ROOM TEMPERATURE IONIC LIQUIDS CONTAINING IONIZED SOLVENT MOLECULE AS AN IN-VOLATILE ADDITIVE FOR A LITHIUM BATTERY ELECTROLYTE

Hajime Matsumoto, Hikari Sakaebi, Kuniaki Tatsumi

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST)

1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan

ABSTRACT

Ionic liquids based on TFSI anion and quaternary ammonium cations, containing the chemical structure of organic solvents such as diethylcarbonate, were prepared to use as an in-volatile organic additives for EMI systems. The addition of both the additive salt and a lithium salt effectively suppressed the reductive decomposition of EMI cation on Ni.

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 to be one of the attractive electrolyte media for a safe lithium battery electrolyte. Recently, ionic liquids based on quaternary ammonium systems have been reported as an electrolyte for the lithium battery system due to its electrochemical stability comparing with that of EMI systems (1). However, the viscosity and melting points of such quaternary ammonium systems are generally much higher than that of EMI system. This disadvantage limits the rate property of lithium battery using such viscous system is limited by the slow diffusion of lithium ions (2).

EMI systems have been the best cation to form low melting and low viscous RTILs with various anions (3). However, the electrochemical windows of these melts are limited by both the reduction and the oxidation of EMI cations. To improve the apparent electrochemical stability of EMI systems, additives such as SOCl₂ and H₂O was added into EMI systems. These molecular additives could form a good SEI film onto an electrode, which suppress the electrochemical decomposition of EMI system. The qualities of the SEI film were much preferable for lithium battery systems since the good plating and stripping peak of lithium can be observed, however, the molecular additives are volatile compound, which might reduce the merit of the use of ionic liquids.

Carbonate compounds such as diethylcarbonate, ethylene carbonate and propylene carbonate have been used for the solvent for a lithium battery. These compounds are used not only a liquid media for electrolytes but also a reagent for modify an electrode surface. The addition of these compounds into ionic liquids as an additive...
has been reported by the same reason. However, this approach to improve the electrochemical stability of ionic liquids contain the volatile and the combustible problem.

In this paper, we report on the preparation of new ionic liquids containing TFSI anion and tetraalkylammonium cation, which include the molecular structure of diethylcarbonate, as a non-volatile and thermally stable additive for a lithium battery electrolyte based on ionic liquids. The effect of the addition of the new ionic liquid into EMI-TFSI on the electrochemical property was also investigated.

EXPERIMENTAL

Materials

Preparation of the ionic liquid containing carbonate structure: The preparation scheme of the ionic liquid containing carbonate structure was shown in scheme 1. At first (1-Ethoxy carbonyloxy-ethyl)-trimethylammonium chloride (ECETMA-C1) was prepared by mixing 20% excess mount of trimethylamine acetone solution and carbonic acid 1-chloroethylethylester (Tokyo Kasei) in acetone for 24 h at room temperature. After the resulting solution was vacuum evaporated, almost the theoretical amount of white solid was obtained. This solid was washed with acetone and diethylether. Then the anion exchange from ECETMA-C1 to ECETMA-TFSI was done in Milli-Q water. ECETMA-TFSI was precipitated by mixing a slightly excess amount (1 wt%) of Li-TFSI (Aldrich, 99.98%) and the ECETMA-C1. The precipitated sample of ECETMA-TFSI was extracted by CH$_2$Cl$_2$ and washing with water twice. The CH$_2$Cl$_2$ was removed by rotary evaporation at 50 °C. Resulting ECETMA-TFSI was dried under vacuum at 80 °C. The chemical structure of the prepared salts was confirmed by $^1$H-, $^{13}$C- $^{19}$F-NMR and the element analysis (C, H, and N). ECETMA-TFSI was liquid at room temperature. EMI-TFSI was prepared by following the literature methods.

![Scheme 1 Preparation of new ionic liquid containing carbonate structure.](image_url)

Measurements

Electrochemical Measurements. Linear sweep voltammetry (LSV) was performed using an automatic polarization system (ALS model 600) in an argon-filled glove box (O$_2$ and water < 5 ppm), by using a 5 mL beaker-type three-electrode cell equipped with a disk electrode (Pt (d=1.6mm), Ni (d=1.5mm)), a Pt wire counter electrode, and an I$_3$/I$^-$/I$^-$ reference electrode consisting of Pt wire/0.015 mol dm$^{-3}$ I$_2$ + 0.060 mol dm$^{-3}$ [I$^{-}$/I$^-$].
C₃H₇dN]I in EMITFSI (EMI = 1-ethyl-3-methylimidazolium, TFSI = bis(trifluoromethylsulfonyl)-imide). The EMI-TFSI containing ca. 1.0 M ECETMA-TFSI was dried under vacuum at 100 °C for 30 min. The metal electrode was polished with alumina powder (d=0.05 μm) and then rinsed with Milli-Q water.

**Thermal analysis.** The TGA was performed on a thermal analysis system (Seiko Instruments, TG/DTA 6200). An average sample weight of 5 mg was placed in a platinum pan and heated at 10°C min⁻¹ from ca. 40°C to 600°C under a flow of nitrogen.

**RESULTS AND DISCUSSION**

Figure 1 shows the result of thermal gravimetric analysis of diethylcarbonate (DEC) and the prepared salts in this study (ECETMA-CI and ECETMA-TFSI). This figure indicates that the addition of trimethylammonium group into DEC successfully improved the thermal stability. The kind of anion was influenced the thermal stability of ECETMA salt as seen in the other ionic liquids such as EMI-TFSI. In case of ECETMA-TFSI, the first thermal decomposition was observed at 300 °C. The 25% decrease of the weight of ECETMA-TFSI (MW = 456.4) at 300°C might be explained by an elimination of DEC (MW = 118) from ECETMA-TFSI. This indicates the carbonate structure might be maintained in the ionic liquid over 200 °C.

![Figure 1. The result of the thermal gravimetric analysis of diethylcarbonate (DEC), ECETMA-CI and ECETMA-TFSI. Scan rate: 10 °C/min.](image)

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Figure 2 The cyclic voltammogram of EMI-TFSI on Ni with (solid line) and without (dotted line) 0.4 M of Li-TFSI. (T=25°C, 50 mV sec⁻¹).

Figure 2 shows the cyclic voltammogram of EMI-TFSI on Ni. The apparent cathode limit potential was shifted toward much negative potential comparing with neat EMI-TFSI. As previously reported, such negative shift was observed even in the addition of small amount of lithium salts (10 mM). Other alkali metal salts such as K-TFSI and tetraalkylammonium salts such as tetraethylammonium carbonate did not influence the cathodic stability any more (x). Then such negative shift must be caused by the formation of SEI film on the Ni, which might be consisted of the electrochemically reduced EMI cation and lithium cation. The SEI film inhibits the reduction of EMI cation. However, the quality of the SEI film was not enough to perform the plating and the stripping of lithium since the stripping peak of the deposited Li was not observed at −3.0 V vs \( \Gamma^-/\Gamma^0 \).

Figure 3 shows the cyclic voltammogram of EMI-TFSI containing ECETMA-TFSI (ca. 1.0 M) on Ni with and without Li-TFSI. The cathodic limit of EMI-TFSI was not shifted toward negative potential with the addition of relatively large amount of ECETMA-TFSI. Even after the potential range was enlarged from −2.3 V to −3.0 V and the scanning were repeated 5 times, the cathodic limit of EMI-TFSI was not changed any more. This suggests that the SEI film was not formed on Ni only the existing the ECETMA-TFSI. On the other hand, when Li-TFSI was existed in the mixed ionic liquid, the typical plating and stripping of lithium could be observed. This indicates that much preferable SEI film for the plating and stripping of lithium was formed on Ni. The quality of the film was much improved comparing with that seen in case of the addition of only Li-TFSI (Figure 2). It is noted that the sample containing EMI-TFSI, ECETMA-TFSI and Li-TFSI was dried under vacuum (10⁻⁴ Torr) at 100 °C before taking the cyclic voltammogram. The ECETMA-TFSI can be used as nonvolatile and thermally stable additives for improve apparent cathodic stability of EMI-TFSI.
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REFERENCES

1. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kayanasundaram and M. Grätzel, Inorg. Chem., 35, 1168, (1996).
2. N. Papageorgiou, Y. Athanassou, M Armand, P. Bonhôte, H. Pettersson, A. Azam, and M. Grätzel, J. Electrochem. Soc., 143, 3099. (1996).
3. Y. Chauvin, L. Maussmann, and H. Olivier, Angew. Chem. Int. Ed. Engl., 34 2698 (1995)
4. Y. Chauvin and H. Olivier-Bourbigou, Chemtech, 25(9), 26 (1995).
5. R. T. Carlin, and J. Fuller, in Molten Salts X, R. T. Carlin, S. Deki, M. Matsunaga, D. S. Newman, J. R. Selman, and G. R. Stafford, Editors, PV 96-7, p. 362, The Electrochemical Society Proceedings Series, Pennington, NJ (1996).
6. R. T. Carlin, H. C. De Long, J. Fuller, and P. C. Trulove, J. Electrochem. Soc., 141, L73, (1994).
7. J. Fuller, R. T. Carlin, and R. A. Osteryoung, J. Electrochem. Soc., 144 3881, (1997).
8. J. Fuller, A. C. Breda, and R. T. Carlin, J. Electrochem. Soc. 144, L68, (1997).
9. J. Fuller, A. C. Breda, and R. T. Carlin, J. Electroanalytical Chem. 459, 29 (1998).
10. R. T. Carlin and J. Fuller, Chem. Commun., 1345 (1997)
11. R. A. Mantz, H. C. De Long, R. A. Osteryoung, and P. C. Trulove, in Proceedings of the 12th International Symposium on Molten Salts, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99–41, The Electrochemical Society: Pennington NJ, 2000, pp. 169–176.
12. A. Noda and Masayoshi Watanabe, in *Proceedings of the 12th International Symposium on Molten Salts*, Paul C. Trulove, Hugh C. De Long, Gery R. Stafford, and Shigehito Deki, Eds.; Vol. 99–41, The Electrochemical Society: Pennington NJ, 2000, pp. 202–208.

13. A. Noda, K. Hayamizu, and M. Watanabe, *J. Phys. Chem. B*, 105, 4603 (2001).

14. P. Stilbs, *Progress in NMR Spectroscopy*, 19, 1 (1987).

15. E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, 42, 288 (1965).

16. F. Lemaitre-Augier and J. Prud’homme, *Electrochem. Acta*, 46, Issue 9, pg. 1359 (2000).