



Short communication

Imidazolium ionic liquids containing LiBOB electrolyte for lithium battery

Hidesato Saruwatari^{*}, Takashi Kuboki¹, Takashi Kishi¹, Satoshi Mikoshiba², Norio Takami¹

Corporate Research & Development Center, Toshiba Corporation, 1, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 212-8582, Japan

ARTICLE INFO

Article history:

Received 19 February 2009
 Received in revised form 14 July 2009
 Accepted 26 August 2009
 Available online 2 September 2009

Keywords:

Room-temperature ionic liquids
 1-Ethyl-3-methyl-imidazolium
 tetrafluoroborate
 Lithium bis(oxlate)borate
 Li battery

ABSTRACT

Bis(oxlate)borate anion (BOB^-) has high reduction potential for 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMIBF_4) and forms solid electrolyte interface (SEI) on lithium (Li) metal surface. The addition of BOB^- may make possible the use of EMIBF_4 for Li metal battery. The electrochemical properties of ionic liquids containing EMIBF_4 were analyzed. We investigated the stability of $\text{LiBOB}/\text{EMIBF}_4$ and $\text{LiBF}_4/\text{EMIBF}_4$ electrolyte for Li metal and the performance of Li/MnO_2 batteries with the electrolytes by ^1H NMR, ac impedance spectra and the electrochemical method. From the ^1H NMR spectra, $\text{LiBOB}/\text{EMIBF}_4$ was stable for Li metal and $\text{LiBF}_4/\text{EMIBF}_4$ was reduced on the surface of Li metal. The discharge capacity of MnO_2 cathode with $\text{LiBOB}/\text{EMIBF}_4$ was 235 mAh g^{-1} . Li metal plating and stripping and Li–Al alloying reaction were reversible in $\text{LiBOB}/\text{EMIBF}_4$. Charge–discharge reaction of Li–Al alloy in $\text{LiBOB}/\text{EMIBF}_4$ had a high coulomb efficiency. The coulomb efficiency at 1st cycle was 86% and the efficiency at 5th cycle was up to 94%.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Room-temperature ionic liquids (RTILs) consisting of organic cation and inorganic anion are a focus of keen interest since they are promising electrolytes for electrochemical devices owing to their highly flame-resistant properties, negligible vapor pressure and high thermal stability. Much effort has been devoted to improving safety for lithium (Li) batteries. The high flame resistance and negligible vapor pressure of RTILs makes them attractive candidates for safe Li-battery electrolytes. Properties of several ionic liquids, namely imidazolium salt [1–5], ammonium salt [6–8], piperidinium salt [8] and pyrrolidinium salt [9,10] were investigated as safer electrolytes for Li batteries.

Some RTILs have problems of low ionic conductivity and/or a narrow electrochemical window. 1-Ethyl-3-methyl-imidazolium tetrafluoroborate (EMIBF_4) has a high ionic conductivity of 13.0 mS cm^{-1} at 25°C , which is comparable to those of organic solvent electrolytes. In addition, the viscosity of EMIBF_4 is low. Therefore, EMIBF_4 is expected to be a good electrolyte for Li batteries. However, EMIBF_4 has not been practically used as a Li metal battery electrolyte, because of its narrow electrochemical window. The reduction potential of EMIBF_4 is around 1 V versus Li/Li^+ . Thus,

EMIBF_4 decomposes on the surface of Li metal that is the negative electrode used for Li metal batteries.

Some reduction films such as solid electrolyte interface (SEI) prevent the decomposition of EMIBF_4 [11]. The ionic liquid electrolyte is prepared in order to dissolve Li salt in ionic liquids. Li salt that has a reduction potential of above 1 V versus Li/Li^+ may result in the formation of reduction film and prevent the decomposition of EMIBF_4 . Lithium bis(oxlate)borate (LiBOB) has a reduction potential of 1.75 V versus Li/Li^+ [12] and it has been reported to form SEI at the anode [13,14]. Thus, we have taken note of the addition of LiBOB as the Li salt for ionic liquid electrolyte containing EMIBF_4 . We investigated the electrochemical property of $\text{LiBOB}/\text{EMIBF}_4$ and the stability of $\text{LiBOB}/\text{EMIBF}_4$ with Li metal. Furthermore, we evaluated the Li battery with EMIBF_4 containing LiBOB .

2. Experimental

Ionic liquids containing EMIBF_4 were prepared in order to investigate electrochemical properties of ionic liquid electrolyte. LiBOB and LiBF_4 were dissolved in EMIBF_4 to get a 1-M ionic liquid electrolyte separately. Mixed Li salt with different composition of LiBOB and LiBF_4 were dissolved in EMIBF_4 to get a 1-M ionic liquid electrolyte. These samples were stirred for 12 h at room temperature. Li salts were completely dissolved in EMIBF_4 . Li salts and EMIBF_4 (Li-battery grade) were obtained from Tomiyama Pure Chemical Industries Ltd. We prepared conventional organic solvent electrolyte, 1 M LiClO_4 , in a mixed solvent of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) with 50:50 vol.% (Li-battery grade, Tomiyama Pure Chemical Industries Ltd.).

^{*} Corresponding author. Tel.: +81 44 520 2120; fax: +81 44 520 1286.

E-mail addresses: hidesato.saruwatari@toshiba.co.jp (H. Saruwatari), takashi.kuboki@toshiba.co.jp (T. Kuboki), takashi.kishi@toshiba.co.jp (T. Kishi), satoshi.mikoshiba@toshiba.co.jp (S. Mikoshiba), norio.takami@toshiba.co.jp (N. Takami).

¹ Tel.: +81 44 520 2120; fax: +81 44 520 1286.

² Tel.: +81 44 520 2053; fax: +81 44 520 1301.

The cathodic behavior of ionic liquid electrolyte was measured by linear sweep voltammetry (LSV). LSV was performed using a potentiogalvanostat (Solartron, SI1287) equipped with a three-electrode cell (working electrode: platinum microelectrode (1.6 mm, ϕ), counter electrode: platinum wire, and reference electrode: Ag/Ag⁺).

The ionic conductivity of ionic liquid electrolyte was measured by a conductivity meter (Toa Electronics, CM-50S/CGT-551B).

Two different states of ionic liquid electrolyte containing EMIBF₄ were prepared. One state is as prepared. The other is after storing for 12 h at room temperature with Li metal. Ionic liquids electrolyte (0.1–0.2 ml) was stored with Li metal 20 mm in diameter and 0.15 mm in thickness. The stability of ionic liquid electrolyte to Li metal is well understood by comparing ¹H NMR spectra of the two electrolytes.

¹H NMR spectra were obtained with a JEOL GSX FT-NMR spectrometer. Dimethyl sulfoxide-d₆ (DMSO-d₆) was used as the external standard and sealed into a capillary.

The fabrication process of Li/MnO₂ cell is as follows. Manganese dioxide (MnO₂) (TOSOH Corporation) mixture was used as positive electrode. 83 wt.% of MnO₂ as positive-electrode active material, 10 wt.% of acetylene black and 5 wt.% of graphite as conductive agent and 2 wt.% of polytetrafluoroethylene as binder were mixed, and then pressed and formed in film to prepare a positive-electrode mixture. Li metal foil was used as a negative electrode. Polyester membrane (NIPPON KODOSHI Corporation) including ionic liquid electrolyte was used as a separator. The thickness of the polyester membrane is 50 μ m and the porosity is 65%. The negative electrode on a nickel mesh collector, the separator, and the positive electrode on a SUS mesh collector were stacked. These stacks were placed in the negative-electrode SUS container. In succession, a metal positive-electrode SUS container was fixed to a negative-electrode SUS container by means of an insulating gasket, thereby assembling a coin battery 20 mm in diameter and 1.6 mm in thickness.

The time dependence of Li/MnO₂ cell resistance at 20 °C was determined by the ac impedance method using a Solartron electrochemical interface model 1286 connected to a frequency-response analyzer model 1255.

The Li/MnO₂ cells discharged at a constant current with a current density of 0.1 mA cm⁻² or 0.5 mA cm⁻² until the battery voltage reached 2 V at 20 °C.

The cyclic voltammetry was performed using the potentiogalvanostat (Solartron, SI1287). A three-electrode test cell was assembled using nickel or aluminum as the working electrode and Li as the counter and reference electrodes.

The charge and discharge curves of 1-M LiBOB/EMIBF₄ were measured by potentiogalvanostat (Solartron, SI1287) equipped with a three-electrode cell (working electrode: nickel or aluminum plate, counter electrode: platinum plate, and reference electrode: Li metal). The three-electrode cell charged at a constant current with a current density of 0.025 mA cm⁻² for 20 min, and discharged at a constant current with a current density of 0.025 mA cm⁻² until the cell voltage reached 2 V at 20 °C.

3. Results and discussion

3.1. Electrochemical behavior of ionic liquid electrolyte

The LSV experiment results for 1-M LiBOB/EMIBF₄ and 1-M LiBF₄/EMIBF₄ on the platinum electrode are shown in Fig. 1. The potential of working electrode was swept in the negative direction from open circuit voltage of the three-electrode cell. The cathodic current at around -2.0 V versus Ag/Ag⁺ appears for 1-M LiBOB/EMIBF₄ and 1-M LiBF₄/EMIBF₄ electrolytes. This cathodic current corresponds to reduction of EMI⁺ cation. The reduction

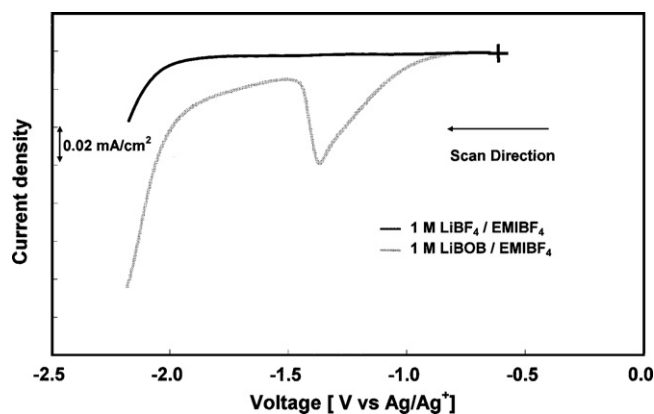


Fig. 1. Linear sweep voltammograms of 1-M LiBOB/EMIBF₄ and 1-M LiBF₄/EMIBF₄ at a scan rate of 5 mV s⁻¹ at 20 °C. Working and counter electrodes are Pt, reference electrode is Ag/Ag⁺.

potential of BF₄⁻ anion is lower than that of EMI⁺ cation [15]. The cathodic current at around -1.3 V versus Ag/Ag⁺ for 1-M LiBOB/EMIBF₄ electrolyte corresponds to the decomposition of BOB⁻ anion. BOB⁻ anion is reduced at around 1.7 V versus Li/Li⁺ [12]. The potential of 1.7 V versus Li/Li⁺ agrees with that of -1.3 V versus Ag/Ag⁺. Fig. 1 also shows that BOB⁻ anion is reduced prior to the decomposition of EMI⁺ cation in 1-M LiBOB/EMIBF₄.

3.2. Ionic conductivity of ionic liquid electrolyte

Temperature dependence of the ionic conductivity of imidazolium ionic liquid electrolyte containing different amounts of LiBF₄ and LiBOB is shown in Fig. 2. The concentration of Li salt in EMIBF₄ is 1 M. The content ratio of LiBOB/LiBF₄ changes in the order: 1/0, 1/1, 1/3 and 0/1. The ionic conductivity of pure EMIBF₄ is also shown in comparison with Fig. 2.

At 30 °C, the conductivities of the 1-M LiBOB/EMIBF₄ and 1-M LiBF₄/EMIBF₄ are 4.5 and 10.1 mS cm⁻¹, respectively. The ionic conductivity decreases with an increase in LiBOB concentration. This reason is explained by the strong van der Waals interactions operated between imidazolium cation and orthoborate anion. In this experiment, the strong van der Waals interactions operated between EMI⁺ cation and BOB⁻ anion. Similar behavior was found for ionic liquids with 1-butyl-3-methyl-imidazolium cation (BMI⁺) by Xu et al. [16]. The Arrhenius activation energy calculated from the linear region in Fig. 2 is listed in Table 1. The increase in activation energy with LiBOB concentration in the low-temperature region is much stronger than that in the high-temperature region. The increase in activation energy means that ionic mobility decreases. In the low-temperature region, the

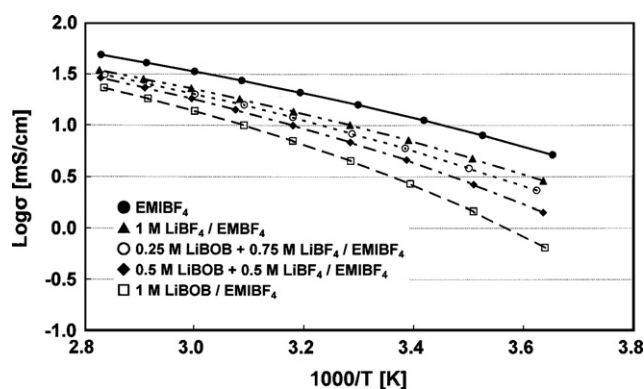


Fig. 2. Temperature dependence of ionic conductivity of ionic liquid electrolyte.

Table 1
Activation energy of ionic conductivity of 1-M (LiBF₄ + LiBOB)/EMIBF₄.

LiBOB concentration [M]	Activation energy [kJ mol ⁻¹]	
	48–80 °C	0–30 °C
0.00	21.7	29.6
0.25	23.1	31.6
0.50	25.2	37.3
1.00	28.6	45.6

decrease in ionic mobility is caused by the increase in ionic liquid electrolyte viscosity.

3.3. ¹H NMR spectra of ionic liquid electrolyte

We investigated the stability of ionic liquid electrolyte for Li metal by ¹H NMR. Fig. 3 a and b shows the ¹H NMR spectra of 1-M LiBOB/EMIBF₄ and ¹H NMR spectra of 1-M LiBOB/EMIBF₄ stored with Li metal. Fig. 4a and b shows the ¹H NMR spectra of 1-M LiBF₄/EMIBF₄ and ¹H NMR spectra of 1-M LiBF₄/EMIBF₄ stored with Li metal.

Peaks of 8.9, 7.6, 4.2, 3.8 and 1.3 ppm in Fig. 3a are assigned to proton of EMIBF₄. These spectra indicate EMI⁺ cation framework. ¹H NMR spectrum of 1-M LiBOB/EMIBF₄ with Li metal and that of 1-M LiBOB/EMIBF₄ as prepared are unchanged. However, some new peaks appear in a ¹H NMR spectrum of 1-M LiBF₄/EMIBF₄ with Li metal. These new peaks indicate decomposition of EMI⁺ cation. After 12 h storage with Li metal, 1-M LiBOB/EMIBF₄ remains transparent and clear. 1-M LiBF₄/EMIBF₄ changed to yellowish brown. These results show that EMI⁺ cation is stable for Li metal in 1-M LiBOB/EMIBF₄, but EMI⁺ cation is decomposed by Li metal in 1-M LiBF₄/EMIBF₄. In 1-M LiBOB/EMIBF₄, SEI may be formed on Li metal surface. The film prevents the decomposition of EMIBF₄.

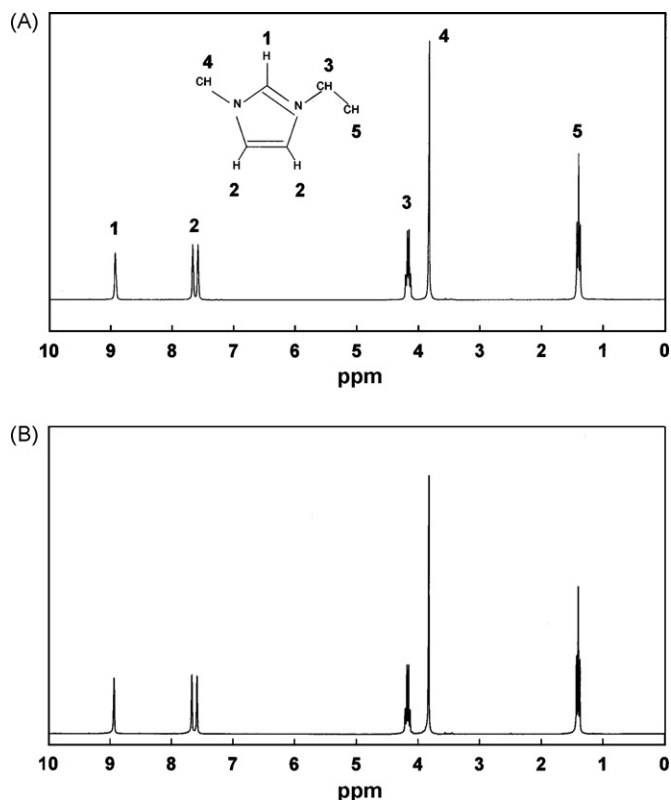


Fig. 3. ¹H NMR spectra of: (a) 1-M LiBOB/EMIBF₄ and (b) 1-M LiBOB/EMIBF₄.

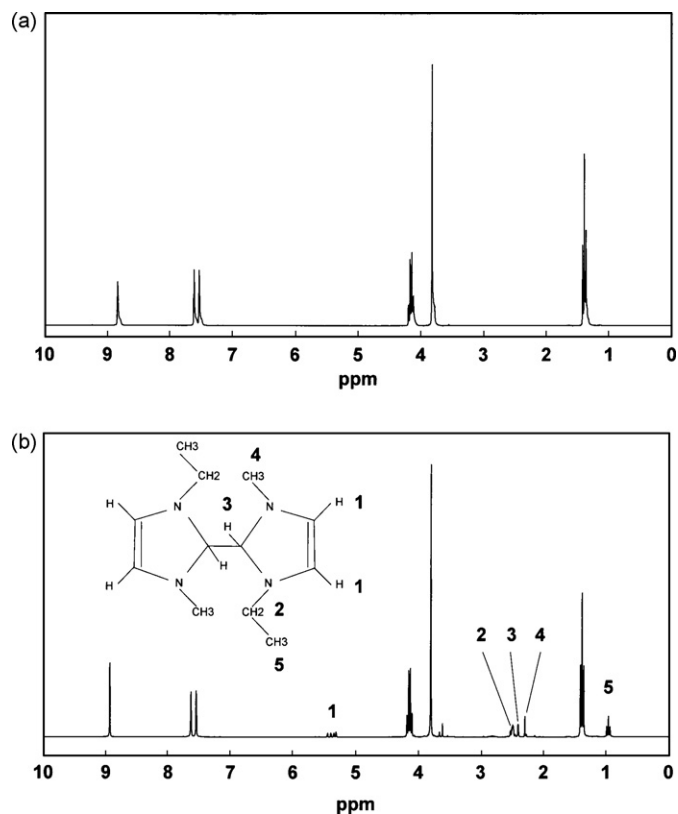


Fig. 4. ¹H NMR spectra of: (a) 1-M LiBF₄/EMIBF₄ and (b) 1-M LiBF₄/EMIBF₄ storage with Li metal for 12 h.

Peaks of 5.4, 2.6, 2.5, 2.4 and 0.9 ppm in Fig. 4a indicate the reduction product of EMI⁺ cation. Peak of 5.4 ppm shows olefin proton peaks. Appearances of these peaks indicate disappearance of aromaticity. We conjecture dimerization of EMI⁺ cation from disappearance of aromaticity. The reduction product of EMI⁺ cation would be the structural formula shown in Fig. 4b.

Xiao and Jhonson have reported the electrolysis of 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIBF₄) [17]. This paper has reported that BMIBF₄ is reduced at the cathode, and then BMI⁺ cation undergoes dimerization.

3.4. Li/MnO₂ cell with the ionic liquid electrolyte

Li/MnO₂ cell resistances were analyzed by the ac impedance method at a frequency of from 0.1 Hz to 1 MHz. Fig. 5a shows the time dependence of Li/MnO₂ cell with 1-M LiBOB/EMIBF₄ resistance. Fig. 5b shows the time dependence of Li/MnO₂ cell with 1-M LiBF₄/EMIBF₄ resistance.

The resistance of the cell with 1-M LiBOB/EMIBF₄ maintains a constant value during prolonged storage time. 1-M LiBOB/EMIBF₄ is stable in Li/MnO₂ cell. The reduction films such as SEI are formed on Li metal surface by the reduction of BOB⁻ anion.

On the other hand, the resistance of the cell with 1-M LiBF₄/EMIBF₄ increases gradually during prolonged storage time. The cross-sectional part of the semicircle at high-frequency region corresponds to the resistance of electrolyte. The increase in resistance of electrolyte means the ionic conductivity of electrolyte decreases. The decrease in the ionic conductivity is caused by EMI dimer that inhibits ion transfer in electrolyte. The increase in electrolyte resistance of the cell with 1-M LiBF₄/EMIBF₄ suggests that EMI⁺ cation is reduced by Li and EMI⁺ cation undergoes dimerization.

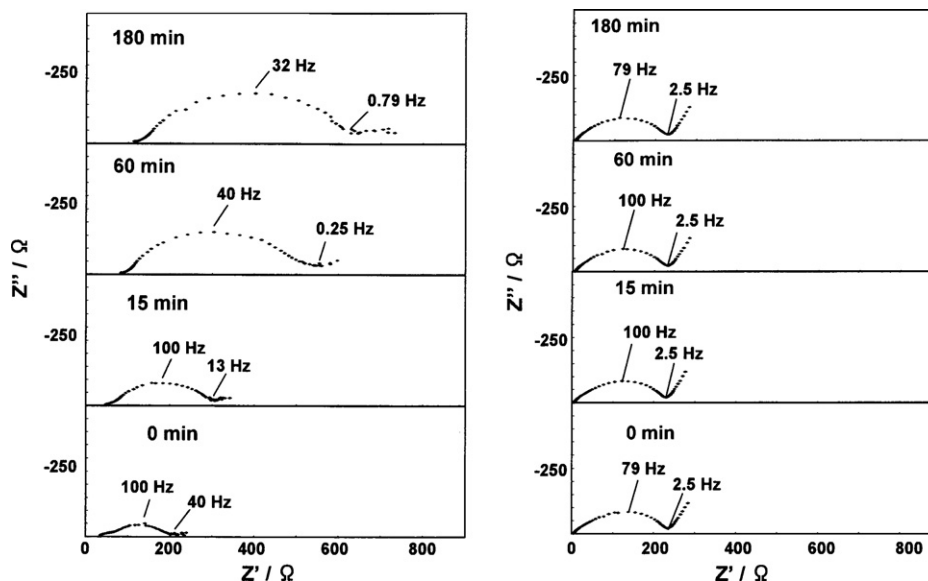


Fig. 5. The time dependence of Li/MnO₂ cell resistance with (a) 1-M LiBOB/EMIBF₄ and (b) 1-M LiBF₄/EMIBF₄ at 25 °C.

Discharge curves of Li/MnO₂ cells with 1-M LiBOB/EMIBF₄, 1-M LiBF₄/EMIBF₄ and conventional organic electrolyte 1-M LiClO₄/PC:DME(1:1) at 20 °C are shown in Fig. 6. The current density is 0.1 mA cm⁻². The discharge capacity of the Li/MnO₂ cell with LiBOB/EMIBF₄ is 235 mAh g⁻¹. The capacity of the cell with 1-M LiBOB/EMIBF₄ is comparable to that of the cell with 1-M

LiClO₄/PC:DME (1:1). We confirm that the addition of LiBOB for EMIBF₄ as Li salt makes possible the use of EMIBF₄ for Li/MnO₂ cell. The discharge capacity of the cell with 1-M LiBF₄/EMIBF₄ is only 10 mAh g⁻¹. This small discharge capacity means EMI⁺ cation is decomposed in the cell with 1-M LiBF₄/EMIBF₄.

We evaluated the high-rate discharge characteristics of Li/MnO₂ cells with the ionic liquid electrolyte (1-M LiBOB/EMIBF₄, 0.5-M LiBF₄+0.5-M LiBOB/EMIBF₄, and 0.75-M LiBF₄+0.25-M LiBOB/EMIBF₄) and organic electrolyte (1-M LiClO₄/PC:DME (1:1)).

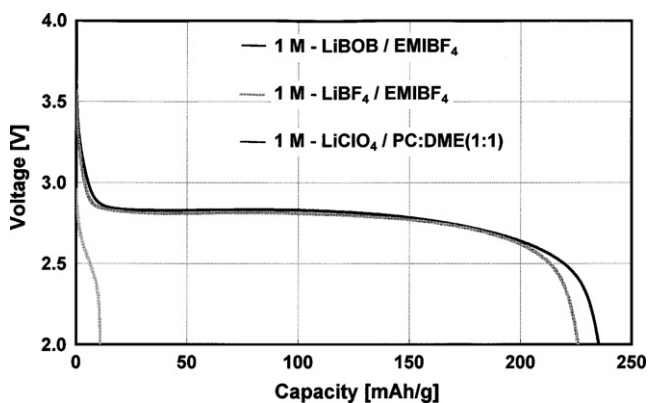


Fig. 6. Discharge curves of Li/MnO₂ coin cells. Current density: 0.1 mA cm⁻², temperature: 20 °C.

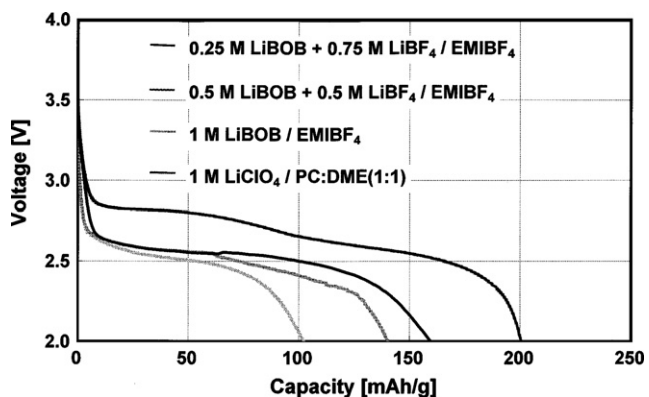


Fig. 7. Discharge curves of Li/MnO₂ coin cells. Current density: 0.5 mA cm⁻², temperature: 20 °C.

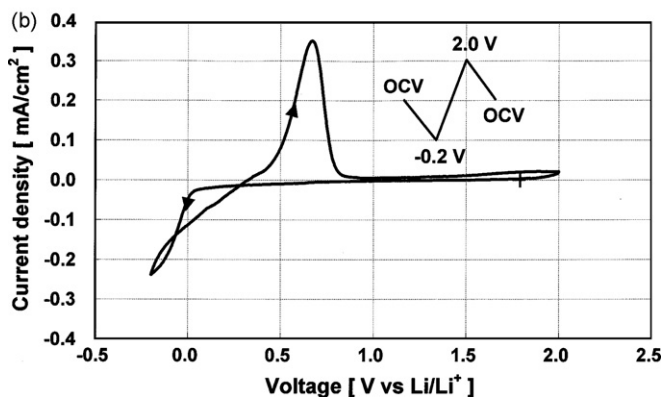
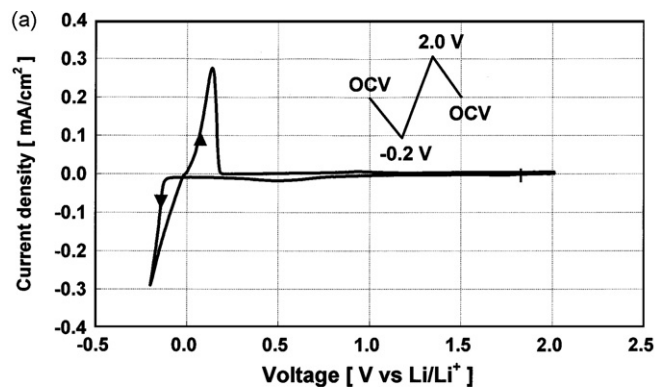


Fig. 8. Cyclic voltammograms of 1-M LiBOB/EMIBF₄ at a scan rate of 5 mV s⁻¹ at 20 °C. Working electrode are (a) Ni, (b) Al, and reference and counter electrode are Li.

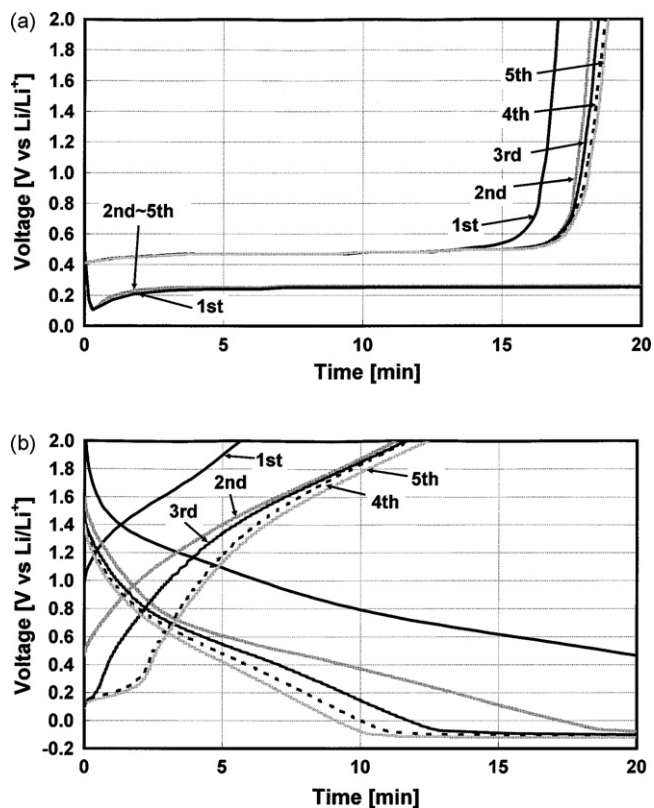


Fig. 9. Charge and discharge curves for Li on Al and Ni substrate in 1-M LiBOB/EMIBF₄. W.E.: (a) Al and (b) Ni; C.E.: Pt; R.E.: Li; charge time: 20 min, current density: 0.025 mA cm⁻², and temperature: 20 °C.

The cell has a current density of 0.5 mA cm⁻². The discharge curves at 20 °C and 0.5 mA cm⁻² are shown in Fig. 7. The cell with 0.75-M LiBF₄ + 0.25-M LiBOB/EMIBF₄ has the largest capacity among the cells with ionic liquid electrolyte. The addition of LiBF₄ is effective to improve the high-rate capability of the Li/MnO₂ cell. However, the discharge capacity and the discharge voltage of the cell with ionic liquid electrolyte are lower than those of the conventional cell. Further improvement of these features is required.

The discharge potential is decided by the relationship among polarization potential (η), open circuit potential (Φ_0), discharge potential (Φ), discharge current (I) and internal resistance (R). The relationship is expressed as the following equation [18]:

$$\Phi = \Phi_0 - (\eta + IR) \quad (1)$$

As shown in Fig. 7, the cells with ionic liquid electrolyte have large internal resistance. The addition of LiBF₄ to LiBOB/EMIBF₄ improves the large polarization of the Li/MnO₂ cell.

3.5. Investigation of LiBOB/EMIBF₄ for Li secondary battery

Cyclic voltammograms for 1-M LiBOB/EMIBF₄ on the nickel and aluminum electrode are shown in Fig. 8. The voltammograms in Fig. 8a shows Li metal plating/stripping and that in Fig. 8b show

Li–Al alloying reaction in LiBOB/EMIBF₄. These voltammograms indicate that Li metal plating/stripping and Li–Al alloying reaction are reversible in LiBOB/EMIBF₄. The working electrode of Ni or Al without surface treatment was used. So, the passive film on the Ni or Al may suppress the reduction of BOB⁻ anion. Hence, the reduction current at ca. 1.7 V versus Li/Li⁺ was very small in Fig. 8.

Charge–discharge curves for Li in LiBOB/EMIBF₄ are shown in Fig. 9. From the result of charge–discharge curves in Fig. 9a, Li–Al alloying reaction in LiBOB/EMIBF₄ has high coulomb efficiency with low over-potential. Though 1st charge and discharge efficiency is 86%, 5th efficiency is up to 94%. Li–Al alloy is stable in LiBOB/EMIBF₄. Li metal plating/stripping reaction in LiBOB/EMIBF₄ has low coulomb efficiency with large over-potential as shown in Fig. 9b. 1st charge and discharge efficiency is 28% and that of the 5th is 62%. The naked Li metal by Li metal electrodeposition reacts with LiBOB/EMIBF₄. These results indicate that Li–Al alloying reaction is possible in LiBOB/EMIBF₄ and suggest the possibility of applying LiBOB/EMIBF₄ electrolytes for Li secondary battery.

4. Conclusion

We confirmed that it is possible to use LiBOB/EMIBF₄ as the electrolyte for Li/MnO₂ cell. The addition of LiBOB to EMIBF₄ restrained the reaction of Li metal with EMI⁺ cation. The cell impedance with LiBF₄/EMIBF₄ increased gradually owing to the reaction of Li metal with EMI⁺ cation. The LiBOB/EMIBF₄ was stable for Li metal. The Li/MnO₂ cell with LiBOB/EMIBF₄ showed a large discharge capacity of 235 mAh g⁻¹ at 20 °C. Li metal plating and stripping and Li–Al alloying reaction were reversible in LiBOB/EMIBF₄. Charge–discharge reaction of Li–Al alloy in LiBOB/EMIBF₄ had a high coulomb efficiency. The LiBOB/EMIBF₄ was also a promising electrolyte for rechargeable Li batteries using Li alloy anode.

References

- [1] V.R. Koch, C. Nanjundiah, G.B. Appetecchi, B. Scrosati, J. Electrochem. Soc. 142 (1995) L116.
- [2] N. Koura, K. Etoh, Y. Idemoto, F. Matsumoto, Chem. Lett. (2001) 1320.
- [3] Y.S. Fung, R.Q. Zhou, J. Power Sources 81 (1999) 891.
- [4] H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, J. Electrochem. Soc. 150 (2003) A695.
- [5] M. Egashira, T. Kiyabu, I. Watanabe, S. Okada, J. Yamaki, Electrochemistry 71 (12) (2003) 1114.
- [6] T. Sato, G. Masuda, K. Takagi, Electrochim. Acta 49 (2003) 3603.
- [7] H. Matsumoto, H. Sakaebe, K. Tatsumi, J. Power Sources 146 (2005) 45.
- [8] H. Sakaebe, H. Matsumoto, K. Tatsumi, J. Power Sources 146 (2005) 693.
- [9] H. Sakaebe, H. Matsumoto, Electrochem. Commun. 5 (2003) 594.
- [10] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, Electrochem. Solid-State Lett. 7 (2004) A97.
- [11] D. Aurbach, A. Zaban, Y. Ein-Eli, I. Weissman, O. Chusid, B. Markovsky, M. Levi, A. Schechter, E. Granot, J. Power Sources 68 (1997) 91.
- [12] J.C. Panotz, U. Wietelmann, M. Wachtler, S. Strobele, M.W. Mehrens, J. Power Sources 153 (2006) 396.
- [13] W. Lu, Z. Chen, H. Joachin, J. Prakash, J. Liu, K. Amine, J. Power Sources 163 (2007) 1074.
- [14] J. Liu, Z. Chen, S. Busking, I. Belharouak, K. Amine, J. Power Sources 174 (2007) 852.
- [15] M. Ue, Curr. Top. Electrochem. 7 (2000) 49.
- [16] W. Xu, L. Wang, R.A. Nieman, C.A. Angell, J. Phys. Chem. B 107 (2003) 11749.
- [17] L. Xiao, K.E. Jhonson, J. Electrochem Soc. 150 (2003) E307.
- [18] W. Guoping, Z. Qingtang, Y. Zuolong, Q. Meizheng, Solid State Ionics 179 (2008) 267.