

The Corrosion Study of Al Current Collector in Phosphonium Ionic Liquid as Solvent for Lithium Ion Battery

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(Received July 29, 2011 : Accepted August 26, 2011)

Abstract : A room temperature ionic liquid (RTIL) based on trihexyl (tetradecyl)phosphonium bis(trifluoromethanesulfonyl) imide ($[(C_6H_{13})_3P(C_{14}H_{29})]$ [TFSI]; P_{66614} TFSI) was synthesized and analyzed to determine their characteristics and properties. The bis(trifluoromethanesulfonyl)imide (TFSI) anion is widely studied as an ionic liquid (IL) forming anion which imparts many useful properties, notably electrochemical stability. Especially its electrochemical and physical characteristics for solvent of lithium ion battery were investigated in detail. P_{66614} TFSI exhibits fairly low conductivity (0.89 mS cm^{-1}) and higher viscosity (298 K: 277 cP; 343 K: 39 cP) than other ionic liquids, but it exhibits a high thermal stability (over 400°C). Especially corrosion behavior on Al current collector was tested at room temperature and further it was confirmed that thermal resistivity for Al corrosion was highly increased in 1.0 M LiTFSI/ P_{66614} -TFSI electrolyte comparing with other RTILs by linear sweep thermometry.

Keywords: Ionic liquid, Phosphonium, Bis(trifluoromethylsulfonyl)imide, Al corrosion, Lithium ion battery

1. Introduction

Global warming becomes one of the most serious problems in the world owing to increasing greenhouse-gas concentrations from the growing usage of fossil fuel. Therefore, high fuel-efficient hybrid electric vehicle (HEV) has received considerable attention and further, the plans for full electric vehicle (EV) have been introduced^{1,2)}. For them, the large-scale lithium ion batteries (LIB) become important to maximize energy capacity for HEVs and EVs and accordingly the safety issues loomed larger than before³⁾. When the large heat was given to LIB from such as overcharging, abnormal high current by internal short and exposure to high temperature, oxygen from metal oxide cathode and flammable materials in LIB accelerate firing of LIB. Among

the several components in LIB related with safety issues, the carbonate electrolytes have been regarded one of the critical reasons, due to high flammability of these electrolytes.

Room temperature ionic liquids (RTIL) for electrolyte of LIB have been investigated because of their unique physical properties such as non-volatility and non-flammability⁴⁾. At the first research stage of RTIL, imidazolium cation based RTILs appeared on the spotlight from high conductivity and low viscosity⁵⁾ However, their narrow electrochemical windows owing to the presence of acidic protons restrict their further applications for solvents of electrolytes for LIBs. And several kinds of cations such as pyrrolidinium, piperidinium and phosphonium were introduced as candidates for electrolyte of LIBs. Among these, recently phosphonium based RTIL were studied vigorously due to its high electrochemical stability window. We also prepared phosphonium with long substituent which can exist as a liquid phase at room temperature, trihexyltetradecylphosphonium (P_{66614})

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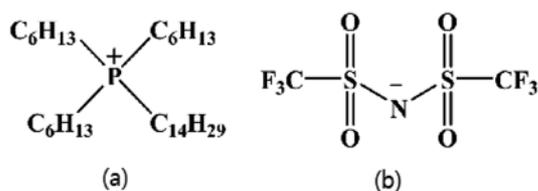
bis(trifluoromethylsulfonyl)imide (TFSI).

On the other hand, high potential cathode is adopted for high energy density to increase operating voltage from graphite. Due to its vigorous condition of cycling, electrochemically stable electrolyte should be used to hinder the side reaction of electrolyte during cycling. Accordance with this, RTILs are applied as the electrolyte which can endure high potential from high electrochemical stability. Mostly RTILs were composed of TFSI anion to delocalize electron on anion to hinder coulombic interaction between ions, but TFSI anion is severely electrochemically-corrosive to Al substrate which is a conventionally requisite as current collector⁶⁾. Although RTIL having TFSI is not corrosive to Al even at oxidative potential, however Al was corroded at elevated temperature⁷⁾. From these, we studied Al corrosiveness of phosphonium along temperature to solve the problem of Al corrosion at elevated temperature.

2. Experiment

The desired P₆₆₆₁₄TFSI were synthesized effectively to the reported papers (Scheme 1)⁸⁾. Li-TFSI (100.0 mmol) was added to a solution of Trihexyl(tetradecyl) phosphoniumchloride (100.0 mmol) in distilled water (100 mL). The reaction mixture was stirred for 24 hours at 80°C. After the reaction mixture was cooled to room temperature, distilled water was added to the mixture and the mixture was extracted with CH₂Cl₂. The obtained CH₂Cl₂ solution which contains P₆₆₆₁₄TFSI was washed with distilled water several times to eliminate LiCl residue. The extracted CH₂Cl₂ solution was filtered by MgSO₄ layer and aluminium oxide layer. After elimination of solvent by evaporation, the obtained high viscous liquid was dried under vacuum oven at 120°C overnight. The molecular structure of obtained product was confirmed by NMR (Bruker AM-300 MHz NMR spectrometer (operating at 116 MHz for Li).

Thermal analysis of samples was performed using a



Scheme 1 the chemical structure of (a) P66614 (b) TFSI.

TA instruments differential scanning calorimeter (DSC Q100) at a scanning rate of 10°C·min⁻¹ over a temperature range of -150 to 150°C. Glass transition (T_g) and melting points (T_m) were determined as a function of composition. Impedance measurements were carried out in a small conductance cell from 25 to 65°C using the Eurotherm 2240E. Thermogravimetric analyzer (Perkin Elmer) was used to test thermal stability of the ionic liquids and the scan rate was 10.0°C·min from room temperature to 800°C under a nitrogen atmosphere. Viscosity of the ionic liquids was measured with an AMVn Automated Microviscometer at 25°C, 70°C and the ionic liquids were sealed in the sample tube under a nitrogen atmosphere.

Coin-type cells (2032 size, Hohsen) were assembled with an Al foil (Donghae, >99.85%, 20 μm thickness), lithium foil (Cyprus), a glass filter separator (Advantec, GA-55, 0.21 mm thickness) and electrolyte to conduct cyclic voltammetry (OCV ~5 V vs. Li/Li⁺, scan rate = 10 mV s⁻¹) and linear sweep thermammetry (LSTA). For LSTA, the cell was charged to 5.0 V at a scan rate 10 mV s⁻¹ and stabilized till the current was lower than 3 μA cm⁻² (Wonatech). The charged cell was heated with a ramp of 0.1°C·min⁻¹ under 5 V and the current was measured.⁷⁾ In coin cells, the electrolytes were prepared with dissolving 1.0 M Li-TFSI (3 M, battery grade). The potential of Al electrode was linearly swept to 5.0 V (vs. Li/Li⁺) at a scan rate of 10 mV s⁻¹ and the given 5 V was stabilized till the current reach under 3 μA cm⁻².

3. Result and Discussion

Synthesized P66614TFSI was confirmed by H-NMR and water and halide content was analyzed (P₆₆₆₁₄TFSI); ¹H NMR δH(300 MHz; CDCl₃) 2.0~2.3(8H, m, CH₂), 1.4~1.5(16H, m, CH₂), 1.2~1.3 (32H, m, CH₂), 0.79~0.85(12H, m, CH₃)ppm.ES-MS : m/z 483[P₆₆₆₁₄]+ ES m/z 279[TFSI] Water content (Karl-Fisher) : 141 ppm, Cl content : < 100 ppm.

Fig. 1(a) shows the thermal trace of P₆₆₆₁₄TFSI. As you can see, the transition temperature (T_g) of P₆₆₆₁₄TFSI exhibited fairly high and exhibits the lower conductivity (0.89 mScm⁻¹) than other ionic liquid, emImTFSI (8.8 mScm⁻¹), N₁₁₃₄TCM (8 mScm⁻¹) and emImDCA (22 mScm⁻¹). The reason why it is quite viscous by comparison with related ionic liquids, this presumably reflects strong electrostatic interactions between ions. The

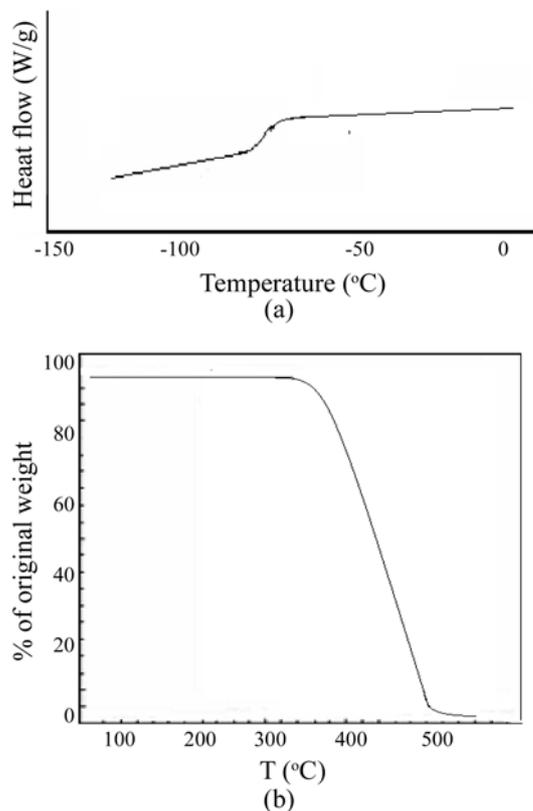


Fig. 1. (a) DSC thermogram of P_{66614} TFSI (b) Thermogravimetric trace for P_{66614} TFSI.

conductivity and viscosity provide the information on the mobility and aggregation of ions and ion-pairing phenomenon.⁸⁾

The thermogravimetric trace for P_{66614} TFSI was shown by Fig. 1(b). It was shown that the phosphonium ionic liquid was thermally stable over 400°C. The Gravimetric decrease of P_{66614} TFSI was slower than those of exhibited more thermal stability than that of pure ionic liquid (a).⁸⁾

For staying liquid state at room temperature, cation which can highly delocalize charge on its own structure such as imidazolium can have wide range of anion. High coulombic force between ions makes them be solid, however, highly delocalized cation can not strongly counteract with anion, so that it stays as liquid even with small anion. For electrochemical stability, several new cations such as pyrrolidinium and piperidinium have been introduced, however, normally its charge delocalization properties is poor so that they should have large anion such as TFSI and BETI to make a pertur-

bation between ion ordering. However, when TFSI anion is used as counter anion to lithium, it makes pitting corrosion on Al current collector over 3.2 V⁶⁾. Because operating potential is higher than Al/Al³⁺ equilibrium potential (-1.676 V vs. NHE) and moreover electrolyte with TFSI can not passivate Al surface with AlF₃. Fortunately, several RTILs having TFSI do not corrode Al surface because of passivation layer from RTIL. CV was conducted to elucidate the oxidative electrochemical characteristics of Al current collector in P_{66614} TFSI electrolyte. As shown in Fig. 2, the oxidative current decreased as cycle number increases. This voltammogram electrochemical behavior explains that passivation layer is formed on the surface of Al at the 1st scan and additional Al corrosion is suppressed owing to resistance of the passivation layer. If native oxide layer on Al surface is broken during oxidative condition, the bare surface of Al is exposed to electrolyte side and it is rapidly corroded due to low equilibrium potential of Al/Al³⁺ (-1.676 V vs. NHE). In Fig. 2 current at the 1st cycle is relative high, however it decreases along cycling processing. This phenomena is explained by passivation theory from previous papers^{7,9)}.

FE-SEM analysis was conducted to visualize the surface of electrode to confirm absent of Al corrosion on the electrode. On the Al electrode cycled in 1.0 M LiTFSI/EC:DEC at 25°C, many pits around 10 μm were presented which were come from corrosion reaction (Fig. 3(a)). These pits enlarge the surface area of Al electrode and the current related Al corrosion also

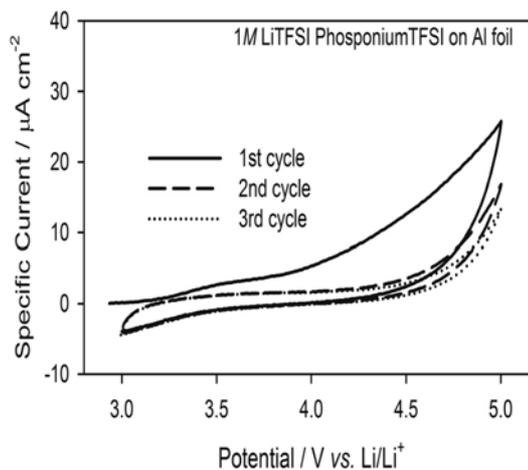


Fig. 2. Cyclic voltammogram of P_{66614} TFSI.

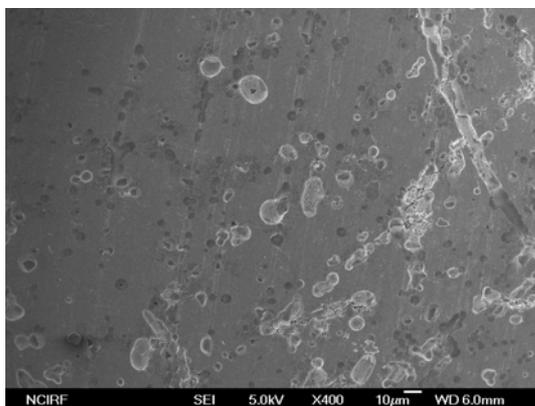


Fig. 3. (a) FE-SEM image on the Al electrode cycled in 1.0 M LiTFSI/EC : DEC at 25°C.

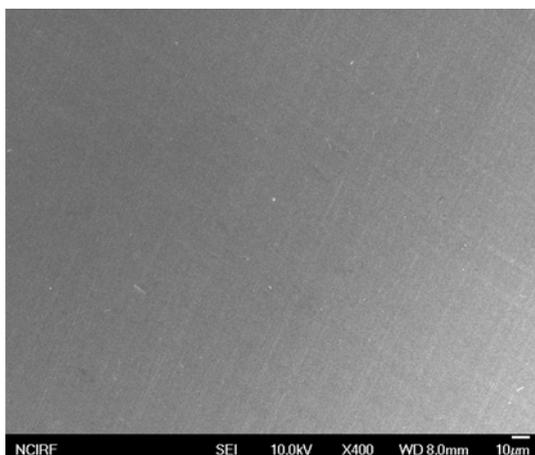


Fig. 3. (b) FE-SEM images on the Al electrode cycled in 1.0 M LiTFSI/ P₆₆₆₁₄TFSI at 25°C.

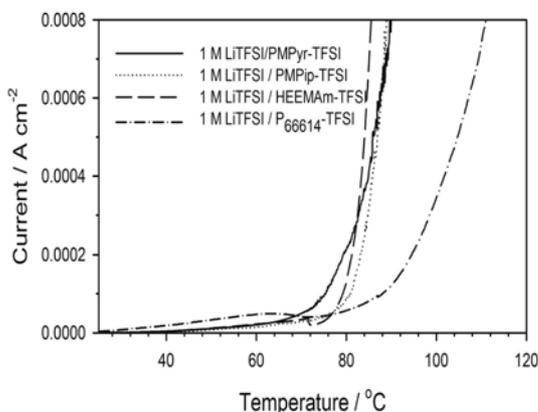


Fig. 4. Linear sweep thermometry profiles obtained in four different electrolytes. The potential of Al electrode was fixed at 5.0 V vs. Li/Li⁺ during the temperature sweep.

increase after the pits appeared. These pits are not observed from Al electrode cycled in the P₆₆₆₁₄TFSI electrolyte at the room temperature. The FE-SEM images clearly show that 1.0 M LiTFSI/ P₆₆₆₁₄TFSI is resistive even at the same temperature (Fig. 3(b)).

But its passivation layer is no longer stable over at the thermally onset temperature. Because this firm passivation layer start to be broken at the elevated temperature. To elucidate these phenomena, linear temperature thermometry is introduced to confirm onset temperature without difficulty comparing with previous CV methods. Accordingly, LSTA experiments with several kinds of RTIL electrolytes with Li-TFSI salt were conducted to grasp the corrosiveness of Al along a temperature gradient and the results are presenting on Fig. 3^{7,10}. The current which was stabilized at room temperature, abruptly augments after onset temperature. From these, it is ascertained that LSTA method is proper tool to evaluate the Al corrosion at high temperature. From LSTA results, the onset temperature of corrosion as well as corrosion-resistant order is obtained; dihexyldiethylammonium-TFSI (HEEHAm-TFSI) < propylmethylpyrrolidinium-TFSI (PMPyr-TFSI) < propylmethylpiperidinium-TFSI (PMPip-TFSI) < P₆₆₆₁₄TFSI with 4 mA cm⁻² as cut off current. As a result, if 1.0 M LiTFSI/PMPyr-TFSI is used as electrolyte for LIB, Al corrosion can be hindered well till 55°C, however, the passivation layer is broken over 65°C⁷. Consequently, temperature condition affects the Al corrosiveness in the RTIL electrolytes. On the other hand, the current from the cells in the P₆₆₆₁₄TFSI electrolyte is well stabilized till 90°C. From these, it is concluded P₆₆₆₁₄TFSI RTIL is better candidate with blocking Al corrosion even with TFSI anion to be used as solvent for electrolyte at the elevated temperature.

4. Conclusion

In 1.0 M LiTFSI/P₆₆₆₁₄TFSI ionic liquid electrolyte, passivation layer on Al is successfully formed on the Al surface and Al corrosion is blocked at the room temperature and this phenomena is analyzed with CV and FE-SEM. Furthermore, thermal stability of this passivation layer is higher than that of PMPyr-TFSI electrolyte. From this, P₆₆₆₁₄TFSI electrolyte is very promising candidate for using it for solvent of lithium ion batteries at the elevated temperature.

Acknowledgement

This work is supported by Hoseo University grant (2010-0107).

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