 wt.% of VC, *c*: 0.9 M of LiTFSI.

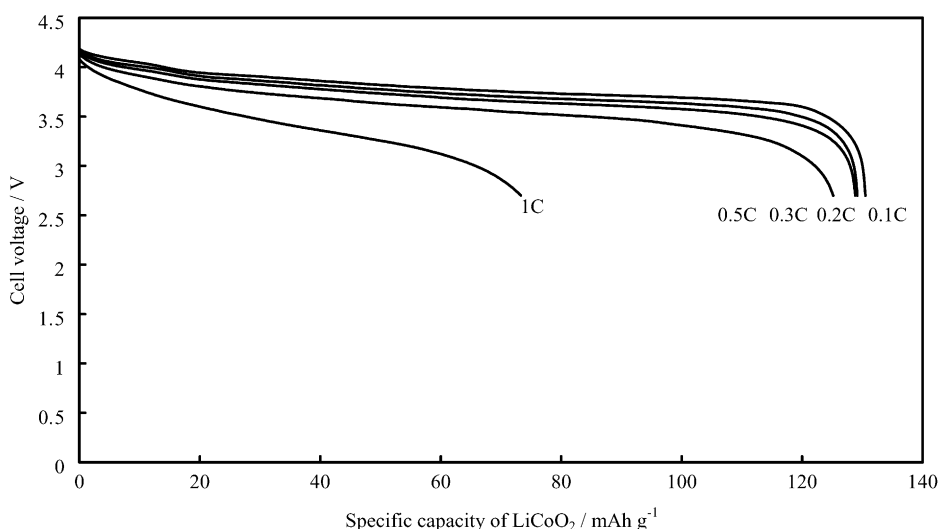


Fig. 7. The discharge curves of the cell at various current density at 25 °C; graphite/electrolyte/LiCoO₂, composition, where the electrolyte was Li–DEME–TFSI containing 10 wt.% of VC, *c*: 0.9 M of LiTFSI. The current density 78.6 $\mu\text{A cm}^{-2}$ corresponds to 0.1 C.

discharge was approximately 50% compared to that at 0.1 C discharge. Most likely, the greater decrease at large discharge currents in the capacity of the cell using Li–DEME–TFSI resulted from a large internal resistance of the cell caused by this high viscosity electrolyte. A highly viscous ionic liquid decreases the mobility of the ionic species. However, in operation at 45 and 60 °C, as shown in Fig. 8, the capacity of cell improved remarkably. The capacities of the cell at 1 C discharge were 73, 98, 102 mA h g⁻¹ for temperatures of 25, 45, and 60 °C, respectively; these levels corresponded to 56, 75, and 78% of the discharge capacity at 0.1 C discharge at 25 °C. The small amount of heating apparently decreased the

viscosity of the ionic liquid, since the effect of a temperature change on the viscosity of ionic liquids is known to be large. We suggest that at temperatures of 45 °C or above, the performance of a cell using Li–DEME–TFSI is quite adequate for practical use.

The cycling behavior of the cells, plotted in Fig. 9, indicated a cycle durability equivalent to that of a conventional lithium ion cell. The cell with higher concentration of LiTFSI showed somewhat better cycle durability. We also plotted (Fig. 9d) the cycle properties of a similar cell, using Li–DEME–TFSI containing 10 wt.% of VC and 10 wt.% of EC. Both the cycle performance and the cell performance of

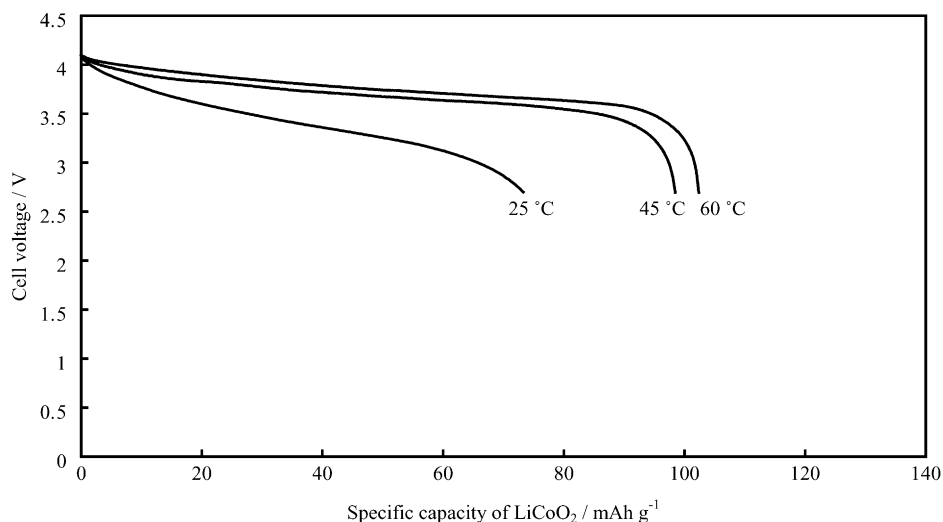


Fig. 8. The 1C discharge curves of the cell at various temperature; graphite/electrolyte/LiCoO₂, composition, where the electrolyte was Li–DEME–TFSI containing 10 wt.% of VC, *c*: 0.9 M of LiTFSI. The current density 786 $\mu\text{A cm}^{-2}$ corresponds to 1 C.

the cell containing VC and EC were comparable to that of the cell containing VC alone (Fig. 9c). It could be considered that about 10 wt.% of carbonate solvent addition was enough for the SEI formation.

Fig. 10 depicts the TG and DTA curves of the electrolyte before charging and after the charge–discharge cycles. The electrolyte, Li–DEME–TFSI containing 10 wt.% of VC before charging, showed a decrease in weight at around 100 °C, with a total weight decrease of about 8% by 300 °C, probably due to evaporation of the VC. However, after 10 or more

cycles, a similarly composed electrolyte exhibited no rapid weight decrease at around 100 °C and the total weight decrease was only about 2.4% by 300 °C. Therefore, at least 5.6% of the VC was consumed by SEI formation. Thus, the addition of VC would not spoil the incombustibility of ionic liquids. We observed no ignition in a nail penetration test of the cell using Li–DEME–TFSI with 10 wt.% of VC. However, there will be the necessity of checking the practical safety level of this type of cell by the nail penetration and overcharge examination with commercial size cell.

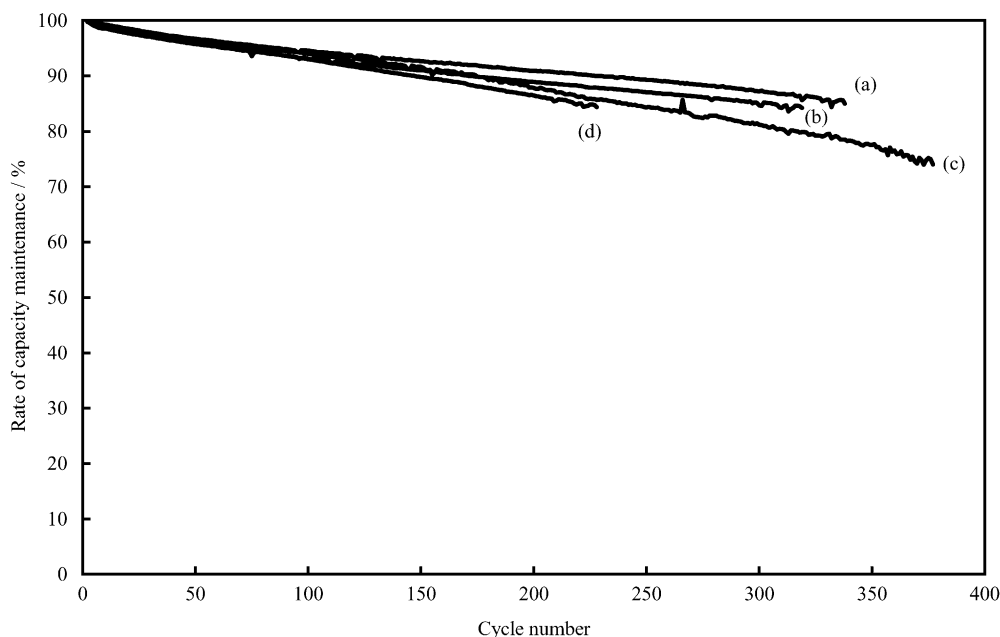


Fig. 9. The cycle life of the cells. The charge–discharge process was performed at 78.6 $\mu\text{A cm}^{-2}$ (0.1 C) constant current. The cut-off limit voltages were 4.2 and 2.7 V for the charge and discharge, respectively. The cells were graphite/electrolyte/LiCoO₂. The electrolytes were based on the Li–DEME–TFSI, containing: (a) 10 wt.% of VC, *c*: 1.2 M of LiTFSI; (b) 10 wt.% of VC, *c*: 1.35 M of LiTFSI; (c) 10 wt.% of VC, *c*: 0.9 M of LiTFSI; (d) 10 wt.% of VC and 10 wt.% of EC, *c*: 0.9 M of LiTFSI.

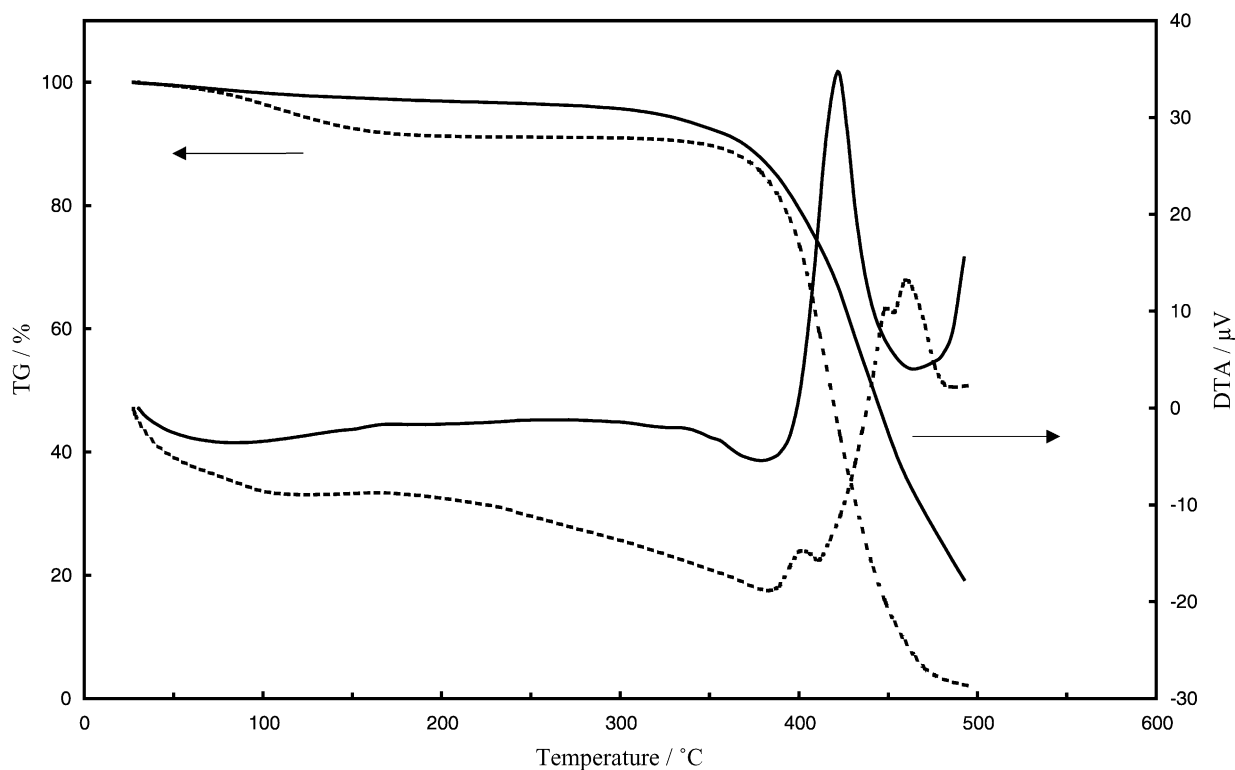


Fig. 10. TG and DTA curves plotted vs. temperature for electrolyte samples: Li–DEME–TFSI containing 10 wt.% of VC, c : 0.9 M of LiTFSI from a non-charged cell (dashed line), and a cell after 10 times charge–discharge cycles (solid line).

We suggest that certain kinds of organic electrolytes, such as VC and EC, are very useful additives, which can provide a SEI on the graphite surface of the anode in Li-binary aliphatic quaternary ionic liquids. In these liquids, the formation of an SEI effectively protects against the further decomposition of the electrolyte. Our cell is the first example of a graphite/Li-binary ionic liquid/LiCoO₂ cell system with a level of cycle durability sufficient for practical use.

4. Conclusions

Two kinds of organic solvent, such as VC and EC, are effective as SEI forming additives on the graphite used as an active material in the anode of a lithium ion cell, even in the electrolyte Li–DEME–TFSI, composed of an ionic liquid, DEME–TFSI, and Li–TFSI. The efficiencies of the lithium deposition and dissolution processes in the cell made of graphite/Li–DEME–TFSI, containing 10 wt.% of VC/LiCoO₂, were sufficient for practical use as a lithium ion battery. We have achieved for the first time a reasonable cycle performance of over 350 in the graphite/Li-binary ionic liquid/LiCoO₂ cell system. Although the capacity at 1 C discharge of a cell using the highly viscous Li-binary ionic liquid was inferior to that of a conventional cell using an organic solvent below room temperature, these liquids did offer a good, practically useful, discharge performance at temperatures of 45 °C or above. In this case, the addition of VC did

not spoil the incombustibility of the ionic liquids because the SEI formation in the initial charging cycles consumed the added organic solvent.

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