



Supercapacitive Properties of Carbon Electrode in an Electrolyte Containing a Newly Synthesized Two-Cation Salt

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ABSTRACT :

To examine the effects of a two-cation ionic liquid as an electrolyte component of a supercapacitor, 1,4-bis(3-methylimidazolium-1-yl)butane tetrafluoroborate (MIBBF₄), dissolved in propylene carbonate (PC) or acetonitrile (ACN), is newly synthesized and tested here for potential use as an electrolyte of capacitor. The MIBBF₄ salt exhibits higher ionic conductivity in ACN than in PC. The supercapacitive properties of capacitors containing an activated carbon electrode and various electrolytes are evaluated using cyclic voltammetry and electrochemical impedance spectroscopy. The capacitor adopting the MIBBF₄/ACN electrolyte shows the largest specific capacitance at low scan rates, whereas the capacitor adopting the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄)/ACN electrolyte shows the largest specific capacitance at high scan rates.

Keywords: Supercapacitive property, Two-Cation salt, Activated carbon electrode, Cyclic voltammetry, Impedance spectroscopy

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1. Introduction

Recently, attempts have been made to improve energy storage capacity to support exploration in the field of material science. Electrochemical capacitors have been proven to have high power density and cycle stability, which are critical requirements for a good power source. Carbon showing high conductivity and good chemical stability is of great value for supercapacitor applications, particularly given its low cost and availability in high purity. Several studies have also been conducted for the improvement of supercapacitive properties by matching carbon electrodes with electrolytes having ionic liquid as a component.¹⁻⁵⁾ Ionic liquid is advantageous in preparing a dried electrolyte

system suitable for electrochemical applications without moisture for long periods of operation.⁶⁾ It is generally accepted that at least one ion has a delocalized charge with one organic component to maintain its liquid form. In addition, the electrolytic activity in the ionic liquid strongly depends on the substituent of the organic component and the counterion.^{5,7)} The most popular ionic liquids are based on the couples of 1-ethyl-3-methylimidazolium cation (EMI⁺), which has a cathodic stability of -1.8 V vs. NHE, with several anions such as BF₄⁻, PF₆⁻, CF₃SO₃⁻, and so on. The effect of the amount of cation-anion couples in the ionic liquid may be considered as a next step of research.

In this study, 1,4-bis(3-methylimidazolium-1-yl)butane tetrafluoroborate (MIBBF₄) is newly synthesized as a two-cation electrolyte component of a supercapacitor. MIBBF₄ salt is used in the dissolved state of the solvent,

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such as acetonitrile (ACN) and propylene carbonate (PC). 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) dissolved in the same solvents is also used for comparison. Thus, the four electrolyte systems of MIBBF₄/PC, MIBBF₄/ACN, EMIBF₄/PC, and EMIBF₄/CAN are characterized here for supercapacitor applications.

2. Experimental

1-Methylimidazole (Aldrich) was mixed with 1,4-dichlorobutane (Aldrich) in 30 ml of ACN and the mixture was refluxed for 48 h at 80°C. Then, the solvent ACN and residue were removed using a vacuum evaporator at 70°C. The sample synthesized was then collected and its structure was elucidated using ¹H-NMR spectroscopy (Varian Gemini 200 NMR). The structure of the sample was identified as 1,4-bis(3-methylimidazolium-1-yl)butane chloride. The collected compound was then dissolved in 30 ml of acetone, and then NaBF₄ was also added for metathesizing. After stirring at room temperature for 24 h, a white precipitate was formed which was collected by filtration, washed with water and dried in a vacuum oven at 70°C for 24 h. Subsequently, the sample was purified using Al₂O₃ in ACN to remove inorganic ion residues such as Na⁺ and Cl⁻. The metathesized sample was finally collected and the structure was again elucidated using ¹H-NMR spectroscopy. The structure of the metathesized sample was identified as a two-cation salt, MIBBF₄. The synthesized salt was dissolved separately in PC and ACN such that 0.5 mol dm⁻³ concentrations of electrolytes were formulated. The same is true with the EMIBF₄ (Aldrich) being dissolved separately with the two solvents. The ionic conductivities of the four electrolytes were then measured using electrochemical impedance spectroscopy. The concentration of salt in each electrolyte was 0.5 mol dm⁻³.

A 1 × 1 cm² sheet electrode of activated carbon powder was attached as an anode to a 5 × 10 cm² aluminum pouch. A separator (Rayon) wet with the electrolyte was placed adjacent to the anode, which was then sandwiched with another activated carbon powder sheet acting as a cathode to make a supercapacitor cell. The resulting cell containing anode/separator/cathode/separator in the electrolyte was pressed using a vacuum sealer.

To examine the redox behavior of the fabricated supercapacitor, cyclic voltammetry was carried out using an Autolab instrument (Eco Chemie, PGstat 100) at different scan rates of 20-400 mV s⁻¹ within a potential range of 0-2.75 V (vs. Ag/AgCl). A three-electrode cell

was used with Ag/AgCl (saturated KCl, 0.222 V vs. SHE) as a reference electrode, platinum as a counter electrode and the activated carbon electrode as a working electrode. Impedance measurement was also conducted in a three-electrode cell using an Autolab instrument (Eco Chemie, PGstat 100) within the frequency range of 10⁻²-10⁵ Hz at an applied potential of 1.4 V.

3. Results and Discussion

Fig. 1(a) shows the chemical structure of the synthesized two-cation salt MIBBF₄ with a molecular weight of 393.92 g mol⁻¹. The MIBBF₄ salt bears two cations and the EMIBF₄ has one, where the molecular anion is BF₄⁻. EMIBF₄ is a common ionic liquid used in several studies either in its neat form or in combination with other ionic liquids or organic solvents,⁸⁻¹² and it shows a good influence on the capacitive performances of conductive materials.^{3,13-16} With regards to its good qualities as an electrolyte, the ionic conductivity and the effect on specific capacitance of EMIBF₄ are compared with the MIBBF₄ dissolved in PC and CAN solvents. Ionic conductivities of the four electrolyte systems, which are evaluated from their impedance spectra, are summarized in Fig. 2. It can

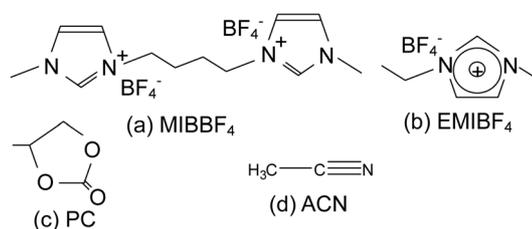


Fig. 1. Chemical structures of (a) MIBBF₄, (b) EMIBF₄, (c) PC, and (d) ACN.

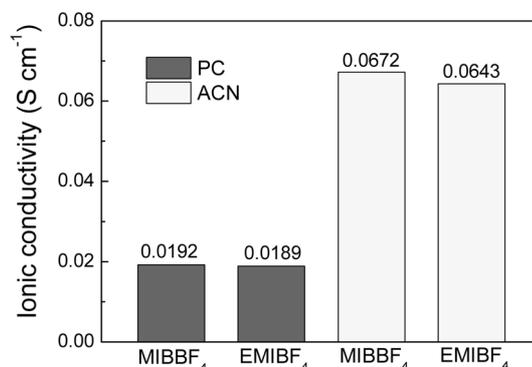


Fig. 2. Room temperature ionic conductivities of MIBBF₄ and EMIBF₄ for different solvents of PC and ACN.

be seen that the ionic conductivity is almost the same, regardless of the kind of salt, when fixing the solvent. Also, the ionic conductivity of the electrolyte adopting ACN solvent is higher than that of the electrolyte adopting PC solvent.

Raman spectroscopy study of ACN by Garcia *et al.*¹⁷⁾ indicates that the effect of changing the anion is more important than that of the EMI^+ cation, suggesting strong sensitivity on the Lewis acidity of cations. However, a polarity study of ionic liquid¹⁸⁾ indicates that the most important effect arises from the hydrogen bond basicity given by the anion. Based on Fig. 2, there is almost no significant difference between the ionic conductivities of MIBBF₄ and EMIBF₄ dissolved in the same solvent. With similar anions in both salts and with the difference in their cationic species, the ionic conductivity results agree with the previous reports.^{17,18)} The obvious difference is that the ionic conductivities of both salts are far higher in ACN than in PC.

The judicious choice of a solvent is a fundamental step in synthesis, because the outcome of a chemical process might be heavily dependent on the characteristic features of the reaction medium. PC and ACN are both polar aprotic solvents, with dielectric constants of approximately 65 and 37.5, respectively. The dielectric constant of a liquid is a simple single physical constant which helps to discern the ability of a solvent to favor ionic or polar species appearing along the chemical reaction. The more important parameters in different ionic liquids are the ones related to dipolar and H-bond basicity. Neat PC shows a negligible H-bond donating acidity, whereas the H-bond accepting basicity and dipolarity/polarizability are significant.^{19,20)} However, PC can also act as Lewis acid/base with an ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF₆), which demonstrates higher ionic conductivity for a 2 : 8 mol% mixture of BMIPF₆ and PC.²¹⁾ The higher dielectric constant of PC may be a cause for its poor H-bond donating acidity, and the same can be true in the PC mixed with BMIPF₆. Although the dielectric constant of PC is much higher than that of ACN, a molecular dynamic simulation shows the advantage of possessing an amphiphilic nature allowing itself distributed within the bulk of the ionic liquid because CH₃CN molecules can be found either close to the imidazolium ring and anion or close to the long alkyl chain.²²⁾ In addition, the H-bond basicity/acidity of ACN is also significant in the ion migration within solvent molecules.

An ideal cyclic voltammogram of a double-layer capacitor is rectangular in shape. As shown in Figs. 3 and 4, the

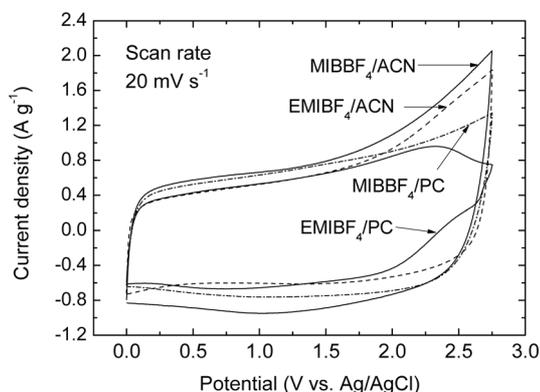


Fig. 3. Cyclic voltammograms of carbon electrode at 20 mV s^{-1} in different electrolytes.

carbon electrode exhibits typical double-layer capacitive behavior. However, there are only slight slants on the shapes for all carbon electrodes containing their respective mixed salt electrolytes. As shown in Fig. 3, with images obtained at the scan rate of 20 mV s^{-1} , the carbon electrode demonstrates a shape nearer to a rectangular shape in the low potential range. This implies that the ions are effectively adsorbed or desorbed in accordance with the applied potential within the electric double layer at the electrode surface by the electrostatic force. As shown in Fig. 4, the cathodic and anodic charging currents also increase with increasing scan rates, implying the dependence of capacitance on the scan rate and a pure capacitive behavior. The slight slants are due to the Faradaic current that is brought about by the presence of either carbonyl or quinine functional groups which cause oxidation and reduction reactions.

Specific capacitance values calculated from cyclic voltammograms are shown in Fig. 5. The highest value of capacitance (49.30 F g^{-1}) can be obtained by the electrode with MIBBF₄/ACN electrolyte at 20 mV s^{-1} . This is still a concern with the capacitance dependence of electroactive material on the dielectric media and also with the better solvation property of ACN compared to PC, which is discussed above. As the scan rate increases, the capacitance decreases for all test electrodes, due to the inner active sites that cannot sustain redox transitions completely at higher scan rates. It can be suggested that the specific capacitance obtained at the slow scan rate is the closest to the full utilization of the electrode material.

As shown in Fig. 6(a), all the electrolytes demonstrate similar characteristics, i.e., a line with a slight deviation to a straight vertical line. The invisibility of any semicircles

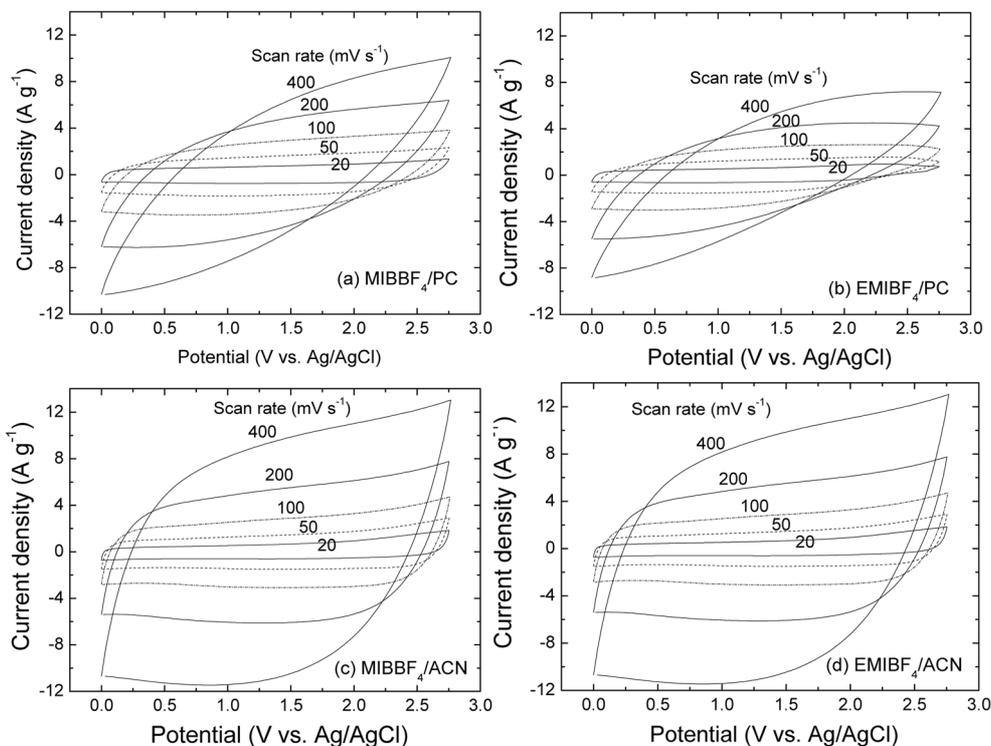


Fig. 4. Cyclic voltammograms of carbon electrode at different scan rates of 20-400 mV s⁻¹ with different electrolytes of (a) MIBBF₄/PC, (b) EMIBF₄/PC, (c) MIBBF₄/ACN, and (d) EMIBF₄/ACN.

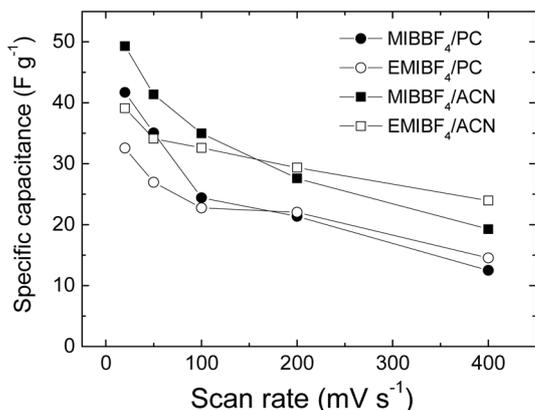


Fig. 5. Specific capacitance of carbon electrode at various mixed salt electrolytes as a function of scan rate.

in the spectra clearly indicates that the formulated mixed salt electrolytes are better conductors and are therefore strong electrolytes. The impedance spectra of electrolytes only differ in their position in the frequency regions wherein the electrolytes containing salts dissolved in

PC appear to be in the lower frequency region, compared to the electrolytes with ACN as a solvent.

As shown in Fig. 6(b), all carbon electrodes exhibit semicircles in the high frequency region and straight lines in the low frequency region. However, the carbon electrodes adopting MIBBF₄/PC and EMIBF₄/PC show larger diameter semicircles, compared to the electrodes adopting the electrolytes with ACN. Therefore, a larger charge transfer resistance is exhibited by the carbon electrode with electrolytes containing PC. The larger the resistance, the poorer is the capacitive performance of the electroactive material. This can be supported by a larger specific capacitance which is obtained by the carbon electrodes containing electrolytes with ACN solvent.

4. Conclusions

There is only slight difference in the ionic activities of the electrolyte containing the newly synthesized salt MIBBF₄ and the electrolyte containing the standard salt EMIBF₄ when dissolved in the same solvent. This indicates that the effect in changing the cation is less significant than

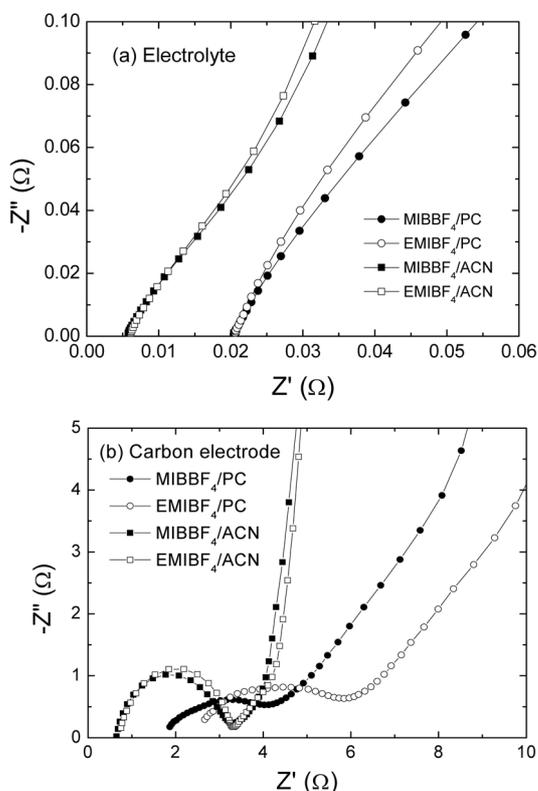


Fig. 6. Nyquist impedance plots of (a) mixed salt electrolytes and (b) carbon electrode at different electrolytes.

changing the anion. Ionic conductivity values of both salts are favorably high in the organic solvent CAN, which is mainly attributed to the solvent's amphiphilic nature favoring its distribution on both the polar and the nonpolar domains within the bulk of ionic liquids. However, a higher specific capacitance value of the full cell carbon electrode was displayed in the MIBBF₄/ACN mixed salt electrolyte compared to EMIBF₄/ACN at lower scan rates based on cyclic voltammetric measurements.

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