

## Effect of Li<sup>+</sup> solvation structure in phosphonium ionic liquids on charge-discharge characteristics of LIBs

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### Abstract

Phosphonium ionic liquids (P-ILs), which contain both a phosphonium group (P<sup>+</sup>) and ether group (R-O-R'), are promising materials for electrochemical applications because they have a lower viscosity than the phosphonium compound of the similar structure consisting only of alkyl chains. For the graphite negative electrode, the solvation and desolvation process at the SEI|electrolyte interface may also have an impact on it. In this study, the discharge rate characteristics of graphite/Li cells were evaluated, and high performance was confirmed in ILs with high ionic conductivity. Furthermore, the solvation structures were also investigated by Raman spectroscopy, which confirmed that the solvation number of FSA<sup>-</sup> to Li<sup>+</sup> decreases with the introduction of ether groups. This may affect the solvation/desolvation processes at the SEI.

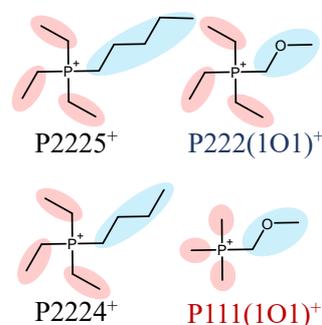


Fig.1 Structural illustration of cations of ILs investigated in this work.

### 1. Introduction

ILs have unique properties such as flame resistance and low volatility. P-ILs, particularly those with ether groups, are well-suited for applications in electrochemical devices due to their higher ionic conductivity compared with conventional ILs.<sup>1)</sup> Thus, we focused on P-ILs as electrolytes for LIBs.

Previously, we have evaluated the discharge rate characteristics of LCO/Li cells and reported that ionic conductivity in ILs significantly affects discharge rate performance.<sup>1)</sup> For the graphite negative electrode, however, the desolvation process at the SEI|electrolyte interface may also play a role. In this study, we evaluated the discharge rate characteristics of graphite/Li cells and analyzed the solvation structure of Li<sup>+</sup> in the electrolyte, which is believed to significantly influence the desolvation process.

Table I Self-diffusion coefficients (*D*), ionic transference numbers (*t*) (25 °C) and ionic conductivities (*σ*) (27 °C) of C<sub>Li</sub><sup>+</sup> = 1 M ILs.

ILs	<i>D</i> / × 10 <sup>-11</sup> m <sup>2</sup> s <sup>-1</sup>			<i>t</i> / × 10 <sup>-2</sup>			<i>σ</i> / mS cm <sup>-1</sup>
	Li <sup>+</sup>	Cation	Anion	Li <sup>+</sup>	Cation	Anion	
P2225-FSA	0.87	0.89	1.06	10.3	35.3	54.4	2.40
P2224-FSA	1.01	1.03	1.34	9.42	34.0	56.6	2.32
P222(1O1)-FSA	2.07	2.21	2.64	8.87	36.3	54.8	4.75
P111(1O1)-FSA	2.61	2.13	3.36	7.27	40.2	52.5	5.72

## 2. Experiment

Lithium salt (LiFSA) added in Bis(fluorosulfonyl)amide (FSA)-based P-ILs, such as P2225-FSA, P2224-FSA, P222(1O1)-FSA and P111(1O1)-FSA. The cell was assembled using Li metal and graphite as the positive and negative electrodes, respectively, with a separator in between. For the discharge rate test, charging was performed under CCCV conditions and fixed at 0.2 C. Raman spectra of the ILs were measured by micro-Raman spectroscopy with a continuous-wave green laser.

## 3. Results and discussion

Fig. 2 shows the results of the discharge rate test with LiFSA dissolved P2225-FSA(Li<sup>+</sup>:P2225<sup>+</sup>=2:8), P222(1O1)-FSA(C<sub>Li<sup>+</sup></sub> = 1 M) and P111(1O1)-FSA(C<sub>Li<sup>+</sup></sub> = 1 M) as electrolytes. The discharge capacity in P222(1O1)-FSA electrolyte which includes an ether structure, was superior to that in P2225-FSA electrolyte under the high-rate condition above 2 C. Furthermore, P111(1O1)-FSA composed of even smaller cation exhibited excellent discharge rate characteristics, maintaining capacity even at 7 C. These results suggest that ionic conductivities( $\sigma$ ) and self-diffusion coefficients( $D$ ) (Table I) are primary influencing factors, similar to the discharge rate characteristics obtained for LCO/Li cells, as previously reported.

Raman spectroscopy was used to evaluate the interaction between Li<sup>+</sup> and FSA<sup>-</sup>, allowing the estimation of the solvation number of FSA with respect to Li<sup>+</sup> by measuring at different concentrations.<sup>2)</sup> The solvation structure in ILs may influence the charge-discharge rate characteristics, particularly the solvation/desolvation process at the SEI. The results are summarized in Table II. These results indicate that the solvation number tends to decrease when ether is introduced.

## 4. Conclusions

The excellent rate capability observed in the P111(1O1) ionic liquid electrolyte is primarily attributed to ion conduction. The introduction of an ether group reduces the viscosity of the ionic liquid itself, enhancing its ionic conductivity. Although the solvation number of Li<sup>+</sup> has decreased, the improved ionic conductivity effect of the phosphonium cation is substantial. Consequently, the diffusion coefficient of Li<sup>+</sup> is also believed to increase relatively.

## Acknowledgments

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## References

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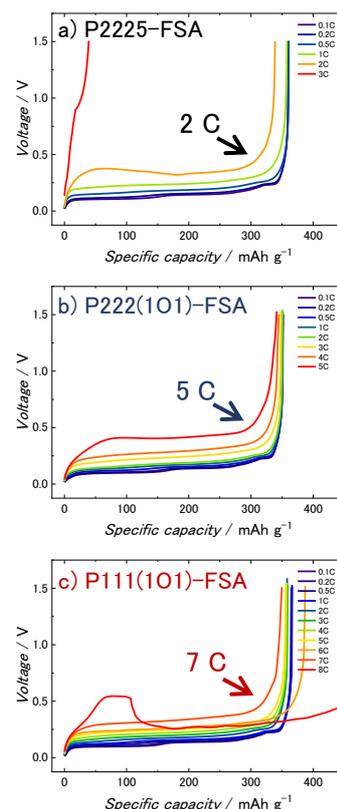


Fig.2 Discharge curves of LiFSA dissolved a)P2225-FSA (Li<sup>+</sup>:P2225<sup>+</sup>=2:8), b)P222(1O1)-FSA(1 M) and c)P111(1O1)-FSA(1 M) at each rate.

Table II Solvation number of FSA<sup>-</sup> to Li<sup>+</sup> in each ILs.

ILs	Solvation Number
	<i>n</i>
P2224-FSA	3.0
P222(1O1)-FSA	2.6
P111(1O1)-FSA	2.7