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Alkylimidazolium-Based Ionic Liquids as Lithium-Ion Battery Electrolyte

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The two alkylimidazolium-based ionic liquids of 1-methyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) are synthesized andtheir electrochemical properties are investigated by using cyclic voltammetry and galvanostatic charge-discharge techniques. The results reveal that the electrochemical windows of these two ionic liquids are both about 4.3 V and their ionic conductivity are 13.7 and 3.0 mS/cm respectively at 25 ºC. The demonstration battery with graphite anode and $LiCoO_2$ cathode are prepared by using $EMIBF_4$, $BMIBF_4$ and 1 mol L^{-1} $LiPF_6$ as electrolyte and 5 % of vinylene carbonate (VC) as additive. The coulombic efficiency of the $EMIBF_4$-involved electrolyte is up to 90 % after 50 cycles and the capacity remaines above 91 $mAhmg^{-1}$ during the whole cycle, while the coulombic efficiency of the $BMIBF_4$-based battery droppes directly after 10 cycles. The capacity of the $EMIBF_4$-based battery with C/5 rate is 80 % of C/15 rate in 25 ºC.

Key Words: Room temperature ionic liquid, Electrolyte, Lithium-ion battery, $LiCoO_2$ cathode.

INTRODUCTION

Room temperature ionic liquids (RTILs) are made of only ions at or near room temperature, with desirable properties include wide electrochemical window, good thermal and chemical stability, high ionic conductivity. They have been attracted considerable interest in the field of electrochemistry device as solvent and electrolyte, such as rechargeable batteries, photoelectrochemical cells, electroplating, electrodeposition and electro-organic-synthesis[1-4].

Lithium based rechargeable batteries are technically interesting energy storage devices. They show high energy density, high operating voltage, good cycle durability and 'greenness' among the applicable chemical and electrochemical energy storage systems. Indeed, the present lithium-ion battery, using conventional organic solvent mainly, has a pressing problem of safety and environment, while the specific properties of RTILs, which are non-flammability and negligible vapour pressure, make them favourable especially for lithium-ion battery electrolytes[5-10].

RTILs investigated for battery use can be classified into several groups depending on cationic, such as quaternary ammonium, pyridinium, pyrrolidinium, pyrazolium, triazolium, phosphonium andimidazolium, which combined with variety of anionic species. RTILs containing alkylimidazolium has been intensively studied because the conductivity of these RTILs is high enough to be applied to the electrochemical devices. Low cathodic stability of EMI-based ionic liquids,however, seems insufficient as lithium battery electrolytes.

The fact that lithium-ion batteries can function is due to the use of some additives, which form a solid electrolyte interphase (SEI) on the active material surface of negative electrode, overcoming the reduction of the electrolyte. The additives are usually ethylene carbonate (EC), ethylene sulphite(ES), acrylonitrile, especially vinylene carbonate (VC).

In this paper, two alkylimidazolium-based Ionic Liquids were synthesized, 1- butyl -3- methyl imidazolium tetrafluoroborate ($BMIBF_4$) and 1-ethyl-3- methyl- imidazolium tetrafluoroborate ($EMIBF_4$). Also, the charge-discharge profile of the lithium-ion batteries with graphite anode and $LiCoO_2$ cathode were studied, containing $EMIBF_4$ or $BMIBF_4$ and 5 % of vinylene carbonate (VC) as additive.

EXPERIMENTAL

$EMIBF_4$ and $BMIBF_4$ were prepared by the reaction of 1-butyl-3-methylimidazolium bromide and 1-ethyl-3- methylimidazolium bromide with argentum tetrafluoroborate in methyl alcohol respectively. The purity of the products was checked by infrared and NMR measurements. $LiPF_6$ (battery) was obtained from Tianjin Research & Design Institute of Chemical Industry. Carbonaceous Mesophase Spheres (CMS) and $LiCoO_2$ were purchased by Shanshan Tech Group. Their water contents were confirmed to be below 50 mg L^{-1} by a Karl-Fisher titration. All products were carried out in a glove box filled with argon (< 1 ppm H_2O, O_2).

Property measurements of RTILs: Thermal analysis of $EMIBF_4$ and $BMIBF_4$ were realized by differential scanning calorimeter (Perkin Elmer Thermal Analysis DSC7), which were cooled down to -150 ºC with liquid nitrogen and successively heated at the rate of 5 ºC/min.. The conductivity (DDS-11A conductivity meter) and viscosity (Pinkevich viscosimeter) measurement were carried out at different temperature with a thermostatic oil bath. The temperature of the samples was maintained during 15 min before each measurement. The electrochemical window was measured by the linear sweep voltammetry using a highly sensitive electrochemical workstation(CHI660B, Shanghai Chenhua Co., China). In this measurement, Platinom electrode was used as working and counter electrode with a diameter of 100 μm in a 3-electrodes glass cell and a silver wire was used as reference electrode. The linear sweep voltammetry tests were performed at 50 mV s^{-1} scan rate.

Fabrication of Li-ion batteries: In order to prepare the anode, 85 wt % of $LiCoO_2$, 7 wt % of acetylene black and 8 wt % of poly(vinylidene) fluoride (PVdF) were dissolved in 1-methyl-2-pyrrolidinone (NMP) and then spread the mixture onto a aluminum foil. The cathode was prepared in the same manner, except that, instead of aluminum foil, copper foil was used as a current collector, composed of 88 wt % of CMS and 12 wt % of PVdF. Electrolyte solution was soaked into the separator (Celgard 2300, Daramic LLC, Shanghai). All of these fabrication processes were carried out in a dry glove box filled with argon.

RESULTS AND DISCUSSION

Physical properties: DSC curves of $EMIBF_4$ and $BMIBF_4$ are showed in Fig. 1. The curve of $EMIBF_4$ shows that the glass transition, crystallization and melting point are -96, -60 and 7 ºC, respectively, while $BMIBF_4$ does not exhibit crystallization and its glass transition point is -92 ºC. Two RTILs are both liquid in the range of the most applied temperature of Lithium-ion batteries.

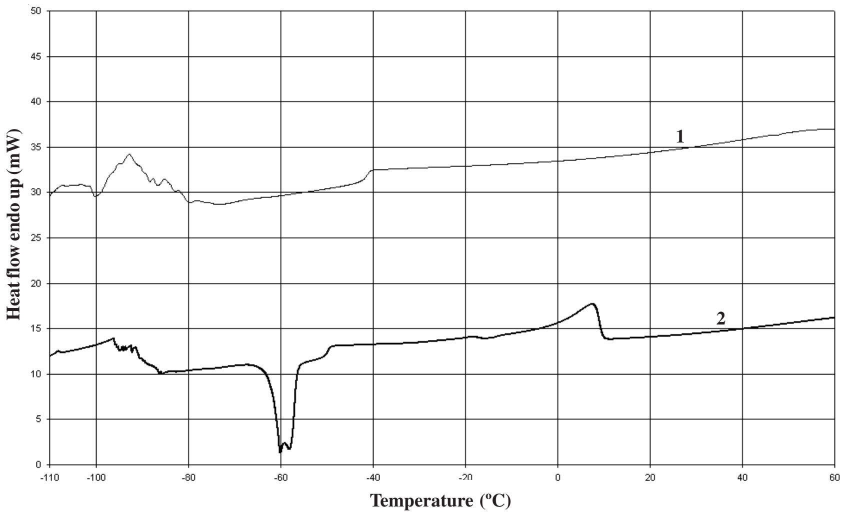

Fig. 1. Differential scanning calorimeter (DSC) thermograms of $EMIBF_4$ (1) and $BMIBF_4$ (2) on warming at 5 ºC/min

The viscosity of RTILs is mostly in relation to H-bonding and Van der Waals interaction[11], which increases with the increase of the length of alkyl chain of the cationic substituent group. The viscosity of EMIBF$_4$ is less than that of BMIBF$_4$. Fig. 2 displays the viscosity variation of EMIBF$_4$ and BMIBF$_4$ with the temperature. The viscosity decreases obviously with the increase of the temperature, but increased drastically with the addition of the lithium salt. The viscosity of EMIBF$_4$ increased from 34.3 to 94.7 mm^2 s^{-1} with the addition of the LiPF$_6$ at 25 ºC, while from 119.7 to 201.4 mm^2 s^{-1} for BMIBF$_4$.

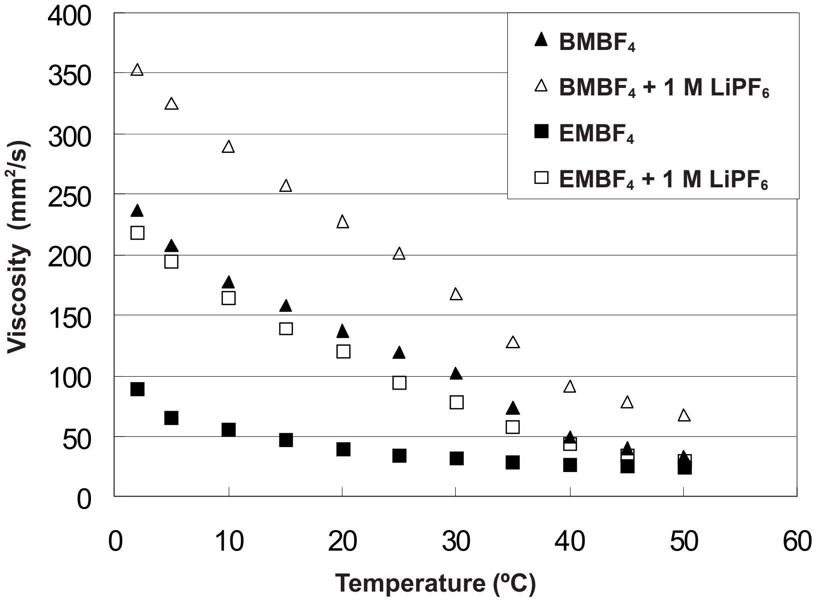

Fig. 2. Variation of viscosity of EMIBF$_4$ and BMIBF$_4$ with temperature

The key factors which influence the conductivity of the RTILs are the viscosity, temperature, density and size of ion. Fig. 3 shows the variation of conductivity of EMIBF$_4$ and BMIBF$_4$ with temperature. The conductivity increases as the temperature increases, however, the addition of the lithium salt leads to the decrease of the conductivity. For instance, the conductivity of EMIBF$_4$ decrease from 13.7 to 7.4 mS cm^{-1} with the addition of the LiPF$_6$ at 25 ºC, while BMIBF$_4$ from 3.0 to 1.5 mS cm^{-1}.

However, these values of conductivity of two RTILs are all in the expected range for the lithium-ion batteries application (1~2 mS cm^{-1}) at 0 ºC and above.

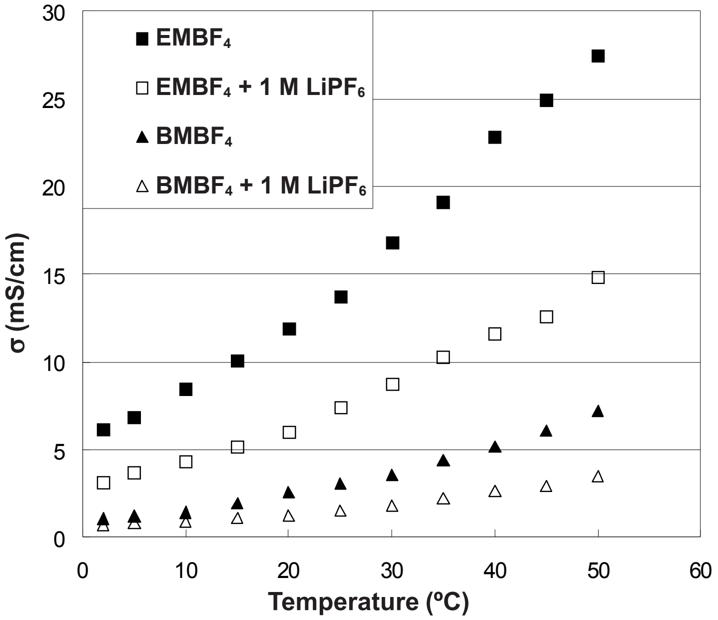

Fig. 3. Variation of conductivity of $EMIBF_4$ and $BMIBF_4$ with temperature

Electrochemical windows: The voltammograms by the linear sweep voltammetry at 50 mV s^{-1} scan rate on platinum electrode with silver as reference electrode are presented in Fig. 4. The potential windows of two RTILs were both 4.3 V approximately. It had the good stability at highly anodic potentials up to +2.7 V *vs.* Ag (+5.4V *vs.* Li^+/Li) and the cathodic limit is around -1.6V *vs.* Ag (+1.1V *vs.* Li^+/Li).

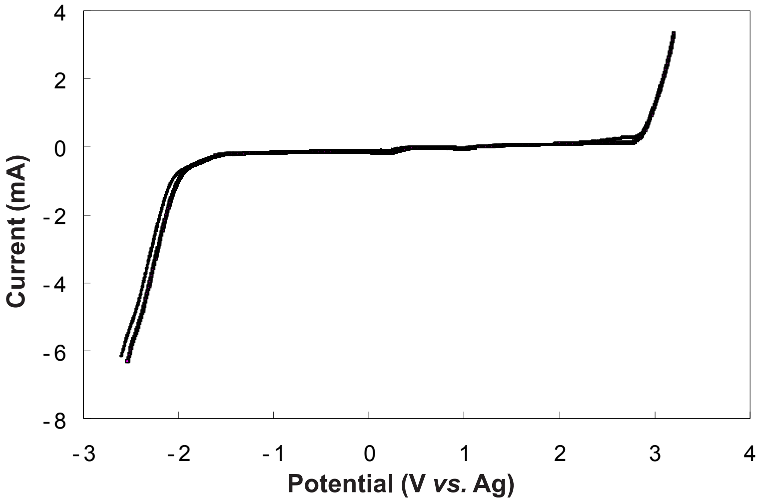

Fig. 4. Voltammograms of $EMIBF_4$ and $BMIBF_4$ (above) at 25 ºC

The cathodic limit potential of the alkylimidazolium-based ionic liquids was positive against the insert potential of graphite. Therefore, from the viewpoint of cycle durability, these two RTILs can not be used as the electrolyte for lithium-ion batteries with the graphite (such as CMS)as anode directly. We add vinylene carbonate (VC) in the RTILs, which can be reduced firstly, formed a SEI film on the graphite electrode surface[12-15], thus prevents reduction of the electrolyte.

Battery tests: The demonstration batteries use commercial graphite (CMS) and $LiCoO_2$ as anode and cathode materials respectively, where 1 mol L^{-1} $LiPF_6$ and 5 wt % of VC are used as the electrolyte. The coulombic efficiency of first cycle of $EMIBF_4$-based battery is low, but over 90 % in succeeding cycles. The rate of charge-discharge is C/15, which means a charge-discharge in 1/15 h. An adequate SEI formation presumably occurred on the graphite surface during the first cycle[9].

The variation of charge-discharge capacity of the two alkylimidazolium-based batteries respectively is shown in Fig. 5 and 6 during 50 cycles. The discharge capacity of $EMIBF_4$ battery declined from 102 to 91 mAh g^{-1} after 50 cycles, however, the coulombic efficiency maintains about 90 %, which indicated its stable cyclic properties. The charge-discharge capacity of $BMIBF_4$-based battery is not bad during the initial cycles, but it declines

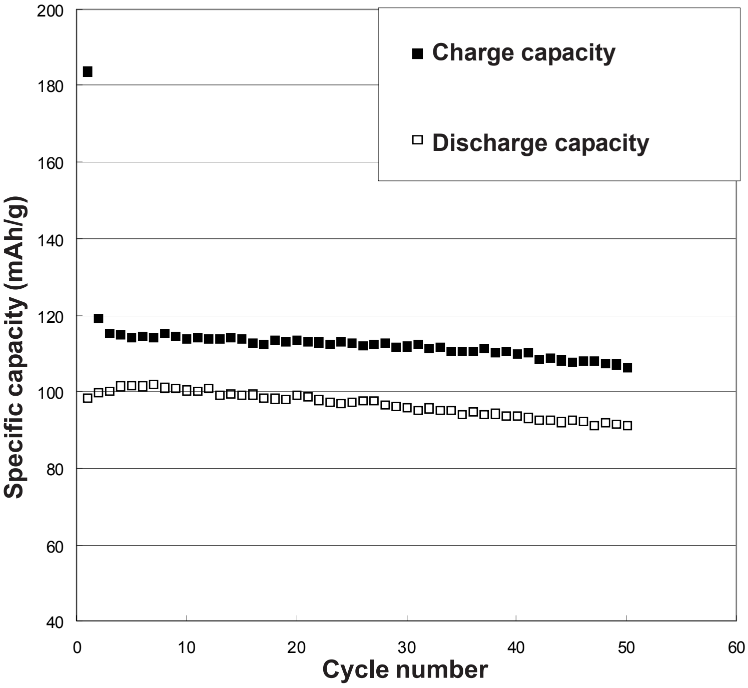

Fig. 5. Charge-discharge capacity during cycling of the $EMIBF_4$-based battery (C/15) at 25 ºC

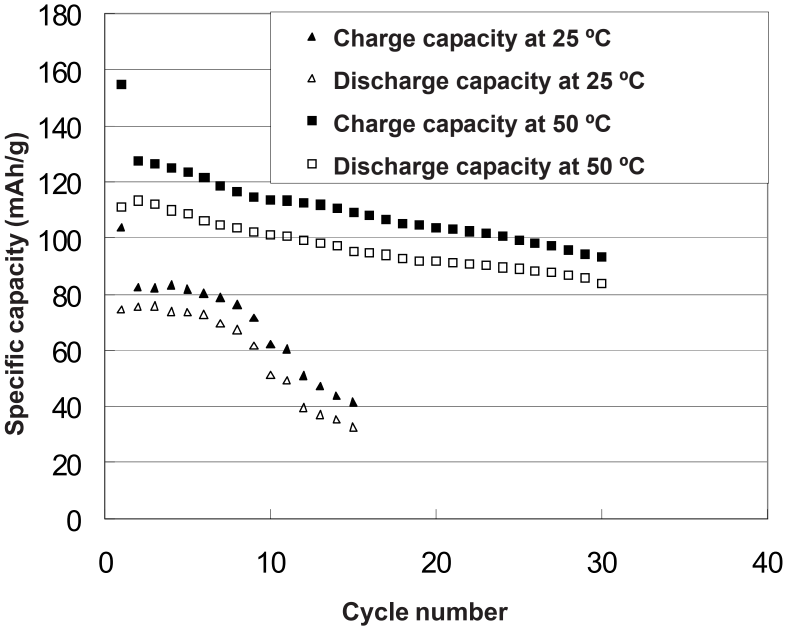

Fig. 6. Charge-discharge capacity during cycling of the $BMIBF_4$-based battery (C/15) at 25 and 50 °C

quickly after about 10 cycles. The reason may be that $BMIBF_4$ possesses a relatively high viscosity, which do not facilitates the wetting of surfaces, particles and the pores of the composite electrodes used in batteries. Although the increase of temperature caused the decreasement of the viscosity and the cycle properties of $BMIBF_4$-based battery is improved, but the capacity is still decline fleetly.

The rate of Charge-discharge has significant influence on the capacity of battery (Fig. 7). The capacity of $EMIBF_4$-based battery at the rate of C/5 is only 80 % of that at the rate of C/15. This is explained by assuming that the lithium ion in the electrolyte can not be supplied in time at higher charge-discharge current density, by reason of the high viscosity of $EMIBF_4$, which are in agreement with the work of Markevich *et al.*[16].

Conclusion

The two alkylimidazolium-based ionic liquids of 1-methyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$), which were synthesized in this work, possess high conductivity, wide potential windows (4.3 V) and high anodic stability (over 5 V *vs.* Li^+/Li). They can be used as electrolyte for lithium-ion batteries with vinylene carbonate additive, which could

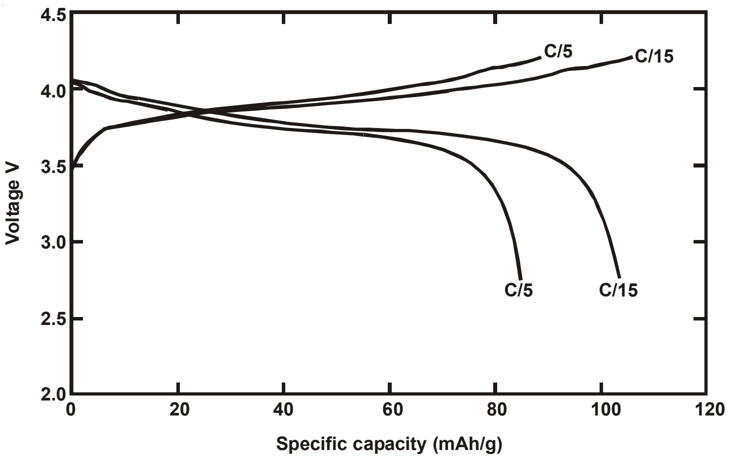

Fig. 7. Charge-discharge curve of the $EMIBF_4$- based battery at different rate

form a SEI against the reduction of the electrolyte. The coulombic efficiency of the $EMIBF_4$-based battery was up to 90 % after 50 cycles, which indicates the stable charge-discharge properties at low charge-discharge rate,while the coulombic efficiency of the the $BMIBF_4$-based battery dropped directly after 10 cycles.

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