# Functionalized tetraalkylammonium ionic liquid electrolytes for use in lithium batteries

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# Introduction

A series of ionic liquids containing tetraalkyl ammonium cations exhibit higher cathodic stability than those containing imidazolium cations. These levels, however, are not yet sufficient for the liquids' use as lithium battery electrolytes[1-3]. The authors introduce several functional groups, such as cyano CN- and acetyl CH<sub>3</sub>CO-, on tetraalkyl ammonium cation-based ionic liquid in order to improve the interfacial stability toward lithium.

## **Experimental**

The structural formulae of onium cation synthesized here are shown in Figure 1. We first synthesized the iodides of these cations, and then exchanged their anions under an aqueous condition with LiTFSI (Fluka). After separation from the water phase, washing, and drying, ionic liquids were obtained[1,3,4]. The products were identified by means of <sup>1</sup>H-NMR measurement[1]. The ionic conductivities of ionic liquids were measured using the AC impedance method.

The ionic liquids prepared here could not contain a large amount of lithium salt, their saturated contents being 0.5 M. Thus we dissolved about 0.2 M of LiTFSI into PTMA-TFSI and CTMA-TFSI. Electrochemical deposition – dissolution tests were performed using a 2-electrode cell consisting of an SS electrode as the working electrode, and lithium metal electrodes as counter and reference electrodes. All of these electrochemical measurements were done at room temperature.

#### **Results and Discussion**

The room-temperature conductivities of the ionic liquids prepared in the present study are summarized in Table 1. It should be noted that the conductivity value of CTMA-TFSI showed some extent of deviation because this salt exhibits an overcooling status at room temperature. ATMA-TFSI exhibited a rather high conductivity among this kind of ionic liquids. The conductivities of CTMA-TFSI and PTMA-TFSI after the addition of LiTFSI are also included in Table 1. CTMA-TFSI showed similar conductivity even after adding LiTFSI salt, while PTMA-TFSI showed drastic decrease conductivities by the addition of lithium salt.

Figure 2 illustrates the electrochemical lithium deposition-dissolution behaviors in LiTFSI / CTMA-TFSI solutions. As shown clearly by these voltammograms, lithium can be deposited and dissolved stably in LiTFSI-CTMA-TFSI, while no peaks indicating such reactions appeared in LiTFSI-PTMA-TFSI. The cathodic stabilities of these ionic liquids themselves did not differ; therefore, it is expected that an effective surface film may be formed on lithium metal in CTMA-TFSI electrolyte. From this result we expect that CTMA-TFSI is available for electrolyte solvent, or at least additive to another ionic liquid, for advanced lithium batteries.

# References

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$$\begin{array}{c} CH_{3} & CH_{3} & CH_{3} \\ CH_{3} - CH_{2} - CH_{2} - \underbrace{\overset{N}{\overset{+}{N}} CH_{3}}_{CH_{3}} & CN - CH_{2} - \underbrace{\overset{N}{\overset{+}{N}} CH_{3}}_{CH_{3}} \\ PTMA & CTMA & CTMA \\ CH_{3} - C - CH_{2} - \underbrace{\overset{N}{\overset{+}{N}} CH_{3}}_{O & CH_{3}} \\ CH_{3} - C - CH_{2} - \underbrace{\overset{N}{\overset{+}{N}} CH_{3}}_{O & CH_{3}} \\ H_{3} & CH_{3} \\ CH_{3} - C - CH_{2} - \underbrace{\overset{N}{\overset{+}{N}} CH_{3}}_{O & CH_{3}} \\ H_{3} & CH_{3} \\ CH_{3} - C - CH_{3} \\ H_{3} \\ CH_{3} \\ CH_{$$

Fig 1. Onium cations prepared in this study.

# Table 1. Conductivities of ionic liquids

	Pristine / mS cm <sup>-1</sup>	w/ LiTFSI / mS cm <sup>-1</sup>
PTMA-TFSI	3.8	2.1
CTMA-TFSI	0.5-0.7	0.53
CTMA-TFSI	5.5	



