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Short Communication

Vinylene Carbonate Modified 1-Butyl-3-Methyle-Imidazolium Tetrafluoroborate Ionic Liquid Mixture as Electrolyte

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Vinylene carbonate (VC) has higher reduction potential than that of 1-butyl-3-methyl-imidazolium tetrafluoroborate ($BMIMBF_4$) and can form solid electrolyte interface (SEI) film on lithium (Li) metal surface. VC modified the mixed electrolyte based on $BMIMBF_4$ and γ-butyrolactone (γ-BL) has been investigated. The result indicates that the optimized mixed electrolyte, γ- BL / $BMIMBF_4$ (70/30, volume ratio) -1 M $LiBF_4$, has high conductivity(14.87 mS cm^{-1}) at 25 °C. Electrochemical impedance spectroscopy discloses that the addition of VC improves the compatibility of the mixed electrolyte towards lithium anodes and enhances the formation of SEI film to protect lithium anodes from corrosion. Accordingly, the Li/$LiFePO_4$ battery with VC modified the $BMIMBF_4$/γ-BL - 1 M $LiBF_4$, has a high discharge capacity of 123.1 mAh g^{-1} without any considerable fading during the first 20 cycles at a current density of 0.1C.

Keywords: Ionic liquid; electrolyte; Li-ion battery; lithium iron phosphate

1. INTRODUCTION

Ionic liquids (ILs) have aroused the attention to be used as one of the safest electrolytes in lithium-ion batteries because of its excellent thermal stability, negligible volatility, non-flammability, high-ionic conductivity and wide electrochemical window. The use of a lithium metal electrode in conjunction with ILs electrolyte offers a potential solution to the safety concerns. Hence, various ILs have been tested for application in lithium batteries [1–28]. Unfortunately, pure ILs are highly viscous and exhibit relatively low conductivity, which impedes their application in rechargeable lithium batteries. It is found that the addition of organic dipolar diluents into the neat ILs is a good way to decrease the viscosity of the neat ILs [9-14].

In the case of ionic liquids used as electrolyte bases, ionic liquids containing imidazolium cation have been intensively studied owing to its low viscosity[2]. However, the application was restricted because of their low cathodic stability toward lithium [15,16]. For this reason, much effort has been made to improve the performance of lithium batteries by developing alternative ionic liquids with more stable cations [17-22], or selecting the appropriate anode materials [18,19], or using a small quantity of film-forming additives [6-8, 23-27]. Among them, the addition of an appropriate additive, vinylene carbonate (VC), to IL electrolytes was proposed to facilitate lithium cycling and protect the IL from reduction on the electrode.

$BMIMBF_4$ ionic liquid is a relatively inexpensive imidazolium salts. It has been reported that the mixture of $BMIBF_4$ with γ-butyrolactone (γ-BL) in the presence of lithium tetrafluoroborate ($LiBF_4$) exhibited better thermal stability than the conventional organic electrolyte [10, 11]. In this work, VC modified the mixed $BMIMBF_4/\gamma$-BL based electrolyte for $Li/LiFePO_4$ batteries was reported and its performance was investigated in details.

2. EXPERIMENTAL

2.1. Preparation of $BMIMBF_4$ ionic liquid mixture electrolytes

The $BMIMBF_4$ was prepared and purified through a usual route [27-29]. The chemical structure of product was checked by IR (Aratar-360，American) and 1H NMR (400MHz, $CDCl_3$) (AvanceⅢ, Bruker). γ- BL (purity > 99.99%, Aldrich) was pre-treated with activated molecular sieve. $LiBF_4$ and VC were provided by Guangzhou Tinci Materials Technology Co., Ltd (China). The mixed $BMIBF_4$ based electrolytes were prepared in an argon-filled glove box (Mbraun, Germany). Water content of the electrolytes was controlled below 20 ppm, which was examined by 831 KF Coulometer.

2.2. Ionic conductivity and viscosity measurements

Ionic conductivity of these electrolytes was determined by a conductometer (DDS-307, Shanghai, China) and a conductivity cell equipped with a platinum (Pt) electrode. Viscosity measurement was performed using a determination of kinematic viscosity (SYD-265C, Shanghai).

2.2. Tests of stability of Li electrodes in IL mixed electrolytes

The time-evolution dependence of the Li/electrolyte interfacial resistance (R_i) was measured in Li/electrolyte/Li symmetric cell through the ac impedance on a Zahner-Elektrik IM6 electrochemical workstation (Germany) with the frequency ranging from 100 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation at room temperature. The measurement was performed with 1 day interval.

2.3. Cell assemblies and electrochemical measurements

The cathode was constructed by $LiFePO_4$ (Tianjin STL Energy Technology Co., Ltd , China), acetylene black, and polytetrafluoro ethylene (PTFE) in the weight ratio of 85:10:5. The slurry was coated onto a stainless steel current collector (*Ø* 9 mm). The CR 2016 coin cells were assembled in an argon-filled glove box with a lithium foil as the counter electrode and a Celgard membrane as the separator.

The galvanostatic charge-discharge was performed at 2.5–4.0 V (vs. Li^+/Li) by a battery test system (LAND CT2001A, China). Electrochemical impedance spectroscopy (EIS) was also recorded under the same condition as in Section 2.2.

3. RESULTS AND DISCUSSION

3.1 Ionic conductivity and viscosity

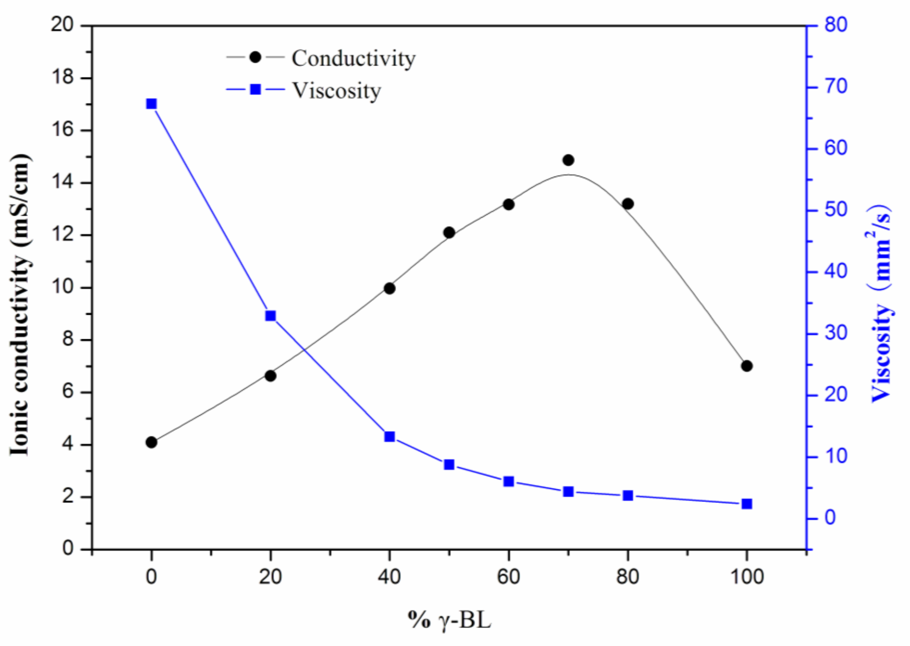

Figure 1. Conductivity and viscosity of $BMIMBF_4$ - 1 M $LiBF_4$ with *γ*-BL at 25 °C.

The conductivities and viscosities of 1M $LiBF_4$ based electrolytes in binary solvent mixtures at different ratios at 25 °C are shown in Fig. 1. As observed, with increasing of the volume ratio of γ- BL, the viscosity of the mixture decreases, while the conductivity increases first and then declines. When the concentration in the diluent γ- BL is raised, the number of charge carriers decreases. At the same time, the viscosity decreases. As a result, the ionic mobilities inevitably increase. The competition between the decrease in number of charge carriers and the increase of their mobilities leads to a maximum in the conductivity-concentrationship. There is the maximum conductivity (14.87 mS/cm) in the electrolyte containing γ-BL/ $BMIMBF_4$ (70/30, volume ratio) at 25 °C. The volume ratio don't agree with the reported [10, 11] due to the addition $LiBF_4$.

3.2. Tests of stability of Li electrodes in IL mixed electrolytes

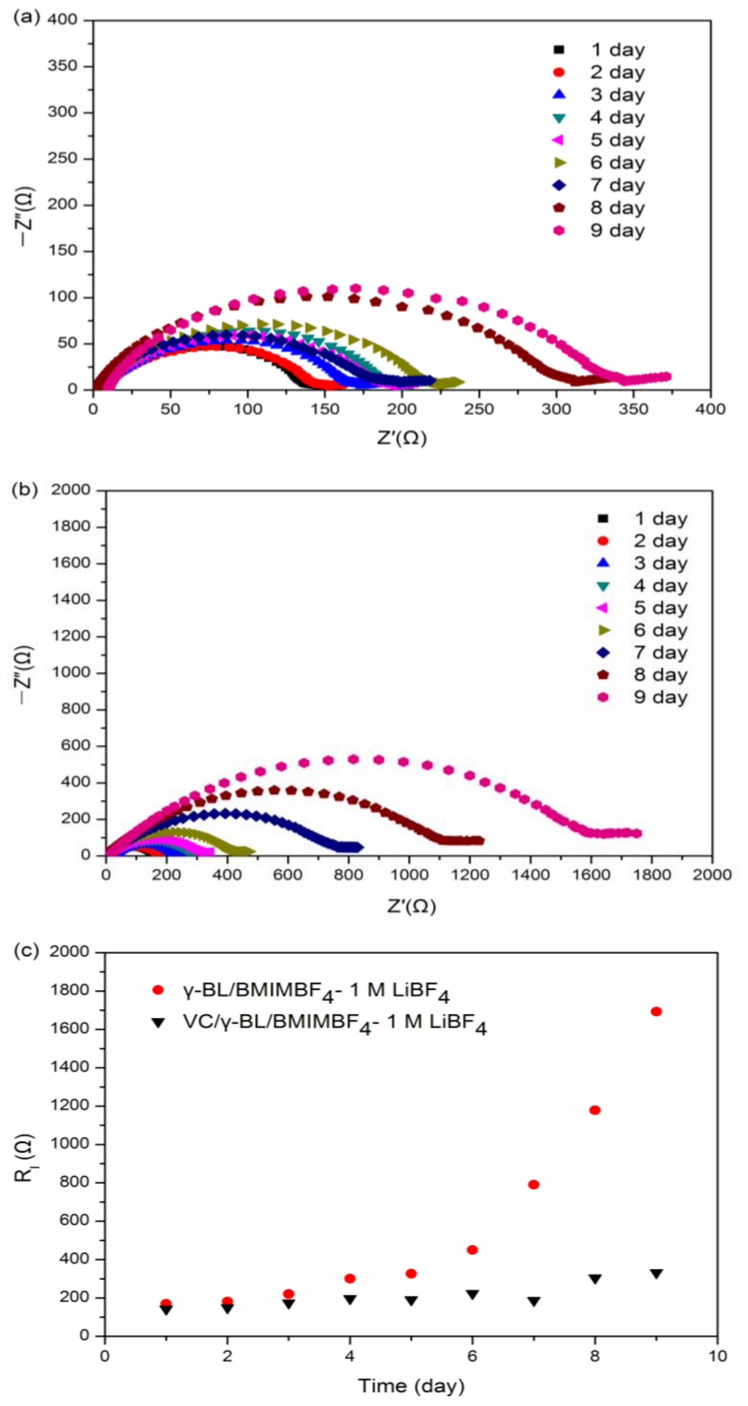

Figure 2. Time evolution of impedance spectra of a Li/electrolyte/Li symmetric cell with (a) VC modified $BMIMBF_4$/γ-BL -1 M $LiBF_4$, (b) $BMIMBF_4$/γ-BL -1 M $LiBF_4$ and (c) Interfacial resistance for Li/electrolyte/Li symmetric cells at open circuit condition at room temperature.

The stability of $BMIMBF_4$ mixture electrolyte against lithium was investigated by monitoring the time evolution of the impedance response of a symmetric Li/ electrolyte /Li cell under open-circuit conditions. As shown in Fig. 2, the impedance evolves with the expected semicircles trend. Their amplitude, determined by the two intercepts with the real axis, may be associated to the impedance of the Li/electrolyte interfaces. The time-dependant behavior of the interfacial impedance (Ri) was composed of charge transfer resistance and SEI film resistance [31-33]. As seen from Fig. 2a, this impedance continuously was increased during the 9 days of contact, implying that a reaction between the lithium metal and VC modified the mixture electrolyte as well as the formation and build-up of a solid electrolyte interface (SEI) layer should occur. However, it also clearly shows that the width of the semicircles, and thus the value of the interface resistance remain more or less constant on the value of 200 Ω for 5 days to then expand after 6 days of contact, see Fig.2a. and 2c. This indicates that lithium could react with the electrolyte, however, the reaction is expected to be eventually prevented by the formation of a passivating layer.

For comparison, the same impedance analysis was carried out on a cell using a $BMIMIBF_4$/γ-BL – $LiBF_4$ electrolyte solution. A much faster growth of the interfacial impedance was demonstrated, from an initial value of ca. 200 Ω to several thousand ohms within 9 days of storage, shown in Fig.2b. and 2c.

The result demonstrates excellent compatibility of VC modified the $BMIMBF_4$/γ-BL- $LiBF_4$ electrolyte with Li metal at room temperature under open circuit conditions. It should be attributed to the fact that the additive VC (1.17 V vs. Li/Li^+) had higher reductive potential than the electrolyte solvents (γ-BL, 1.15 V vs. Li/Li^+, and $BMIMBF_4$, 1.0 V vs. Li/Li^+)[34, 35]. Prior to electrochemical reduction of the electrolyte solvents, the additive is preferably reduced to form an insoluble solid product, which subsequently is covered onto the surface of Li foil as a preliminary film to deactivate catalytic activity. Therefore, VC additive would provide the better efficient SEI in the mixed electrolyte and could improve better compatibility towards Li metal[8, 30].

3.3 Battery tests

Charge–discharge of different electrolytes were further measured in $Li/LiFePO_4$ cells. Fig. 3 displays the cycling performance of $Li/LiFePO_4$ cells in different electrolyte at a current density of 17 $mA\cdot g^{-1}$ (0.1C) between 4.0 V and 2.5 V. It indicated that the addition of VC played a significant role in improving the cyclic performance. The initial discharge capacity of the cell with VC was 123.1 $mAh\cdot g^{-1}$. However, the initial reversible capacity of the cell without VC was only 90.7 $mAh\cdot g^{-1}$ with the columbic efficiency of 40.8%, which was consistent with the reported result[11]. After 10 cycles, the discharge capacity of the cell with VC modified electrolyte was 135.9 $mAh\cdot g^{-1}$, which was much higher than that without VC (53.5 $mAh\cdot g^{-1}$). Moreover, the discharge capacity of 129.1 $mAh\cdot g^{-1}$ was maintained after 20 cycles.

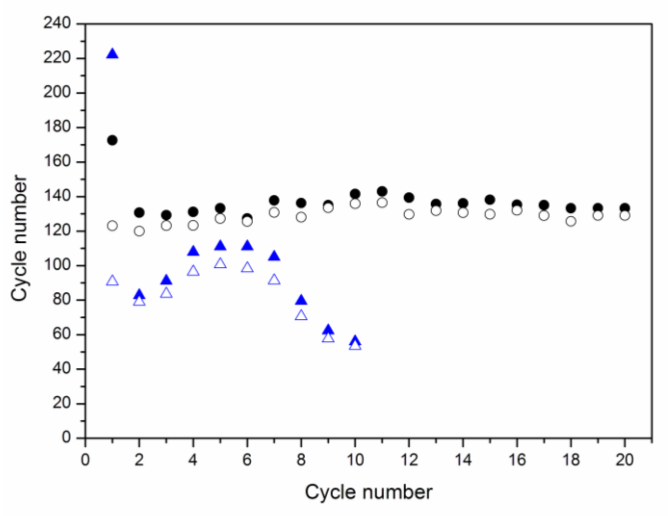

Figure 3. Cyclic performance of Li/LiFePO$_4$ cells in BMIMBF$_4$ /γ-BL – 1 M LiBF$_4$ with VC additive (filled circles: charge, open circles: discharge) or without (filled triangles: charge, open triangles: discharge)

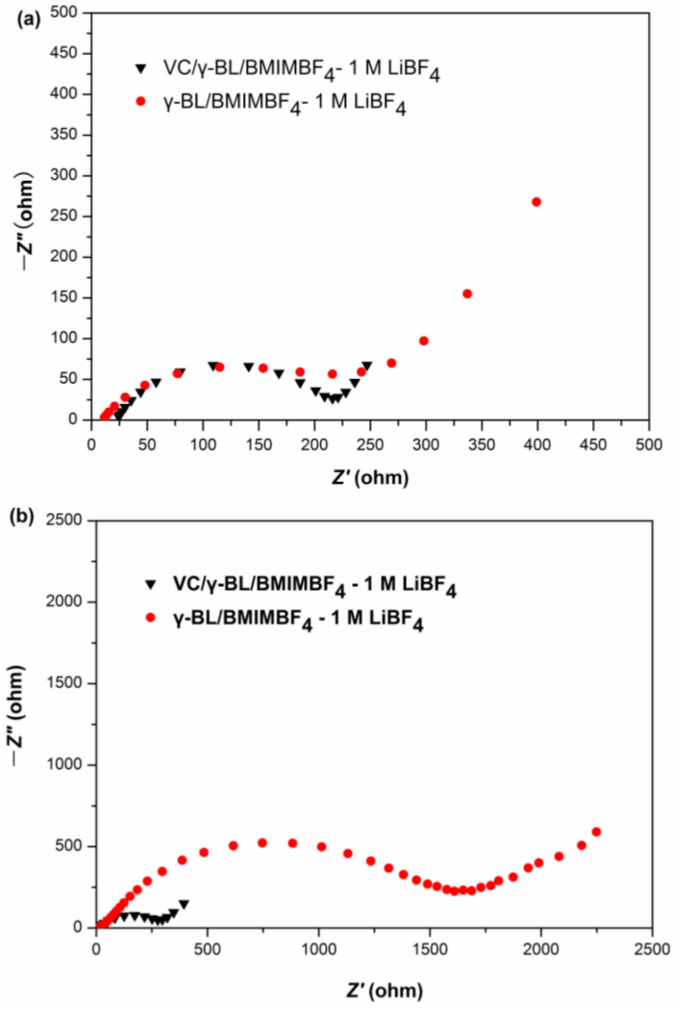

Figure 4. Nyquist plots of Li/electrolytes/LiFePO$_4$ cells: (a) fresh cell, and (b) after 10 cycles.

To clarify the effect of VC on battery, the impedance spectra of the related Li/LiFePO$_4$ cells before and after cycling are shown in Fig. 4. Each impedance spectra exhibited a semicircle in the high-frequency range and an inclined line in the low-frequency range. The high-frequency semicircle represented the resistance of the SEI film[36], and the inclined line corresponded to the lithium-ion diffusion process, Warburg diffusion. Before SEI formation in different electrolytes (Fig. 4a), Li/LiFePO$_4$ cells with and without VC showed similar size of semicircle at high frequency, with the resistance of ca. 195 ohm and 187 ohm, respectively. A dramatic difference appeared after 10 cycles (Fig. 4b): the resistance was increased a little to 287 ohm for the cell with VC, but increased rapidly up to 1668 ohm for the cell without VC. The EIS results demonstrated that VC addition can form an improved SEI film, which not only decreased the impedance on the electrode/electrolyte interphase but also could protect lithium from corrosion. Therefore, the electrochemical performance of Li/LiFePO$_4$ cell with VC was improved.

4. CONCLUSIONS

In the present work, VC modified the BMIMBF$_4$/γ-BL - 1 M LiBF$_4$ was proposed as the electrolyte for Li/LiFePO$_4$ cell. The cell impedance with BMIMBF$_4$/γ-BL – 1 M LiBF$_4$ increased gradually owing to the reaction of Li metal with BMIM$^+$ cation. However, the addition of VC into BMIMBF$_4$/γ-BL greatly restrained the reaction of Li metal with BMIM$^+$ cation. The related results revealed that the VC modified electrolyte was stable for Li metal. When used as electrolyte for the Li/LiFePO$_4$ battery, it had a high discharge capacity of 123.1 mAh g^{-1} without any considerable fading during the first 20 cycles.

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