

Preparation of room temperature ionic liquids based on aliphatic onium cations and asymmetric amide anions and their electrochemical properties as a lithium battery electrolyte

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Available online 7 July 2005

Abstract

The physical and electrochemical properties of room temperature ionic liquids (RTILs) based on asymmetric amide anions (TSAC: 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)acetamide, C1C2: *N*-(trifluoromethylsulfonyl)pentafluoroethylsulfonamide) and aliphatic onium cations, such as ammonium, phosphonium, and sulfonium, were reported. The melting point of the C1C2 salts decreased compared to the corresponding TFSI salts (TFSI: bis(trifluoromethylsulfonyl)imide), however, the viscosity was about twice that of the TFSI salts. Relatively low viscosity RTILs based on aliphatic onium cations could be prepared using the TSAC anion and tetraalkylammonium cation containing an alkoxy group. The linear sweep voltammogram of these RTILs with and without Li-TFSI were investigated in order to estimate the electrochemical windows and possible use as a lithium battery electrolyte.

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Keywords: Aliphatic onium cations; Tetraalkylammonium cation; TFSI

1. Introduction

Room temperature ionic liquids (RTILs) have been extensively studied due to their unique properties, which could not be obtained with conventional molecular liquids. Especially, the nonvolatile and noncombustible natures of the RTILs seem make them attractive candidates for a safe lithium battery electrolyte, but only a few studies have been reported on this subject [1,2].

In these reports, aromatic cations, such as 1-ethyl-3-methylimidazolium (EMI), have been used for as the cationic component of the RTILs. The EMI cation is the best cation to form the RTIL, which has a low viscosity and low melting point, with various anions. However, the electrochemical stability as a lithium battery electrolyte was not satisfactory since the cathodic limiting potential is ca. +1.0 V versus Li/Li⁺, and additives, such as thionyl chloride, were essential for improving the coulombic efficiency for lithium deposition in an RTIL based on EMI [2b–d].

Aliphatic quaternary ammonium (AQA) salts are often used as a supporting electrolyte in electrochemical studies due to their good electrochemical stability. Therefore, an RTIL consisting of the AQA cation might be better for use as a lithium battery electrolyte compared to the EMI systems. There are only a few reports on such RTILs based on AQA [3], however, the viscosity was generally an order of magnitude higher than that of the EMI systems until the RTIL containing AQA and TFSI (TFSI: bis(trifluoromethylsulfonyl)imide) anion was reported [4].

Our group showed that AQA-TFSI possesses a high cathodic stability compared with EMI-TFSI and that lithium plating and stripping behavior could be observed in the RTIL based on AQA and TFSI (AQA-TFSI) without any additives [5]. A greater than 97% coulombic efficiency could be achieved in the charge/discharge test of the Li/LiCoO₂ half cells using AQA-TFSI [6]. However, the viscosity of AQA-TFSI remained about twice that of the EMI system. Therefore, lowering the viscosity of the AQA systems is necessary in order to use these melts in electrochemical devices such as a lithium battery. For

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this purpose, we also reported that the 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl)-acetamide (TSAC) anion with an asymmetrical structure and lower molecular weight than that of bis(trifluoromethylsulfonyl)imide anion forms low melting and low viscous RTILs [7]. Introducing an alkoxy group into the tetraalkylammonium reduced the viscosity and the melting point [5].

We would like to report the preparation of relatively low viscosity RTILs based on aliphatic onium cations that were developed by our group and focus on the electrochemical properties of the relatively low viscous and low-melting RTILs based on AQA with amide (or imide) anions such as TFSI, TSAC and *N*-(trifluoromethylsulfonyl)-pentafluoroethylsulfonamide, which is denoted as C1C2. In this paper, not only TSAC and C1C2, but also TFSI, all of which contain the “–N[–]–” structure, are called “amides” and not “imides”.

2. Experimental

The preparation of the amide salts was basically followed the reference method [8]. Since the RTILs based on amide anions and quaternary onium cations used in this study are hydrophobic, a relatively pure sample can be obtained by the simple metathesis reaction in water. The desired RTILs were immediately precipitated by mixing the aqueous solutions containing the onium bromide and lithium or potassium salts consisting of amide anions as shown in Fig. 1. The amount of alkali metal salts were slightly in excess versus that of the onium salts due to the fact that the alkali metal cation contained in the hydrophobic RTILs can be easily removed by washing with water, however, the halide anion could not be reduced any more. This fact was confirmed by fluorescence X-ray spectrometry (XRF, JEOL JSX-3201). The precipitated RTILs were extracted by CH₂Cl₂ and then the extract was washed with water, that is, adding water to the CH₂Cl₂ solution in a separatory funnel and vigorously shaking. After

complete dissociation of the water and the CH₂Cl₂ layer was confirmed, the CH₂Cl₂ was distilled off using a rotary evaporator. Finally, the RTIL was dried under vacuum at 105 °C for 2 h. The residual water in the dried RTIL was below 10 ppm which was measured using a Karl–Fisher moisture meter (Mitsubishi CA-07). The C1C2 salts and the TSAC salts were prepared by the same methods as that for the TFSI salts. The anionic source was Li-C1C2 and K-TSAC, respectively.

For use of Li-TFSI as an anion source, the residual amount of the Li cation in the resultant RTILs was below the detection limit (5 ppm) of an inductively-coupled plasma spectrometer (ICP, Shimadzu ICPS-8100). That of the bromide anion was below 25 ppm, which is the detection limit of the XRF. Based on ion chromatography, the bromide anion was not observed above the detection limit (<50 ppm). However, a relatively high amount of bromide anion (>500 ppm) in the resultant RTILs was observed for the RTILs based on AQA containing the methoxyethyl group. In such cases, a neutralization reaction between the acid (H-TFSI) and tetraalkylammonium hydroxide was used for the preparation of the bromide-free RTILs. The tetraalkylammonium hydroxide was prepared using a cation-exchange column (Mitsubishi Chem).

The ethylammonium or triethylammonium salts were prepared by neutralization between the amines and acid such as H-TFSI in pure water. All the samples were checked by NMR (¹H, ¹³C, ¹⁹F) and an elemental analysis (CHN).

The measurements of the physical properties of the RTILs were done in an open dry chamber (dew point in chamber greater than –50 °C, Daikin HRG-50A). The viscosity was measured using a cone-plate type viscometer (Brookfield DV-III+). The conductivity was estimated using a conductivity meter (Radiometer Analytical, model CDM230). The melting point was by DSC (Perkin-Elmer, Pyris 1).

The linear sweep voltammetry (LSV) was performed (ALS model 600) in an argon-filled glove box (O₂ and water <5 ppm). A glassy carbon electrode (GC, surface area: 7.85 × 10^{–3} cm²), a Pt electrode (surface

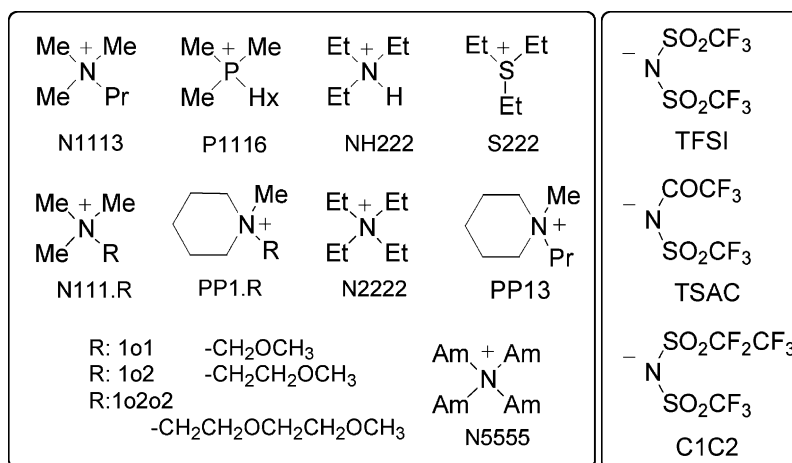


Fig. 1. Structure of cation and anion components in this study: Me, methyl; Et, ethyl; Pr, *n*-propyl; Am, *n*-amyl (*n*-pentyl); Hx, *n*-hexyl.

area: $2.0 \times 10^{-2} \text{ cm}^{-2}$) and Ni electrode (surface area: $1.7 \times 10^{-2} \text{ cm}^{-2}$) were used as the working electrodes. The GC electrode was polished with diamond paste ($d=1 \mu\text{m}$), while the Pt and Ni were both polished with an alumina paste ($d=0.1 \mu\text{m}$). The polished electrodes were washed with Milli-Q water and dried under vacuum. The I_3^-/I^- reference electrode for the RTILs consisted of Pt wire/ $0.015 \text{ mol dm}^{-3} \text{ I}_2 + 0.060 \text{ mol dm}^{-3} [(n\text{-C}_3\text{H}_7)_4\text{N}]\text{I}$ in EMI-TFSI (EMI, 1-ethyl-3-methylimidazolium). The potential was referenced to the ferrocene (Fc)/ferrocenium (Fc^+) redox couple in each RTIL.

3. Results and discussion

3.1. Physical properties of various RTILs based on amide anions

Fig. 1 shows the structures of the ionic component of the RTILs evaluated in this study. Table 1 indicates the physical properties of the various RTILs based on the aliphatic onium cations and amide anions as shown in Fig. 1.

For the same cation, the melting point decreased with the use of an asymmetric anion, such as TSAC and C1C2,

compared with a symmetric one, such as TFSI except for EMI-TSAC and P1116-C1C2. The asymmetry in the anionic structure might have an effect on blocking the close packing between a cation and an anion as well observed in RTILs containing an asymmetric cation such as EMI and N1113 to reduce the melting points. To understand the reason why the melting point of EMI-TSAC and P1116-C1C2 was higher than that of EMI-TFSI and P1116-TFSI, respectively, we must further study the various imidazolium and phosphonium systems.

On the other hand, the viscosity decreased with the decreasing molecular weight of the anion with the same cation. This observation was also seen for the same anion. For example, the viscosity of the N1113 system was much lower than that of the N5555 system. These results suggest that the molecular weight of both the anion and cation should be decreased as low as possible to make a low viscosity RTIL, which must be necessary for Li battery applications. However, the molecular weight of the cation and anion cannot be too much decreased since the melting point increases over room temperature.

The TSAC anion is apparently the most preferable among the three amide anions studied here to form low melting and low viscosity RTILs with small aliphatic ammonium cations.

Table 1
Physical properties of various RTILs based on aliphatic onium cations and amide anions at 25 °C

Cation	Anion	MW ^a	Density (g mL ⁻¹)	T_m^b (°C)	η^c (cP)	σ^d (mS cm ⁻¹)	Reference
EMI	TSAC	355	1.46	-1.5	25	9.9	[7]
EMI	TFSI	391	1.52	-12	33	8.7	[5b]
EMI	C1C2	441	1.56	(-93)	48	4.4	This work
N1113	TSAC	346	1.38	10	46	4.3	[12]
N1113	TFSI	382	1.44	19	72	3.1	[5b]
N1113	C1C2	432	1.48	19	174	1.2	This work
N2222	TSAC	374	1.37	21	60	3.6	[7]
N2222	TFSI	410	-	114	-	-	[14]
N2222	C1C2	460	-	69	-	-	This work
N5555	TSAC	542	1.11	16	391	0.20	This work
N5555	TFSI	578	1.16	25	554	0.15	[14]
N5555	C1C2	628	1.18	25	650	0.11	This work
PP13	TSAC	386	1.37	(-83)	98	2.1	This work
PP13	TFSI	422	1.43	12	151	1.4	[6]
PP13	C1C2	472	1.46	-4	281	0.71	This work
PP1.1o1	TFSI	424	1.47	(-85)	68	2.2	This work
PP1.1o2	TFSI	438	1.45	(-91)	55	2.7	This work
PP1.1o2o2	TFSI	483	1.44	(-82)	88	1.7	This work
N111.1o1	TFSI	384	1.51	4.5	50	4.7	[7]
N111.1o2o2	TFSI	442	1.44	(-80)	63	2.6	This work
NHHH2	TFSI	326	-	48	-	-	This work
NH222	TFSI	382	1.42	3	48	4.4	This work
P1116	TSAC	405	1.28	7.3	91	1.4	This work
P1116	TFSI	441	1.34	21	150	0.92	This work
P1116	C1C2	491	-	40	-	-	This work
S222	TSAC	363	1.42	(-102)	28	9.0	This work
S222	TFSI	399	1.49	-14	33	8.5	[9]
S222	C1C2	449	1.53	(-93)	55	3.7	This work

^a Molecular weight.

^b Melting point determined by DSC on heating. The data in parentheses is glass transition temperature (T_g) of the RTILs, which did not show any other peaks.

^c Viscosity at 25 °C.

^d Specific conductivity at 25 °C.

However, unfortunately, the electrochemical stability of the TSAC systems was very limited by the low electrochemical stability of the TSAC anion itself as stated below.

Table 1 also indicates another method to lower both the melting point and viscosity of the aliphatic ammonium system. The relatively high melting PP13-TFSI can be much improved by introducing an alkoxy group into the *N*-methylpiperidinium such as PP1.1o2. Not only melting points but the viscosity also decreased. However, the electrochemical stability of the quaternary ammonium systems was limited by the presence of the alkoxy group as stated in the next section.

The physical properties of the S222 salt was almost the same as that of EMI even for the aliphatic onium cation which was not expected to form a low viscosity RTIL compared to the aromatic EMI cation due to its poor charge dispersibility. The flat shape of the S222 might be the cause of the low viscosity. Indeed, the triethylammonium (NH222) also forms relatively low viscosity RTILs even in aliphatic ammonium systems as shown in Table 1. However, the electrochemical stability of NH222-TFSI was poor compared to the fully alkylated tetraalkylammonium salt as stated below. The sulfonium salt also exhibited a poor electrochemical stability as already reported [9].

Based on these results, a new anion, which forms low-melting and low viscosity RTILs consisted of a fully alkylated quaternary ammonium cation to maintain its electrochemical stability, will be necessary. Recently, a new fluoroborate anion, such as perfluoroethyltrifluoroborate and trifluoromethyltrifluoroborate, was reported [10,11a]. The perfluoroethyltrifluoroborate anion forms RTILs with AQA having relatively low melting points and low viscosities compared with the tetrafluoroborate systems [11b]. It is

interesting that these anions possess an asymmetric structure as in the case of TSAC and C1C2.

3.2. Electrochemical windows of various RTILs based on amide (or imide) anions

Fig. 2 shows linear sweep voltammograms of various RTILs based on amide anions and aliphatic onium cations. Fig. 2(a) shows a LSV of the AQA salt and other related ammonium salts and the TFSI anion. A good cathodic and anodic stability was seen only for the fully alkylated ammonium and phosphonium salts and not for the mono- or tri-alkylated ammonium salts. This figure suggests that the cathodic limit potential (E_{CL}) was determined by the reduction of the cation, and the anodic limit potential (E_{AL}) was determined by the oxidation of the anion if the TFSI anion would be more stable for reduction than a quaternary ammonium cation, such as N1113, and a quaternary ammonium cation more stable for oxidation than TFSI. However, this was not valid for the EMI systems. As shown in Fig. 2(b), which shows the LSV of the C1C2 salts compared with that of the corresponding TFSI salts, the E_{AL} for the EMI systems (+2.0 V versus Fc/Fc^+) was much positive than that of the PP13 systems (+2.5 V versus Fc/Fc^+) even when both systems consisted of the same anion such as TFSI. As previously reported [5a], the oxidation potential of Li-TFSI in an acetonitrile solution was observed at +2.5 V versus Fc/Fc^+ , which was almost the same as the E_{AL} of PP13-TFSI. These results suggest that the E_{AL} of the EMI systems must not be determined by the anion oxidation, but the EMI oxidation, and the electrochemical stability of the C1C2 anion was almost the same as that of TFSI.

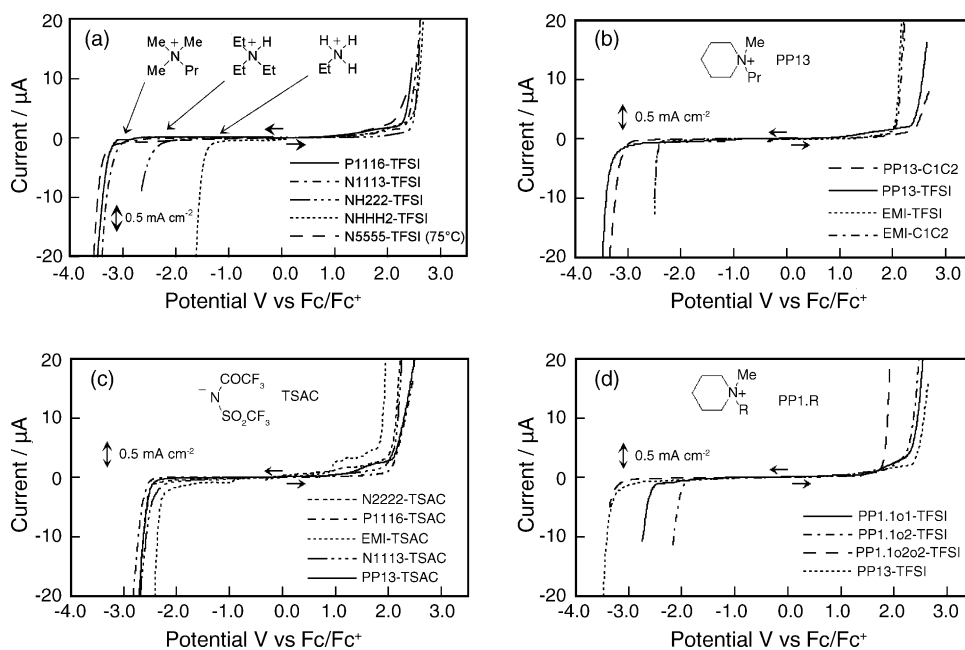


Fig. 2. Linear sweep voltammograms (the first cycle) of GC in various RTILs at 25 °C. For NH222-TFSI, the sample was heated at 50 °C since this salt has a high melting point (ca. 48 °C), scan rate = 50 mV s⁻¹.

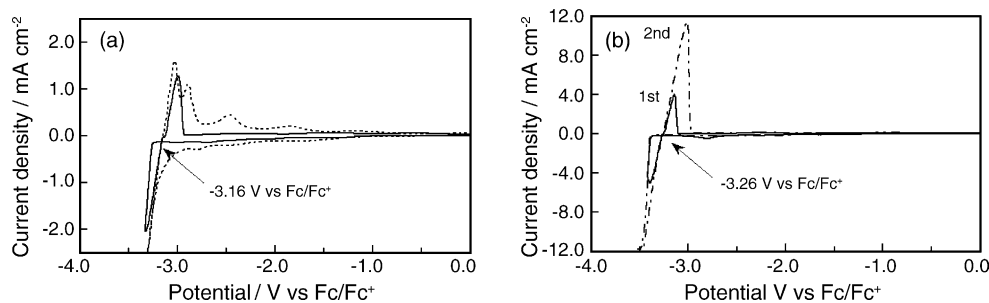


Fig. 3. The first cycle of cyclic voltammogram of metal electrode at 25 °C: (a) in N1113-TFSI containing 0.4 mol dm⁻³ of Li-TFSI. Working electrode, Pt (dotted line), Ni (solid line); (b) in propylene carbonate containing 1.0 mol dm⁻³ Li-TFSI. Working electrode, Ni. Scan rate = 50 mV s⁻¹.

On the other hand, for the TSAC salts (Fig. 2(c)), both the cathodic limit potential (E_{CL}) and anodic limit potential (E_{AL}) shifted in an unfavorable direction, viz., E_{CL} went positive, and E_{AL} went negative for the AQA systems. These results can be explained by the poor electrochemical stability of the TSAC anion compared with TFSI and C1C2. As previously reported [5a], the oxidation and reduction potentials of K-TSAC in acetonitrile were observed in +2.0 V versus Fc/Fc⁺ and -2.7 V versus Fc/Fc⁺, respectively, which were almost the same as that the E_{AL} and E_{CL} of various TSAC salts. Therefore, the TSAC anion has an excellent ability to lower both the melting point and the viscosity; however, the electrochemical stability of TSAC seems unsuitable for a lithium battery application. The reason for this might be the existence of the carbonyl group in TSAC.

As stated above, the viscosity of the AQA melts could be decreased by introducing an alkoxy group into the side chain of AQA. Fig. 2(d) shows the LSV of TFSI salts containing various piperidinium cations with an alkoxy group. In this case, both the E_{CL} and E_{AL} depend on the kind

of alkoxy group in the cationic structure. The E_{CL} of the methoxymethyl and methoxyethyl piperidiniums shifted to a positive potential compared with PP13-TFSI. On the other hand, the E_{CL} of the methoxyethoxyethyl piperidinium was almost the same as that of PP13-TFSI, however, the E_{AL} shifted to a negative potential, which indicated that the methoxyethoxyethyl group is easily electrochemically oxidized. In the range of our investigation, the electrochemical stability of AQA with an alkoxy group and TFSI did not maintain the advantage of using the AQA cation.

The lack of a good electrochemical stability of these salts might seem unsuitable for lithium battery applications. However, the addition of a lithium salt to these RTILs apparently improves the cathodic limit potential as stated below.

3.3. Lithium redox in RTILs based on aliphatic ammonium salts.

As shown in Fig. 3(a), lithium metal can be deposited on a Ni electrode at ca. -3.2 V versus Fc/Fc⁺ in RTILs based on

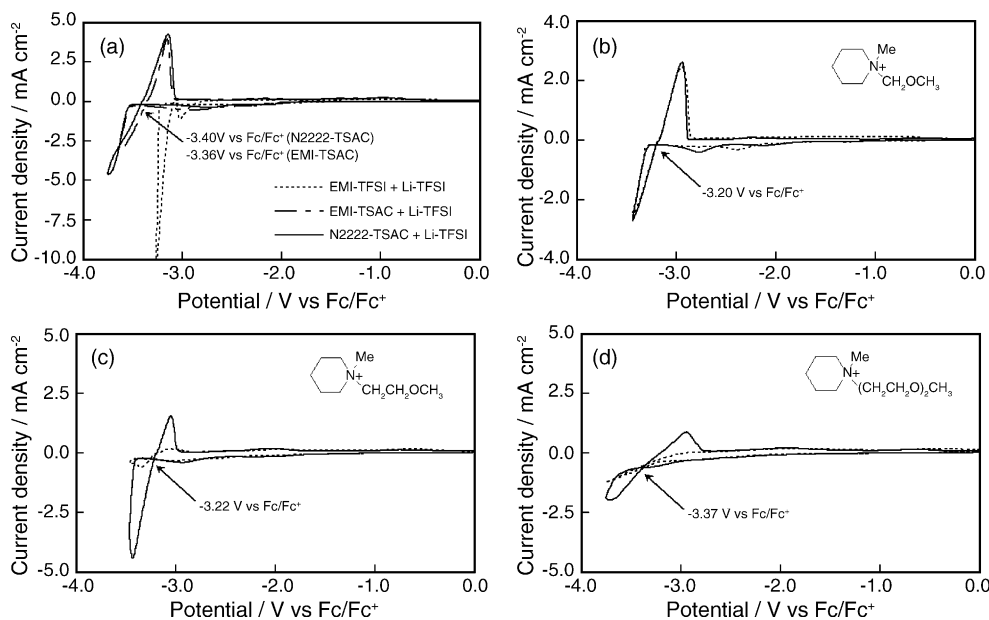


Fig. 4. The first cycle of cyclic voltammogram of Ni in various RTILs containing 0.5 mol dm⁻³ of Li-TFSI at 25 °C. Scan rate = 50 mV s⁻¹. Dotted lines of (b), (c) and (d) were taken after 10 cycles. The data of EMI-TFSI shown in (a) were taken from [13].

N1113-TFSI. The potential was slightly positive from that observed in propylene carbonate (Fig. 3(b)). In case of the Pt electrode, many peaks due to the formation of a Li–Pt alloy could be clearly observed. The shape of the plating/stripping peaks in N1113-TFSI was not notably changed at least after 20 cycles.

As shown in Fig. 2, the relatively low viscosity RTILs, such as the TSAC salts and TFSI salts containing AQA with an alkoxy group, were not electrochemically stable compared with the TFSI salts containing AQA without an alkoxy group. However, as shown in Fig. 4, the lithium plating/stripping behaviors could be observed with the addition of Li-TFSI to these salts except for EMI-TFSI (Fig. 4(a)). This means that the E_{CL} of these salts shifted to a negative potential compared to that without Li-TFSI. Though the reason why the plating/stripping of lithium could not be observed in EMI-TFSI is still unknown at this time, one of the reasons might be attributed to the difference in the properties of the SEI film on Ni compared with the other salts. Recently, we showed that the E_{CL} of EMI-TFSI was dramatically shifted about 1.0 V more negative with the addition of Li salts, however, other alkali metal salts had no effect on the shift of the E_{CL} . We then speculated that the SEI would consist of the lithium cation and reduced ions derived from the RTIL [13].

The shape of the lithium plating/stripping peaks, which might reflect a smooth redox reaction through the SEI film, was different among these RTILs with the poor electrochemical stability. Since the shape did not depend on the viscosity and the E_{CL} of the RTILs, the quality of the SEI depends on the lithium redox behavior. It will be necessary to further investigate the chemical and/or electrochemical properties on the electrode surfaces.

4. Conclusion

We prepared various RTILs based on three different amide anions and aliphatic onium cations. The physical and electrochemical properties of the RTILs depend on the type of cation and anion. The attempt to lower the viscosity, by using the TSAC anion and tetraalkylammonium with an alkoxy group resulted in a decreased E_{CL} or increased E_{AL} compared with the TFSI salt, such as N1113-TFSI and PP13-TFSI. The addition of Li-TFSI improved the cathodic stability as seen in EMI-TFSI [13]. However, the shape of the lithium plating/stripping does not depend on the viscosity and the E_{CL} but on the kind of RTILs. These results imply that the

properties of the SEI on Ni might be different based on the kind of RTILs.

Acknowledgements

A part of this work was supported by the project concerning Li battery by NEDO and METI. Authors are also grateful for Tokuyama Corp. for supply of K-TSAC, and for Central Glass Co. Ltd., for supply of Li-C1C2.

References

- [1] A. Webber, G.E. Blomgren, in: W. van Schalkwijk, B. Scrosati (Eds.), *Advances in Lithium-Ion Batteries*, Kluwer Academic/Plenum Publishers, 2002, p. 185, and references therein.
- [2] (a) V.R. Koch, C. Nanjundiah, G.B. Appetecchi, B. Scrosati, *J. Electrochem. Soc.* 142. J (1995) L116;
(b) R.T. Fuller, R.A. Carlin, Osteryoung, *J. Electrochem. Soc.* 144 (1997) 3881;
(c) N. Koura, K. Etoh, Y. Idemoto, F. Matsumoto, *Chem. Lett.* (2001) 1320;
(d) Y.S. Fung, R.Q. Zhou, *J. Power. Sources* 81 (1999) 891;
(e) H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, *J. Electrochem. Soc.* 150 (2003) A695.
- [3] (a) W.T. Ford, R.J. Hauri, D.J. Hart, *J. Org. Chem.* 38 (1973) 3916;
(b) E.I. Cooper, C.A. Angell, *Solid State Ionics* 9–10 (1983) 617;
(c) E.I. Cooper, C.A. Angell, *Solid State Ionics* 18–19 (1986) 570;
(d) T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta* 49 (2004) 3603.
- [4] J. Sun, D.R. MacFarlane, M. Forsyth, *Ionics* 3 (1997) 356.
- [5] (a) H. Matsumoto, M. Yanagida, K. Tanimoto, K. Kojima, Y. Tamiya, Y. Miyazaki, *Molten Salts XII*, P.C. Trulove, H.C. DeLong, G.R. Stafford, S. Deki, (Eds.), *Proceedings of the Electrochemical Society*, vol. 99-41, Pennington, NJ, 2000, p. 186;
(b) H. Matsumoto, M. Yanagida, K. Tanimoto, K. Kojima, Y. Tamiya, Y. Miyazaki, *Chem. Lett.* (2000) 922.
- [6] H. Sakaebe, H. Matsumoto, *Electrochem. Commun.* 5 (2003) 594.
- [7] H. Matsumoto, H. Kageyama, Y. Miyazaki, *Chem. Commun.* (2002) 1726.
- [8] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Graetzel, *Inorg. Chem.* 35 (1996) 1168.
- [9] H. Matsumoto, T. Matsuda, Y. Miyazaki, *Chem. Lett.* 1430 (2000).
- [10] Z.B. Zhou, M. Takeda, M. Ue, *J. Fluorine Chem.* 125 (2004) 471.
- [11] (a) Z.B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* (2004) 680;
(b) Z.B. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Lett.* (2004) 886.
- [12] H. Matsumoto, et al., *Molten Salts XIII*, in: P.C. Trulove, H.C. DeLong, R.A. Mantz, G.R. Stafford, M. Matsunaga (Eds.), *Proceedings of the Electrochemical Society*, vol. 2002-19, Pennington, NJ, 2002, p. 1057.
- [13] H. Matsumoto, H. Kageyama, Y. Miyazaki, *Electrochemistry* 71 (2003) 1058.
- [14] H. Matsumoto, H. Kageyamam, Y. Miyazaki, *Chem. Lett.* (2001) 183.