A study of spiro-type quaternary ammonium salt propylene carbonated electrolyte for high voltage electric double layer capacitors
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INTRODUCTION
Electric double layer capacitors (EDLCs), have received much attention recently because their excellent performance. However, the drawback of low energy density limits their application. According to the equation E=1/2CV^2, it is obviously that increasing voltage is more effective because the energy density increases in proportion to squared voltage. Therefore, novel electrolytes with wide work potential and high electrical conductivity can be explored to improve the electrochemical stability at electrode/electrolyte interface. Spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBP-BF4), which is a spiro-type quaternary ammonium salt, has received much attention for its excellent electrochemical properties in recent years[1].

EXPERIMENTAL
Test cells were assembled in an argon dry glove box and were filled with 1.5M SBP-BF4 and TEMA-BF4 in PC based electrolytes. Cell testing includes cyclic voltammetry and galvanostatic charge-discharge to evaluate the withstand voltage, power and energy characteristics, and capacitance.

RESULTS AND DISCUSSION
The value of electrical conductivity and viscosity measured using 1.5M SBP-BF4 in PC are shown in Table 1. At the same concentration, the specific conductivity of SBP-BF4/PC is higher than that of TEMA-BF4/PC, because the SBP cations may have smaller volume than TEMA cations[2]. The viscosity of the SBP-BF4 is smaller than that of the TEMA-BF4, therefore the SBP-BF4 solution has better mobility. Table 1: Conductivity and viscosity of investigated electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (mol/L)</th>
<th>Conductivity (mS·cm(^{-1}))</th>
<th>Viscosity (mPa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBP-BF4/PC</td>
<td>1.5</td>
<td>16.96</td>
<td>4</td>
</tr>
<tr>
<td>TEMA-BF4/PC</td>
<td>1.5</td>
<td>14.62</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The cyclic voltammetry curves for EDLCs based on the 1.5M SBP-BF4 and TEMA-BF4 in PC are presented in Fig.1. The degree of distortion of SBP-BF4/PC based EDLCs is lower than that of TEMA-BF4/PC based EDLCs, and this may relate with the high conductivity of SBP-BF4/PC electrolyte and the higher mobility of SBP cations at high scan rate. The galvanostatic charge-discharge profiles of SBP-BF4 and TEMA-BF4 in PC electrolytes based EDLCs under various constant charging voltages are shown in Fig.2. When the constant charging voltages are no more than 3.5 V, the symmetric straight lines indicate that the cations and anions could both simply adsorp/desorp at electrode/electrolyte interface. The SBP-BF4/PC electrolyte has higher withstand voltage than that of TEMA-BF4/PC which may relate with its wide potential window and the high electrical conductivity.

Fig.1 CV curves of 1.5M SBP-BF4 and TEMA-BF4 in PC for EDLCs (a) SBP-BF4 (b) TEMA-BF4

Fig.2 Charge-discharge curves of 1.5M SBP-BF4 and TEMA-BF4 for EDLCs in PC (a) SBP-BF4 (b) TEMA-BF4

The charge/discharge rates performance shown in Fig.3 has been obtained from galvanostatic charge/discharge tests in the current density range from 50 mA/g to 10 A/g. The cell using 1.5M SBP-BF4/PC reaches 120 F/g specific capacitance at charge current density of 100mA/g, and the energy density and power density could reach 31.5 Wh/kg, 7000 W/kg, respectively. It suggests that the mobility of SBP ions in electrolyte is high compared with those of TEMA ions in PC.

Fig.3 (a) Relationship between discharge capacitance and discharge current density at 298K completed using 1.5M SBP-BF4 and TEMA-BF4 in PC and (b) Ragone plots for the EDLCs

CONCLUSION
The SBP-BF4/PC electrolyte own well upper voltage hold feature and higher discharge capacitance than that of TEMA-BF4/PC which can be a promising high voltage electrolyte for the energy type EDLCs.

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