IV-SFG studies on the effect of Li^+ in extending the electrochemical window at the $\text{Pt}||[\text{C}_2\text{mim}][\text{FSA}]$ interface

*Takashi Iwahashi,^a Yujiro Miwa,^a Wei Zhou,^b Yasunari Sakai,^a Masaki Yamagata,^c Masashi Ishikawa,^c
Doseok Kim,^d and Yukio Ouchi^{*a}*

Department of Materials Science and Engineering, Tokyo Institute of Technology, O-okayama,
Meguro-ku, Tokyo, 152-8552, Japan.

Department of Chemistry, Shanghai University, Shanghai 200444, China.

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and
Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

Department of Physics, Sogang University, Seoul, 121-742, Republic of Korea.

*To whom correspondence should be addressed. E-mail: ouchi.y.ab@m.titech.ac.jp Phone: +81-3-5734-2436. Fax: +81-3-5734-2876.

^aDepartment of Materials Science and Engineering, Tokyo Institute of Technology

^bDepartment of Chemistry, Shanghai University

^cDepartment of Chemistry and Materials Engineering, Kansai University

^dDepartment of Physics, Sogang University

Abstract

The effect of Li^+ addition at the interface of a 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide ($[\text{C}_2\text{mim}][\text{FSA}]$) 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 $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]$ system results in the extension of the electrochemical window (EW) by more than 1.0 V at its negative edge. The potential dependence of the SF signal reveals that the $[\text{FSA}]^-$ anion of neat $[\text{C}_2\text{mim}][\text{FSA}]$ 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 $[\text{FSA}]^-$ anion at the $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]$ interface interacts with Li^+ at the interface with the negatively-charged Pt electrode. This $[\text{FSA}]^-$ anion layer anchored through Li^+ suppresses $[\text{C}_2\text{mim}]^+$ cation adsorption on the negatively-charged Pt electrode, resulting in a wider electrochemical window.

Keywords: IR-visible sum-frequency generation vibrational spectroscopy, ionic liquid, RTIL, electrical double layer

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 ($[\text{C}_2\text{mim}][\text{FSA}]$, 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 more than 1.0 V at the negative edge is obtained for the $\text{Pt}[\text{C}_2\text{mim}][\text{FSA}]$ system with Li^+ . A comparative analysis of electrochemical and SFG results demonstrates that the $[\text{FSA}]^-$ anion layer anchored by Li^+ on the negatively-charged Pt surface effectively prevents the adsorption of $[\text{C}_2\text{mim}]^+$ 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 signal contribution from the bulk of the electrolyte [14,15]. The observed SF signal intensity I_{sf} is given by

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

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 q th vibrational mode, respectively. A_q is related to molecular hyperpolarizability A_q by

$$\chi^{(2)} = N_s \langle \alpha^{(2)} \rangle \quad (2)$$

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 [C₂mim][FSA] sample (H₂O <20ppm; halogens and metals <10ppm) 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 [C₂mim][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 (ϕ 10 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 $[\text{C}_4\text{mim}][\text{OTf}]$) 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/sec and 50 mV/sec, 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 $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]$ system with and without Li^+ are shown in Fig. 1. The negative edge of the EW of the $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]$ system is extended by more than 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 $[\text{C}_2\text{mim}]^+$ cations, this result indicates that the reduction of $[\text{C}_2\text{mim}]^+$ 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 $[\text{C}_2\text{mim}]^+$ at negative potentials.

Fig. 2 shows the SFG spectra of the $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]]$ 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 ($\text{SO}_2\text{-op}$) and in-phase SO_2 symmetric stretch ($\text{SO}_2\text{-ip}$) modes, respectively [21,22].

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

It is noteworthy that the $\text{SO}_2\text{-ip}$ 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 $\text{SO}_2\text{-ip}$ 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 around $-0.5\text{ V vs. Ag/Ag}^+$ [23,24], we can safely conclude that the red-shift is due to a

vibrational Stark shift of the $[\text{FSA}]^-$ anion interacting with an electric field from the positively-charged Pt electrode. In contrast, the observation that the $\text{SO}_2\text{-ip}$ peak position of $[\text{C}_2\text{mim}][\text{FSA}]$ with added Li^+ is located at 1225 cm^{-1} even at high negative potentials suggests that the $[\text{FSA}]^-$ anion is adsorbed on the negatively-charged Pt surface due to the interaction with Li^+ . According to the Raman spectroscopy data obtained by Fujii and co-workers [22], $[\text{FSA}]^-$ anions solvated with Li^+ were found to provide the $\text{SO}_2\text{-ip}$ peak at 1230 cm^{-1} . This result, together with the observation of Li-UPD at -1.8 V , strongly suggests that the Li^+ is adsorbed on the negatively-charged Pt surface and is solvated by $[\text{FSA}]^-$ anions. Such a strong interaction between the $[\text{FSA}]^-$ anion and the Li^+ cation, and the layering nature of RTILs [25-27], should lead to a stable adsorbed structure of the $[\text{FSA}]^-$ anion on the negatively-charged Pt surface and suppress the approach of $[\text{C}_2\text{mim}]^+$ cations to the Pt electrode [10,11], resulting in the extension of the negative edge of the EW. The small but remaining $\text{SO}_2\text{-ip}$ with a different intensity ratio to SNS even at -2.0 V after Li-UPD implies the presence of polar-oriented $[\text{FSA}]^-$ anions anchored by Li^+ on the Li-UPD layer with a different orientational distribution. Bearing in mind that the infrared dipole derivative unit vectors of SNS and $\text{SO}_2\text{-ip}$ modes are nearly parallel and perpendicular to the vector formed by the two S atoms in the $[\text{FSA}]^-$ anion (S-S vector), respectively, we can interpret the increase in the SNS peak with decreasing $\text{SO}_2\text{-ip}$ peak as being due to the orientational change in the S-S vector from parallel to perpendicular relative to the surface plane [28].

Finally, it is worth noting that the peak assigned to $\text{SO}_2\text{-op}$ at 1190cm^{-1} still remains, even at -1.9 V . In view of the fact that the $\text{SO}_2\text{-op}$ is observed at high negative potentials even before starting the reduction of the $[\text{C}_2\text{mim}]^+$ cation, the remaining $\text{SO}_2\text{-op}$ peak is likely to be derived from $[\text{FSA}]^-$ anions near the interface but not adsorbed directly on the Pt surface, as has been reported for other RTIL/Pt cases [14,15]. This is partly due to the fact that the position of $\text{SO}_2\text{-op}$ peak is almost the same within the EW irrespective of the presence of Li^+ . Layering observed on the electrode [25-27] may also cause SF active complex configurations of $[\text{FSA}]^-$ with $[\text{C}_2\text{mim}]^+$ and Li^+ .

Here we propose a model for the applied potential dependence of the $\text{Pt}[[\text{C}_2\text{mim}][\text{FSA}]$ interface with and without Li^+ . The schematic illustrations for the interface model are given in Fig. 4. Without Li^+ , the

[FSA][−] anion strongly adsorbed on the positively-charged Pt surface starts desorbing as the potential shifts from positive to negative, resulting in the gradual decay of the SO₂-ip amplitude accompanied by a vibrational Stark shift. The [FSA][−] anion is totally desorbed from the Pt surface at a negative potential of −1.5 V. In the case with added Li⁺, the [FSA][−] anion configuration under high positive potential is similar to the previous case. The [FSA][−] anion remains on the Pt surface even at −1.0 V, possibly due to a strong interaction through Li⁺ bound on the negatively-charged Pt surface. The [FSA][−] anion strongly interacting with Li⁺ remains even at a negative potential of −2.0 V after the Li-UPD [11]. The presence of the [FSA][−] anion interacting with Li⁺ prevents [C₂mim]⁺ cation adsorption and reduction at the negatively-charged Pt surface [10,11]. Some [FSA][−] anions may weakly align on or near the interface [25-27], resulting in the appearance of SO₂-op peak even at high negative potentials irrespective of the presence of Li⁺.

5. Summary

In summary, we have revealed the effect of Li⁺ addition on the applied potential response of the [FSA][−] anion configuration at the Pt[[C₂mim]][FSA] interface using IV-SFG vibrational spectroscopy. An extension of the negative edge of the electrochemical window of more than 1.0 V was obtained for the Pt[[C₂mim]][FSA] with Li⁺. The redox pair centered at −1.8 V was observed in the CV profile only with Li⁺, suggesting the presence of Li-UPD. The [FSA][−] anion adsorption/desorption behavior was monitored by SFG, to show from the SO₂-ip mode that the [FSA][−] anion is desorbed at −1.5 V without Li⁺ while it remains even at −2.0 V with Li⁺. Strong interaction with Li⁺ anchors the polar-oriented [FSA][−] anion layer even at high negative potentials, preventing the adsorption and reduction of the [C₂mim]⁺ cation onto the Pt electrode. A more detailed study on the effect of Li⁺ addition to electrode|RTIL systems, including quantitative analysis of the [FSA][−] anion orientation and the anion/electrode species dependence, is now in progress and will be presented in the near future.

Acknowledgements This work is supported in part by KAKENHI; Grant-in-Aid for the Scientific Research in Priority Areas “Science of Ionic Liquids”, for Scientific Research (A) (No.26248004) and for Young Scientists (B) (No. 16K21030) from MEXT, Japan. M. Y. also acknowledges Grant-in-Aid for Encouragement of Young Scientists (B) (No.16K17974) from MEXT, Japan. W. Z. acknowledges support from the National Science Foundation of China (No. 21573144 and 21003088). D. K. acknowledges Korean Government (MEST) grant No. 2011-0017435 of the Republic of Korea. We thank Dr. H. Matsumoto at AIST, Japan for kindly donating us [FSA]⁻ anion at the initial stage of experiments.

References

- [1] H. Sakaebe, H. Matsumoto, *N*-Methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) – novel electrolyte base for Li battery, *Electrochem. Commun.*, 2003, 5, 594–598.
- [2] B. Garcia, S. Lavallée, G. Perron, C. Michot, M. Armand, Room temperature molten salts as lithium battery electrolyte, *Electrochim. Acta*, 2004, 49, 4583–4588.
- [3] H. Matsumoto, H. Sakaebe, K. Tatsumi, Preparation of room temperature ionic liquids based on aliphatic onium cations and asymmetric amide anions and their electrochemical properties as a lithium battery electrolyte, *J. Power Sources*, 2005, 146, 45–50.
- [4] Z. Li, J. Huang, B. Y. Liaw, V. Metzler, A review of lithium deposition in lithium-ion and lithium metal secondary batteries, J. Zhang, *J. Power Sources*, 254 (2014) 168–182.
- [5] X. H. Huang, J. P. Tu, X. H. Xia, X. L. Wang, J. Y. Xiang, L. Zhang, Y. Zhou, Morphology effect on the electrochemical performance of NiO films as anodes for lithium ion batteries, *J. Power Sources*, 188 (2009) 588–591.
- [6] P. Verma, P. Maire, P. Novák, A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries, *Electrochim. Acta*, 55 (2010) 6332–6341.
- [7] J. D. Holbrey, K. R. Seddon, The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals, *J. Chem. Soc., Dalton Trans.*, (1999) 2133–2139.
- [8] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, Ionic-liquid materials for the electrochemical challenges of the future, *Nature Mat.* 8 (2009) 621–629.
- [9] V. Borgel, E. Markevich, D. Aurbach, G. Semrau, M. Schmidt, On the application of ionic liquids for rechargeable Li batteries: High voltage systems, *J. Power Sources*, 189 (2009) 331–336.

- [10] M. Yamagata, N. Nishigaki, S. Nishishita, Y. Matsui, T. Sugimoto, M. Kikuta, T. Higashizaki, M. Kono, M. Ishikawa, Charge-discharge behavior of graphite negative electrodes in bis(fluorosulfonyl)imide-based ionic liquid and structural aspects of their electrode/electrolyte interfaces, *Electrochim. Acta*, 110 (2013) 181–190.
- [11] K. Kiyohara, M. Yamagata, M. Ishikawa, Electrochemical and structural properties of the electrical double layer of two-component electrolytes in response to varied electrode potential, *J. Chem. Phys.*, 144 (2016) 134701.
- [12] X. Zhuang, P. B. Miranda, D. Kim, Y. R. Shen, Mapping molecular orientation and conformation at interfaces by surface nonlinear optics, *Phys. Rev. B*, 59 (1999) 12632–12640.
- [13] T. Iimori, T. Iwahashi, K. Kanai, K. Seki, J. Sung, D. Kim, H. Hamaguchi, Y. Ouchi, Local structure at the air/liquid interface of room-temperature ionic liquids probed by infrared-visible sum frequency generation vibrational spectroscopy: 1-Alkyl-3-methylimidazolium tetrafluoroborates, *J. Phys. Chem. B*, 111 (2007) 4860–4866.
- [14] W. Zhou, S. Inoue, T. Iwahashi, K. Kanai, K. Seki, T. Miyamae, D. Kim, Y. Katayama, Y. Ouchi, Electrochemical double-layer structure of Pt electrode/ionic liquids interface studied by in situ IR-visible sum frequency generation spectroscopy, *ECS Trans.*, 16 (2009) 545–557.
- [15] W. Zhou, S. Inoue, T. Iwahashi, K. Kanai, K. Seki, T. Miyamae, D. Kim, Y. Katayama, Y. Ouchi, Double layer structure and adsorption/desorption hysteresis of neat ionic liquid on Pt electrode surface – an in-situ IR-visible sum-frequency generation spectroscopic study, *Electrochem. Commun.*, 12 (2010) 672–675.
- [16] T. Iwahashi, T. Miyamae, K. Kanai, K. Seki, D. Kim, Y. Ouchi, Anion configuration at the air/liquid interface of ionic liquid [bmim]OTf studied by sum-frequency generation spectroscopy, *J. Phys. Chem. B*, 112 (2008) 11936–11941.

- [17] S. Menne, R.-S. Kühnel, A. Balducci, The influence of the electrochemical and thermal stability of mixtures of ionic liquid and organic carbonate on the performance of high power lithium-ion batteries, *Electrochim. Acta*, 90 (2013) 641–648.
- [18] C. A. Paddon, R. G. Compton, Underpotential deposition of lithium on platinum single crystal electrodes in tetrahydrofuran, *J. Phys. Chem. C*, 111 (2007) 9016–9018.
- [19] L. H. S. Gasparotto, N. Borisenko, N. Bocchi, S. Z. E. Abedin, F. Endres, *In situ* STM investigation of the lithium underpotential deposition on Au(111) in the air- and water-stable ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide, *Phys. Chem. Chem. Phys.*, 11 (2009) 11140–11145.
- [20] R. Wibowo, S. E. W. Jones, R. G. Compton, Kinetic and thermodynamic parameters of the Li/Li^+ couple in the room temperature ionic liquid *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide in the temperature range 298–318 K: A theoretical and experimental study using Pt and Ni electrodes, *J. Phys. Chem. B*, 113 (2009) 12293–12298.
- [21] L. Li, S. Zhou, H. Han, H. Li, J. Nie, M. Armand, Z. Zhou, X. Huang, Transport and electrochemical properties and spectral features of non-aqueous electrolytes containing LiFSI in linear carbonate solvents, *J. Electrochem. Soc.*, 158 (2011) A74-A82.
- [22] K. Fujii, H. Hamano, H. Doi, X. Song, S. Tsuzuki, K. Hayamizu, S. Seki, Y. Kameda, K. Dokko, M. Watanabe, Y. Umebayashi, Unusual Li^+ ion solvation structure in bis(fluorosulfonyl)amide based ionic liquid, *J. Phys. Chem. C*, 117 (2013) 19314–19324.
- [23] S. Baldelli, Probing electric fields at the ionic liquid-electrode interface using sum frequency generation spectroscopy and electrochemistry, *J. Phys. Chem. B*, 109 (2005) 13049–13051.

- [24] M. T. Alam, Md. M. Islam, T. Okajima, T. Ohsaka, Capacitance measurements in a series of room-temperature ionic liquids at glassy carbon and gold electrode interfaces, *J. Phys. Chem. C*, 112 (2008) 16600–16608.
- [25] M. Mezger, H. Schröder, H. Reichert, S. Schramm, J. S. Okasinski, S. Schöder, V. Honkimäki, M. Deutsch, B. M. Ocko, J. Ralston, M. Rohwerder, M. Stratmann, H. Dosch, Molecular layering of fluorinated ionic liquids at a charged sapphire (0001) surface, *Science*, 322 (2008) 424–428.
- [26] S. A. Kislenko, I. S. Samoylov, R. H. Amirov, Molecular dynamics simulation of the electrochemical interface between a graphite surface and the ionic liquid [BMIM][PF₆], *Phys. Chem. Chem. Phys.* 11 (2009) 5584–5590.
- [27] A. Lahiri, T. Carstens, R. Atkin, N. Borisenko, F. Endres, In situ atomic force microscopic studies of the interfacial multilayer nanostructure of LiTFSI–[Py_{1,4}]TFSI on Au(111): Influence of Li⁺ ion concentration on the Au(111)/IL interface, *J. Phys. Chem. C*, 119 (2015) 16734–16742.
- [28] C. Hirose, N. Akamatsu, K. Domen, Formulas for the analysis of the surface SFG spectrum and transformation coefficients of Cartesian SFG tensor components, *Appl. Spectroscopy*, 46 (1992) 1051–1072.

Figure Captions

- Figure 1.** (a) LSV and (b) CV profiles of Pt|[C₂mim][FSA] system with and without Li⁺. Molecular structures of [C₂mim]⁺ cation and [FSA]⁻ anion are given in the inset. The redox pair shown by red arrows represents Li-UPD.
- Figure 2.** Applied potential dependence of SFG spectra at Pt|[C₂mim][FSA] interfaces (a) without Li⁺ and (b) with Li⁺.
- Figure 3.** Applied potential dependence of (a) amplitude and (b) position of SO₂-ip mode of [FSA]⁻ anion in the SFG spectra of the Pt|[C₂mim][FSA] interfaces with and without Li⁺. The thick lines are guides to the eye.
- Figure 4.** Schematic illustrations of applied potential dependence of Pt|[C₂mim][FSA] interface structure (a) without Li⁺ and (b) with Li⁺. Three types of [FSA]⁻ anions are modeled: “Free” orienting randomly as in the bulk, “Weakly” bound near the interface, and “Strongly” interacting with Pt surface or Li⁺ with polar orientation. The red dotted line represents a possible solvation of [FSA]⁻ anion to Li⁺.

(a) without Li^+

(b) with Li^+