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Short communication

Tetramethylammonium difluoro(oxalato)borate dissolved in ethylene/propylene carbonates as electrolytes for electrochemical capacitors

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HIGHLIGHTS

- TMADFOB dissolved in EC/PC as electrolyte for electrochemical capacitors.
- Ionic conductivity rises with the addition of ethylene carbonate.
- Ethylene carbonate suppresses the DFOB$^-$ intercalation into graphite.

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ABSTRACT

Tetramethyl ammonium difluoro(oxalato)borate (TMADFOB) dissolved in the mixed solvents of ethylene and propylene carbonates (EC/PC) instead of neat PC have been proposed as the electrolyte solutions for electrochemical capacitors. The ionic conductivity of 1 M TMADFOB-EC/PC electrolyte solutions has been measured. It climbs up monotonously as EC content increases. Accordingly, the power density of electric double-layer capacitors is enhanced with certain EC addition. The optimum EC content for the power of EDLCs is about 30 volume percentage in the mixed EC/PC solvents. This tendency has been testified by impedance study. The electrochemical behavior of activated carbon/graphite capacitors using these electrolyte solutions has also been studied by galvanostatic charge–discharge test and the charge storage mechanism at the graphite positive electrode has been investigated by *in situ* XRD and *ex situ* Raman. The effect of EC addition on DFOB$^-$ intercalation into graphite has also been addressed at both room and elevated temperatures.

1. Introduction

Accompanying the intemperate consumption of energy and resources on the earth, human society starts to care the worldwide problem of energy storage and transformation. In the past decades, there are two families of electric energy storage devices, lithium-ion batteries and electrochemical capacitors, have caught the eyes of many researchers. Both boomed in the 1990's. Soon after lithium-ion batteries outpaced electrochemical capacitors in various application fields. Then the balance between these two families got more and more tilted towards lithium-ion batteries. Once an electrode or electrolyte material was discovered or devised, it was more likely considered to meet the needs of lithium-ion batteries instead of electrochemical capacitors.

Recently, lithium difluoro(oxalato)borate (LiDFOB) has appeared as a promising electrolyte salt in lithium-ion batteries by virtue of its hydrolytic and thermal stability, compatibility with some cathode materials and beneficial effect on the solid electrolyte interface (SEI) formation at graphite anodes, etc. [1–9]. In contrast, electrolyte salts based on DFOB$^-$ anion have received much less attention in the community of electrochemical capacitors. In order to enhance the storage ability of the porous carbon negative electrode in an non-aqueous electric double-layer capacitor, Sasaki et al. first proposed tetramethyl ammonium difluoro(oxalato)borate (TMADFOB) as the electrolyte salt because of its high solubility in propylene carbonate (PC) and the small cation size [10]. Afterward, we utilized TMADFOB in the asymmetric capacitor of activated carbon/graphite [11]. The practical application of this electrolyte salt,

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however, is problematic because of the low ionic conductivity of TMADFOB dissolved in PC, even inferior to most electrolyte solutions commercialized today (say, 1 M tetraethyl ammonium tetrafluoroborate ($TEABF_4$) dissolved in PC, 13 mS cm^{-1}). This shortcoming may decrease the power density of an electrochemical capacitor. Therefore, we attempted to enhance the ionic conductivity of TMADFOB solutions by using ethylene carbonate (EC) as a co-solvent mainly due to its high dielectric constant. Moreover, the molecular structures of EC and PC are very near, only differing by one methyl group. So both the solvents are quite miscible because like dissolves like.

Since solvents can considerably influence the properties of an electrode/electrolyte interface, EC addition into TMADFOB-based electrolyte solutions may play an important role in determining the behavior of electrochemical capacitors. In this study, we applied the electrolyte solutions of TMADFOB-EC/PC in both the symmetrical AC/AC and asymmetric AC/graphite capacitors. The electrochemical performance of both types of capacitors was tested and its dependency upon the EC content in the binary mixed solvents was investigated.

2. Experimental

2.1. Preparation of TMADFOB salt

The TMADFOB salt was synthesized according to the procedure introduced in the reference [12] and confirmed by H NMR (hydrogen nuclear magnetic resonance) and ITMS (ion trap mass spectroscopy).

2.2. Electrochemical measurements

The AC sample was PW15M13130 from Kureha Co. Ltd. and its physical properties have been described in a previous report [13]. The graphite sample was natural graphite flakes purified by Kansai Coke and Chemicals Co. Ltd. Their morphological features are shown in Fig. 1. In a capacitor (coin cell), the weight ratio of negative to positive electrode materials was kept at 1. Main electrolyte solutions were 1 M TMADFOB dissolved in the mixed solvents of EC and PC. 1 M $TEABF_4$-PC and $TEAPF_6$-EC/PC were also employed for comparison. The coin cell fabrication and glove box conditions were similar to those described in the past reports [13,14]. Unless otherwise specified, the galvanostatic charge-discharge tests of the coin cells were performed at the constant current density of 0.4 mA cm^{-2}. The cut-off voltages were 0 and 2.7 V for the EDLCs with two symmetrical AC electrodes. In the case of asymmetric capacitors, the cut-off voltages were set at 0 and 3.5 V. Charge storage ability of the total capacitor (coin cell) was expressed in the terms of capacity (mAh g^{-1}). The capacity values were calculated according to the following formula: $Q = IT/w_+$ (I, the constant current (mA); T, the time for charge or discharge between cut-off voltages (hour); w_+, the weight of the positive electrode material (gram)).

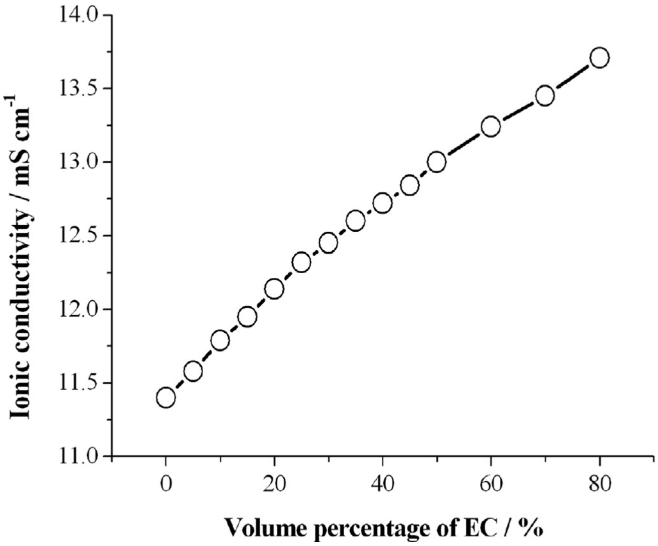

Fig. 2. Relationship between the ionic conductivity of a 1 M TMADFOB-EC/PC electrolyte solution and the EC content in the mixed solvents.

The details of *in situ* XRD measurements on the graphite positive electrode in an asymmetric AC/graphite capacitor were described in the reference [13]. The Al foil was used as both the current collector and X-ray window.

3. Results and discussion

In the electrolyte solutions using neat PC solvent, the conductivity reaches the maximum value at the concentration of 1.6 M [10]. At lower concentrations, the conductivity strongly relies on the number of free ions, rather than the mobility of ions in the electrolyte solutions [15]. Fig. 2 depicts the relationship between the ionic conductivity of the 1 M TMADFOB solution and the EC content in the mixed solvents. The conductivity value monotonously rises up as the EC content increases. This clear trend can be interpreted as follows. Along with the addition of EC, the dielectric constant of the binary solvent apparently gets higher, and then helps enlarge the number of free ions. On the other hand, EC has a slightly higher viscosity than PC, which may somehow retard the motion of ions in the electrolyte solutions. But this influence can be neglected at the concentration of 1 M. As a result, these two conflicting factors contribute to the monotonous increase in conductivity with the EC addition. It should

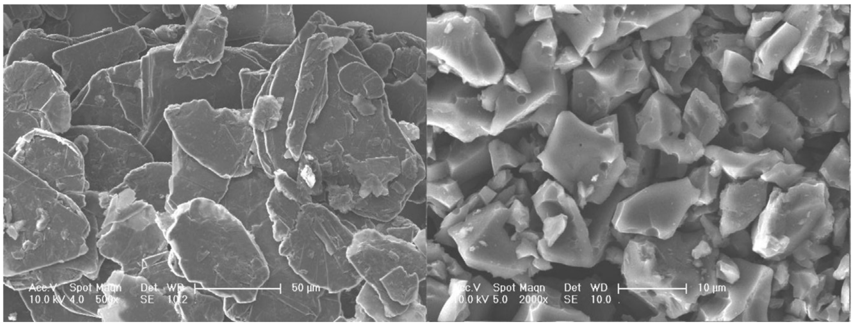

Fig. 1. SEM images of natural graphite flakes (left side) and activated carbon (right side).