Electric Double-Layer Capacitor with Binary Salt Electrolyte

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INTRODUCTION

Electric double layer capacitors (EDLCs) as energy storage devices have deserved our attention; they can store substantial large energy in an electric double layer at an interface between an electrode and electrolyte. Since there is intrinsically no chemical reaction involved, EDLCs can discharge stored energy much faster and have much longer cycle life than conventional rechargeable batteries. To realize wide use of EDLCs in energy storage application, safety enhancement of EDLC systems is requisite especially to mobile energy systems such as an electric and fuel-cell vehicle.

In this context, room-temperature molten salts or ionic liquids have attracted a growing interest for application to electrochemical devices due to their nonflammabilty and negligible vapor pressure. Ue et al. reported EDLC performances with several ionic liquids [1]. EDLC performances using a binary salt electrolyte with an ionic liquid, however, have not been well understood while the binary salt electrolytes for rechargeable lithium battery systems have been reported [2]. This paper reports the effect of a binary salt electrolyte with an ionic liquid on the performance of EDLCs.

EXPERIMENTAL

We examined the performance of EDLC using three sorts of electrolytes: a conventional organic electrolyte (TEMABF$_4$/PC 3 moldm^{-3}(M)), ionic liquid (EMIBF$_4$) and binary salt electrolyte (EMIBF$_4$+LiBF$_4$) (TEMA=Triethylmethylammonium, EMI=1-ethyl-3-methylimidazolium). The composite salt electrolyte (EMIBF$_4$+ LiBF$_4$) was prepared by dissolving weighed LiBF$_4$ in liquid EMIBF$_4$, and then stirring at a room temperature for 6h. The concentration of the dissolved LiBF$_4$ was 0.5M in EMIBF$_4$. Electrochemical stability of these electrolytes was measured by running a liner sweep voltammetry in a three-electrode cell.

To examine the performance of the EDLCs, a typical model capacitor was used. It was composed of the pair of activated carbon cloth electrodes, an electrolyte and separator as main components. The charge-discharge characteristics of the model capacitors were measured under a constant current cycling condition.

RESULTS AND DISCUSSION

Figure 1 shows the linear sweep voltammograms for the electrolytes. The observed potential window of EMIBF$_4$ was narrower when compared to that of TEMABF$_4$/PC. Cathodic decomposition voltage of EMIBF$_4$+LIBF$_4$ was observed at about -4V vs. Ag/Ag$^+$, which was lower than that of EMIBF$_4$; Matsumoto et al. also reported the same results previously [2].

Since the overall potential window of EMIBF$_4$+LiBF$_4$ was wider than the others, we examined withstand voltages for the model capacitors with the respective electrolyte. Charge-discharge curves for the model capacitor with EMIBF$_4$+LiBF$_4$ were excellent even at a high-voltage operation. The approximate decomposition voltages were estimated to be 3.4, 3.2 and 3.6V for TEMABF$_4$/PC, EMIBF$_4$ and EMIBF$_4$+LiBF$_4$, respectively. These results could be consistent with the potential windows for these electrolytes.

Figure 2 shows cycling performance with various rates for the model capacitors. The TEMABF$_4$/PC system provided the best high-rate performance among the three electrolytes. EMIBF$_4$ is a high viscosity liquid and the interface resistance between the electrode and electrolyte is high. This should inevitably lead to the lower discharge capacitance under the high current density conditions. On the other hand, the addition of LiBF$_4$ to EMIBF$_4$ resulted in an increase of the discharge capacitance. This may imply that the addition of a suitable Li salt to an ionic liquid can enhance the EDLC capacitance.

REFERENCES
1. M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, J. Electrochem. Soc., 150, A499 (2003).
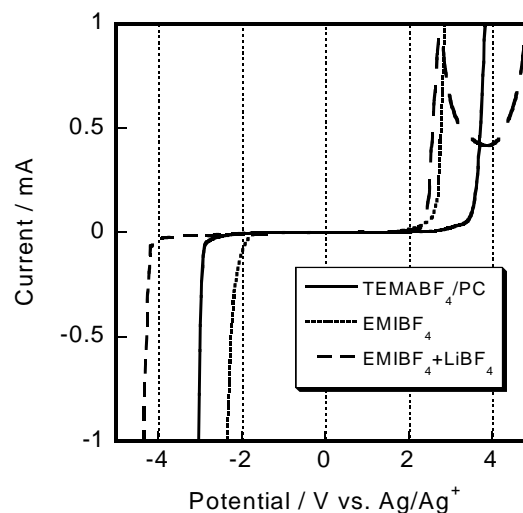2. H. Matsumoto, H. Kageyama, The Electrochemical Society of Japan, Meeting Abstract, p. 212 (2003).

Fig. 1 Linear sweep voltammograms for the electrolytes.
Scanning rate: 5mV s^{-1}
Working electrode: Pt wire
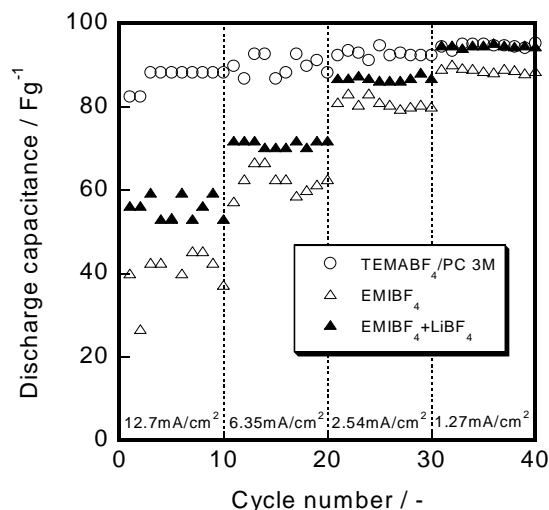Counter electrode: Pt prate
Reference electrode: Ag wire

Fig. 2 Rate performance for the model capacitors.
Operating voltage: 0-1V