

IV-SFG studies on the effect of zwitterion additive on the anodic-stability of Lithium-ion battery

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[Abstract] Glyme–Li salt system has been widely studied as an electrolyte in Li-ion battery. The stability of the electrolyte on anode is one of the most important factors allowing the Li-ion battery operation at high voltages. Fujita and co-workers have reported that the electrochemical stability of glyme-based electrolytes is improved by the incorporation of zwitterion 1-butylimidazolium-3-(n-butanesulphonate) ([Bimps]) [1]. But the oxidation-stability enhancement mechanism with adding zwitterion in glyme-Li salt system is still unclear. In this work, infrared-visible sum frequency generation (IV-SFG) spectroscopy has been successfully applied to elucidate the anodic-stability enhancement mechanism in [Bimps] added glyme-Li[TFSA] system.

[Introduction] Glyme-Li salt (LiX)-based electrolytes have been extensively studied as potential electrolytes in lithium-based batteries. However, they are not compatible with a high voltage electrode, due to oxidation of ether group at a potential higher than 4 V vs. Li/Li⁺. Recently, it is found that an anodic limit of glyme-LiX electrolytes can shift to a higher potential with the incorporation of zwitterion [1][2]. But an oxidation-stability enhancement mechanism with adding zwitterion in glyme-Li salt system is still unclear. In this study, infrared-visible sum frequency generation (IV-SFG) spectroscopy has been applied to elucidate the anodic-stability enhancement mechanism of 1-butylimidazolium-3-(n-butanesulphonate) (zwitterion: [Bimps]) added tetraglyme (G4) with lithium bis(trifluoromethylsulfonyl)amide (Li[TFSA]) system (Fig.1).

[Methods] G4-Li[TFSA] (8:1 mole ratio) electrolyte and G4-Li[TFSA]-[Bimps] (8:1:0.11 mole ratio) electrolyte are prepared in glove box. The electrochemical cell is based on a three-electrode design. The working electrode is a polycrystalline Pt disk. The reference and counter electrodes are Ag/Ag⁺ and Pt wire, respectively. HZ-5000 electrochemical workstation is employed to control the potential of Pt disk in the SFG measurement and to carry out linear sweep voltammetry (LSV). In addition, *ab initio* calculations with B3LYP/6-311G** basis set are carried out to estimate the hyperpolarizability tensor elements of Li⁺-G4 complex cation.

[Results and Discussion] Fig.2 shows the LSV of G4-Li[TFSA] with and without [Bimps] measured at a

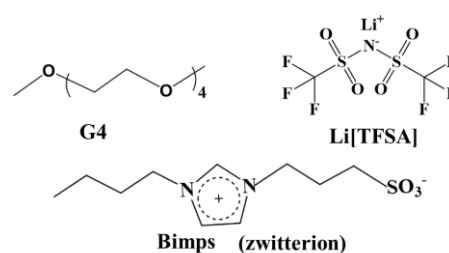


Fig.1 Structures of G4, Li[TFSA] and [Bimps].

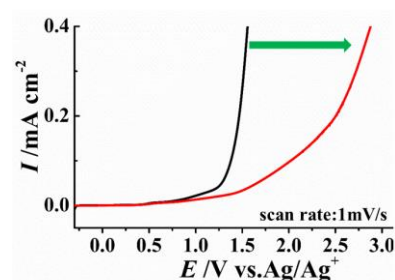


Fig.2 LSV results of G4-Li[TFSA] (black) and G4-Li[TFSA]-[Bimps] (red)

scan rate of 1 mV s^{-1} . The anodic reaction of G4-Li[TFSA] system starts at around 1.0 V, and the oxidized current is rapidly increased above 1.2 V. But, the initial oxidation potential shifts to 1.5 V by adding [Bimps] to G4-Li[TFSA]. The anodic current does not increase appreciably even beyond 1.5 V. LSV results demonstrate that the electrochemical stability of G4-Li[TFSA] on the anode can be enhanced with addition of [Bimps], which allows glyme-LiX based electrolytes being compatible with high voltage.

Fig.3 shows the potential dependent SFG spectra at Pt/G4-Li[TFSA] electrolyte interface at -2.4 V and 1.0 V. The peak at 1020 cm^{-1} is from free G4, and the peak at 1074 cm^{-1} is due to G4-Li⁺ complex. The peak derived from the [TFSA]⁻ anion was not observed, indicating that only free G4 and Li⁺-G4 complex adsorb on the Pt surface and [TFSA]⁻ anion are repelled from Pt surface. When the potential changes from negative to positive, the peak intensity of Li⁺-G4 is increased. *Ab initio* calculations indicated that the increased peak amplitude is attributable to the orientation of Li⁺-G4 complex changes from a flat configuration at negative potential to a vertical configuration at positive potential.

Fig.4 shows the potential dependent SFG spectra at Pt/G4-Li[TFSA]-[Bimps] electrolyte interface at -2.5 V and 1.0 V. The peak at 1137 cm^{-1} is related with [TFSA]⁻ anion and the peak at 1062 cm^{-1} is derived from Li⁺-[Bimps] complex. The extra peak at 1078 cm^{-1} at 1.0 V is assigned to Li⁺-G4 complex. These results indicated that Pt surface is mainly occupied by Li⁺-[Bimps] complex cation, and Li⁺-G4 complex starts to adsorb on Pt surface at positive potential. [TFSA]⁻ anion also exists in the interfacial region.

Here we compare the two systems with and without [Bimps]. At the positive potential, we found that Pt surface is occupied with G4-Li⁺ complex and free G4 molecule in G4-Li[TFSA] system. But, the Pt surface is mainly occupied by Li⁺-[Bimps] complex cation in G4-Li[TFSA]-[Bimps] system. Here we should note that free G4, which is weakest moiety against oxidation [3], are absent from Pt surface after adding [Bimps]. Therefore, we can conclude that free G4 are repelled from the Pt surface by the addition of [Bimps], resulting in the suppression of oxidation of G4 and then in the improvement of anodic-stability.

[References]

- [1] S. Yamaguchi et al. *Electrochim. Acta.* **186**, 471–477, (2015).
- [2] M. Suematsu et al. *Electrochim. Acta.* **175**, 209–213, (2015).
- [3] K. Yoshida et al. *J. Am. Chem. Soc.* **133**, 13121–13129 (2011).

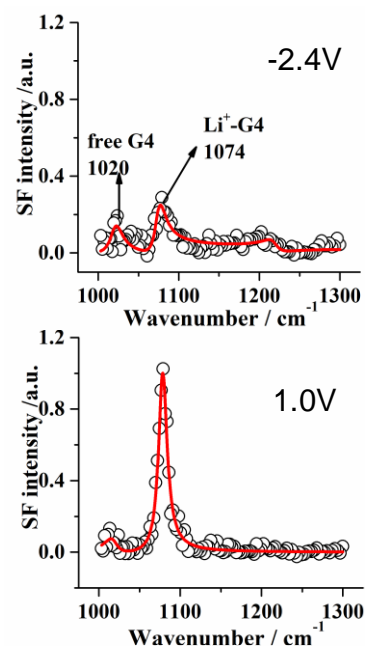


Fig.3 SFG spectra of G4-Li[TFSA]

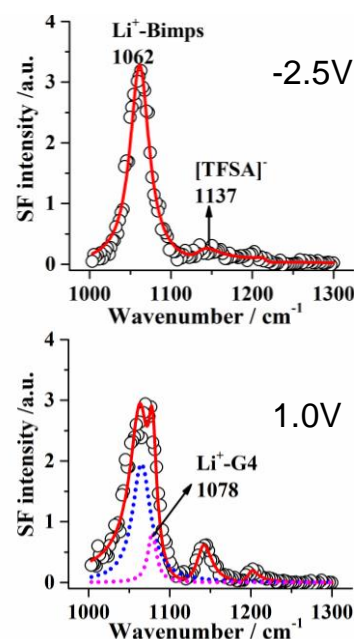


Fig.4 SFG spectra of G4-Li[TFSA]-[Bimps]