

## Electrochemical intercalation/deintercalation of cations into/from graphite electrode in ionic liquid

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### Introduction

Recently, ionic liquids have attracted much attention as higher safety liquid electrolyte solution replacing organic solvent for energy conversion devices because of non-volatile, incombustibility and high ionic conductivity. Among the ionic liquids, 1-ethyl-3-methylimidazolium (EMI<sup>+</sup>)-based ionic liquids have lower viscosity, and N,N-diethyl-N-methyl-N-2-methoxyethylammonium (DEME<sup>+</sup>)-based ionic liquids have wider potential window, so the ionic liquids are very attractive for electrochemical scientists. As an energy conversion device using ionic liquid as active material, Dual Intercalating Molten Electrolyte Battery has been proposed [1]. However, electrochemical intercalation/deintercalation of cations composing ionic liquid into/from graphite electrode has not been clarified in detail. Therefore, we focused on the behavior of cation intercalation at graphite electrode in ionic liquid. Here we report the electrochemical intercalation behavior of cation at graphite electrodes in ionic liquids.

### Experimental

Three-electrode cell was used for electrochemical measurements. Highly oriented pyrolytic graphite (HOPG) was used as a working electrode and graphite composite electrode or platinum mesh was used as a counter electrode. Using vycor® glass electrode, silver electrode in each internal liquid was used as a quasi-reference electrode. Internal liquids were silver trifluoromethanesulfonate in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMITFSA), and in DEMETFSA. As electrolyte solutions, EMITFSA and DEMETFSA were used. Cyclic voltammetry was carried out between -0.5 V and -2.75 V or -3.2 V (vs. Ag<sup>+</sup>/Ag) at a scan rate of 1.0 mV s<sup>-1</sup>. HOPG held at constant potential was investigated by Raman spectroscopy and X-ray diffraction (XRD) measurement. Electrochemical impedance spectroscopy was carried out over a frequency region of 100 kHz – 100 mHz with applied voltage amplitude of 10 mV. All cell assembly and electrochemical measurements were conducted in Ar-filled glove box.

### Results and discussion

Fig. 1 shows cyclic voltammograms (CV) measured in EMITFSA and in DEMETFSA. In the CVs, reduction current and oxidation current were observed below -2.5 V. These redox peaks would be attributed to the intercalation/deintercalation of EMI<sup>+</sup> or DEME<sup>+</sup> into/from graphite electrode. From Raman spectra and XRD patterns of HOPG held at constant potential, intercalation of EMI<sup>+</sup> or DEME<sup>+</sup> into graphite electrode and formation of graphite intercalation compound (GIC) was revealed. About HOPG held at constant potential in DEMETFSA, stage 5 at -2.7 V, stage 4 at -2.73 V, stage 3 at -2.8 V

and stage 2 at -2.9 V GIC were formed assuming that the interlayer distance of graphite layer DEME<sup>+</sup> intercalated was 0.81 – 0.82 nm and interlayer distance of graphite was 0.335 nm. From electrochemical impedance spectroscopy, only one semi-circle appeared below -2.6 V in EMITFSA and -2.7 V in DEMETFSA. The diameter of the semi-circle was highly dependent on the electrode potentials. Hence, the semi-circle can be attributed to the charge (EMI<sup>+</sup> or DEME<sup>+</sup>) transfer resistance at graphite electrode / electrolyte interface. Fig. 2 shows the Arrhenius plots of the interfacial conductivities at graphite electrode / electrolyte interface with the electrode potential held at -2.7 V. The activation energies were evaluated from the slop of the Arrhenius plots. When using EMITFSA, the activation energy was evaluated to be 55 kJ mol<sup>-1</sup>. On the other hand, when using DEMETFSA, the activation energy was evaluated 32 kJ mol<sup>-1</sup>, which was lower than that of EMITFSA. Based on these results, it was suggested that interaction between EMI<sup>+</sup> and TFSA<sup>-</sup> would be different from that between DEME<sup>+</sup> and TFSA<sup>-</sup>.

### Acknowledgement:

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### Reference

[1] R. T. Carlin, H. C. De Long, J. Fuller and P. C. Trulove, *J. Electrochem. Soc.*, **141** (1994) 7.

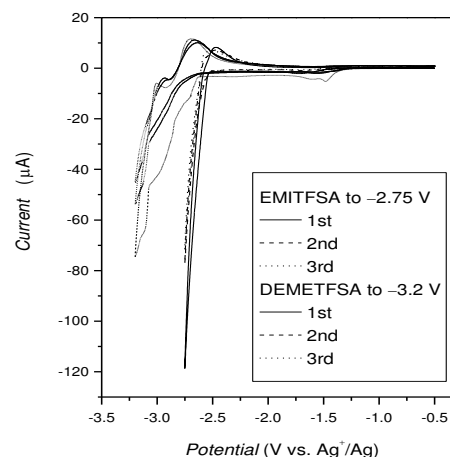


Fig. 1 Cyclic voltammograms of HOPG in EMITFSA and DEMETFSA. Sweep rate was 1.0 mV s<sup>-1</sup>.

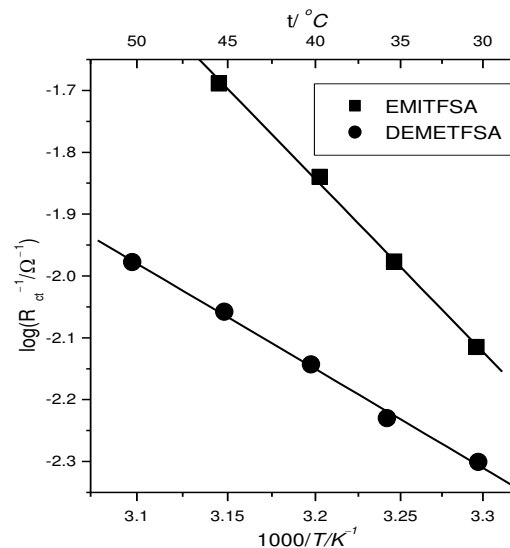


Fig. 2 Temperature dependence of the interfacial conductivities for graphite electrode / ionic liquid.