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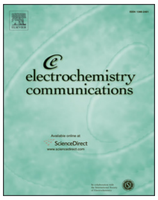

IV-SFG studies on the effect of Li^+ in extending the electrochemical window at the Pt|[C_2mim][FSA] interface

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ABSTRACT

The effect of Li^+ addition at the interface of a 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide ([C_2mim][FSA]) room-temperature ionic liquid (RTIL) and a Pt electrode is investigated by infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy. Addition of Li^+ to the Pt|[C_2mim][FSA] system results in the extension of the electrochemical window (EW) by >1.0 V at its negative edge. The potential dependence of the SF signal reveals that the $[FSA]^-$ anion of neat [C_2mim][FSA] is desorbed at −1.5 V while it remains in place even at −2.0 V when Li^+ is added. The SFG spectra indicate that the $[FSA]^-$ anion at the Pt|[C_2mim][FSA] interface interacts with Li^+ at the interface with the negatively-charged Pt electrode. This $[FSA]^-$ anion layer anchored through Li^+ suppresses $[C_2mim]^+$ cation adsorption on the negatively-charged Pt electrode, resulting in a wider electrochemical window.

1. Introduction

The adsorption/desorption of ions at an electrolyte/electrode interface plays a vital role in the electrochemical reactions used in various applications, including supercapacitors and batteries [1–3]. In the case of the lithium-ion battery, the formation of a Li dendrite at an anode surface during charging-discharging processes results in a degradation of battery performance due to narrowing of the active area and shunt [4]. Such degradation is known to be suppressed by the formation of a solid electrolyte interphase (SEI) at the anode surface, which is composed of Li precipitated with reduced anion components [4–6]. Therefore, controlling the electrolyte/electrode interface structure should be highly beneficial to the development of more efficient electrochemical systems [4–6].

Room-temperature ionic liquids (RTILs), which are liquid at room temperature [7], have attracted much interest as potential electrolytes in various electrochemical applications, including lithium batteries [1,8]. When using RTILs as an electrolyte in lithium batteries, an extension of the electrochemical window (EW) at the negative edge has been reported when Li^+ is added to the RTIL electrolyte [9,10]. Several models for the EW extension, including SEI [9] and anion/Li^+ double-layered structure [10,11], have been proposed, but the actual mechanism of the EW extension caused by the added Li^+ is still unclear due to lack of information on the microscopic structure of the RTIL/electrode interface.

In this communication, we study the applied potential response of adsorption/desorption behavior of the anion at the interface of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide ([C_2mim][FSA], shown in an inset of Fig. 1) and a Pt electrode, with and without Li^+, using infrared-visible sum-frequency generation (IV-SFG) vibrational spectroscopy. The EW extension of >1.0 V at the negative edge is obtained for the Pt|[C_2mim][FSA] system with Li^+. A comparative analysis of electrochemical and SFG results demonstrates that the $[FSA]^-$ anion layer anchored by Li^+ on the negatively-charged Pt surface effectively prevents the adsorption of $[C_2mim]^+$ cations and the associated reduction processes.

2. Theory

The basic theory of IV-SFG has been described previously [12,13]. IV-SFG is a vibrational spectroscopy based on a second-order nonlinear optical process which is allowed only at the region where centrosymmetry is broken. The bulk structure of an isotropic liquid, including an electrolyte solution, possesses centrosymmetry, while the electrolyte/electrode interface intrinsically loses such symmetry, and therefore SFG only probes the electrolyte/electrode interface selectively without any

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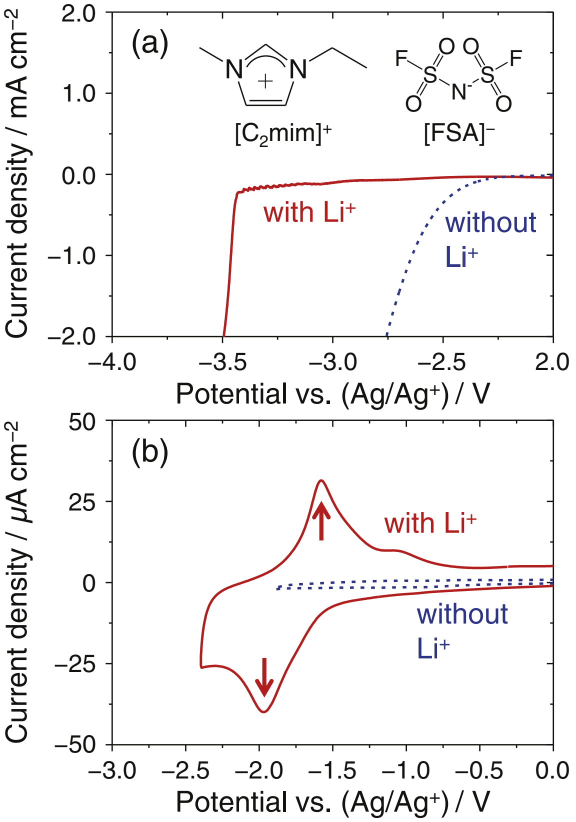

Fig. 1. (a) LSV and (b) CV profiles of Pt|[C$_2$mim][FSA] system with and without Li$^+$. Molecular structures of [C$_2$mim]$^+$ cation and [FSA]$^-$ anion are given in the inset. The redox pair shown by red arrows represents Li-UPD. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

signal contribution from the bulk of the electrolyte [14,15]. The observed SF signal intensity I_{sf} is given by

$$I_{sf}(\omega_{ir}) \propto \left| \chi_{NR} + \sum_q \frac{A_q}{\omega_q - \omega_{ir} - i\Gamma_q} \right|^2 \qquad (1)$$

where χ_{NR} is the non-resonant contribution to the susceptibility, and A_q, ω_q, Γ_q are the amplitude, frequency, and the damping constant of the qth vibrational mode, respectively. A_q is related to molecular hyperpolarizability A_q by

$$\chi^{(2)} = N_S \left\langle \alpha^{(2)} \right\rangle \qquad (2)$$

where N_S is the surface number density of molecules and the angular bracket represents the average over the distribution of molecular orientations.

3. Experiment

The ultra-pure [C$_2$mim][FSA] sample (H_2O <20 ppm; halogens and metals <10 ppm) was purchased from Kanto Chemical Co. and used as received. Li$^+$ was added by dissolving Li[FSA] (purchased from Nippon Shokubai Co., Ltd.) powder into neat [C$_2$mim][FSA] with a concentration of 0.45 M in accordance with Ref. [10]. The electrochemical cell was of a three-electrode design. A polycrystalline Pt disk (ϕ10 mm) served as a working electrode, which was polished and cleaned by electrochemical stripping in an aqueous solution of H_2SO_4 (0.5 M). The reference and counter electrodes were Ag/Ag$^+$ (0.1 M Ag trifluoromethanesulfonate (OTf) in [C$_4$mim][OTf]) and Pt wire, respectively. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed using an electrochemical workstation (HZ-5000, Hokuto Denko Corp.) [14,15]. The LSV and CV scan rates were 5 mV/s and 50 mV/s, respectively [10].

Details of the electrochemical SFG setup are described elsewhere [13,16]. A tunable IR laser pulse (2.5–10 μm in wavelength) was overlapped with a visible laser pulse (532 nm) to generate the SF beam. The polarization combination in the experiments was ssp (denoting the s-polarized SF, s-polarized visible, and p-polarized IR beam, respectively). During SFG measurement, the Pt disk was pressed onto a BaF$_2$ window to form a thin layer of electrolyte on the electrode. No SF signal was observed when the Pt electrode was backed away from the BaF$_2$ window, indicating that the signal was entirely generated at the electrolyte/Pt interface [14,15]. All SFG spectra were obtained under equilibrium conditions; this was confirmed by monitoring the change of SF signal intensity after the potential step.

4. Results and discussion

LSV and CV profiles of a Pt|[C$_2$mim][FSA] system with and without Li$^+$ are shown in Fig. 1. The negative edge of the EW of the Pt|[C$_2$mim][FSA] system is extended by >1.0 V by the addition of Li$^+$ relative to that without Li$^+$. Since the negative edge of the EW of the neat RTIL is determined by the reduction potential of [C$_2$mim]$^+$ cations, this result indicates that the reduction of [C$_2$mim]$^+$ cations on Pt is suppressed by adding Li$^+$, as observed in other RTIL/electrode systems [9,10,17]. A small redox pair centered at −1.8 V is attributable to under-potential-deposition (UPD) of Li$^+$ and the corresponding Li stripping process on the Pt surface, respectively [18,19]. This is partly due to the facts that (1) the deposition potential is much more positive than that of the bulk Li deposition; (2) the deposition charge of the redox pair is comparable to a ~1.3 monolayer relative to H-UPD on the same electrode. A similar Li-UPD process has been observed by Endres et al. on a polycrystalline Pt electrode in a different ionic liquid [19]. It should be noted that a Li-Pt alloy could possibly form because the UPD charge decreases with CV cycling numbers, suggesting that an irreversible redox process occurs [20]. Thus Li$^+$ is adsorbed on the Pt electrode before [C$_2$mim]$^+$ at negative potentials.

Fig. 2 shows the SFG spectra of the Pt|[C$_2$mim][FSA] interface with and without Li$^+$ taken at the SO stretch region within the EW. All the SFG spectra are fitted to Eq. (1) with three vibrational modes [12,13]; the peaks at 1130 cm^{-1}, 1190 cm^{-1} and 1225 cm^{-1} are attributed to the S-N-S asymmetric stretch (SNS), out-of-phase SO$_2$ symmetric stretch (SO$_2$-op) and in-phase SO$_2$ symmetric stretch (SO$_2$-ip) modes, respectively [21,22].

The SFG spectral features change as the applied potential shifts from positive to negative. The SNS and SO$_2$-ip peaks for neat [C$_2$mim][FSA] disappear when the potential reaches −1.5 V. In the case where Li$^+$ has been added to [C$_2$mim][FSA], however, both the SNS and SO$_2$-ip peaks remain at −1.5 V and are still detectable even at −2.0 V beyond the Li-UPD of −1.8 V. A change in the peak intensity ratio of SNS and SO$_2$-ip modes at −2.0 V suggests a change in the orientational distribution of the [FSA]$^-$ anion at the Pt surface [12,13]. To compare the [FSA]$^-$ anion configuration at the interface for the cases with and without Li$^+$, the potential dependence of the SF amplitude and peak position of the SO$_2$-ip mode are plotted in Fig. 3a and b. When the potential moves from positive to negative, the SO$_2$-ip amplitude of neat [C$_2$mim][FSA] gradually decreases, indicating that the [FSA]$^-$ anion starts desorbing from the negatively-charged Pt surface. On the other hand, the SO$_2$-ip peak for the added Li$^+$ case remains at the same amplitude level even at −1.0 V. This result indicates that the [FSA]$^-$ anion can keep its polar orientation on the negatively-charged Pt surface with Li$^+$.

It is noteworthy that the SO$_2$-ip peak position in the Li$^+$ added case remains at 1225 cm^{-1} for all the applied potentials, even beyond the Li-UPD, while the one without Li$^+$ red-shifts linearly from 1225 cm^{-1} to 1221 cm^{-1} at −1.0 V. Considering that the corresponding bulk value of the SO$_2$-ip peak position is about 1220 cm^{-1} [22] and that the potential of zero charge (PZC) for RTIL/Pt systems has been estimated to be