

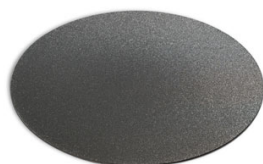
OPEN ACCESS

## Piperidinium-Based Ionic Liquids as an Electrolyte Solvent for Li-Ion Batteries: Effect of Number and Position of Oxygen Atom in Cation Side Chain on Electrolyte Property

To cite this article: Masahiro Shimizu *et al* 2020 *J. Electrochem. Soc.* **167** 070516

View the [article online](#) for updates and enhancements.

**elementsix**  
DE BEERS GROUP



Element Six's boron doped diamond (BDD) is the ultimate material for electrochemical advanced oxidation processes

Free-standing BDD is the ideal electrode material for electrochemical applications as it possesses an extended solvent window and low capacitive current. It's also chemically and catalytically inert as well as extremely resistant to corrosion. BDD has no substrate and can withstand pH 1 - 14 operation.

Find out more and contact the team at [ustechnologies@e6.com](mailto:ustechnologies@e6.com)



[e6.com/en/products/diamond-water-solutions](https://e6.com/en/products/diamond-water-solutions)



# Piperidinium-Based Ionic Liquids as an Electrolyte Solvent for Li-Ion Batteries: Effect of Number and Position of Oxygen Atom in Cation Side Chain on Electrolyte Property

Masahiro Shimizu,<sup>1,2,\*</sup> Kazuki Yamaguchi,<sup>1,2</sup> Hiroyuki Usui,<sup>1,2</sup> Naoya Ieuji,<sup>1,2</sup> Takuya Yamashita,<sup>1,2</sup> Takuro Komura,<sup>1,2</sup> Yasuhiro Domi,<sup>1,2</sup> Toshiki Nokami,<sup>1,2,\*</sup> Toshiyuki Itoh,<sup>1,2</sup> and Hiroki Sakaguchi<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Tottori 680-8552, Japan  
<sup>2</sup>Center for Research on Green Sustainable Chemistry, Tottori University, Tottori 680-8552, Japan

In the pursuit of developing reliable Li-ion batteries with high performance and safety, the use of ionic liquids is one of the most promising approaches due to its high thermal stability. There is, however, the critical issue concerning the significantly low Li-ion diffusion in an electrolyte solution, which is directly linked to the degradation of their rapid charge–discharge properties. Ionic liquids with ether-substituted cation have generated much interest as electrolyte solvents for Li-ion batteries because the ether group functions to reduce the coordination number and increase ionic conductivity. In the present study, we synthesized six types of ionic liquids consisting of bis(trifluoromethanesulfonyl)amide (TFSA) anions and piperidinium-based cations in which the attached side chains are 1-((2-methoxyethoxy)methyl)-1-methylpiperidinium (PPIMEM), 1-butoxymethyl-1-methylpiperidinium (PP1BM), 1-methyl-(2-propoxyethyl)piperidinium (PP1PE), 1-(3-ethoxypropyl)-1-methylpiperidinium (PP1EP), 1-(4-methoxybutyl)-1-methylpiperidinium (PP1MB), and 1-hexyl-1-methylpiperidinium (PP16). It was found that the ionic liquid with PPIMEM cations with two oxygen atoms in the side chain exhibited the lowest solvation number of TFSA anions (1.56), whereas PP1BM (1.78), PP1PE (1.86), PP1EP (2.08), and PP1MB-TFSA (2.07) resulted in a larger number, as the oxygen atoms in the alkyl side chain are located far from the positively charged nitrogen atoms. PPIMEM-TFSA with small solvation numbers enhanced the ionic conductivity and thereby achieved high electrode performance.

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab6a89]



Manuscript submitted November 25, 2019; revised manuscript received December 20, 2019. Published January 27, 2020. *This paper is part of the JES Focus Issue on Challenges in Novel Electrolytes, Organic Materials, and Innovative Chemistries for Batteries in Honor of Michel Armand.*

Supplementary material for this article is available [online](#)

Application of room temperature ionic-liquids to energy-storage devices including Li-,<sup>1–4</sup> Na-,<sup>5,6</sup> Mg-,<sup>7,8</sup> Al-ion batteries,<sup>9</sup> metal-air batteries,<sup>10</sup> and electrochemical capacitors<sup>11</sup> has great potential because of their unique properties such as high thermal stability, negligible vapor pressure, and wide electrochemical window. It is possible to provide above-mentioned functionality to ionic liquids using a combination of cations and anions. Among them, ionic liquids with bis(trifluoromethanesulfonyl)amide (TFSA) and bis(fluorosulfonyl)amide (FSA) as counter anions have been studied for electrolyte solvents due to their non-flammability or high ionic conductivity originating from low viscosity.<sup>12–14</sup> Matsumoto and Sakaebe et al. synthesized *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)amide (PP13-TFSA) which has a wide electrochemical window and they demonstrated that the electrolyte consisting of the attained ionic liquid prolonged the life of the Li/LiCoO<sub>2</sub> cell.<sup>15,16</sup> Aurbach et al. for first time applied PP13-TFSA to amorphous silicon (*a*-Si) thin-film with a 100 nm-thickness prepared using magnetron sputtering. Although the film thickness was thinner compared to that of a typical composite electrode, the *a*-Si thin-film exhibited a high electrode performance with a reversible capacity of ca. 3000 mA h g<sup>-1</sup> at the 30th cycle.<sup>17</sup> As a matter of course, growing interest in ionic-liquid electrolytes originates from ensuring the safety of batteries due to their high thermal stability, but still these reports also have sparked the use of ionic liquids in recent years.<sup>18–21</sup> In many cases, ionic liquids are very promising candidates as electrolyte solvents for developing batteries with long lifetimes; however, there is the critical issue of the rapid charge–discharge properties of the batteries equipped with ionic liquids.

The ionic conductivity of charge carriers such as Li- and Na-ions are inevitably decreased due to the high viscosity of ionic liquids. This is responsible for unfavorable degradation of rate performance.<sup>22</sup> In a lot of research, commercially available ionic-liquid electrolytes have been used. On the other hand, Passerini et al. investigated the effect of introducing ether functional groups to pyrrolidinium cations on the physicochemical properties of TFSA-based ionic-liquid electrolytes. They elucidated that the coordination number of TFSA anions, meaning the solvation shell of Li-ion, is reduced when using 1-(2-ethoxyethyl)-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (Pyr<sub>1</sub>[2O<sub>2</sub>]-TFSA) compared to the ionic liquid with pyrrolidinium cations with alkyl side chains of the same length.<sup>23</sup> We have also demonstrated that the addition of methoxyethoxymethyl (MEM) groups to piperidinium cations decreased the number (*x*) of TFSA anions in [Li(TFSA)<sub>*x*</sub>]<sup>1–*x*</sup> complexes, and enhanced the rate performance of a Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> electrode in comparison with the alkyl-substituted one because of the improved diffusion of the Li-ion in the electrolyte solution.<sup>24</sup> The introduction of oxygen atoms (ether functional group) into a side chain is remarkably effective to control cation-anion interaction involved in the solvation environment and ionic conductivity. Understanding the solvation environment of Li-ion in electrolytes is extremely important when designing an ionic liquid for use as an electrolyte solvent, which leads to achieving high-performance batteries. To the best of the authors' knowledge, there have been few systematic studies that investigate the influence of the position and number of oxygen atoms in the fixed-length functional groups on physicochemical properties.<sup>23</sup> In the present study, we synthesized five types of ionic liquids with piperidinium cations in which the position and number of oxygen atoms are different while fixing the side-chain length with focusing on the methoxyethoxymethyl (MEM) group. Then, we studied the influence of the functional group on Li<sup>+</sup>–TFSA interaction, the formation of [Li(TFSA)<sub>*x*</sub>]<sup>1–*x*</sup> complexes, and the physicochemical properties of the ionic liquids. The electrode performance of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and

\*Electrochemical Society Member.

<sup>†</sup>Present address: Department of Materials Chemistry, Faculty of Engineering, Shinshu University, 4–17–1 Wakasato, Nagano 380–8553, Japan.

<sup>‡</sup>E-mail: sakaguch@chem.tottori-u.ac.jp; shimizu@shinshu-u.ac.jp

Li-deposition/stripping behavior in the respective electrolyte solutions were examined for the purpose of applying the ionic liquids to various rechargeable battery systems.

### Experimental

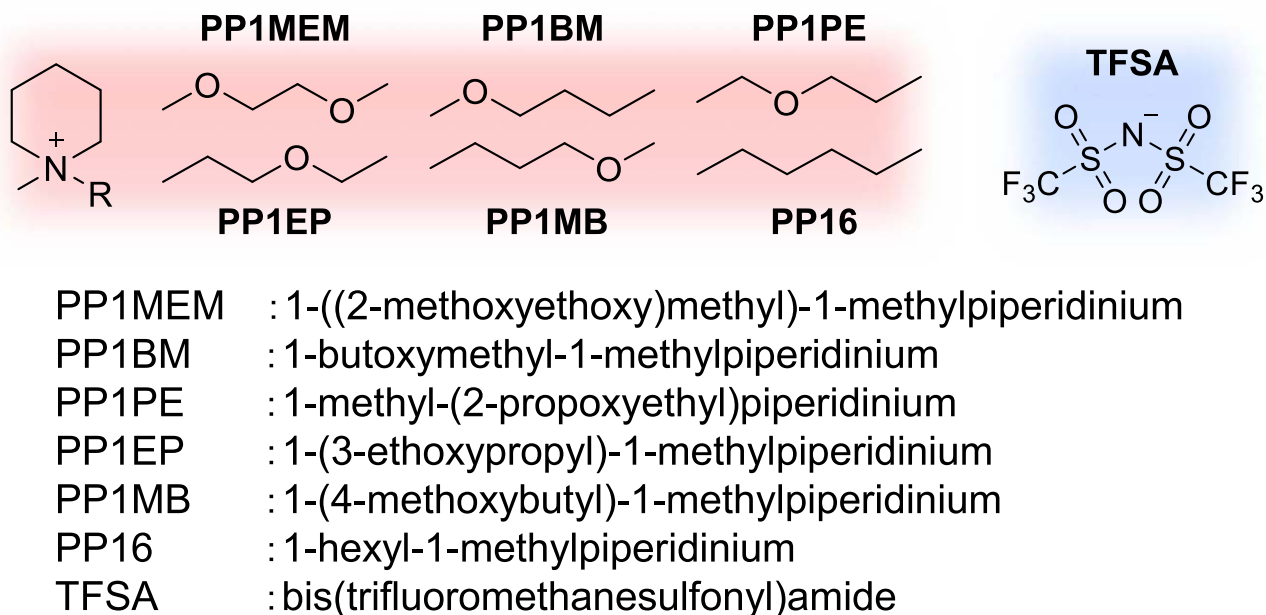
Six kinds of ionic liquids consisting of piperidinium-based cations and bis(trifluoromethanesulfonyl)amide (TFSA) anions were synthesized. Figure 1 displays the cation structure of 1-((2-methoxyethoxy)methyl)-1-methylpiperidinium (PP1MEM), 1-butoxymethyl-1-methyl (PP1BM), 1-methyl-(2-propoxyethyl)piperidinium (PP1PE), 1-(3-ethoxypropyl)-1-methylpiperidinium (PP1EP), 1-(4-methoxybutyl)-1-methyl (PP1MB), and 1-hexyl-1-methylpiperidinium (PP16) used in this study. Viscosity and ionic conductivity were measured using a cone-plate type viscometer (Brookfield) and an electrochemical cell equipped with two Pt electrodes, respectively, at various temperature from 298 to 353 K. Electrolyte solutions of  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  were prepared by dissolving Li salt, lithium bis(trifluoromethanesulfonyl)amide (LiTFSA, 99%, Kishida Chemical Co., Ltd). To study the Li-deposition/stripping behavior in each of the electrolytes, a three-electrode type cell was fabricated and cyclic voltammetry (CV) measurement was conducted with a sweep rate of  $0.1 \text{ mV s}^{-1}$  at 303 K. The working electrode is a Ni substrate (99.9%, 20- $\mu\text{m}$  thickness; Nilaco Co., Ltd), and both the counter and the reference electrodes are Li sheets (99.90%, 1.0-mm thickness; Rare Metallic). All operations including electrolyte preparation and cell assembly were carried out completely within a purge-type glovebox (DBO-2.5LNKP-TS; Miwa MFG) filled with an argon atmosphere from which the oxygen and water had been completely removed. The glovebox maintained a dew point below  $-100^\circ\text{C}$  and an oxygen content below 1 ppm. A Raman spectroscopy system (NanofinderFLEX, Tokyo Instruments, Inc.) with 532 nm line of Nd:YAG laser was used to analyze the solvation environment of Li ions.<sup>24</sup> In order to avoid the effects of humidity, we put the electrolyte solution into a quartz cell, and tightly sealed in it within an argon atmosphere.

### Results and Discussion

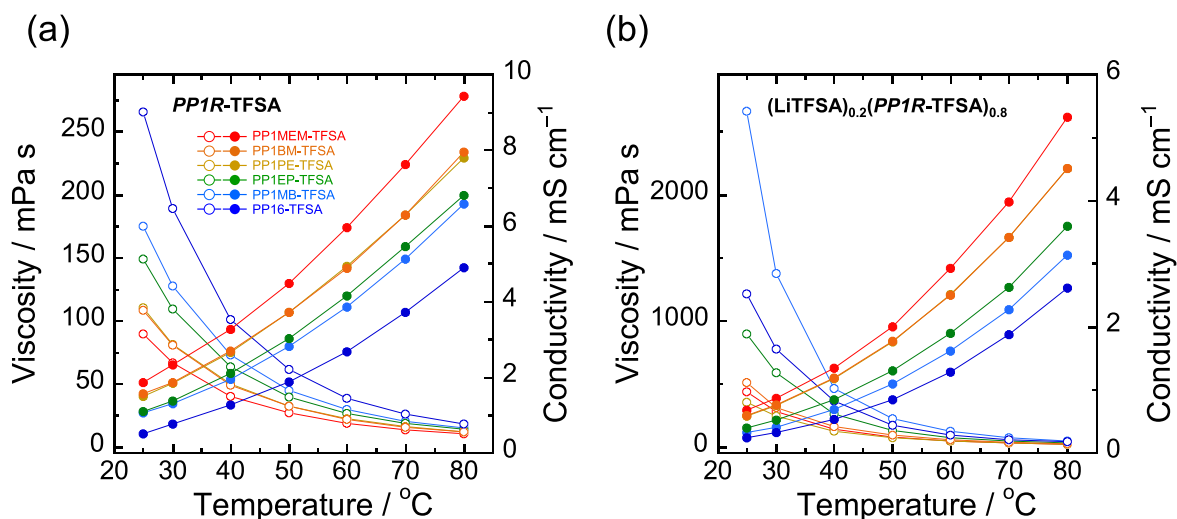
Figure 2a shows the temperature dependence of viscosity and ionic conductivity for the newly synthesized ionic liquids, which indicates how much the functional group attached to the cation structure reduces their central positive charge. The viscosity at room

temperature ( $25^\circ\text{C}/298 \text{ K}$ ) was 89 for PP1MEM-TFSA, 108 for PP1BM-TFSA, 110 for PP1PE-TFSA, 149 for PP1EP-TFSA, 175 for PP1MB-TFSA, and 266 mPa s for PP16-TFSA. As viscosity decreases, ionic conductivity increases (Tables SI–SII and Fig. S1, available online at [stacks.iop.org/JES/167/070516/mmedia](https://stacks.iop.org/JES/167/070516/mmedia)). The low viscosity of PP1MEM-TFSA means that the electrostatic interaction between dissociated cations and anions is much reduced, and the functional group of methoxyethoxymethyl (MEM) has more of an influence as an electron-releasing substituent on the central charge of the cations than any of the others in the present study. What needs to be emphasized is that the viscosity of PP1BM-TFSA was smaller than those of PP1PE-TFSA, PPEP-TFSA, and PP1MB-TFSA in spite of the equal molecular weight of their ionic liquids. Therefore, it is found that the functional group of butoxymethyl has a greater electron-donating ability in comparison with those of propoxyethyl, ethoxypropyl, and methoxybutyl, and that PP1BM-TFSA has an ability to provide superior ionic transport properties. In the ether-substituted ionic liquids, the closer the oxygen atom is to the positively charged nitrogen atom, the weaker the cation charge and the results in enhancement of ionic conductivity due to the reduction of cation-anion interaction. The higher ionic conductivity in PP1MEM-TFSA was observed even after the dissolution of LiTFSA salt (Fig. 2b and Table SIII). Although ionic conductivities between PP1BM-TFSA and PP1PE-TFSA and between PP1EP-TFSA and PP1MB-TFSA almost overlapped each other, there was a marked difference in  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  systems, which implies different solvation states in the respective electrolyte solutions.

The coordination environment of the Li-ion as a charge carrier is determined by an electrolyte solvent and has a great influence on charge–discharge behavior. With respect to commercially available ionic liquids such as PP13-TFSA and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMI-TFSA), it is well known that Li ions are inevitably solvated by an electrostatic interaction between Li-ions and TFSA anions to form negatively charged  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes, and the solvation number ( $x$ ) results in “2”.<sup>25</sup> As for the electrolyte solution including LiTFSA with a molar fraction of 0.2, we previously demonstrated that the two oxygen atoms in the functional group of methoxyethoxymethyl (MEM) play a key role in weakening the interaction between Li-ions and TFSA anions by forming the PP1MEM-Li-TFSA complex; the average solvation number of TFSA anions per Li-ion becomes smaller due to



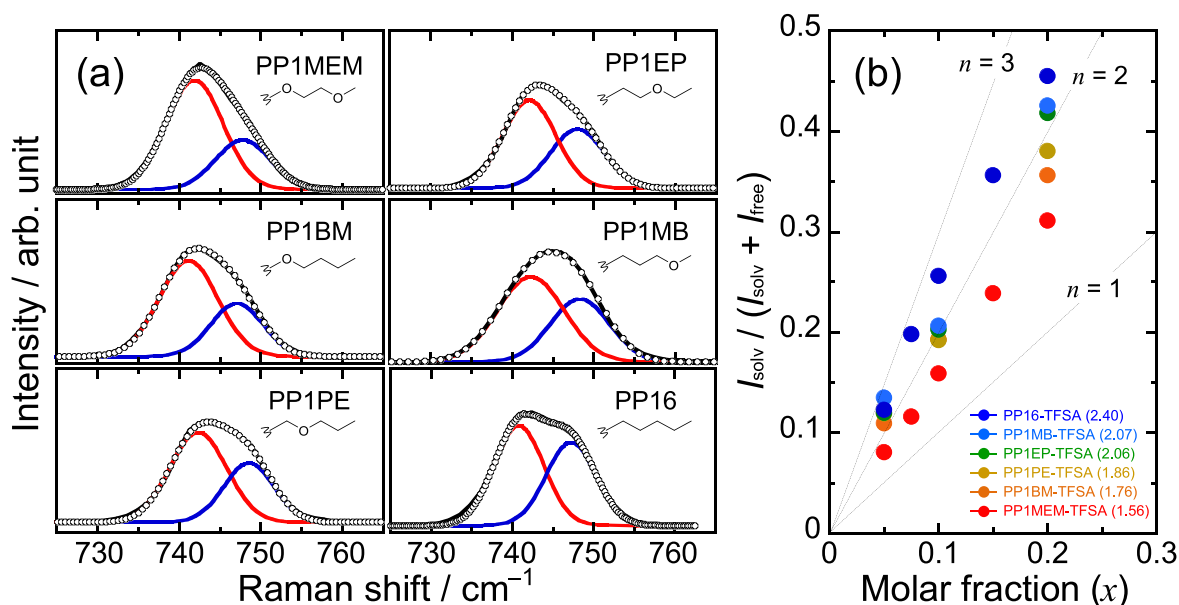
**Figure 1.** Cation and anion structures of ionic liquids used in this study. Ionic liquids with piperidinium cations were synthesized in which position and number of oxygen atoms are different while fixing the side-chain length with a focus on the methoxyethoxymethyl (MEM) group.



**Figure 2.** Temperature dependences of viscosity and ionic conductivity of (a) neat ionic liquids and (b) piperidinium-based ionic-liquid electrolyte solutions of  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$ . The plots for PP1BM-TFSA and PP1PE-TFSA are almost overlapping in panel (b).

the attractive force induced by the negatively-charged oxygen atoms.<sup>24,26</sup> The lower number made Li-ions relatively free from the constraint generated by the cation-anion electrostatic interaction and improved the transport ability of Li-ions, and thereby improved rate the performance of the Si electrode and the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode.<sup>20,21,24</sup> However, there is room to reconsidering the matter. In order to further understand the phenomenon, it is necessary to investigate the relationship between the number and the position of oxygen atoms in the side chain groups to achieve the effect mentioned above. Figure 3a compares the Raman spectra of  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  electrolyte solutions in the wave-number range from 725 to 765  $\text{cm}^{-1}$ , which offers insight into behavior of Li-ions and TFSA anions. The intense band of 742  $\text{cm}^{-1}$  derives from the  $\text{CF}_3$  bending vibration coupled with the S–N stretching vibration of the TFSA anions.<sup>27</sup> The band shows that TFSA anions in the respective electrolyte solutions do not interact with Li-ions, which means that the anions are not involved in the stabilization of  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes. It was observed in only

one band before dissolving Li-salt (not shown here), whereas the additional band appeared at around 748  $\text{cm}^{-1}$  in the presence of LiTFSA. The appearance indicates the existence of  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes formed by the Coulomb force. In respect to a neat EMI-TFSA and its mixtures of the ionic liquid and Li ions at room temperature, Kurisaki and Umebayashi et al. used X-ray photoelectron spectroscopy for analyzing the composition and structure of its near-surface region. They revealed that Li ions are easily solvated C1 TFSA anions C1 than C2 TFSA anions and proposed that Li ions are concentrated in the near-surface region.<sup>28</sup> In all cases, the band intensity at 742  $\text{cm}^{-1}$  was consistently larger compared to that at 748  $\text{cm}^{-1}$ , that is, TFSA anions are often present to be free rather than involved in the solvation. When attention is paid to the number of oxygen atoms in the respective functional groups, it is found that the formation of  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes tend to be suppressed in the presence of oxygen atoms. From a viewpoint of the position of the atom, it is indicated that Li-ions become free from TFSA anions as oxygen atoms approach the positively charged nitrogen atoms.



**Figure 3.** (a) Raman spectra of  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  electrolyte solutions from 725 to 765  $\text{cm}^{-1}$ . The black, dotted, red, and blue lines correspond to observed spectrum, the total Raman spectrum, the deconvoluted components of free TFSA anions ( $\text{TFSA}_{\text{free}}^-$ ) and TFSA anions interacting with  $\text{Li}^+$  ( $\text{TFSA}_{\text{solv}}^-$ ), respectively. (b) Plot of  $I_{\text{solv}} / (I_{\text{solv}} + I_{\text{free}})$  as a function of  $(\text{LiTFSA})_x(\text{PP1R-TFSA})_{1-x}$ . The cations are PP1MEM, PP1BM, PP1PE, PP1EP, PP1MB, and PP16, respectively.

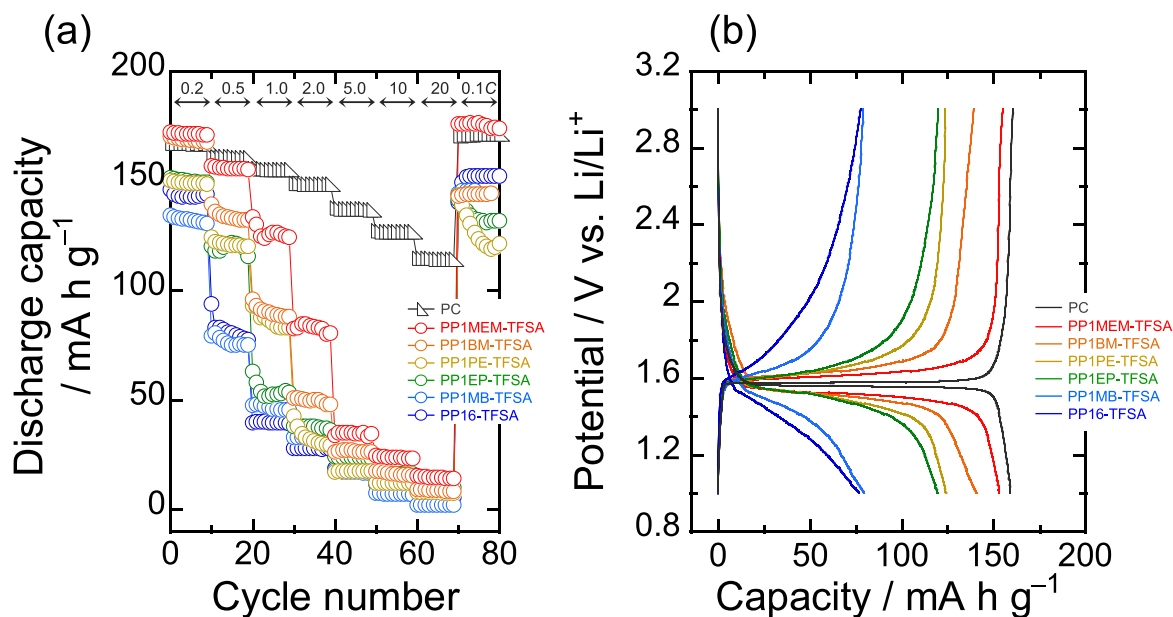


We think that the resulting free Li-ions interact through oxygen atoms in cations. Based on the results for the ratios of band intensity ( $I_{\text{solv}}/I_{\text{free}} + I_{\text{solv}}$ ) vs the molar fraction of LiTFSA (Fig. 3b), the average solvation numbers of TFSA anions per Li-ion in the respective electrolyte solutions were calculated through the method reported by Lassègues and Balducci et al.<sup>29,30</sup> The average solvation numbers in each of the electrolyte solutions of  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  are 1.56 for PP1MEM-TFSA, 1.76 for PP1BM-TFSA, 1.86 for PP1PE-TFSA, 2.06 for PP1EP-TFSA, 2.07 for PP1MB-TFSA, and 2.40 for PP16-TFSA. The higher ionic conductivity obtained in  $(\text{LiTFSA})_{0.2}(\text{PP1MEM-TFSA})_{0.8}$  should be responsible for the lower solvation number and is related to enhanced Li-ion diffusion property. To investigate the applicability of these ionic liquids to electrolyte solvents for Li-ion batteries, the effects of the physicochemical properties and solvation number on charge–discharge behavior were studied using  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes which can operate within the potential windows of the ionic liquids. In addition, we also evaluated Li-deposition/stripping properties.

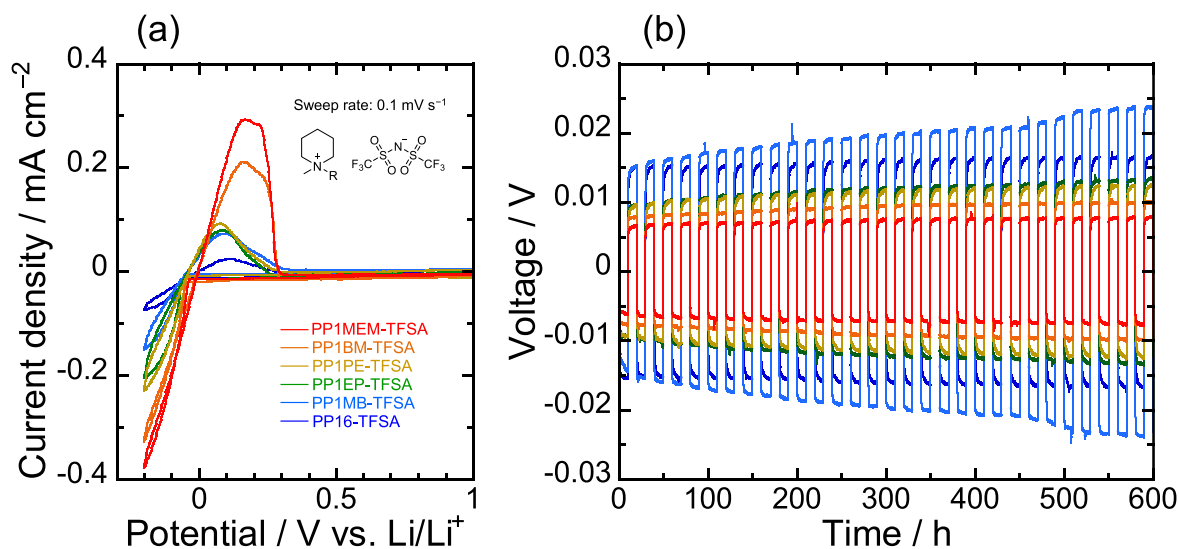
Figure 4a summarizes the rate performance of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes in  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  electrolyte solutions at various C-rates from 0.1 C (17.5 mA g<sup>-1</sup>) to 20 C (3500 mA g<sup>-1</sup>). For comparison, the performance in an organic electrolyte of 1 M LiTFSA/propylene carbonate (PC) was also shown. Ionic liquid electrolytes except for PP1MEM-TFSA showed only a low reversible capacity below 150 mA h g<sup>-1</sup> even at a low current density region with low influence from the concentration polarization (0.5 C). Clear polarization for charge–discharge was observed in PP1MB-TFSA and PP16-TFSA systems (Figure 4b). At a relatively high rate of 2 C, PP1MEM-TFSA displayed a higher reversible capacity of 85 mA h g<sup>-1</sup> than any other ionic liquid, showing the good Li-ion transport properties in PP1MEM-TFSA originating from the small average solvation number and low viscosity.

Figure 5 displays the cyclic voltammograms of Ni/Li cells with a Li reference electrode in a potential range from 2.0 to -0.2 V and voltage profiles of symmetric cells consisting of Li metal under a constant current density of 0.01 mA cm<sup>-2</sup>. No obvious peak for cathodic and anodic decomposition of ionic liquid was observed in the sweep range. PP1MEM-TFSA showed smallest overvoltage for Li-deposition/stripping and the reaction was stable for 600 h. In the

voltammograms, the reduction and oxidation current density involved with Li-deposition/stripping increased in order of decreasing solvation number, indicating that lower solvation has the effect of showing good conductivity in the charge carriers. In the TFSA-based ionic-liquid electrolyte, Li ions have a negative charge rather than a positive charge because TFSA anions work as a ligand to form the  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complex. Therefore, in the vicinity of the Ni substrate which is negatively charged during the cathodic reaction, the cations of the ionic liquids are preferentially accumulated to compensate for the negative charge, and  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes align opposite to the cations. This is the reason why the kinetics of the charge transfer reaction are lower than that in an organic electrolyte system. It is considered that the higher conductivity comes from the relatively free Li-ions from the constraint generated by the electrostatic interaction with TFSA anions. In the previous study, we revealed that PP1MEM cations attract Li-ions bound to TFSA anions through the two oxygen atoms to form the PP1MEM-Li-TFSA complex.<sup>24</sup> The complex enables Li-ions to be closer to the electrode, which is why a good rate performance and the largest current densities during Li-deposition/stripping were obtained. Comparing PP1BM-TFSA, PP1PE-TFSA, PP1EP-TFSA and PP1MB-TFSA in which the position of oxygen atoms in the functional group differs, the higher solvation number was acquired with PP1MB-TFSA (2.07). However, PP16-TFSA caused the largest number of 2.40. The results show that solvation environment is also affected by the position as well as the number of oxygen atoms. Oxygen atoms located nearer to the center of the cation structure than the end of the side chain exert a controlling influence on lower solvation. Furthermore, the favorable number of oxygen atoms for lower solvation number is not one but rather two or more because of the chelating effect. Mere modification and addition of functional groups raises the molecular weight of cations and enhances Van der Waals' force increasing the viscosity of the electrolyte solution. Therefore, there should be a threshold in the chain length of the functional moiety. In a future study, we are going to investigate the interaction between Li-ions and other anions such as FSA<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, and PF<sub>6</sub><sup>-</sup> in PP1MEM-based ionic liquids. Given the functionality of ether groups in enhancing high ionic conductivity and their relatively high thermal stability,<sup>31</sup> ionic liquids consisting of ether-substituted piperidinium cations and TFSA anions are promising electrolyte solvents not only for Li-ion batteries but also Li-Sulfur, and Li-Air batteries.



**Figure 4.** (a) Rate capability of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrodes in  $(\text{LiTFSA})_{0.2}(\text{PP1R-TFSA})_{0.8}$  electrolytes at various C-rates from 0.1 to 20 C (3500 mA g<sup>-1</sup>). (b) Charge–discharge (Li-insertion/extraction) curves at 0.5 C. For comparison, the performance in the organic electrolyte of 1 M LiTFSA/PC is shown.



**Figure 5.** (a) Cyclic voltammograms of Ni/Li cells with a Li reference electrode corresponding to Li-deposition/stripping in electrolytes of  $(\text{LiTFSA})_{0.2}(\text{PPiR-TFSA})_{0.8}$ . (b) Voltage profiles of symmetric Li/Li. The charge/discharge capacities and current density were set to  $0.1 \text{ mA h cm}^{-2}$  and  $0.01 \text{ mA cm}^{-2}$ , respectively.

### Conclusions

TFSA-based ionic liquids with piperidinium cations with various substitution groups were synthesized to study the effect of the position and number of oxygen atoms within the group on the solvation environment of Li-ions in the respective ionic-liquid electrolytes. Raman spectroscopic analysis revealed that the methoxyethoxymethyl group plays a key role to suppress the formation of  $[\text{Li}(\text{TFSA})_x]^{1-x}$  complexes. The solvation number ( $x$ ) of TFSA anions per Li-ion in PP1MEM-TFSA was 1.56, and the number was lower than any other electrolyte solutions.  $(\text{LiTFSA})_{0.2}(\text{PP1MEM-TFSA})_{0.8}$  displayed relatively high rate performance due to good Li-ion diffusion properties originating from its low viscosity and small solvation numbers.

### Acknowledgments

This work has been supported by Japan Society for the Promotion of Science (JSPS) for research fellowship (2611485) and a Grant-in-Aid for Scientific Research (B) (24350094) from Scientific Research of Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan. M. Shimizu gratefully acknowledge T. Elliot for her heartfelt advice.

### References

- K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko, and M. Watanabe, *J. Am. Chem. Soc.*, **133**, 13121 (2011).
- M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, and M. Kono, *J. Power Sources*, **162**, 658 (2006).
- A. Basile, A. I. Bhatt, and A. P. O'Mullane, *Nat. Commun.*, 711794 (2016).
- H. Sano, H. Sakaebe, H. Senoh, and H. Matsumoto, *J. Electrochem. Soc.*, **161**, A1236 (2014).
- T. Hosokawa, K. Matsumoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, and K. Nitta, *J. Phys. Chem. C*, **120**, 9628 (2016).
- J. Koster, M. Schonhoff, and N. A. Stolwijk, *J. Phys. Chem. B*, **117**, 2527 (2013).
- G. A. Giffin, A. Moretti, S. Jeong, and S. Passerini, *J. Phys. Chem. C*, **118**, 9966 (2014).
- T. Watkins, A. Kumar, and D. A. Buttry, *J. Am. Chem. Soc.*, **138**, 641 (2016).
- Y. Fang, K. Yoshii, X. Jiang, X.-G. Sun, T. Tsuda, N. Mehio, and S. Dai, *Electrochim. Acta*, **160**, 82 (2015).
- G. A. Elia et al., *Nano Lett.*, **14**, 6572 (2014).
- M. P. Mousavi, B. E. Wilson, S. Kashefolgheta, E. L. Anderson, S. He, P. Buhlmann, and A. Stein, *ACS Appl. Mater. Interfaces*, **8**, 3396 (2016).
- J.-W. Song, C. C. Nguyen, and S.-W. Song, *RSC Adv.*, **2**, 2003 (2012).
- K. Tsunashima, A. Kawabata, M. Matsumiya, S. Kodama, R. Enomoto, M. Sugiya, and Y. Kunugi, *Electrochem. Commun.*, **13**, 178 (2011).
- N. Yabuuchi, K. Shimomura, Y. Shimbe, T. Ozeki, J.-Y. Son, H. Oji, Y. Katayama, T. Miura, and S. Komaba, *Adv. Energy Mater.*, **1**, 759 (2011).
- H. Sakaebe and H. Matsumoto, *Electrochem. Commun.*, **5**, 594 (2003).
- H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, and M. Kono, *J. Power Sources*, **160**, 1308 (2006).
- V. Baranchugov, E. Markevich, E. Pollak, G. Salitra, and D. Aurbach, *Electrochem. Commun.*, **9**, 796 (2007).
- D. Molina Piper et al., *Nat. Commun.*, **6**, 6230 (2015).
- H. Usui, M. Shimizu, and H. Sakaguchi, *J. Power Sources*, **235**, 29 (2013).
- M. Shimizu, H. Usui, K. Matsumoto, T. Nokami, T. Itoh, and H. Sakaguchi, *J. Electrochem. Soc.*, **161**, A1765 (2014).
- M. Shimizu, H. Usui, T. Suzumura, and H. Sakaguchi, *J. Phys. Chem. C*, **119**, 2975 (2015).
- L. Chancelier, A. Benayad, T. Gutel, S. Mailley, and C. C. Santini, *J. Electrochem. Soc.*, **162**, A1008 (2015).
- M. Kunze, E. Paillard, S. Jeong, G. B. Appetecchi, M. Schönhoff, M. Winter, and S. Passerini, *J. Phys. Chem. C*, **115**, 19431 (2011).
- M. Shimizu, H. Usui, and H. Sakaguchi, *Phys. Chem. Chem. Phys.*, **18**, 5139 (2016).
- Y. Umebayashi, S. Mori, K. Fujii, S. Tsuzuki, S. Seki, K. Hayamizu, and S. Ishiguro, *J. Phys. Chem. B*, **114**, 6513 (2010).
- S. Tsuzuki, K. Hayamizu, S. Seki, Y. Ohno, Y. Kobayashi, and H. Miyashiro, *J. Phys. Chem. B*, **112**, 9914 (2008).
- Y. Umebayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanzaki, M. Takeuchi, and S. Ishiguro, *J. Phys. Chem. B*, **111**, 3028 (2007).
- T. Kuriasaki, D. Tanaka, Y. Inoue, H. Wakita, B. Minofar, S. Fukuda, S. Ishiguro, and Y. Umebayashi, *J. Phys. Chem. B*, **116**, 10870 (2012).
- S. Duluard, J. Grondin, J.-L. Bruneel, I. Pianet, A. Grélard, G. Campet, M.-H. Delville, and J.-C. Lassègues, *J. Raman Spectrosc.*, **39**, 627 (2008).
- S. Menne, T. Vogl, and A. Balducci, *Phys. Chem. Chem. Phys.*, **16**, 5485 (2014).
- M. Shimizu, H. Usui, K. Yamane, T. Sakata, T. Nokami, T. Itoh, and H. Sakaguchi, *Int. J. Electrochem. Sci.*, **10**, 10132 (2015).