Communication

**EDLC Performance of Various Activated Carbons in Spiro-Type Quaternary Ammonium Salt Electrolyte Solutions**

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In this study, we investigated the electrochemical behavior of various types of activated carbons with different properties, such as the specific surface area and pore size distribution in an electrolyte containing TEA-BF₄ and in that containing a spiro-type quaternary ammonium salt (SBP-BF₄). EDLC cells using 1 M SBP-BF₄/DMC + PC showed higher capacitances for the various activated carbons and good rate capabilities even for an activated carbon with a small pore size distribution compared to EDLC cells using 1 M TEA-BF₄/PC. These results may be attributed to the higher mobility of SBP with a smaller cation size and the lower viscosity of 1 M SBP-BF₄/DMC + PC due to the addition of DMC.

**Key Words** : EDLC, Spiro-type Quaternary Ammonium Salt, Activated Carbon

1 Introduction

Recently, electric double layer capacitors (EDLC) have been used in many devices such as the HEV, UPS and solar cell, and its use has significantly expanded. ⁵ EDLCs have a better safety, cyclability and power density when compared to secondary batteries because the energy-storage in the EDLC is based on the electric double layer formed at the interface between a polarizable electrode and electrolyte. However, the weakness of the EDLC is its low energy density. Therefore, many investigations about the electrode materials and electrolyte have been carried out to improve the energy densities. ⁴ ⁵

Spiro-1,1’-bipyridinium tetrafluoroborate (SBP-BF₄), i.e., a spiro-type quaternary ammonium salt, is highly soluble in various solvents and has excellent electrochemical properties, such as a highly conductivity. ⁵⁶ The solubility of SBP-BF₄ in PC is about three times higher compared to that of tetracylammonium tetrafluoroborate (TEA-BF₄) (TEA-BF₄ : 1.10 mol dm⁻³, SBP-BF₄ : 3.55 mol dm⁻³ at 303 K). Therefore the maximum conductivity of SBP-BF₄ is higher than those of TEA-BF₄. The internal resistance of EDLC using SBP-BF₄ was smaller than those using TEA-BF₄. In addition, the internal resistance of the EDLC using the DMC + PC solvent mixture is reduced about 20% at 233 K compared to that using the single PC solvent.

In this study, we investigated the electrochemical behavior of various types of activated carbons with different properties, such as the precursors, the specific surface area and pore size distribution in a conventional electrolyte and the spiro-type electrolyte in order to demonstrate the superiority of the SBP-BF₄ salt compared to TEA-BF₄.

2 Experimental

The various activated carbons with different properties as summarized in Table 1 (i.e., precursors, activation methods, specific surface areas, pore size distributions and grain sizes) were used as the electrode materials. Slurries dispersing the activated carbon, acetylene black and PVDF in NMP at the weight ratio of 80: 9: 11 were coated on a Ti film or etched Al film. These electrodes were dried at 150°C under vacuum for 4 h and then used as a working electrode for all the tests.

A CR2032 type coin cell was used for the charge-dis-

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( \delta_{\text{BET}} ) (m² g⁻¹)</th>
<th>( d_\text{por} ) (nm)</th>
<th>( d_\text{grain} ) (µm)</th>
<th>Group</th>
<th>Precursor</th>
<th>Activation</th>
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<tr>
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<td>H₂O</td>
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<td>A</td>
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<td>0.42</td>
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</tr>
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<td>29.2</td>
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<td>Coal</td>
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</tbody>
</table>

*Specific surface area. †Average pore size. ‡Average grain size. §Surface functional group.
charge tests. The electrolytes were 1 M TEA-BF₄ in PC (TEA-BF₄/PC) and 1 M SBP-BF₄ in a 3:7 volume ratio of DMC and PC (SBP-BF₄/DMC + PC). The charge-discharge tests were performed in the constant current voltage mode at current densities from 50 to 5000 mA g⁻¹ between 0 and 2.7 V to investigate the capacitances and rate capabilities of the EDLC cells using each material.

To investigate the behaviors of the cation and anion, cyclic voltammetry was performed at scan rates from 5 to 200 mV s⁻¹ using a three-electrode cell consisting of the prepared electrodes as the working and counter electrodes and Li metal foil as the reference. As the electrolyte, 1 M TEA-BF₄/PC, 1 M SBP-BF₄/PC and 1 M SBP-BF₄/DMC + PC were used.

3 Results and Discussion

Figure 1 shows the specific capacitances calculated from the linear part of each discharge curve plotted versus the specific surface areas. This figure demonstrates that the coin type cells using 1 M SBP-BF₄/DMC + PC showed a higher capacitance than those using 1 M TEA-BF₄/PC for all the activated carbons, and the specific capacitance of the cells using 1 M SBP-BF₄/DMC + PC more linearly increased with the specific surface areas, indicating a higher capacitance compared to the cells using the other electrolyte solutions.

The effect of the discharge current density on the capacity of the cells using activated carbons with different pore sizes that ranged from 1.65 to 1.82 nm was studied in 1 M TEA-BF₄/PC and in 1 M SBP-BF₄/DMC + PC as shown in Fig. 2. For 1 M TEA-BF₄/PC (Fig. 2 (a)), the capacity retention ratio of the cell using the activated carbon with the average pore size of 1.65 nm (B-1) decreased with the increasing current density. On the contrary, the capacity of the cells using 1 M SBP-BF₄/DMC + PC (Fig. 2 (b)) did not decrease between the discharge current densities of 100-5000 mA g⁻¹. In addition, even at a low current density (50 mA g⁻¹), the charge-discharge profiles of the coin type cells using B-1 in 1 M TEA-BF₄/PC showed a remarkable IR drop (Fig. 3). These results suggest that the TEA cation with a larger size compared to that of the SBP cation cannot easily diffuse into the micro pores as small as 1.65 nm at the higher current densities. This was also confirmed by the cyclic voltammetries (CVs), in which they were measured using the activated carbon with the average pore size of 1.65 nm in 1 M TEA-BF₄/PC, 1 M SBP-BF₄/PC and 1 M SBP-BF₄/DMC + PC. The remarkable distortion of the CV of B-1 at 5 mV s⁻¹ in 1 M TEA-BF₄/PC (Fig. 4) was observed in the potential region more negative than

![Fig. 1](image1.png)  
**Fig. 1** Relationship between specific surface area and specific capacitance for various activated carbons in 1 M TEA-BF₄/PC and 1 M SBP-BF₄/DMC + PC.

![Fig. 2](image2.png)  
**Fig. 2** Capacity retentions of coin type cells using activated carbons with different pore diameters at various discharge rate. Electrolyte : (a) 1 M TEA-BF₄/PC, (b) 1 M SBP-BF₄/DMC + PC.

![Fig. 3](image3.png)  
**Fig. 3** Charge-discharge curves of coin-type cells using an activated carbon with the average pore size of 1.65 nm in 1 M TEA-BF₄/PC and 1 M SBPBF₄/DMC + PC. The current density was 50 mA g⁻¹.
the OCV (ca. 3.2 V vs. Li/Li⁺), where the cations are absorbed and desorbed, while the CV in 1 M SBP-BF₄/DMC + PC showed the maximum current values over the entire potential region. Figure 5 shows the CVs of B-1 in (a) 1 M TEA-BF₄/PC, (b) 1 M SBP-BF₄/PC and (c) 1 M SBP-BF₄/DMC + PC at scan rates from 5 to 200 mV s⁻¹. The distortion of the CV shape with the increasing scan rate is especially observed in the 1 M TEA-BF₄/PC. The degree of distortion in the 1 M SBP-BF₄/DMC + PC is lower than those in 1 M TEA-BF₄/PC and 1 M SBP-BF₄/PC. In addition, the rectangular shape of the CV in the 1 M SBP-BF₄/DMC + PC is maintained even at the scan rate of 200 mV s⁻¹. These results suggest that the SBP cation has a higher mobility than that of the larger size TEA cation in the very small pores (below 1.65 nm) of the activated carbon, and the addition of DMC with a low viscosity causes not only an improvement in the mobility of the cation, but also improves the mobility of the anion.

4 Conclusion

This work demonstrated the superiority of the SBP-BF₄ salt as the electrolyte for EDLCs compared to TEA-BF₄. EDLC cells using various activated carbons in a 1 M SBP-BF₄/DMC + PC showed higher specific capacitances than those in 1 M TEA-BF₄/PC. For the activated carbon with the average pore size of 1.65 nm, the cell using 1 M SBP-BF₄/DMC + PC showed a better rate capability, while the capacity of the cell using 1 M TEA-BF₄/PC significantly decreased with the increasing discharge current density.

These results may be due to the higher mobility of the SBP cation with the smaller ion size than the TEA cation in the small pores of the activated carbons and to the addition of DMC with a low viscosity which may cause an improvement in the mobility of both the cation and anion.

Fig. 4 Cyclic voltammograms of the activated carbon with the average pore size of 1.65 nm in 1 M TEA-BF₄/PC, 1 M SBP-BF₄/PC and 1 M SBP-BF₄/DMC + PC. The scan rate was 5 mV s⁻¹.

Fig. 5 Cyclic voltammograms of the activated carbon with average pore size of 1.65 nm in (a) 1 M TEA-BF₄/PC, (b) 1 M SBP-BF₄/PC and (c) 1 M SBP-BF₄/DMC + PC.

References