



Electrochemical properties of non-aqueous electrolytes containing spiro-type ammonium salts



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ABSTRACT

Electrochemical properties of organic solvent electrolytes containing salt additive were investigated by means of cyclic voltammetry, ionic conductivity and charge–discharge curve. The electrolyte was prepared by a mixture of propylene carbonate (PC) and dimethyl carbonate (DMC), tetraethylammonium tetrafluoroborate (TEABF₄) and spiro-1,1'-bipyrolidinium tetrafluoroborate (SBPBF₄) as a salt additive. The aim of this paper is to evaluate the effect of spiro-type quaternary ammonium salt on electrochemical properties. The bulk resistance of the mixture electrolytes and interfacial resistance were investigated using an AC impedance method. The result shows that SBPBF₄ has good solubility in PC/DMC and the ionic conductivity is comparable to TEABF₄ in PC/DMC. From the experimental results, by using the SBPBF₄ salt, the interfacial resistance was decreased and capacity and ionic conductivity were increased. These results may be due to the higher mobility or ion dissociation of the SBP cation with smaller ion size than the TEA cation against the meso- or micro-pores of the activated carbons electrode.

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1. Introduction

During the last three decades, considerable interest has been focused on the development of electrochemical capacitors for energy storage devices [1–3]. Electrochemical double layer capacitors (EDLCs) are promising charge storage devices and have been used in many devices as a power equipment [4–7]. The EDLCs have better safety, power density, and long cycle life than secondary batteries. However, the weakness of the EDLCs is their low energy density. So, many studies have been carried out to improve the energy density [8,9]. EDLCs are charge storage devices that gather charge at the between electrode and electrolyte double layer interphase. Carbon based materials, which has high surface have been mainly used as electrode material [10–12]. Several types of electrolytes such as aqueous, organic and solid polymer are considered to be proper [13–15]. Most of all, investigations on organic electrolyte, which have wide voltage window, are proceeding briskly. Because the energy density is proportional to the square of the voltage. So, the organic

electrolytes are used for high energy density applications. Generally, the organic electrolytes, which are the solid quaternary ammonium salt dissolved in either acetonitrile (AN) or propylene carbonate (PC), have been used for high voltage EDLCs of the higher than 2 V [16]. Among many solvent candidates, acetonitrile has good electrochemical stability and high conductivity. However, it is harmful solvent and flammable. Propylene carbonate has high flash point, but low conductivity. On the other hand, in the case of salts, the most favorable electrolyte salt is tetraethylammonium tetrafluoroborate (TEABF₄) [17–19]. It has a good electrochemical stability but demonstrates a limited solubility in solvents. Spiro-1,1'-bipyrolidinium tetrafluoroborate (SBPBF₄), a spiro-type quaternary ammonium salt, has a low viscosity and a high solubility in various solvents. Furthermore, it shows an excellent electrochemical stability and a high conductivity [20].

In this work, two salts were investigated by comparing the common tetraethylammonium tetrafluoroborate (TEABF₄) and the spiro-1,1'-bipyrolidinium tetrafluoroborate (SBPBF₄). The aim of this study is to demonstrate and prove the superiority of the SBPBF₄ salt, when it was compared to TEABF₄. Firstly, the conductivity of solvents containing 1 M SBPBF₄ in PC/DMC was studied and compared with 1 M TEABF₄ in PC/DMC. Furthermore, the capacitance and impedance results of electrolytes containing a different content of salt were estimated.

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2. Experiment details

2.1. Materials

TEABF₄ (99%) was purchased from Aldrich. SBPBF₄ (98%) was purchased from SK Chemical Co. Propylene carbonate (99.7%) was also acquired from Aldrich. And dimethylcarbonate (99%) and carbon blacks (99%) were acquired from Alfa Aesar. Sodium carboxymethyl cellulose (Na-CMC, average molecular weights of 1×10^4) was acquired Aldrich. N-methyl-2-pyrrolidone (NMP, 99%) was purchased from Junsei Chemical Co. Ltd. (Japan).

2.2. Preparation of electrolytes and electrode

The electrolytes were prepared by dissolving the salts in propylene carbonate (PC) and dimethylcarbonate (DMC). All the electrolytes were prepared in a glove box of Ar atmosphere. We used X M TEABF₄ in PC/DMC (X = 0, 0.5, 1) and X M SBPBF₄ in PC/DMC (X = 0, 0.5, 1, 1.5, 2.3) as electrolytes. The fabrication of working electrodes was carried out as follows. First, active materials (MSP-20), carbon blacks (Super-P, Alfa Aesar), sodium carboxymethyl cellulose (Aldrich) and styrene-butadiene rubber (SBR) were mixed in a mass ratio of 85:5:6:4 in NMP solution. Then the resulting slurry was coated on nickel foam substrate (1 cm × 1 cm) with a spatula, which was followed by drying at 100 °C for 12 h in a vacuum oven.

2.3. Characterization of electrolytes

All electrochemical tests were done in three electrode system. A nickel foam coated with the slurry used as working electrode. A platinum wire and Ag/AgCl saturated with (3 M NaCl) served as counter and reference electrode. Electrochemical measurements were performed in a Iviumstat (Ivium Technologies, The Netherlands). Cyclic voltammetry (CV) tests were analyzed between 0 V and 1.0 V at different scan rate 5, 10, 30, 50, 100 mV s⁻¹. Also, bulk resistance and interfacial resistance of the various electrolytes were measured by AC impedance spectroscopy over the frequency range from 100 kHz to 253 Hz.

The ionic conductivities of prepared electrolyte were measured by using a conductivity meter (ES-51, HORIBA, Ltd.). Galvanostatic charge–discharge curves of prepared samples were analyzed at a current density of 1 A g⁻¹, and a potential range was between 0 V and 1 V.

3. Results and discussion

3.1. Ionic conductivity of electrolytes

Fig. 1 displays room temperature ionic conductivities of SBPBF₄ or TEABF₄ dissolved electrolytes as a function of salt concentration. The ionic conductivity was increased by increase of molar concentration. And, a slight increase of conductivity was shown for SBPBF₄ in PC/DMC in comparison with TEABF₄. An increase in the ionic conductivity of SBPBF₄ containing electrolytes will be confirmed again by the decreased interfacial resistance from semi-circle size and bulk resistance point, obtained from impedance plots in the following part. It means that the ion mobility of SBPBF₄ in carbonate solvents is higher than TEABF₄. Also, the solubility of SBPBF₄ was found to be higher than TEABF₄. The maximum solubility of TEABF₄ in PC/DMC was 1 M concentration. However, the conductivity of SBPBF₄ was sharply increased from 0.1 M to 1.5 M. At over the 1.5 M, ionic conductivity was slightly increased and saturated until 3 M concentration.

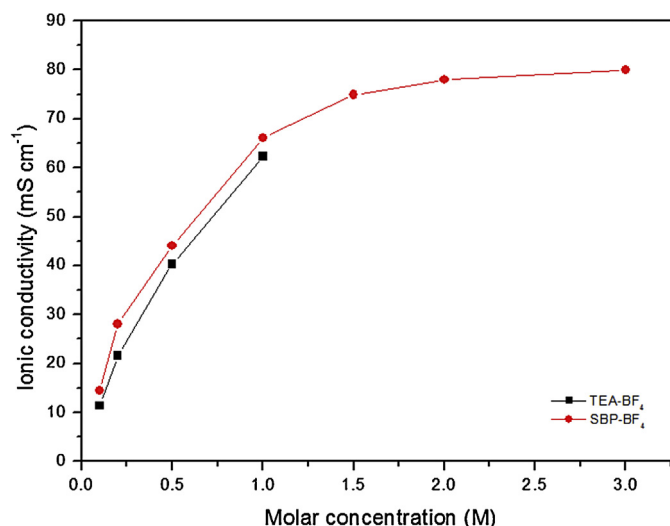


Fig. 1. Ionic conductivity of electrolytes with different concentration of SBPBF₄ or TEABF₄ in PC/DMC.

3.2. Electrochemical property of electrolytes

Figs. 2 and 3 show the impedance plots of the electrolytes containing a different concentration SBPBF₄ or TEABF₄. The beginning point of the impedance plot at high frequency indicates a bulk resistance, which could be related to electrolyte itself resistance. Interfacial resistance, which is estimated from the diameter of semi circle, explains the resistance between electrode and electrolyte. Bulk resistances of electrolyte using SBPBF₄ exhibited lower value than those of TEABF₄ at same salt concentration (0.1 M, 0.5 M, 1 M). The reason for the increased ionic conductivities of SBPBF₄-containing electrolytes could be thought that the ion mobility of SBP cation is the larger than that of TEA cation. Also, interfacial resistance of SBPBF₄ has lower value in compared with TEABF₄. This result may be due to the high mobility or dissociation ability and excellent solubility of SBP with a smaller ion size [21]. The high mobility and solubility can help ion insert into the pore of activated carbon. These reasons could reduce the interfacial resistance between electrode and electrolyte effectively.

The electrochemical performance of electrolytes was analyzed using CV curve. CV curves of various electrolytes are shown in

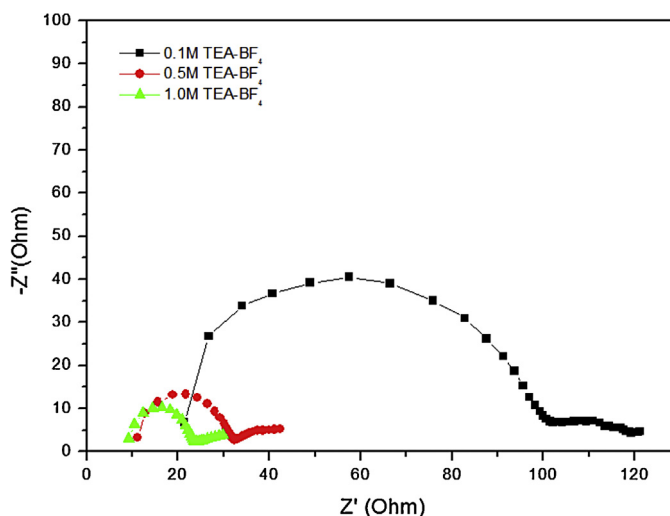


Fig. 2. Impedance plots of electrolytes with different concentration of TEABF₄ in PC/DMC.

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