

IV-SFG studies on lithium salt concentration dependent interface structure of Pt/glyme-lithium solvate ionic liquids

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[Abstract] IV-SFG spectroscopy has been used to explore Li[TFSA] concentration dependence of microscopic structure at Pt/[Li(glyme)_x][TFSA] (*x*: mole ratio of glyme and Li[TFSA]) SILs interface. LSV results show that the anodic stability of [Li(G4)_x][TFSA] SIL is enhanced with an increase in Li[TFSA] concentration. SFG results confirmed that the enhanced anodic stability can be caused by the decreased adsorption in the number of free G4 adsorbed on the electrode surface.

[Introduction] Recently, solvate ionic liquids (SILs) have been developed and extensively studied as electrolytes in lithium-based batteries. SILs are composed of a salt and a solvent that strongly coordinates to the cation or anion of salt to form stable complex ions. One of the most popular SILs is glyme and lithium bis(trifluoromethylsulfonyl)amide Li[TFSA] mixture [Li(glyme)][TFSA], where stable [Li(glyme)]⁺ complex cations can be formed. It has been reported that the electrochemical anodic stability of [Li(glyme)_x][TFSA] SILs depends on the concentration of Li[TFSA]^[1]. However, it is still unclear how Li[TFSA] concentration affects the oxidation stability of [Li(glyme)_x][TFSA] SILs and how [TFSA]⁻ anion and [Li(glyme)]⁺ complexes behave on electrical interface. Elucidating Li[TFSA] concentration dependent interface structure of [Li(glyme)_x][TFSA] SILs on the electrode surface is very helpful to explore these problems. In this work, infrared-visible sum frequency generation (IV-SFG) vibrational spectroscopy is applied to study Li[TFSA] concentration and potential dependence of platinum (Pt)/[Li(G4)_x][TFSA] (*x* = 8, 4, 2, 1) SILs (G4: tetraglyme) interfacial structure. The chemical structures of G4 and Li[TFSA] are shown in Fig.1.

[Methods] Li[TFSA] salt was added into G4 solvent to form different Li concentration [Li(G4)_x][TFSA] SILs, where the mole ratio of G4 and Li[TFSA] was fixed at *x* = 8, 4, 2 and 1. The electrochemical properties of [Li(G4)_x][TFSA] SILs as well as potential dependent SFG measurements are carried out with a three-electrode cell. 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 also to perform linear sweep voltammetry (LSV). A mode-locked picosecond Nd:YAG laser (pulse duration of 20 ps, repetition rate of 10 Hz) system is used to carry out SFG measurement. The polarization combination used in this work is ssp (denoting in order s-polarized SF, s-polarized visible and p-polarized field).

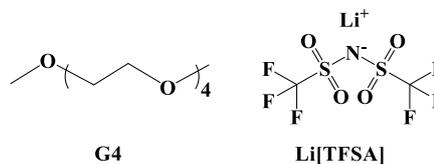


Fig.1 Structure of G4 and Li[TFSA]

[Results and Discussion] Fig.2 shows LSV results of [Li(G4)₈][TFSA] (black line) and [Li(G4)₁][TFSA] (red line) at Pt electrode with a scan rate 50 mV s⁻¹. The oxidation limit in [Li(G4)₁][TFSA] is located at around 1.7 V, which is much higher than that in

[Li(G4)₈][TFSA] (around 1 V). The results show that the anodic stability of [Li(G4)_x][TFSA] SIL is enhanced with an increase in Li[TFSA] concentration. In fact, the anodic limit of [Li(G4)₈][TFSA] is mainly determined by the anodic stability of free G4, which is confirmed to be easily oxidized at positive potential. While in [Li(G4)₁][TFSA] system, the amount of free G4 in SIL is considered to be negligible, and electrochemically stable [Li(G4)]⁺ complexes, are formed in the bulk, possibly resulting in high anodic stability.

Potential dependent SFG spectra of Pt/[Li(G4)₈][TFSA] and Pt/[Li(G4)₁][TFSA] SILs are shown in Fig.3 and Fig.4, respectively. In [Li(G4)₈][TFSA] system, the peaks at around 1040 cm⁻¹ and 1078 cm⁻¹ are due to free G4 and Li⁺-G4 complex, respectively. The peak appeared at 1143 cm⁻¹ is originated from SO₂ symmetric stretching vibration mode (ν_{ss-SO2}) of [TFSA]⁻ anion, which is very small even at positive potential. The SFG spectra of [Li(G4)₈][TFSA] in Fig.3 indicates that Pt electrode surface is mainly occupied by Li⁺-G4 complex and free G4 both at -2.4 V and at 0.5 V. The increased peak intensity of Li⁺-G4 complex is due to its orientation change as potential shifts positively.

In [Li(G4)₁][TFSA] system, two main peaks are attributable to ν_{ss-SO2} and CF₃ anti-symmetric stretching vibration mode (ν_{as-CF3}) of [TFSA]⁻ anion respectively, and there is no peak from Li⁺-G4 complex or free G4 at -2.5 V. It means that [TFSA]⁻ anion may adsorb on the negatively charged Pt surface by interacting with Li⁺ cation. At 1.3 V, the new peak at 1083 cm⁻¹ may be contributed by both Li⁺-G4 complex and SNS anti-symmetric stretching vibration mode (ν_{as-SNS}) of [TFSA]⁻ anion. The very small peak appeared at 1035 cm⁻¹ is due to free G4. Moreover, the increase in ν_{ss-SO2} peak intensity and decrease on ν_{as-CF3} peak intensity may be caused by the orientation change of [TFSA]⁻ anion. Comparing SFG results at positive potential of two systems, the relative intensity ratio of Li⁺-G4 complex to ν_{ss-SO2} is decreased as Li[TFSA] concentration increase in SILs. It demonstrates that the amount of [TFSA]⁻ anion adsorbed on Pt surface is increased. In addition, it should be noted that the amount of free G4 in [Li(G4)₁][TFSA] bulk is just tiny, so the available free G4 adsorbing on the Pt surface is much less than that in [Li(G4)₈][TFSA] system. Finally, we can conclude that positively charged Pt surface in high Li concentration SIL is largely covered by [TFSA]⁻ anion, resulting in the decrease of free G4 adsorbed on the positively charged Pt surface and therefore the enhancement of anodic stability. In the poster presentation, the other two different Li concentration SILs will be discussed.

[Reference]

[1] K. Yoshida *et al.* *J. Am. Chem. Soc.*, **133**, 13121(2011)

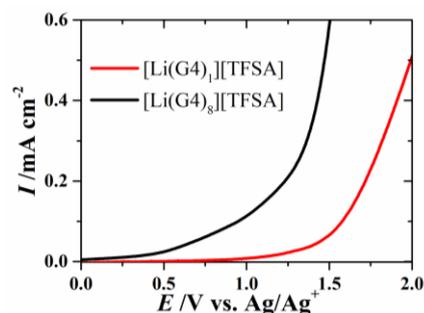


Fig.2 LSV results of [Li(G4)₈][TFSA] and [Li(G4)₁][TFSA] SILs at Pt

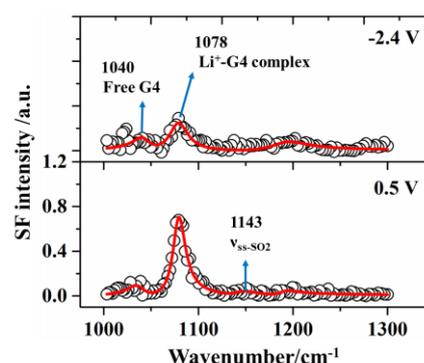


Fig.3 SFG spectra in [Li(G4)₈][TFSA]

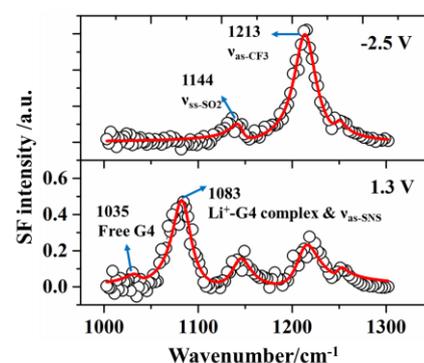


Fig.4 SFG spectra in [Li(G4)₁][TFSA]