

**Electrochemical Properties of the Interfaces
between Water and Room-Temperature Molten Salts
Composed of Surface-Active
Quaternary Ammonium Cations**

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The hydrophobic room-temperature molten salts (RTMSs) are immiscible with water (W). The RTMS|W two-phase system has attracted many researcher's attention for the applications to solvent extraction or ion selective electrodes. In the two-phase system, partition of ions strongly depends on the phase-boundary potential across the RTMS|W interfaces. Therefore, the electrochemistry of the RTMS|W interfaces is indispensable to control the ion partition. We reported some electrochemical properties of the RTMS|W interfaces based on imidazolium RTMSs[1], and symmetrical quaternary ammonium RTMSs[2]. In this study, we studied the electrochemical properties of the interfaces between water and new RTMSs composed of surface-active cations.

The RTMSs used are composed of alkyl-dimethylbenzylammonium cations (C_nBDA^+ ; $n=12,14,16$) and the bis(pentafluoroethylsulfonylethyl)imide anion ($C_2C_2N^-$). Cyclic voltammograms (CVs) were recorded for the ion transfer across the RTMS|W interfaces formed at the end of the micropipette tip with the inner diameter of several micrometers. Electrochemical cell is represented:

Ag/AgCl	100 mM		100 mM	Ag/AgCl
	LiCl		LiCl	
	100 mM			
	LiC_2C_2N		Micropipette	
	(W_{ref})	(RTMS)	(W)	

The potential applied to the Ag/AgCl electrode on the right-hand side with respect to the left is denoted as E . The current corresponding to the flow of a positive charge from W to RTMS is taken to be positive.

In Fig. 1, CVs show the potential window where only charging current can be observed. At more positive (negative) potential over the potential window the current sharply rises, indicating that anions (cations) transfer across the RTMS|W interface from RTMS to water at the potential.

The potential window of the RTMS|W interfaces may be determined by the difference between the standard ion-transfer potential of anion at the positive end of the potential window and that of cation at the negative end[2].

Fig. 1(a) shows the dependence of the potential window on the chain-length of cations. As the increase in the chain-length of cation, the potential window is extended only to the direction of negative potential while the positive end of the window remains unchanged. The temperature-dependence of the potential window is shown Fig. 1(b). Both cation and anion become less hydrophobic at higher temperature.

The differential capacitance of the RTMS|water interface can be estimated from the current at the potential within the potential window. The estimated differential capacitance was $5 \times 10^3 \mu F/cm^2$, which is 100-times greater than the value in the case of the electrochemical oil|water interface. The capacitance also depends both on the chain-length and on temperature; the shorter the chain-length and the higher temperature, the greater the

capacitance.

We will present quantitative analysis of the electrochemical properties in conjunction with a digital simulation to clarify the polarization characteristics of the RTMS|W interfaces.

References

- [1] T. Kakiuchi, N. Tsujioka, S. Kurita, and Y. Iwami, *Electrochem. Commun.*, **5**, 159 (2003).
[2] T. Kakiuchi, and N. Tsujioka, *Electrochem. Commun.*, **5**, 253 (2003).

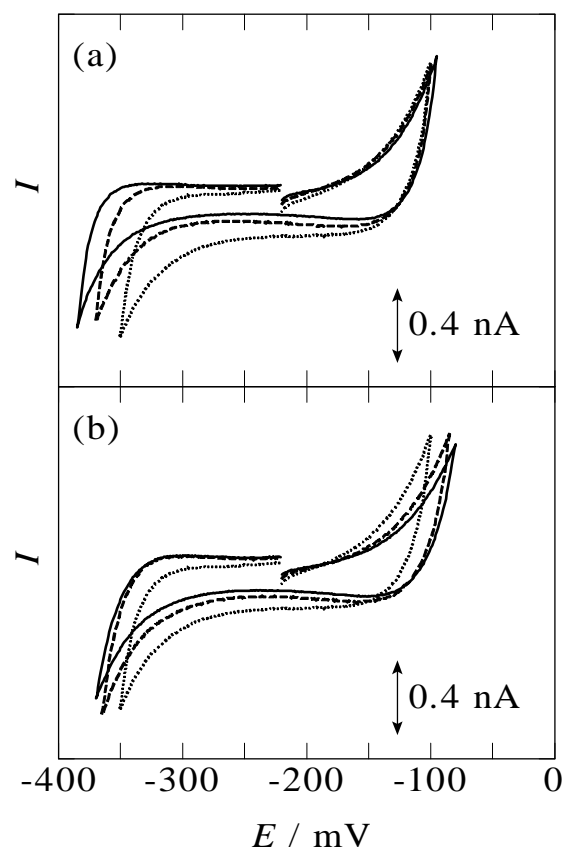


Fig. 1. Cyclic voltammograms for the ion transfer across the $C_nBDAC_2C_2N|W$ interfaces (a) for $n = 16$ (solid), 14 (dashed), and 12 (dotted) at $40^\circ C$, and (b) for $n = 12$ at 25 (solid), 30 (dashed), and $40^\circ C$ (dotted). The inner diameter of the pipette is $5 \mu m$. Scan rate is $100 mV/s$.