Novel ionic liquid electrolyte for electrochemical double layer capacitors

Thamarai Devarajan a, Seiichiro Higashiya b, Christopher Dangler a, Manisha Rane-Fondacaro a,*, Jeremy Snyder a, Pradeep Haldar a

a College of Nanoscale Science and Engineering, University at Albany, SUNY, 251 Fuller Road, CESTM, Albany, New York 12203, USA
b Department of Chemistry, University at Albany, 1400 Washington Avenue, Albany, New York 12222, USA

Article info
Article history:
Received 7 December 2008
Received in revised form 27 December 2008
Accepted 9 January 2009
Available online 13 January 2009

Keywords:
OPBF 4
Electrolyte
Cyclic voltammetry
Acetonitrile
Electrochemical double layer capacitors

Abstract
A novel oxygen containing spiro ammonium salt, oxazolidine-3-spiro-1'-pyrrolidinium tetrafluoroborate (OPBF 4) was synthesized using an innovative technique for use as electrolyte in electrochemical double layer capacitors (EDLC). Comparison of OPBF 4 with commercially available, tetraethyl ammonium tetrafluoroborate (TEABF 4) showed higher voltage window and higher capacitance for the OPBF 4 compound. Moreover, molarity of 3 M was produced with OPBF 4 as compared to a maximum of 1.5 M for TEABF 4 in acetonitrile (AN). This is especially important to enable the fabrication of higher energy density EDLC. This is the first report of testing OPBF 4 compound in an EDLC device, and it qualifies as a reasonable alternative to TEABF 4 for high performance ultracapacitors.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electrical energy storage technologies becomes increasingly important with the growth of portable consumer electronics, increase in hybrid or electric transportation vehicles and the use of renewable energy generation sources (that are intermittent) as they gain higher penetration in the electric grid. A promising technology for energy storage is the EDLC.

EDLC research has focused on improving energy density without compromising power density or cycle life. Aqueous electrolytes typically enable a voltage window of ~1 V, while organic electrolytes allow ~3–3.5 V [1]. Using organic electrolytes and especially ionic liquids (IL) is preferred for high energy density applications [2], since the energy density is proportional to square of voltage window. Other desired characteristics of EDLC electrolytes are high conductivity, wide operating temperature range, large voltage window, and good stability during charge–discharge cycles and low viscosity.

Fused salts with melting points (MP) below 100 °C are typically referred to as ionic liquids, and compounds with MP at or below room temperature are called room temperature ionic liquids (RTILs). RTIL’s have attractive properties as mentioned above, and low conductivity is their only drawback [3]. Many aromatic and aliphatic cations such as pyridinium, imidazolium, pyrrolidinium, tetralkyl ammonium [R 4N] +, sulfonium [R 3S] +, [4,5] form IL and have previously been investigated for EDLC applications. Aromatic quaternary ammonium salts [6] typically have low cathodic stability, while it is higher in aliphatic counterparts; however, most of them are RTILs due to their relatively short alkyl chains. So far, very few ILs (e.g. aliphatic quaternary ammonium salt such as N, N-diethyl-N-(2-methoxyethyl)-N-methylammonium tetrafluoroborate (DEME) with BF 4 as an anion), have been commercialized despite their higher conductivity and wider decomposition potential as compared to aromatic IL such as 1-ethyl-3-methylimidazolium (EMI) BF 4 [7].

Spiro quaternary ammonium salts have low viscosity, and are chemically and electrochemically stable [8,9]. This is the first investigation of oxygen containing spiro ammonium salt, OPBF 4 for room temperature EDLC applications. OPBF 4 was dissolved in AN, and was compared with TEABF 4 in AN. Cyclic voltammetry was used to estimate the electrolyte breakdown potential.

2. Experimental

2.1. Materials

Commercially available activated carbon electrodes (~130 μm), with carbon layer (~100 μm) attached to an aluminum (Al) current collector (~30 μm) was used together with a commercially available ~24 μm thick PTFE separator to fabricate the bag cells.
Ionic liquid was synthesized in-house and dried under vacuum. Table 1 shows the ionic structure of OPBF$_4$ and TEABF$_4$. Anhydrous acetonitrile, 99.99% pure (Sigma Aldrich) was used as the solvent to make multiple molarity solutions.

2.2. Synthesis of OPBF$_4$

Pyrrolidine (28.45 g, 0.40 mol) was added to a mixture of Paraformaldehyde (12.01 g, 0.40 mol), Et$_2$O (150 mL), and 2-chloroethanol (32.20 g, 0.40 mol), and mildly refluxed overnight which led to layer separation. The bottom layer was dissolved in H$_2$O and subsequently filtered. The filtrate was washed with CH$_2$Cl$_2$ and the aqueous layer evaporated, yielding a crude chloride salt, which was subsequently converted to BF$_4$ salt by adding 50% HBF$_4$ and MeOH followed by evaporation [11].

2.3. Fabrication of bag cell

Two pieces of electrodes (2 x 2 cm$^2$) and one piece of separator (2.5 x 2.5 cm$^2$) dried in a vacuum oven at 120 °C for 48 h. OPBF$_4$ salt was dissolved in AN to make 0.2 M, 1 M, 2 M, and 3 M solutions, and TEABF$_4$ was dissolved to make 1 M and 1.5 M solutions. Both the electrodes and separator were soaked in electrolyte for 24 h in the glove box, and the electrode–electrolyte assembly sealed inside a metalized polymer bag. The bag was filled with 0.3 ml of electrolyte, and heat sealed. Three bag cells were prepared for each electrolyte. Prior to testing, the bag cells were clamped under low pressure (<5 lbs) using a C-clamp to reduce the equivalent series resistance (ESR).

2.4. Measurements

Radiometer™ was used to measure conductivity. The breakdown potential of the electrolytes was measured using a three-electrode half-cell using a glassy carbon-working electrode, platinum wire counter electrode, and silver wire as quasi reference electrode. The voltage window was determined from linear voltammetry technique using a PARSTAT 2273A potentiostat.

The capacitance and breakdown potentials were measured in bag cell using cyclic voltammetry (CV) technique. The CV scans were performed between 0 and 1.0, 1.5, 2, 2.5, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0 V at a scan rate of 5 mV/s.

3. Results and discussion

3.1. Conductivity study

The conductivity (Y-axis- left) of ionic liquids OPBF$_4$ (0.2 M, 1 M, 1.5 M, 2 M, 2.5 M, 3 M) and TEABF$_4$ (1 M, 1.5 M) dissolved in AN is
showed in Fig. 1. Higher solubility of OPBF₄ enables higher molar concentration of 3 M, versus 1.5 M for TEABF₄. OPBF₄ has lower conductivity than TEABF₄. The conductivity of OPBF₄ increases up to 2 M and then decreases due to increase in viscosity. Similar behavior was observed by Lewandowski [12] in N-Methyl-N-propylpiperidinium bis (trifluoromethanesulphonyl) imide in AN.

3.2. Half-cell measurements

Fig. 1 shows the plot of electrolyte breakdown potential (Y-axis-right) for OPBF₄ and TEABF₄. The potential was scanned from 0 to +5 V and 0 to −5 V, respectively. OPBF₄ exhibits a higher voltage window than TEABF₄, although no clear correlation exists between breakdown potential and concentration. OPBF₄ in AN was previously shown to have a higher voltage window than EMIBF₄ dissolved in PC, however it was lower than DEMEBF₄ in PC [13].

3.3. Bag cell study

CVs of 2 M OPBF₄ is shown in Fig. 2 (left) at various potential range. The peak at the top right of the CV curve indicate occurrence of irreversible redox reactions. The reversibility factor or Faradaic ratio (R) was calculated in the 8th cycle of each scan in order to quantify the electrolyte breakdown (decomposition) potential

\[ R = \left( \frac{|Q_{\text{charge}}|}{|Q_{\text{discharge}}|} \right) - 1 \]

\( Q_{\text{charge}} \) is the charge build up during charging, and \( Q_{\text{discharge}} \) is the charge consumed during discharge. Ideally, \( R = 0 \) indicates absence of redox reactions. Typically, \( R \geq 0.1 \) indicates excessive irreversible redox reactions. Decomposition potential variation was observed in different electrolytes, and was attributed to dependence of electrolyte properties on operating pH, and the thermodynamic stability of various electrolyte species [14].

The performance of the two electrolytes are almost similar up to an optimum concentration (e.g., from 1–2 M) and then found to drop off at higher concentrations. A minimum concentration is required in the electrolyte to supply ions needed for the charge/discharge process. We investigated a low 0.2 M concentration of OPBF₄ to highlight ion starvation effects, and their prominence at higher potentials (Fig. 2-right). Zheng et al [15] also observed a similar effect of concentration in TEABF₄/PC.

The breakdown potentials (\( R = 0.1 \)) for each electrolyte is shown in Fig. 3 (Y-axis-left). The decomposition potential for TEABF₄ (1 M and 1.5 M) was observed around 3.9 V, which was slightly higher than for OPBF₄ (1 M and 2 M) at 3.7 V. The breakdown potential reduces to 3.5 V at 3 M concentration, which is most likely due to ion pairing effect.

As expected, the breakdown potentials were lower when measured with activated carbon (i.e. the bag cell) than when measured using glassy carbon (i.e. the half-cell). The highly polished glassy carbon has fewer surface defects that can potentially lead to breakdown when compared to activated carbon.

Fig. 3 (Y-axis-right) shows the capacitance at various concentrations of TEABF₄ and OPBF₄. OPBF₄ system exhibits 10% higher specific capacitance at 3 V as compared to TEABF₄. The compact nature of the OP cation (Table 1) facilitates easy access to smaller pores, thus leading to higher surface area utilization. The lower decomposition potential in OPBF₄ system in a bag cell is due to larger degree of interaction with more surface functionalities of carbon. Reduction in capacitance at high concentration may be due to pairing of ions that would prevent them from accessing the pores [16].

4. Conclusion

A novel oxygen containing spiro ammonium salt, OPBF₄ was synthesized using the haloalcohol and haloacetal synthesis route. Characteristics of OPBF₄ including potential window, conductivity, capacitance, and concentration were compared with commercially available TEABF₄. OPBF₄ (1–3 M) had higher voltage window ~ 5 V, as compared to TEABF₄ (1–1.5 M) which was ~4.5–4.6 V. The compact nature of OP cation led to 10% higher specific capacitance in OPBF₄ as compared with TEABF₄ at 3 V. However, this was also responsible for lower electrode breakdown potential in OPBF₄ due to the reaction between OPBF₄ and functionalities in activated carbon electrode. Thus, OPBF₄ is a potential substitute for TEABF₄.

For future investigations, we propose to study both the OPBF₄ and TEABF₄ salts using in situ Raman spectroelectrochemistry, in order to evaluate the electrode-electrolyte interaction between the two compounds.

References