

# Novel Chemically Synthesized Polyaniline Electrodes Containing a Fluoroboric Acid Dopant for Supercapacitors

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**ABSTRACT:** The performance of chemically synthesized dual-acid-doped polyaniline (PANI) electrode material was investigated for supercapacitors for the first time. Three different grades of PANI-containing fluoroboric acid (HBF<sub>4</sub>) as one of the dopants were prepared by a chemical polymerization method. PANI-dodecylhydrogen sulfate-HBF<sub>4</sub> salt was synthesized by an emulsion polymerization pathway. A PANI-HBF<sub>4</sub>-sodium tetrafluoroborate composite and PANI-HBF<sub>4</sub> salt were prepared from different modifications of dopants by a dedoping-redoping process. Capacitative behaviors of the three grades of PANI electrode materials were investigated. Among the three differ-

ent grades of PANI, PANI-HBF<sub>4</sub> electrode showed the best performance in terms of conductivity ( $2.3 \times 10^{-1}$  S/cm), specific capacitance of the supercapacitor (140 F/g), specific energy (9.6 W h/kg), and specific power (58.8 W/kg). An increase in the capacitance of PANI-HBF<sub>4</sub> was achieved, which identified the significant contribution of the dedoping-redoping processes in the PANI system for supercapacitors. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1887–1892, 2008

**Key words:** conducting polymers; electrochemistry; emulsion polymerization

## INTRODUCTION

Supercapacitors are an important device in energy storage and conversion systems. These devices attract significant attention because of their promising applications in high-pulse power devices of energy storage systems. The capacitance of an electrochemical capacitor arises mainly from the redox reaction on/with the electrode materials.<sup>1,2</sup> Transition metal oxides or conducting polymers can be used as electrode materials for the redox process in a supercapacitor.<sup>3</sup> From an economic point of view, the conducting polymer is generally available at a significantly lower cost compared to the metal-oxide-based supercapacitor. Among the conducting polymers, polyaniline (PANI) is representative because of its environmental stability and controllable electrical conductivity in the doped state; it can also be doped and dedoped to a high charge density. Hence, it is considered an active material in redox pseudocapacitors.<sup>4,5</sup>

PANI synthesized with an electrochemical method has already been investigated with regard to its performance as an electrode material for supercapaci-

tors.<sup>6–8</sup> The investigation of PANI synthesized through chemical methods has been reported in the literature.<sup>9–11</sup> The electrochemical method has two disadvantages compared with the chemical polymerization method. One is that the electrochemical method is limited in terms of the mass production of composite electrodes. The other disadvantage is that the electrochemical method is not suitable for the preparation of controllable polymer films with thicknesses above 100  $\mu\text{m}$ , although it is suitable for the preparation of very thin polymer films.

Recently, many attempts have been made to use chemically synthesized conducting PANI as an electrode material in supercapacitors. Ryu et al.<sup>15</sup> synthesized PANI electrode materials such as polyaniline-lithium hexafluorophosphate (PANI-LiPF<sub>6</sub>), PANI-HCl, and PANI-dimethyl sulfate and used PANI with polymer electrolyte<sup>11–14</sup> and with tetraethyl ammonium tetrafluoroborate (Et<sub>4</sub>NBF<sub>4</sub>) liquid electrolyte. The specific capacitance of a capacitor with a polymer electrolyte and a liquid electrolyte was found to be 80 and 100 F/g, respectively. A hybrid type supercapacitor was made by Park et al.<sup>9</sup> with conducting *p*-dopable PANI as the positive electrode material and activated carbon with a high specific surface area as the negative electrode material instead of *n*-dopable conducting polymer. The specific capacitance of the electrode material was 380 F/g. Khomenko et al.<sup>10</sup> focused their capacitance study on the combination of PANI with multiwalled carbon nanotube electrode material. The specific

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capacitance of the capacitor with a PANI/multi-walled carbon nanotube composite electrode was achieved up to 344 F/g. As far as the electrolyte is concerned, the conductivity of the aqueous electrolyte solution is generally higher than that of the organic and solid electrolytes. This is the advantage that the use of aqueous electrolytes because the conductance of the electrolyte relates closely to the equivalent series resistance of the capacitor.

In recent years, emulsion and microemulsion polymerization of aniline have come to the forefront. Emulsion polymerization methods have several distinct advantages. The physical state of the emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than in bulk polymerization. The product of the emulsion polymerization can, in many instances, be used directly without further separations. High molecular weights and high reaction rates can be simultaneously attained by these methods.<sup>16,17</sup>

We prepared soluble PANI salts with cheaper mineral acids by an emulsion polymerization pathway.<sup>18</sup> Recently, we reported the preparation of soluble PANI salt with fluoroboric acid (HBF<sub>4</sub>) by the emulsion polymerization pathway and used it as a recyclable catalyst in organic transformations.<sup>19</sup>

To elucidate the effect of as-synthesized PANI salt containing dual dopants and PANI salt prepared by the dedoping–redoping process on the performance of supercapacitors, in this study, we studied the electrochemical behavior of dual-acid-doped PANI salt containing HBF<sub>4</sub> and dodecylhydrogen sulfate (DHS) prepared by the emulsion polymerization pathway and PANI–HBF<sub>4</sub>·NaBF<sub>4</sub> (NaBF<sub>4</sub> – refers to sodium fluoroborate) and PANI–HBF<sub>4</sub> prepared by the dedoping–redoping process with HBF<sub>4</sub>. As far we know, we carried out the study of the electroactivity of PANI electrode materials containing HBF<sub>4</sub> for supercapacitor application for the first time.

## EXPERIMENTAL

### Synthesis of PANI salts

#### Synthesis of PANI–DHS–HBF<sub>4</sub> salt (method 1)

PANI–DHS–HBF<sub>4</sub> was synthesized via the emulsion polymerization pathway as reported by a procedure reported in an earlier article.<sup>19</sup> In a typical experiment, 3 g of benzoyl peroxide was dissolved in 30 mL of chloroform in 250-mL, round-bottom flask and added to a 20-mL aqueous solution containing 1 g of sodium lauryl sulfate [SLS; or sodium dodecyl sulfate (SDS)]. The reaction mixture was stirred at 40°C. An aqueous solution (50 mL) containing 5.5 mL of HBF<sub>4</sub> and 1 mL of distilled aniline was added dropwise into the initiator–surfactant mixture for 15

min. After this addition, the reaction was continued for 8 h. A chloroform layer containing PANI salt was separated from the aqueous layer and was washed three times with distilled water. PANI salt was precipitated from the chloroform layer with 300 mL of acetone. The precipitate of PANI salt was separated by filtration, washed with water and then acetone and dried at 100°C until a constant mass was reached.

#### Synthesis of the PANI–HBF<sub>4</sub>·NaBF<sub>4</sub> composite (method 2)

The dark green powder of PANI salt (1 g) was treated with 100 mL of 1N NaOH solution. The reaction mixture was kept under stirring for 8 h at ambient temperature. The solution was filtered, washed with distilled water, and dried *in vacuo* at ambient temperature until a constant mass was reached. Then, the dried PANI base was stirred with 100 mL of 1N HBF<sub>4</sub> solution for 8 h. The solution was filtered, washed with distilled water, and dried *in vacuo* at ambient temperature until a constant mass was reached.

#### Synthesis of the PANI–HBF<sub>4</sub> salt (method 3)

The dark green powder of PANI salt (1 g) was treated with 100 mL of 1N NaOH solution. The reaction mixture was kept under stirring for 8 h at ambient temperature. The solution was filtered, washed with distilled water and then methanol, and dried at 100°C until a constant weight was reached. The dried PANI base was again treated with 100 mL of 1N HBF<sub>4</sub> solution for 8 h under constant stirring. The solution was filtered, washed with distilled water, and dried *in vacuo* at ambient temperature until a constant mass was reached.

### Characterization of the electrode materials

The volume resistance of the PANI salt was measured by a two-probe method with a digital multimeter (Keithley, Cleveland, OH, model-2010). The PANI sample was pressed into disks of 16 mm in diameter and about 2 mm in thickness under a pressure of 400 MPa. The resistance was calculated on the basis of the consistent readings of different pressed pellets (the total error involved was <1%).

The electrode material was prepared by the mixing of 20% battery-grade carbon and 80% PANI salt. The electrode material was pelletized on stainless steel mesh (size, 24 μm) by the application of a pressure of 100 kg/cm<sup>2</sup>.

Cyclic voltammetry and galvanostatic charge–discharge experiments were carried out with a WonATech multichannel potentiostat/galvanostat

(WMPG1000, GyeongGi-DO, Korea). Two- and three-electrode cells were used for the measurements. PANI electrodes were tested in a beaker-type three-electrode cell with a PANI working electrode, platinum counterelectrode, and reference electrode (Ag/AgCl) in a 1M H<sub>2</sub>SO<sub>4</sub> electrolyte. The two-electrode cell was built with a polypropylene separator containing 1M H<sub>2</sub>SO<sub>4</sub> solution and PANI electrodes with stainless steel current collectors.

## RESULTS AND DISCUSSION

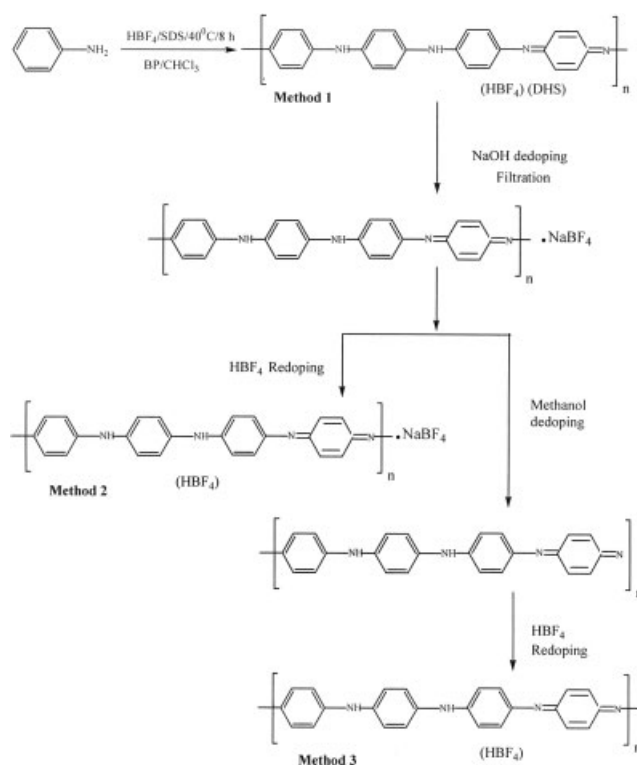
### Synthesis of PANI salts

PANI-DHS-HBF<sub>4</sub> was synthesized via an emulsion polymerization pathway.<sup>19</sup> Aniline was oxidized to the PANI salt by benzoyl peroxide in the presence of SLS (or SDS) and HBF<sub>4</sub>. In the course of polymerization, the surfactant SLS was converted into dodecyl hydrogen sulfate (DHS) under the acidic conditions and incorporated into the PANI system along with HBF<sub>4</sub> (method 1 in Scheme 1).

In this study, in the treatment of PANI-DHS-HBF<sub>4</sub> powder with aqueous sodium hydroxide solution, PANI salt was converted to PANI base, and the dopants, including HBF<sub>4</sub> and DHS, were converted to their corresponding sodium salts, that is, NaBF<sub>4</sub> and SDS, respectively. On filtration, PANI base was obtained along with NaBF<sub>4</sub> (PANI·NaBF<sub>4</sub> composite) because NaBF<sub>4</sub> was not soluble in aqueous sodium hydroxide solution. In method 2, the PANI·NaBF<sub>4</sub> composite was redoped with 1N HBF<sub>4</sub> to obtain the PANI salt composite (PANI-HBF<sub>4</sub>·NaBF<sub>4</sub>). PANI base was obtained by the treatment of the PANI·NaBF<sub>4</sub> composite in methanol followed by filtration. This PANI was converted to PANI-HBF<sub>4</sub> salt by redoping with HBF<sub>4</sub> (method 3). In this study, no efforts were made to determine the percentage of dopants present in the PANI salts because of the nonavailability of sophisticated equipment.

### Electrical conductivity of PANI salts

The electrical conductivity of a material depends on both the number of charge carriers and their mobility. The electrical conductivity of PANI-DHS-HBF<sub>4</sub>, PANI-HBF<sub>4</sub>·NaBF<sub>4</sub>, and PANI-HBF<sub>4</sub> were found to be  $3.0 \times 10^{-3}$ ,  $1.4 \times 10^{-1}$ , and  $2.3 \times 10^{-1}$  S/cm, respectively. PANI-DHS-HBF<sub>4</sub> showed a lower conductivity due to multiple charge dopants present on the PANI salt. Both DHS and HBF<sub>4</sub> were likely to interact with two or more imine nitrogens, and the resultant crosslinking between charge carriers may have restricted their mobility and led to lower conductivities. The higher conductivity for the PANI-HBF<sub>4</sub> may have been due to the partial conversion



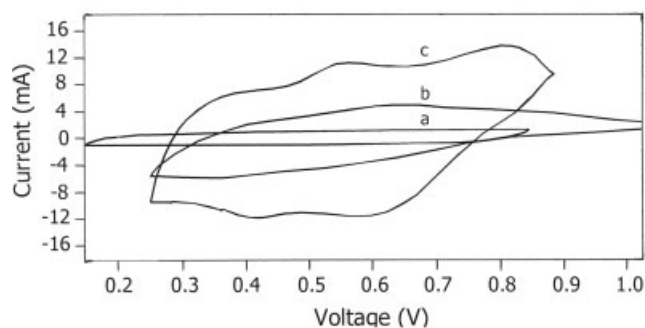
**Scheme 1** Synthesis of different grades of PANI salts containing HBF<sub>4</sub>.

of its tight coil structure to expanded coils during the deprotonation/reprotonation process.<sup>20</sup>

### PANI electrode performance

The electrochemical properties of the PANI electrode materials were studied by cyclic voltammetry in 1M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Typical cyclic voltammograms (CVs) of the electrode materials prepared by three different methods scanned in the voltage range of 0.2–0.8 V at a scanning rate of 5 mV/s are shown in Figure 1.

The CV curves of the PANI electrode showed a pseudocapacitive current, which arose mainly from the redox transition of the PANI chain. The charges on the positive sweep were approximately equal to that on the corresponding negative sweep, which revealed the good electrochemical reversibility of the redox transition of PANI in acid medium. The specific capacitance value (*C*) was obtained from the CV curves according to the equation  $C = i/sm$ , where *i* is the average current, *s* is the potential sweep rate, and *m* is the mass of active material. The specific capacitance values calculated from the voltammogram for PANI-DHS-HBF<sub>4</sub>, PANI-HBF<sub>4</sub>·NaBF<sub>4</sub>, and PANI-HBF<sub>4</sub> were found to be 24, 119, and 301 F/g, respectively. This result means that the ion diffusion for charge compensation during the redox reaction

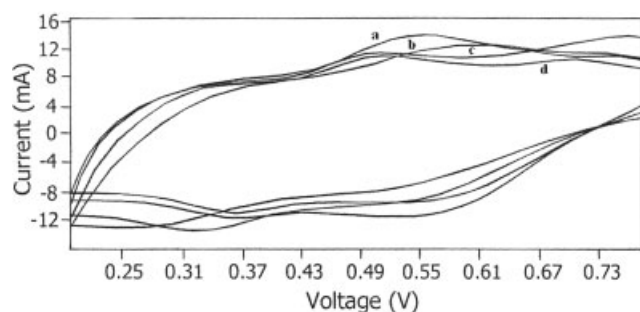


**Figure 1** CV (three-electrode cell) of (a) PANI-DHS-HBF<sub>4</sub>, (b) PANI-HBF<sub>4</sub>·NaBF<sub>4</sub> composite, and (c) PANI-HBF<sub>4</sub> electrode (mass of composite, 8.5 mg; electrolyte, 1 mol/L H<sub>2</sub>SO<sub>4</sub>; scanning rate, 5 mV/s).

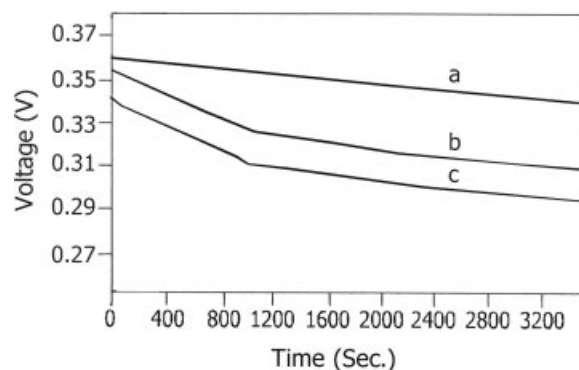
was much faster in the PANI-HBF<sub>4</sub> salt prepared by method 3 than the PANI materials prepared by either method 2 or method 1.

Cyclic voltammetry of the electrode material of higher capacitance (PANI-HBF<sub>4</sub>) at various scanning rates are shown in Figure 2. The data demonstrated that the electrodes were stable in the potential range and that the good shape of the CV was preserved up to the highest scanning rates. This result implies the existence of favorable conduction channels that allowed cations and anions enter and leave the polymer easily.

The fall in voltage during discharge at various current densities for PANI-HBF<sub>4</sub> are shown in Figure 3. The voltage of the electrode was more stable at 2 mA compared to those at 5 and 7 mA. As the current density increased, the voltage rapidly decreased, and the capacitance of the capacitor decreased. A similar behavior was observed for the PANI-DHS-HBF<sub>4</sub> and PANI-HBF<sub>4</sub>·NaBF<sub>4</sub> electrode materials. As the current density increased, the time required to attain the cut-off voltage decreased, and this probably affected the double-layer formation



**Figure 2** CV (three-electrode cell) of PANI-HBF<sub>4</sub> salt (mass of composite electrode, 8.5 mg; electrolyte, 1 mol/L H<sub>2</sub>SO<sub>4</sub>) at scanning rates of (a) 5, (b) 10, (c) 25, and (d) 50 mV/s.



**Figure 3** Galvanostatic discharge curve (three-electrode cell) of a PANI-HBF<sub>4</sub> electrode at (a) 2, (b) 5, and (c) 7 mA.

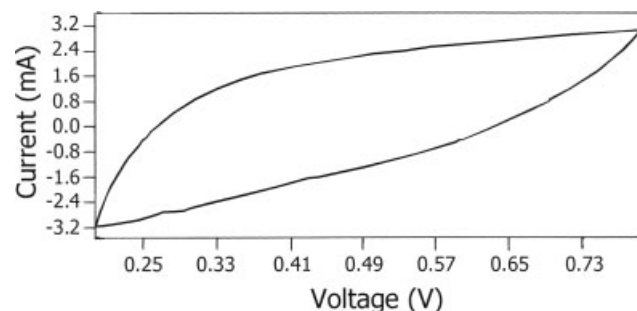
and led to a decrease in capacitance. Similar behavior was observed for a PMMA-PAN-gel-LiClO<sub>4</sub> electrolyte by Liu and Osaka.<sup>21</sup>

## Electrochemical cell

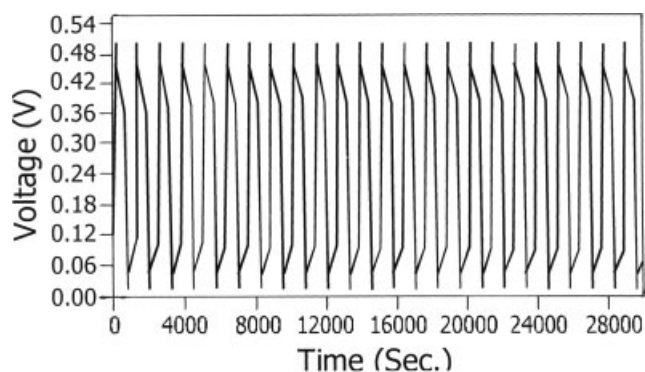
### Cyclic voltammetric studies

Electrochemical cells were constructed with the PANI materials prepared by three different methods. PANI symmetric electrochemical cells were constructed with a polypropylene separator by sandwich-type construction.

As a representative case, cyclic voltammetry of the cell constructed with PANI-HBF<sub>4</sub> is shown in Figure 4. The figure shows that the electrode was stable within the potential range employed and that peaks due to faradic current were not observed for the capacitor cell. The capacitance of the materials obtained for PANI-DHS-HBF<sub>4</sub>, PANI-DHS·NaBF<sub>4</sub>, and PANI-HBF<sub>4</sub> were 23, 96, and 145 F/g, respectively. The PANI-HBF<sub>4</sub> electrode material showed a higher capacitance than other two materials, which



**Figure 4** CV (two-electrode cell) of a (PANI-HBF<sub>4</sub>)-(PANI-HBF<sub>4</sub>) supercapacitor (mass of each electrode, 8.5 mg; electrolyte, 1 mol/L H<sub>2</sub>SO<sub>4</sub>; scanning rate, 5 mV/s).



**Figure 5** Galvanostatic charge–discharge of a symmetric capacitor based on a PANI–HBF<sub>4</sub> electrode (two-electrode cell; current, 2 mA; mass of each electrode, 8.5 mg).

may have been due to the contribution of the fast faradaic pseudocapacitance of PANI.

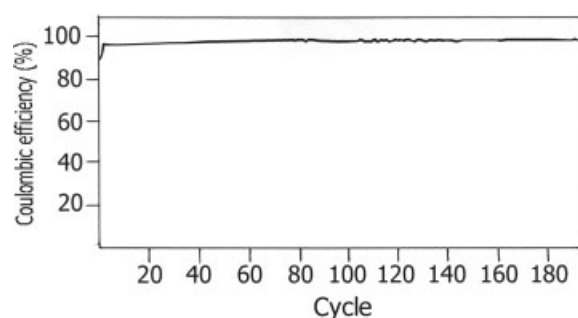
#### Constant charge–discharge characteristics

To illustrate the practical performance of the resulting electrode prepared for supercapacitors, constant current charge–discharge cycling (200 cycles) was performed for PANI–DHS–HBF<sub>4</sub>, PANI–HBF<sub>4</sub>·NaBF<sub>4</sub>, and PANI–HBF<sub>4</sub> supercapacitor cells. As a representative system, constant current charge–discharge cycling (24 cycles) of the PANI–HBF<sub>4</sub> supercapacitor is given in Figure 5.

The specific discharge capacitance, specific energy, and specific power of the supercapacitors were calculated, and the results are given in Table I.

Among the three PANI salts, the PANI–HBF<sub>4</sub> electrode showed the best electrochemical performance, that is, higher specific capacitance (301 F/g) for the electrode material from CV measurement (140 F/g for the supercapacitor), specific energy (9.6 W h/kg), and specific power (58.8 W/kg). This result may have been due to the formation of an open structure from a tight coil structure when a bulkier group (DHS) was replaced by the HBF<sub>4</sub> group during the dedoping–redoping process, which profoundly increased the mobility of the charge carriers from the electrode site to the electrolyte.

In this study, in general, better electrochemical performance was obtained for PANI–HBF<sub>4</sub>; for example, the specific capacitance of the PANI–HBF<sub>4</sub>



**Figure 6** Coulombic efficiency of a PANI–HBF<sub>4</sub> supercapacitor.

supercapacitor showed a higher specific capacitance value (140 F/g) when compared to conductive paste<sup>11</sup> and carbon powder.<sup>9</sup> However, it was lower compared to a high-cost, low-volume multiwalled polymer/nanotube composite electrode.<sup>10</sup>

Coulombic efficiency ( $\mu$ ) of the capacitor was calculated with the formula  $\mu = (t_D/t_C) \times 100$ , where  $t_D$  and  $t_C$  are the discharge and charge times, respectively. Coulombic efficiency of the PANI–HBF<sub>4</sub> supercapacitor is shown in Figure 6, which was obtained from the galvanostatic charge–discharge experiment at a constant current of 2 mA between 0 and 0.5 V for 200 cycles (Fig. 5). The results reveal that the supercapacitor had very stable coulombic efficiencies, about 99%. Similarly, a 99% coulombic efficiency over 200 cycles was obtained for the PANI–DHS–HBF<sub>4</sub> and PANI–HBF<sub>4</sub>·NaBF<sub>4</sub> supercapacitors.

## CONCLUSIONS

In this study, PANI salt containing HBF<sub>4</sub> dopant was successfully used as an electrode material for supercapacitors. Among the three PANI salts, PANI–HBF<sub>4</sub> electrode showed the best electrochemical performance, that is, a higher specific capacitance (301 F/g) for electrode material (140 F/g) for supercapacitors, specific energy (9.6 W h/kg), and specific power (58.8 W/kg). Also, this electrode material had good cycling performance and retained 99% of its initial capacity over 200 cycles. The importance of dedoping and redoping processes in PANI systems was established.

**TABLE I**  
Electrochemical Parameters of the PANI Capacitors

PANI system	Current (mA)	Discharge charge efficiency	Discharge capacitance (F/g)	Specific energy (W h/kg)	Specific power (W/kg)
PANI–DHS–HBF <sub>4</sub>	1.25	99	19	1.22	36.7
PANI–HBF <sub>4</sub> ·NaBF <sub>4</sub>	2	99	88	4.74	58.8
PANI–HBF <sub>4</sub>	2	99	140	9.6	58.8

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