

High energy density capacitor using solvent-free ionic liquids and their mixing effect with propylene carbonate (PC)

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Introduction

Ionic liquids are organic salts with melting points under 100 °C, often even lower than room temperature (room temperature molten salts, RTMSs). Recently they are employed more and more as substitute for the traditional organic solvents in chemical reactions. The most common RTMSs are imidazolium [1] and pyridinium [2] derivatives, while phosphonium [3] or tetralkylammonium [4] compounds can be also used for this purpose. Aprotic solvents, such as propylene carbonate (PC), have generally been applied as a solvent for an electrochemical capacitors due to higher decomposition voltage, that is, wider voltage window, than those of aqueous electrolytes. A wide voltage window, which in turn implies enhancing the energy density of single-cell capacitors while reducing the number of cells required in a series stack. In this respect, we have been adopted and investigated the room temperature molten salt (RTMS) as an electrolyte on electrochemical double layer capacitors (EDLCs). Recently, Nisshinbo industries, Inc. have been synthesized the novel ionic liquid with ammonium salt type cation, which can be considered as a promising candidate for an electrolyte of EDLCs. We demonstrate the molecular structure of RTMS supplied by Nisshinbo Industries, Inc. using NMR, IR, elemental analysis and the capacitance response when it is used in combination with the mesophase pitch based carbon fibers (MPCFs) activated using KOH as an electrode. Furthermore, mixing effect by RTMS (Ionic liquid B with the higher viscosity) in PC has been demonstrated using a fixed molar fraction of RTMS to PC.

Experimental

Two tetralkylammonium RTMSs (designated as B and T, which were supplied by Nisshinbo Industries, Inc.) with different anions are compared with each other about physicochemical, electrochemical properties. The typical electrolyte for an EDLC, 1M of tetraethylene tetrafluoroborate ($(C_2H_5)_4NBF_4$ (TEAN- BF_4) in propylene carbonate (PC), is used as a standard to compare each other. In order to identify the molecular structure of two ionic liquids, FT-NMR (JNM-GX400, JEOL, Japan), IR (Perkin Elmer, 1600-series FT-IR, 4 wave number resolution), elemental analysis have been applied. Furthermore,

the mixture of 1 molar fraction of Ionic liquids to PC solvent is investigated to due to the problematic high viscosity of ionic liquid B.

Mesophase (MPCF, graphitizable carbonaceous material) were chosen as host materials for the EDLC electrodes. After stabilization under an ambient atmosphere, carbonization was performed at 650°C. Subsequently, these carbon fibers were milled mechanically to select the mean length of about 25 μm. Then, the fibers were well mixed with potassium hydroxide (KOH) as an activator. The mixture was heated to 700°C at a fixed programming rate in a nitrogen flow, and held for 2 h. The samples obtained were washed with deionized distilled water to eliminate the excess KOH, and the washing process has repeated until it reached to pH 7. The mixing weight ratios of KOH to the host carbon material were varied from 1.5 to 4. A coin type electrode was made around 0.3mm in thickness by using 5 wt. % of poly-tetrafluoroethylene (PTFE) as a binder, and a glassy carbon plate was used as a current collector. The capacitor was constructed using a couple of electrodes face to face, with a separator (glass filter paper, Oribest Co. Ltd., Japan) inserted between these electrodes. 1M of ((C₂H₅)₄NBF₄) in (PC) is used as a counter part to two kinds of ionic liquids (B with high viscosity, T with low viscosity). Charging was performed at a constant current of 5mA/cm² and charge-discharge cycles were performed at various current densities. The capacitance was calculated from the corresponding voltage variation of the discharge at various discharge current densities in the 1~60mA/cm² range. For cyclic voltammograms (HZ-300, Hokuto Denko, Japan) was fixed at the scan rate of 1mVs⁻¹, and galvanostatic charge/discharge characteristics were performed in the voltage range from 0 - 4V and used to characterize the electrochemical behavior.

Results and Discussion

Figure 1 represent the molecular sizes of the ionic liquids (ILs) used in this study which were obtained from computer simulation. The force fields of the model for ion T and B were taken to be a Lennard-Jones potential integrated over the overall feature using van der Waals surface. The ionic radius of conventional electrolyte (C₂H₅)₄NBF₄/PC was adopted for comparison. The ionic radius of this conventional electrolyte system has been previously reported (cation; 7.4, anion; 4.3Å) [5]. On the calculation for ion radius of T and B ILs, the solvent effect is ignored, because the RTMSs consist of ions, which do not contain the solvent. The RTMS designated T have

Table 1. Fundamental properties of the ILs used in this study

Properties	B	T
Molecular weight	233.1	426.4
Specific gravity	1.17	1.42
Potential window (V vs. Ag/AgCl)	-3.0/+3.0	-3.0/+2.7
Viscosity (mPa, 20°C)	560	120
Melting point (°C)	9	-

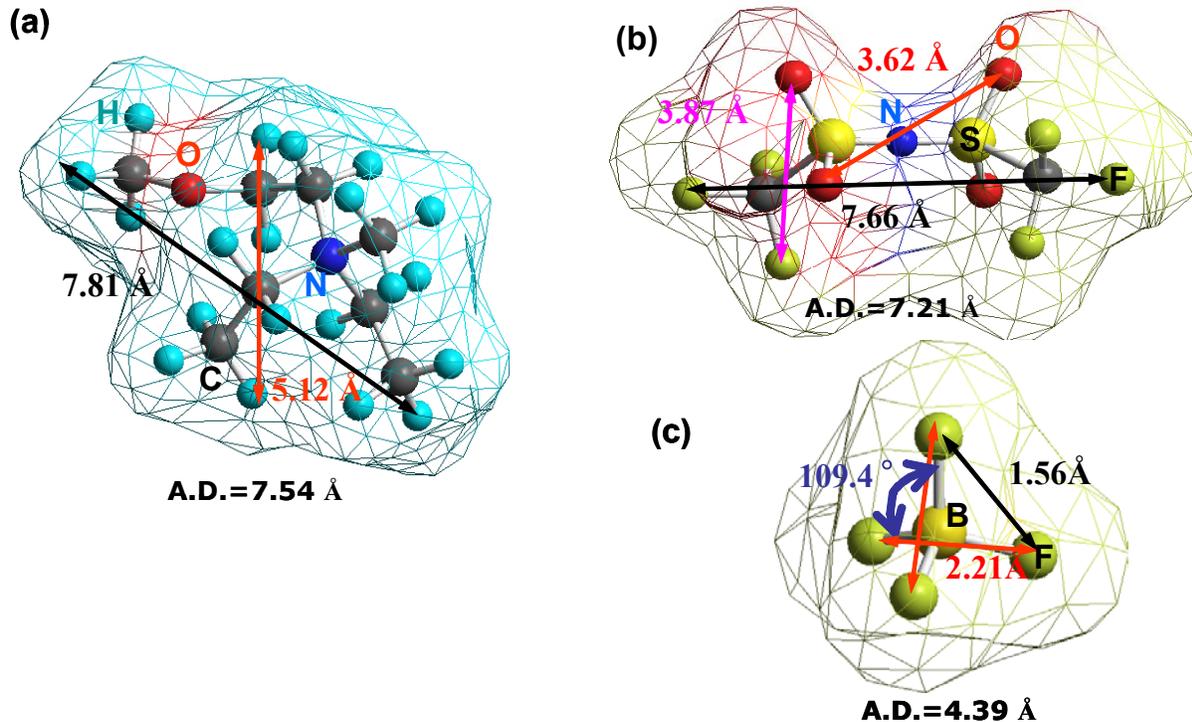


Fig. 1 Simulation results for possible sizes describing both the anion and cation of the ILs that control the kinetics of charge transfer in the relation with electrode's pore sizes

the cation with 8 carbon atoms (Fig. 1(a)) and the anion (Fig. 1(b), TFSI, bis(trifluoromethylsulfonyl)imide). The sample B have the composition of Fig. 1(a) and tetrafluoroborate, BF_4^- , Fig. 1(c). The average diameters obtained from the computer simulation are 7.54, 7.21 and 4.39Å, respectively. In table 1, fundamental properties for these two ILs were summarized.

Figure 2 represent the variations of the specific capacitance per (a) unit weight (F/g), (b) unit volume and (c) unit area using MPCF-based activated carbon as an electrode material that was activated using KOH addition. The details on a host material will be described in the presentation of the day. The charge cycles were carried out up to 3.5 V at a constant current of $5\text{mA}/\text{cm}^2$, and the discharge cycle was performed at $1\text{mA}/\text{cm}^2$. All samples showed an increase in the capacitance as the KOH fraction increased. At the sample with the low KOH addition below the 200 wt. %, conventional PC-based electrolyte has the best capacitance among them. However, as the KOH increased, their order was reversed at the 400 wt. % KOH addition. The increment of the capacitance uptake using IL-B and T is attributed to the correlation between the pore size and the ionic radius. That is, both ions of the ionic liquids are effectively contribute to uptake the capacitance. However, as for the IL-B, the small size of anion is unavailable to get a capacitance.

Figure 3 shows the effect by charging voltage to capacitance uptake using IL-B, IL-T and conventional tetraethyleneammonium tetrafluoroborate ($(\text{C}_2\text{H}_5)_4\text{NBF}_4$) in propylene carbonate (PC) with 1 molar fraction. Fig. 3(a) represents the variation of gravimetric (F/g) and (b) volumetric capacitance (F/cc). The overall tendency of capacitance uptake as a function of applied voltage is clearly indicated. The capacitance obtained by ionic

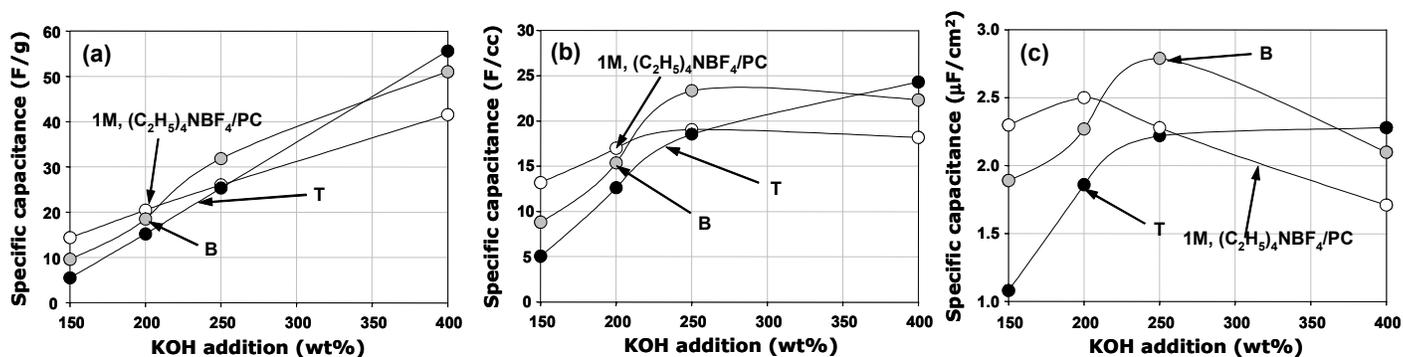


Fig. 2 Variations of the specific capacitance per (a) unit weight (F/g), (b) unit volume and (c) unit area using MPCF-based activated carbon as an electrode material which activated using KOH addition

liquids continuously increase as a function of applied voltage (although it is limited up to 3.5V). In contrast, conventional electrolyte system shows a decrement at the 3.5V charge, which is ascribed to the decomposition of the solvents. This implies that the ionic liquids are quite effective to obtain the high energy density in supercapacitor application.

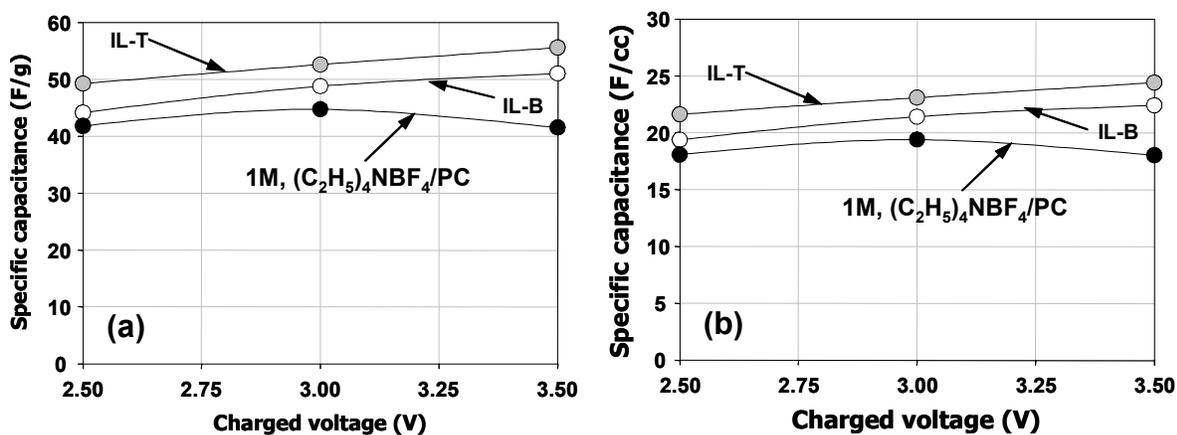


Fig. 3 Effect by charging voltage to capacitance uptake using IL-B, IL-T and conventional tetraethyleammonium tetrafluoroborate ((C₂H₅)₄NBF₄) in propylene carbonate (PC) with 1 molar fraction; (a) represents the variation of gravimetric (F/g) and (b) volumetric capacitance (F/cc)

Figure 4 represents the mixing effect by the IL-B to PC on the capacitance uptake. Each graph shows the variations of the specific capacitance per (a) unit weight (F/g), (b) unit volume and (c) unit area using MPCF-based activated carbon as an electrode material that was activated using KOH addition. The high viscosity of IL-B can be considered as the most problematic obstacle on application to supercapacitors. Its high viscosity prevents the ion alteration in dispersive regime. This would cause a fatal drawback in practical use, in other words, on high speed charge/discharge conditions. Therefore, it was required to mix the IL-B into PC, which can helpful to reduce the viscosity in itself. By mixing with PC (at 1 M fraction), the viscosity abruptly decrease to ca. 1%. This effect is reflected in the capacitance results (It will be demonstrated by our

presentation in 2004 Carbon). Furthermore, effectiveness of each ion can be described in Fig. 4(c). It was confirmed that the capacitance uptake at the current density of $1\text{mA}/\text{cm}^2$ was enhanced by the mixing of IL-B and PC. It is desirable to be applied to high performance capacitor on an application in restricted space.

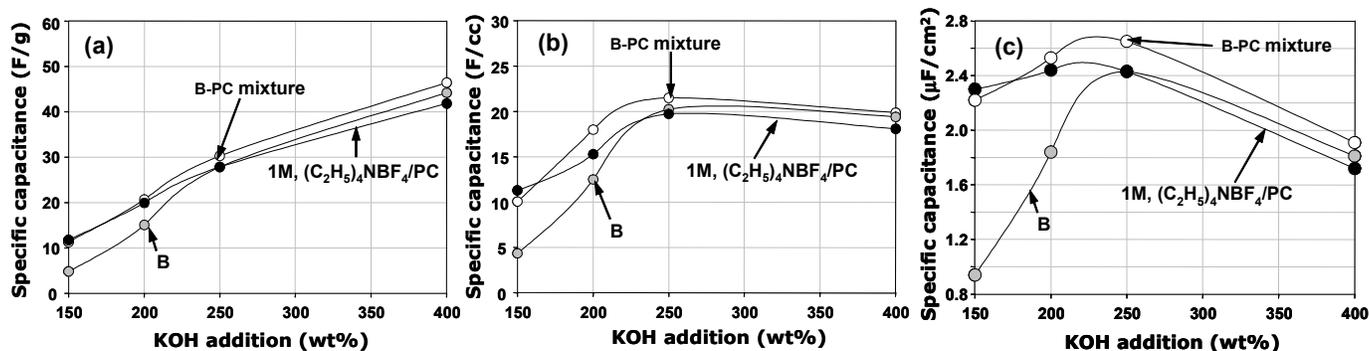


Fig. 4 The mixing effect by the IL-B to PC on the capacitance uptake. Each graph shows the variations of the specific capacitance per (a) unit weight (F/g), (b) unit volume and (c) unit area using MPCF-based activated carbon as an electrode material which activated using KOH addition, respectively.

Conclusions

The results demonstrated that the two kinds of ionic liquids with ammonium salt type is applicable to high performance EDLC as an alternative to conventional PC-based electrolyte. The ILs having diverse special properties are; good solvent for both organics and inorganics, liquid over a wide range of temperature, not volatile, highly thermally stable, non-flammable, less toxic than usual organic solvents etc. That is, IL is very friendly to environments. The appropriate modification of ILs and the choice of proper electrode material can give a potential to future energy device free from environmental problems.

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