Advanced p- and n-Dopable Polymer Supercapacitors


*Crosslink, 950 Bolger Ct., St. Louis, MO, USA, ykim@crosslinkusa.com

ABSTRACT

Metallically conductive PAC 1003, an inherently conductive polymer product of Crosslink, has been developed to have remarkably high electrical conductivity (>1000 S/cm) which can be applied to advanced polymer supercapacitor design. The metallic conductivity of the polymer allows for supercapacitors with low equivalent resistance and high capacitance via efficient redox electrochemical activity. The use of n-dopable polymers can enhance the function of the supercapacitor to achieve higher energy and power densities. In parallel efforts, device structures with strategic technical features including nano-structured interfacial layers, leakage free device design and bipolar device designs have proven to give promising device performance.

Keywords: energy, supercapacitor, polymer, nano, conductivity

1 INTRODUCTION

Inherently conductive polymers (ICPs) that have a broad range of electrical and electrochemical conductivities have attracted a lot of interest due to their application in opto-electronic and electronic devices including solar cells,1 field effect transistors (FETs), light emitting diodes (LEDs), electrochromic devices (ECDs), non-volatile memories (NVMs), fuel cells, batteries and supercapacitors (SCs). In particular, ICP based SCs can provide promising features including high redox capacitive performance along with light weight and conformal characteristics.

Polyaniline is one of the representative polymers for the application area of energy storage, especially in the ICP-SCs since it has proven to show remarkable electrical and electrochemical properties. The properties can be modulated by electrochemical doping processes.2 The efficient and fast energy charge–discharge capabilities of the polyaniline is another property that can be utilized in the ICP-SC. For this application, Crosslink has developed a PAC 1003 electrode which is a doped polyaniline layer having remarkable electrical conductivity of up to 1000 S/cm.

Figure 1 shows a schematic illustration of possible capacitor combinations utilizing polymer electrodes that can be either p- and/or n- dopable. As shown in Figure 2, since energy is proportional to the square of clamping voltage, it is beneficial to build type III and IV SCs that can operate at higher clamping voltages. In this article, poly(bisethylenedioxythiophene-benzobisthiazole) [poly(BEDOT-BBT)] has been considered as the n-dopable polymer.
2 EXPERIMENTALS

2.1 Materials and Procedures

Polyaniline (PAC 1003, Crosslink) was treated with dopants and through the application of novel, proprietary treatment steps, various improvements in electrical and electrochemical properties have been achieved. The polyaniline electrode was coated on well-cleaned stainless steel substrates that were pre-cleaned and pre-treated. The n-dopable monomer (BEDOT-BBT) was synthesized and characterized following the reported procedure and electrochemically polymerized on a charge collector. Ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI-Im, Covalent Associates) was used as the electrolyte with a PTFE separator (GORE) unless otherwise specified. Coin cell parts and a crimer were purchased from NRC-Canada.

2.2 Device Fabrication

The coin cell was assembled for the testing of the polymer electrodes in inert gas conditions using a glove box (m-Braun). Figure 3 shows a schematic illustration of the coin cell. A photo of assembled coin cell is shown in Figure 4. Figure 5 shows a type IV supercapacitor.

2.3 Characterization

Absorption spectra was obtained using UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600). 4-probe DC electrical conductivity measurement was performed using gold contacts. Electrochemical analyses including cyclic voltammetry and chronopotentiometry were conducted using potentiostats (Gamry or CH instruments). Capacitance and the other characteristics were obtained from supercapacitor tester (Arbin instrument).

3 RESULTS AND DISCUSSION

Remarkably high DC electrical conductivity (ca. 1000 S/cm) was measured from the polyaniline film that was developed. This extremely high conductivity was achieved through the application of proprietary doping processes. The analogous polyaniline layer was observed to have
dramatic increase in absorption in the near IR spectral region, indicating molecular rearrangement for enhancing photo-induced charge carrier transfer. Direct visualization for the merit of the higher electrical conductivity can be seen in the CV curve shown in figure 6. The curves exhibit the enhanced charge transport through the well-aligned polyaniline molecules.

![Image](image1.png)

Figure 6: CV curves of polyaniline films. Scan rate: 10 mV/s

As seen in Table 1, the electrical conductivity was observed to have positive contribution for application to high performing SCs. For this test, type I coin cells were fabricated applying identical polymer films on both positive and negative electrodes.

![Image](image2.png)

Table 1: Electrical conductivity of polyaniline film and the characteristics of corresponding SC.

<table>
<thead>
<tr>
<th>Electrical Conductivity (S/cm)</th>
<th>Specific Capacitance (F/g)</th>
<th>Specific Energy (Wh/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.2</td>
<td>0.38</td>
</tr>
<tr>
<td>250</td>
<td>6.13</td>
<td>1.92</td>
</tr>
<tr>
<td>1000</td>
<td>12.48</td>
<td>3.39</td>
</tr>
</tbody>
</table>

The use of the n-dopable polymer electrode along with this novel polyaniline electrode was observed to have a synergy effect. Figure 7 shows typical specific energy and specific power of type IV coin cells.

Parallel efforts have been made for achieving advanced device geometry including a polymer-gel SC and a bipolar SC. Figure 8 shows typical gel electrolytes for use in a leakage free SC. A bipolar SC was fabricated using 4 ft. long electrodes and is depicted in figure 9.
4 CONCLUSION

The inherently conductive polymer, PAC 1003, has proven its superb function in advanced energy storage devices. In particular, the high electrical conductivity of the PAC 1003 layer was observed to have beneficial effect on charge transport translating to enhanced capacitance in supercapacitors. The use of an n-dopable polymer into this SC was found to have synergistic effects on achieving increased energy and power densities. Stacks and modules of the SCs were found to show promise in achieving enhanced electrochemical characteristics. Advanced bipolar SCs were fabricated and found to be promising.

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REFERENCES

