

# Preparation of spiro-type quaternary ammonium salt via economical and efficient synthetic route as electrolyte for electric double-layer capacitor

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**Abstract:** A spiro-type quaternary ammonium salt, spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBP-BF<sub>4</sub>) was successfully prepared by an economical and efficient three-step process comprising the cyclization reaction of 1,4-dibromobutane and pyrrolidine, and subsequent ion exchange pathway with KOH followed by neutralization reaction via HBF<sub>4</sub> in the system of ethanol solution. <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and XPS analyses showed the structure of SBP-BF<sub>4</sub>. The as-obtained SBP-BF<sub>4</sub> was dissolved in AN and used as the electrolyte for supercapacitor. Electrochemical measurements demonstrate that, compared with commercial electrolyte TEMA-BF<sub>4</sub>/AN, SBP-BF<sub>4</sub>/AN exhibits high ionic conductivity, lower resistance and improved cycling performance, which is due to its smaller ion size and stable symmetry structure.

**Key words:** spiro-type quaternary ammonium salt; synthesis; electrolyte; electric double-layer capacitor

## 1 Introduction

Supercapacitor has been partially or fully, to replace conventional chemical batteries, the complement of batteries or fuel as power boosters due to its outstanding properties such as a great power density, long cycle life and high energy density [1–2]. Electrolyte, as the most important part of supercapacitors, is a key factor for the performance of the capacitor. Recently, supercapacitors with nonaqueous electrolytes are mainly represented by quaternary ammonium salt. Especially, spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBP-BF<sub>4</sub>), a new electrolyte salt, causes a wild concern [3].

Supercapacitor using SBP-BF<sub>4</sub> as electrolyte shows excellent performances [4–5] compared with other quaternary ammonium, not only high solubility, high electrical conductivity, high capacitance, low internal resistance and high rate discharge characteristics, but also outstanding durability and remarkable withstand voltage performance. Unfortunately, commercial sources of this electrolyte are few.

In an earlier publication, there are a few methods of synthesis [6–9]. Synthesis of SBP-BF<sub>4</sub> was attempted by HIGASHIYA et al [7] using pyrrolidine, 1,4-dibromobutane, K<sub>2</sub>CO<sub>3</sub>, and KBF<sub>4</sub> in AN. HIGONO et al [8] reported that spiro-(1,1′)-bipyrrolidinium chloride (SBP-Cl) was synthesized by reacting

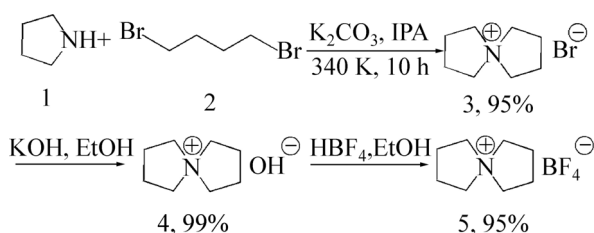
pyrrolidine with 1,4-dichlorobutane and neutralized with addition of an equivalent amount of HBF<sub>4</sub>, thereby obtaining SBP-BF<sub>4</sub> [9]. CHIBA et al [6] synthesized SBP-Br by reacting pyrrolidine with 1,4-dibromobutane and then it was reacted with silver oxide to obtain SBP-OH. The obtained SBP-OH was made to react with HBF<sub>4</sub> to obtain SBP-BF<sub>4</sub>. However, there exist defects either in yield [7–9] or cost [6].

In this work, we present a facile and economic synthesis of SBP-BF<sub>4</sub> for industrialization with high yield in Scheme 1. For comparison with commercial electrolyte, SBP-BF<sub>4</sub> was also blended with AN to obtain the required electrolyte. Subsequently, some electrochemical properties were measured. The electrochemical properties of as-obtained electrolytes were studied to evaluate their potential use in electrochemical double layer capacitors (EDLCs).

## 2 Experimental details

### 2.1 Material

Solvents (Changsha Huihong Chemicals and Glass Apparatus Co., China) were purified and dried according to known methods and then rectified. Active carbon, carbon blacks and poly(vinylidene fluoride) (PVDF) were acquired from Japan. Cellulose separator was purchased from Taiwan, China. TEMABF<sub>4</sub>/AN electrolyte was purchased from Shenzhen Capchem



**Scheme 1** Synthesis of SBP-BF<sub>4</sub>

Polytron Technologies Inc. (China).

## 2.2 Synthesis of spiro-(1,1)-bipyrrrolidinium tetrafluoroborate (SBP-BF<sub>4</sub>)

200 mL of the isopropanol solution of 1,4-dibromobutane (50.0 g, 0.23 mol) was introduced into a large three-necked flask under mechanical stirring in an ice bath, and pyrrolidine (15.0 g, 0.21 mol) was added dropwise over about half an hour. When the addition was completed, the solution was heated to 340 K and reacted in the presence of K<sub>2</sub>CO<sub>3</sub> (34.9 g, 0.23 mol) for 10 h [10]. Then, the potassium bromide was filtered from the solution and the isopropanol was removed with the help of rotary evaporation apparatus at 338 K. The collected salts was washed two or three times by 100 mL acetone and dried in the vacuum drying oven for 12 h at 338 K. The yield of dry SBP-Br was 41.2 g, 95%. FI-IR:  $\bar{\nu}$  = 3431, 2967, 2893, 1635, 1461, 917 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 2.23 (t, 8H),  $\delta$  = 3.60 (d, 8H). <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 63.96 (t, 4C),  $\delta$  = 23.05 (s, 4C). pH = 6.4.

An equivalent amount of potassium hydroxide was added to the spiro-(1,1')-bipyrrrolidinium bromide (40 g, 0.19 mol) in 200 mL ethanol. After dropwise addition, ion exchange reaction was conducted at ambient temperature for 30 min to obtain spiro-(1,1')-bipyrrrolidinium hydroxide (SBP-OH) [11–12]. Then, the solution was filtered for the removal of potassium bromide and the yield of ion exchange was 99%. FI-IR:  $\bar{\nu}$  = 3431, 2967, 2893, 1635, 1461 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 2.23 (m, 8H),  $\delta$  = 3.58 (m, 8H). <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 63.97 (t, 4C),  $\delta$  = 23.05 (s, 4C). pH = 9.0.

The 40% HBF<sub>4</sub>(aq) was added to the filtrate drop by drop until pH = 5–6. The mixture was evaporated under reduced pressure at 388 K to remove water and ethanol, thereby obtaining SBP-BF<sub>4</sub> [13]. The salts were recrystallized from ethanol and dried for 12 h. The yield of SBP-BF<sub>4</sub> was 39.2 g, 95.0%. FI-IR:  $\bar{\nu}$  = 3431, 2967, 2893, 1635, 1461, 1306, 1078, 1040 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 2.21 (m, 8H),  $\delta$  = 3.55 (m, 8H). <sup>13</sup>C NMR (500 MHz, CD<sub>3</sub>OD, 291.1 K):  $\delta$  = 63.84 (t, 4C),  $\delta$  = 22.94 (s, 4C). pH = 5.8.

## 2.3 Preparation of electrode, electrolyte and EDLCs

Active carbon (80%, mass fraction), carbon blacks (10%, mass fraction), and poly(vinylidene fluoride) (PVDF) (10%, mass fraction) with adequate *N*-methyl-2-pyrrolidone (NMP) were mixed, coated on the aluminum foil and dried at 353 K for 12 h in a vacuum oven. Finally, the resulting circular electrode sheet was made with 14 mm in diameter.

The electrolyte was prepared by dissolving SBP-BF<sub>4</sub> salt in AN. Using electrode sheets of the same mass and a cellulose separator and nickel mesh, a 2025 coin cell was assembled. All the operations were prepared in glove box in N<sub>2</sub> atmosphere.

## 2.4 Instrumentation methods

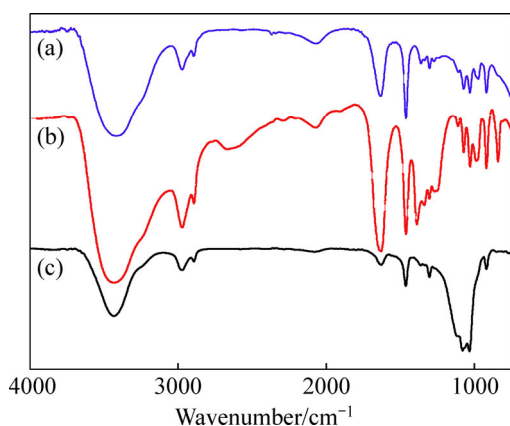
FI-IR spectra were recorded with an American Nicolet 6700 FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE 500 instrument. X-ray-photoelectron spectrograph was recorded with Thermo Scientific ESCALAB 250Xi photoelectron spectroscopy.

The ionic conductivity of the electrolyte was measured using a conductivity meter DDS-11A and refrigerated/heating circulators TEMI880. The bulk resistance and interfacial resistance were measured by AC impedance spectroscopy on CHI660 over the frequency range from 10<sup>5</sup> Hz to 1 Hz. Charge–discharge curves were analyzed on BTS10105C5 at a current density of 0.43 A/g, and a potential range between 0 V and 2.5V.

## 3 Results and discussion

### 3.1 Structure of SBP-BF<sub>4</sub> salt

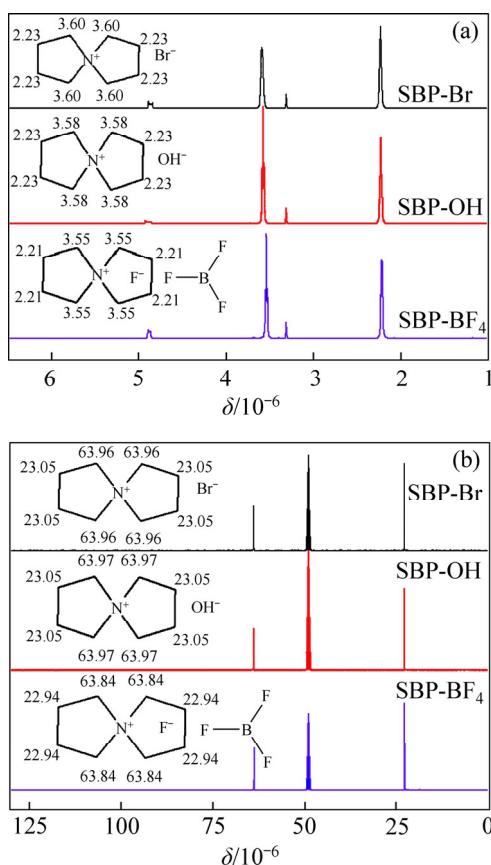
Synthesis of SBP-BF<sub>4</sub> was accomplished in moderate overall yield as shown in Scheme 1. The method was based in part on that used by CHIBA et al [6]. <sup>1</sup>H NMR, <sup>13</sup>C NMR, FI-IR, and X-ray photoelectron spectroscopy were applied to determine the structure of intermediates and final product. Figure 1 presents the FI-IR spectra of SBP-Br, SBP-OH, and SBP-BF<sub>4</sub>. The absorption peaks at about 2967, 2893, 1461 cm<sup>-1</sup> are characteristic ones of the C—H stretching vibration and bending vibration. The presence of the absorption peaks at 1078 and 1031 cm<sup>-1</sup> indicate the existence of the N—B and the stretching vibration of B—F is observed at 1306 cm<sup>-1</sup> in the spectrum of SBP-BF<sub>4</sub>. The absorption peak at 1387 cm<sup>-1</sup> is the stretching vibration of N—O and the absorption peaks at 3431 and 1649 cm<sup>-1</sup> are the bands of O—H in the spectrum of SBP-OH. The absorption peak at 917 cm<sup>-1</sup> assigned to the stretching vibration of N—Br disappears in the spectrum of SBP-Br. Additionally, the FI-IR spectrum also has peaks at 3431 and 1635 cm<sup>-1</sup>. These bands are ascribed to the stretching vibration and bending vibration of O—H group of adsorbed water.



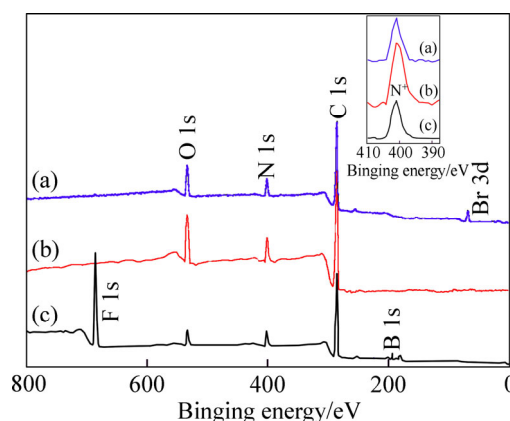
**Fig. 1** FI-IR spectra of SBP-Br (a), SBP-OH (b) and SBP-BF<sub>4</sub> (c)

Furthermore, Fig. 2 demonstrates the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of SBP-Br, SBP-OH and SBP-BF<sub>4</sub>. There are two types of H and two types of C in the spiro-type quaternary ammonium salt, exhibiting the exact structure of spiro-type quaternary ammonium salt.

Figure 3 shows the X-ray photoelectron spectra of SBP-Br, SBP-OH and SBO-BF<sub>4</sub> for the characterization of the nitrogen (N<sup>+</sup>) in quaternary ammonium salt. It is known that the XPS signals at 685 eV, 533 eV, 401 eV, 285 eV, 194 eV and 68 eV are attributed to F 1s, O 1s, N 1s, C 1s, B 1s and Br 3d, respectively. In particular, nitrogen (N<sup>+</sup>) peak at 401 eV is presented, corresponding



**Fig. 2** NMR spectra: (a) <sup>1</sup>H NMR; (b) <sup>13</sup>C NMR spectra



**Fig. 3** XPS spectrum of SBP-Br (a), SBP-OH (b) and SBP-BF<sub>4</sub> (c)

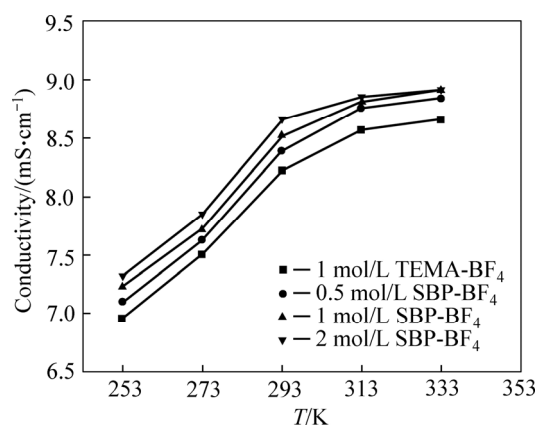
to the C—N group of quaternary ammonium salt, in the high-resolution N 1s spectrum of these three compounds [14–15].

### 3.2 Ionic conductivity of electrolytes

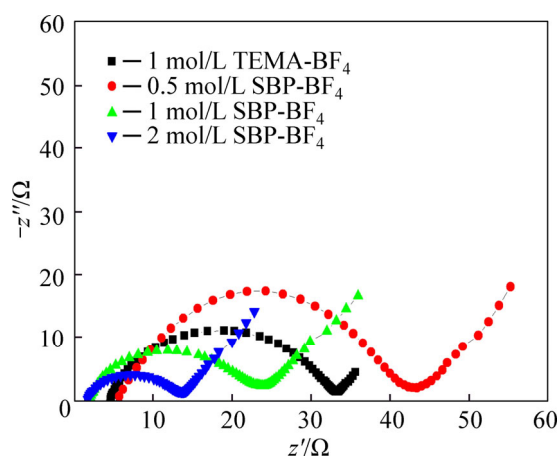
Figure 4 shows the electric conductivity of different concentrations of SBP-BF<sub>4</sub>/AN (0.5 mol/L, 1 mol/L and 2 mol/L) and 1 mol/L TEMA-BF<sub>4</sub> at different temperatures (253 K, 273 K, 293 K, 313 K and 333 K). Obviously, the conductivity of SBP-BF<sub>4</sub> sharply increases from 253 K to 313 K, and then slightly increases and is saturated until 333 K. With the concentration increasing, the conductivity of SBP-BF<sub>4</sub> slight increases at the same temperature for dissolving more salt. The electric conductivity of SBP-BF<sub>4</sub> is better than that of TEMA-BF<sub>4</sub> at the same salt concentration, because the size of SBP cation is smaller than that of TEMA cation. Also, the solubility of SBP-BF<sub>4</sub> is found to be higher than that of TEMA-BF<sub>4</sub>. Thus, SBP-BF<sub>4</sub> has a better mobility compared with TEMA-BF<sub>4</sub>.

### 3.3 Electrochemical property of electrolytes

Figure 5 displays the impedance plots of EDLCs



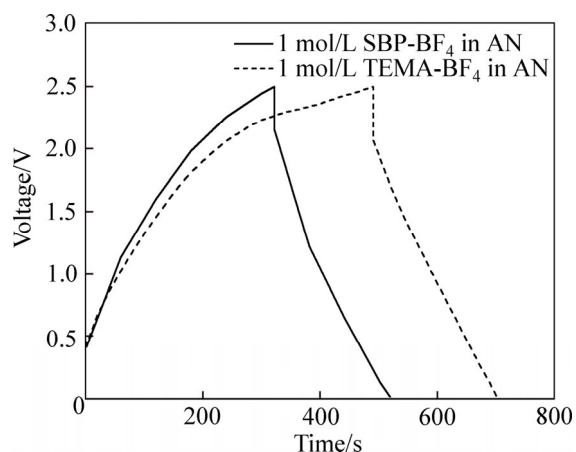
**Fig. 4** Conductivity of electrolytes with different concentrations of SBP-BF<sub>4</sub>/AN (0.5 mol/L, 1 mol/L and 2 mol/L) and 1 mol/L TEMA-BF<sub>4</sub>/AN



**Fig. 5** Impedance plot electrolytes with different concentrations of SBP-BF<sub>4</sub>/AN (0.5 mol/L, 1 mol/L and 2 mol/L) and 1 mol/L TEMA-BF<sub>4</sub>/AN

using different concentrations of SBP-BF<sub>4</sub> (0.5 mol/L, 1 mol/L and 2 mol/L) and 1 mol/L TEMA-BF<sub>4</sub>. The start point of impedance curve is the resistance of the electrolyte itself. The diameter of the semicircle is estimated as the interface resistance, indicating the resistance between the electrode and the electrolyte. The bulk resistance of SBP-BF<sub>4</sub> is smaller than that of TEMA-BF<sub>4</sub>. The reason is that the ion mobility and conductivity of the SBP-BF<sub>4</sub> are better than those of TEMA-BF<sub>4</sub>. And the interface resistance of SBP-BF<sub>4</sub> is also smaller than that of TEMA-BF<sub>4</sub>, probably because of higher mobility, better dissociation ability and smaller ion size of SBP cation, which helps ion insert the pores of the activated carbon, reducing the interfacial resistance. However, the bulk resistance and the interfacial resistance of EDLCs using SBP-BF<sub>4</sub>/AN is reduced from 0.5 mol/L to 2 mol/L.

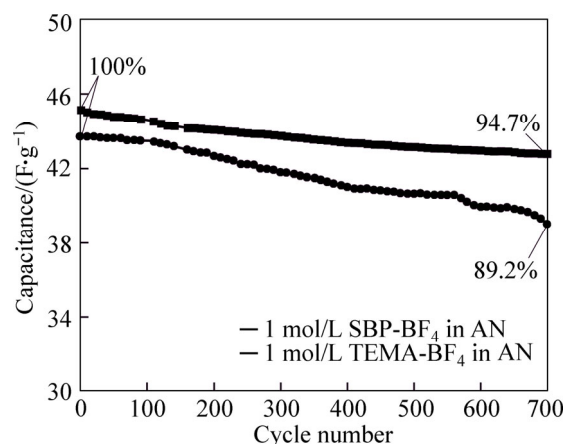
Figure 6 shows the first charge–discharge curves of EDLCs using 1 mol/L SBPBF<sub>4</sub>/AN and 1 mol/L TEMABF<sub>4</sub>/AN. The ideal charge–discharge curve is



**Fig. 6** Charge–discharge curves of electrolytes using SBP-BF<sub>4</sub>/AN and 1 mol/L TEMA-BF<sub>4</sub>/AN at current density of 0.43 A/g

symmetrical triangle, which means excellent electrochemical reversibility. The charge and discharge curve using 1 mol/L TEABF<sub>4</sub>/AN shows a greater IR drop. The equivalent resistance of TEMA-BF<sub>4</sub>/AN electrolyte is larger. This is because the volume of the TEMA cation ratio is larger than that of SBP cation, which can not easily diffuse into the pores of the activated carbon.

Figure 7 illustrates the cycling performance of 1 mol/L SBPBF<sub>4</sub>/AN and 1 mol/L TEMABF<sub>4</sub>/AN. Compared with TEMABF<sub>4</sub>/AN, SBPBF<sub>4</sub>/AN has a greater reversible capacity. The retention rate of the electrolyte SBP-BF<sub>4</sub>/AN is 94.7% after 700 cycles. SBP-BF<sub>4</sub>/AN has a better cycling stability. The reason is that the SBP cation has a stable symmetrical structure, which can form a constant and stabled adsorption–desorption doubled layer on the surface of the electrode.



**Fig. 7** Capacitance retention curves of electrolytes using 1 mol/L SBP-BF<sub>4</sub>/AN and 1 mol/L TEMA-BF<sub>4</sub>/AN

## 4 Conclusions

1) The economical, facile and efficient synthesis of SBP-BF<sub>4</sub> has been successfully carried out from a series of reactions involving 1, 4-dibromobutane, pyrrolidine, potassium carbonate, potassium hydroxide and tetrafluoroboric acid. The identification of the product was confirmed by FI-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and XPS. The overall yield of the synthesis is 89.2%. Further efforts are still in process in order both to optimize the treatment of by-products and improve the yield.

2) SBP-BF<sub>4</sub> has a better conductivity than TEMA-BF<sub>4</sub> because of the smaller size of the SBP cation.

3) EDLCs using SBP-BF<sub>4</sub>/AN have larger capacitance, lower bulk resistance and interfacial resistance, and more stable cycling performance, compared with TEMA-BF<sub>4</sub>/AN. This is because of the stable symmetrical structure and small size of SBP cation.

## References

- [1] WINTER M, BRODD R J. What are batteries, fuel cells, and supercapacitors? [J]. American Chemical Society, 2004, 104(10): 4245–4269.
- [2] PANDOLFO A G, HOLLENKAMP A F. Carbon properties and their role in supercapacitors [J]. Journal of Power Sources, 2006, 157(1): 1–27.
- [3] NAOIL K. ‘Nanohybrid Capacitor’: The next generation electrochemical capacitors [J]. Fuel Cells, 2010, 10(5): 825–833.
- [4] KORENBLIT Y, KAJDOS A, WEST W C, SMART M C, BRANDON E J, KVIT A, JAGIELLO J, YUSHIN G. In situ studies of ion transport in microporous supercapacitor electrodes at ultralow temperatures [J]. Advanced Functional Materials, 2012, 22(8): 1655–1662.
- [5] HIGASHIYA S, FILATOV A S, WELLS C C, RANE-FONDACARO M V, HALDAR P. Crystal structures and quantitative structure–property relationships of spirobipyrrrolidinium and the oxygen-containing derivatives [J]. Journal of Molecular Structure, 2010, 984 (1/2/3): 300–306.
- [6] CHIBA K, UEDA T. Performance of electrolyte composed of spiro-type quaternary ammonium salt and electric double-layer capacitor using it [J]. Electrochemistry, 2007, 75(8): 664–667.
- [7] HIGASHIYA S, DEVARAJAN T S, RANE-FONDACARO M V, DANGLER C, SNYDER J, HALDAR P. Synthesis of oxygen-containing spirobipyrrrolidinium salts for high conductivity room temperature ionic liquids [J]. Helvetica Chimica Acta, 2009, 92(8): 1600–1609.
- [8] HIGONO T, SATO K, SUGA N, CHIBA K, KAMEI T. Electrolyte for electrical double layer capacitor and electrical double layer capacitor using the electrolyte. EP 1583116 [P]. 2005–10–05.
- [9] CHIBA K. Electrolytic solution for electric double layer capacitor and electric double layer capacitor. EP 1724795 [P]. 2006–11–22.
- [10] BLICKEF F, HOTELLING E B. Polycyclic quaternary ammonium salts [J]. Journal of the American Chemical Society, 1954, 76(20): 5099–5103.
- [11] HARLOW G A, WYLD G E A. Nonaqueous quaternary ammonium titrants preparation by the potassium hydroxide method [J]. Analytical Chemistry, 1962, 34 (1): 172–173.
- [12] LIN Ben-cai, QIU Li-hua, LU Jian-mei, YAN Feng. Cross-linked alkaline ionic liquid-based polymer electrolytes for alkaline fuel cell applications [J]. Chemistry of Materials, 2010, 22(24): 6718–6725.
- [13] HOFF R H, HENGGE A C. A facile high-yield synthesis and purification of tetrabutylammonium tetrabutylborate [J]. Journal of Organic Chemistry, 1998, 63(1): 195–195.
- [14] CHEN Shi-guo, CHEN Shao-jun, JIANG Song, XIONG Mei-ling, LUO Jun-xuan, TANG Jiao-ning, GE Zao-chuan. Environmentally friendly antibacterial cotton textiles finished with siloxane sulfopropylbetaine [J]. ACS Applied Materials & Interfaces, 2011, 3(4): 1154–1162.
- [15] KELEMEN S R, AFEWORKI M, GORBATY M L, KWIAK P J. XPS and <sup>15</sup>N NMR study of nitrogen forms in carbonaceous solids [J]. Energy Fuels, 2002, 16(6): 1507–1515.

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