

# Electrochemical Capacitor Composed of Doped Polyaniline and Polymer Electrolyte Membrane

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**ABSTRACT:** We prepared polyaniline doped with  $\text{LiPF}_6$  and HCl, respectively, using chemical methods. The electrode composite was attached to both sides of Al mesh, while the polymer electrolyte mixture was spread on a glass plate. Then, the polyaniline-based redox supercapacitor was fabricated using two electrodes and a polymer electrolyte membrane. The electrochemical performance of the redox supercapacitor was investigated by using the charge/dis-

charge method, cyclic voltometry, and impedance spectroscopy. The initial specific capacitance was  $\approx 115$  F/g and it retained  $\approx 90$  F/g even after 5000 cycles. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1300–1304, 2003

**Key words:** conducting polymers; redox polymer; electrochemistry

## INTRODUCTION

Recently there have been many reports on redoxcapacitors (pseudocapacitors). Ruthenium oxide is the best example of the inorganic class of pseudocapacitive materials, and its hydrous form is demonstrated to have a capacitance of  $\approx 720$  F/g.<sup>1</sup> Conducting polymer is also a promising redox supercapacitor material for its fast charge-discharge kinetics, low cost, suitable morphology, and fast doping-undoping process. Among conducting polymers, polyaniline (Pani) has attracted much attention for its environmental stability, controllable electrical conductivity, and easy processability.

Most of the electrochemical supercapacitors are composed of p- and n-dopable polythiophene derivatives.<sup>2</sup> These materials make the preparation of high energy and high power density capacitors possible. Indeed, a recent study on p-dopable polymer has achieved 10 KW/kg power density, with a cell voltage of 0.6 V.<sup>3</sup> In addition, p-dopable polymers are more stable against degradation than n-dopable polymers. Hence, it is clear that investigations dealing with p-dopable polymers are welcome.

Pani synthesized using electrochemical methods was already investigated as the electrode material for redox supercapacitors.<sup>4–6</sup> However, investigation of Pani synthesized through chemical methods has begun.<sup>7–9</sup> Recently, we reported the preparation of lithium salt-doped Pani and its performance in polymer

based redox supercapacitors.<sup>10,11</sup> In this study, we adopted  $\text{LiPF}_6$  or HCl doped Pani powder as the electrode material. Then a Pani-based redox supercapacitor was fabricated by laminating a Pani- $\text{LiPF}_6$  electrode, a polymer electrolyte membrane, and a Pani-HCl electrode. The laminated capacitor has unitary sheet shape, which does not need external support. We investigated the performance of the asymmetrically fabricated redox supercapacitor with various electrochemical measurements.

## EXPERIMENTAL

The synthesis of Pani powder doped with protonic acid and lithium salt, respectively, was already reported elsewhere.<sup>10,12</sup> To identify the doping state of Pani, we measured the electrical conductivity at room temperature. To measure DC conductivity, a four-probe method was used. To eliminate contact resistance, four thin gold wires were attached parallel to the sample surface using graphite glue.

The electrode composite was fabricated by mixing the Pani- $\text{LiPF}_6$  powder, Super P (MMM Carbon Co.), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (KynarFlex 2801, Elf Atochem N.A. Co.) in acetone in a weight ratio of 42 : 28 : 30. The electrode composite of Pani-HCl was also fabricated by the same method but with a weight ratio of 39 : 20 : 35. The mixture slurry was stirred for 72 h at room temperature in a sealed bottle. The viscous slurry was cast on a glass plate using a doctor blade apparatus in a dry room (moisture content less than 0.1 ppm) and dried in a vacuum oven at 50°C for 12 h. To fabricate the electrode, the electrode films were attached to both

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sides of Al mesh (30  $\mu\text{m}$  thick). The total thickness of the electrodes was  $\approx 115 \mu\text{m}$  (Pani-LiPF<sub>6</sub>) and  $\approx 180 \mu\text{m}$  (Pani-HCl). The mass of polymer active material was 1.580 mg/cm<sup>2</sup>.

To prepare polymer electrolyte membrane, PVdF-HFP and fumed silica (Cab-O-Sil TS-530, Cabot Co.) were used. The polymer film was prepared by mixing PVdF-HFP powder and fumed silica in 25 ml of acetone solvent. The mixture was stirred with a magnetic bar for 3 h at 50°C in a sealed bottle, and then vigorously stirred for 24 h at room temperature. The viscous slurry was cast on a clean glass plate using a doctor blade apparatus in a dry room, and dried in a vacuum oven at 70°C for 12 h. The thickness of this polymer electrolyte membrane was  $\approx 30 \mu\text{m}$ . Surface morphologies of the electrode and polymer electrolyte membrane were observed using a scanning electron microscope (Hitachi S800).

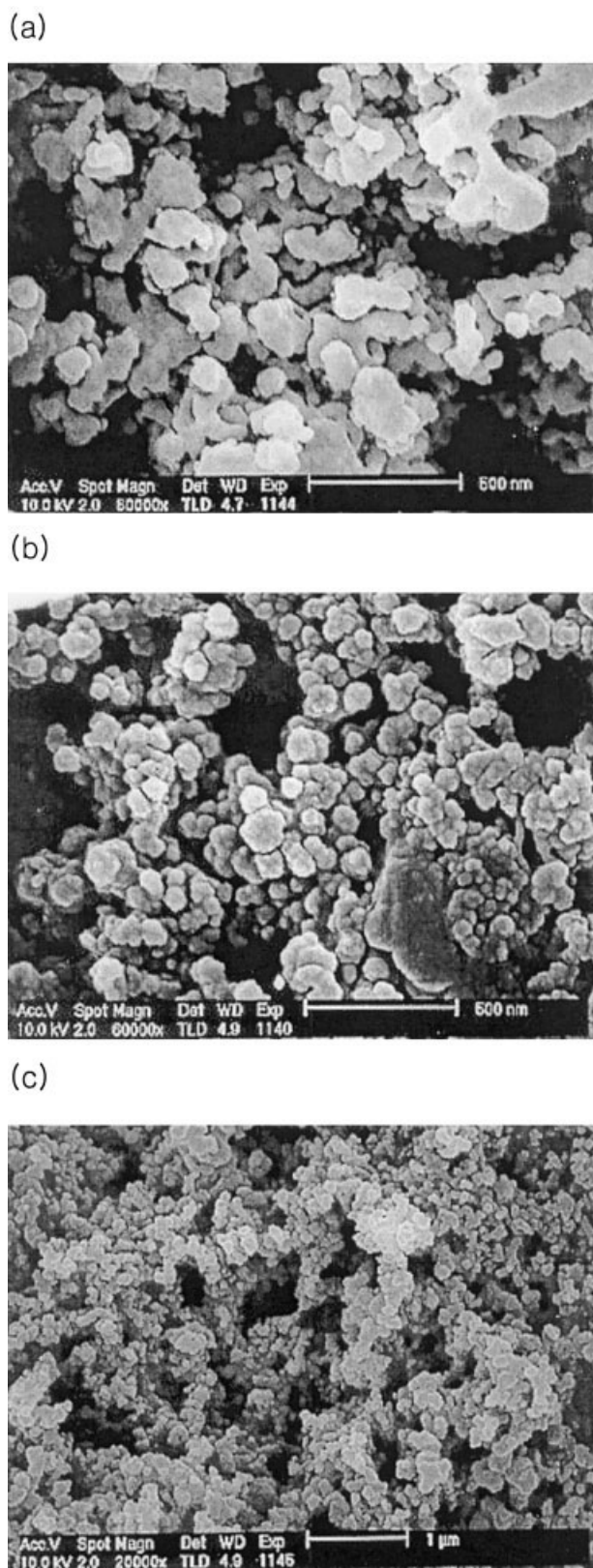
To assemble the redox supercapacitor, we took advantage of the conventional lithium-ion polymer battery fabrication method.<sup>13</sup> The electrochemical capacitor consisted of a Pani-LiPF<sub>6</sub> electrode, a polymer electrolyte membrane, and a Pani-HCl electrode. They were laminated through double roll press under 40 kgf/cm at 120°C. This laminated capacitor (unitary shape) was immersed in 1M Et<sub>4</sub>NBF<sub>4</sub> in acetonitrile. After that, the cell was sealed with an aluminum patch in a dry room.

Cyclic voltammogram was obtained using a MacPile-II potentiostat system at a constant scan rate of 1 mV/sec in the voltage range of -2-2V. Impedance spectroscopy was performed using a frequency response analyzer (FRA, Solatron 1260) in the range of 1MHz-1Hz. The redox supercapacitor was charged and discharged using a Maccor cyler in the voltage range of 1.0-0.01 V with 1.25 mA/cm<sup>2</sup>, 2.50 mA/cm<sup>2</sup>, and 3.75 mA/cm<sup>2</sup> current densities.

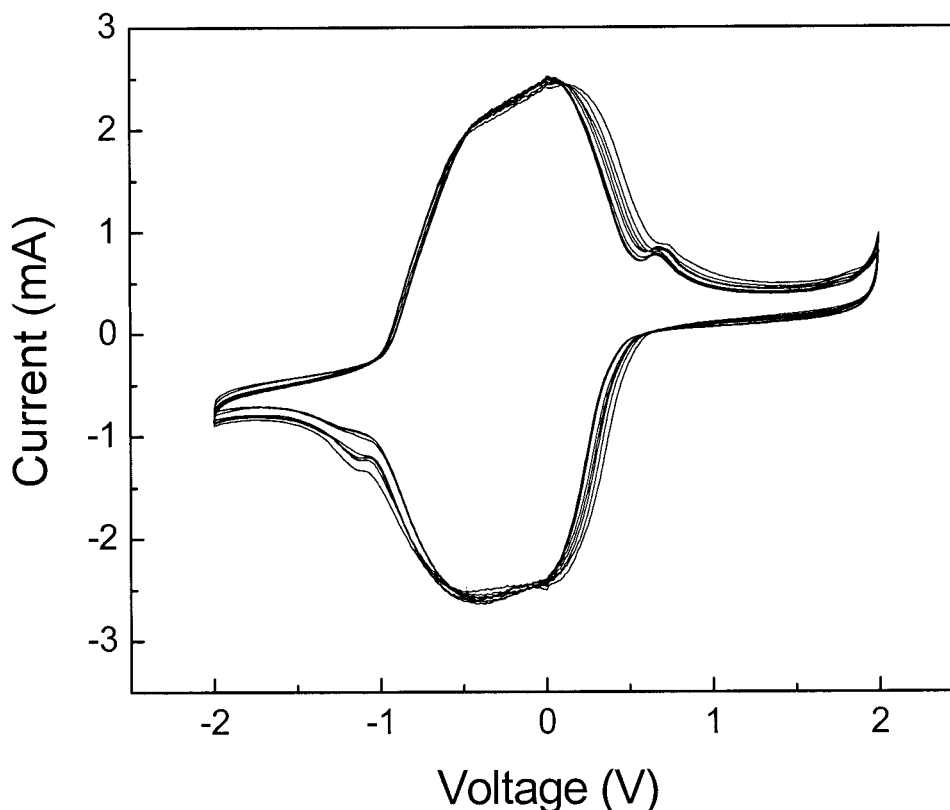
## RESULTS AND DISCUSSION

Pani prepared by the oxidizing method is soluble in organic solvents in a non-conducting state ( $\sigma_{\text{R.T.}} = \approx 10^{-10} \text{ S/cm}$ ). When treated with protonic acid or a Li salt such as HCl or LiPF<sub>6</sub>, it takes a different reaction time. The protonic acid doping occurs within a few minutes, whereas the lithium salt doping is finished only after  $\approx 10$  h. However, the doping process of the two samples is very similar. When Pani is treated with doping agents, an unpaired electron (polaron) is formed at the site of the imine in the quinoid ring and the Li ion bonds to the nitrogen. The polaron formed is delocalized along the polymer backbone due to its conjugated structure, which leads to a conducting state ( $\sigma_{\text{R.T.}} = \sim 10^{-1} \text{ S/cm}$ ).<sup>10</sup>

Figure 1 shows the scanning electron microscope images of Pani-LiPF<sub>6</sub>, the Pani-HCl electrode surface,



**Figure 1** Scanning electron microscope images of (a) Pani-LiPF<sub>6</sub> electrode, (b) Pani-HCl electrode, and (c) polymer electrolyte membrane surface.

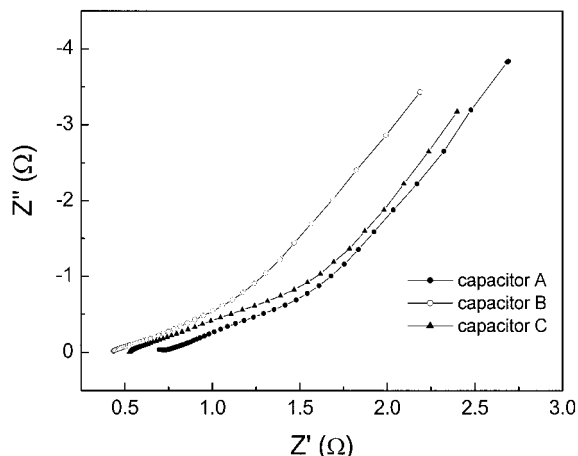


**Figure 2** Cyclic voltammograms of redox supercapacitor composed of Pani-LiPF<sub>6</sub> and Pani-HCl electrodes.

and the polymer electrolyte membrane surface. Figure 1(a,b) shows that the doped Pani are connected to the conductor uniformly. Furthermore, it reveals that the conductor and the pore are homogeneously distributed on the surface of the electrode. Therefore, the contact area between the electrode and electrolyte is broadened, which generates a high capacitance supercapacitor. From pictures of the same magnification, we know that the grain size of HCl doped Pani ( $\approx 90$  nm) is smaller than that of LiPF<sub>6</sub> doped Pani ( $\approx 160$  nm). The size of the well-developed pore is 100–300 nm. The electrical conductivity of the electrode is  $\approx 1.5$  S/cm, and the moisture content is  $\approx 150$  ppm/g. Figure 1(c) shows the highly porous polymer electrolyte. The porous nature might be due to the homogeneously distributed inorganic silica. It is clear that the surface area of the polymer electrolyte film is increased by silica doping, which increases the absorption of the electrolyte solution.<sup>14</sup> In fact, the ionic conductivity of the polymer electrolyte, containing 20% silica, is  $\approx 3 \times 10^{-3}$  S/cm.

Tetraalkylammonium salts have been widely used to support electrolyte salts in nonaqueous solvents for their high solubility, electrolytic conductivity, electrochemical stability, simple preparation, and purification. The oxidation and reduction potential of acetonitrile is  $\approx 3.3$ –2.8 V compared to saturated calomel

electrode (SCE). This potential range is similar to that of propylene carbonate.<sup>15</sup> Therefore, we adopted the salt and solvent as an electrolyte solution. The ionic conductivity of an electrolyte solution containing Et<sub>4</sub>NBF<sub>4</sub> and acetonitrile is  $\approx 70$  mS/cm. This is the highest conductivity of any organic solvent. In order to identify the oxidation/reduction potentials and the electrochemical reaction of the cell, cyclic voltammetry (CV) was performed. Figure 2 shows the cyclic voltammograms of Pani-LiPF<sub>6</sub> and Pani-HCl electrodes. It is clear that the oxidation and reduction peaks are stable with cycling. This proves that the redox reaction occurs with good reversibility in the voltage range of  $-1.2$ – $0.8$  V. Hence, the possible cutoff range is 2.0–0 V. However, if the voltage cutoff range is fixed to 2.0–0.01 V, only a small capacitance appears in the 2.0–1.0 V range and its contribution to the total capacitance is very small. Therefore, the charge/discharge cycle was repeated in the range of 1.0–0.01 V. It is obvious that the large oxidation peak is composed of two peaks. The upper peaks at  $\approx -0.43$  V and  $\approx 0.07$  V corresponded to the oxidation (Li<sup>+</sup>, H<sup>+</sup>, PF<sub>6</sub><sup>-</sup> or Cl<sup>-</sup> doping) and the lower peaks at  $\approx -0.5$  V and  $\approx 0.01$  V correspond to the reduction (Li<sup>+</sup>, H<sup>+</sup>, PF<sub>6</sub><sup>-</sup> or Cl<sup>-</sup> undoping). However, the redox peaks of symmetrically coupled Pani-LiPF<sub>6</sub> redox supercapacitors were composed of two singlet peaks and showed good



**Figure 3** Impedance spectroscopy of redox supercapacitor composed of Pani-LiPF<sub>6</sub> and Pani-HCl electrodes: (A) at a current density of 1.25 mA/cm<sup>2</sup>, (B) at a current density of 2.50 mA/cm<sup>2</sup>, and (C) at a current density of 3.75 mA/cm<sup>2</sup>.

symmetry.<sup>16</sup> From these results, we assumed that the peaks at  $\approx 0.07$  V and 0.01 V in this system can be attributed to the oxidation and reduction of the Pani-LiPF<sub>6</sub> electrode, respectively. The potential difference of redox peaks in this system is  $\approx 0.56$  V. Nevertheless, the area of CV in this system is larger than that of a symmetric system.

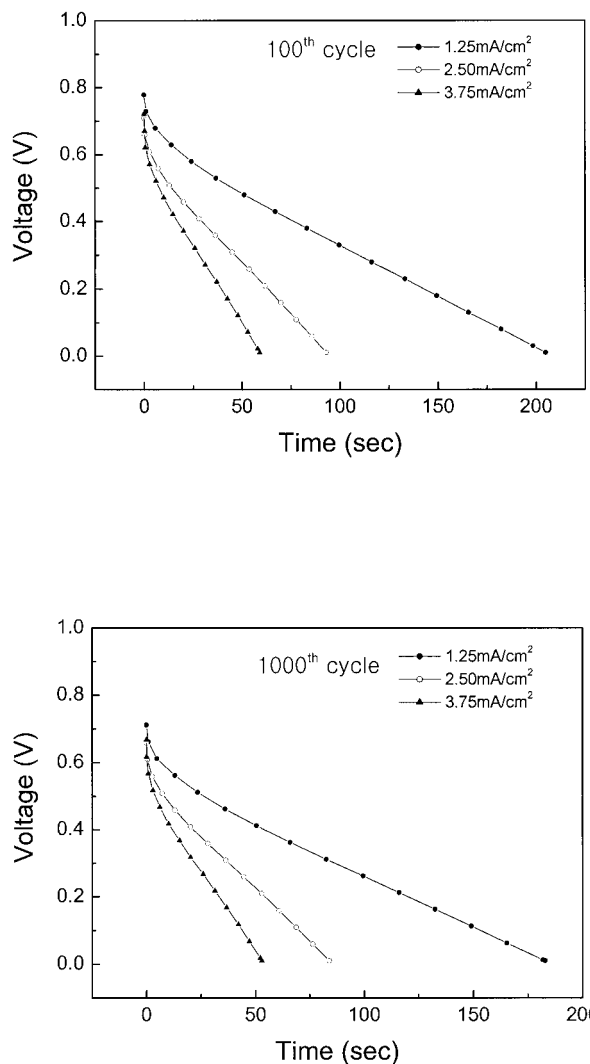
Figure 3 shows impedance spectroscopy of the redox supercapacitor composed of asymmetrically doped Pani and polymer electrolyte membranes. The internal resistances between electrodes are about 68 m $\Omega$  for capacitor A, 43 m $\Omega$  for capacitor B, and 53 m $\Omega$  for capacitor C. The equivalent series resistance (ESR) is 79 m $\Omega$  for capacitor A, 48 m $\Omega$  for capacitor B, and 58 m $\Omega$  for capacitor C at 1 kHz. These values are similar to those for the redox supercapacitor composed of symmetrically doped Pani (Pani-LiPF<sub>6</sub>) and polymer electrolyte membrane. However, the values for the redox supercapacitor composed of symmetrically doped Pani (Pani-LiPF<sub>6</sub>) and porous polyolefin separator are smaller than these.<sup>16</sup>

Figure 4 shows the 100<sup>th</sup> and 1000<sup>th</sup> discharge curves of the redox supercapacitor at different current densities. From these curves, the discharge time is preserved for  $\approx 210$  seconds under the current density of 1.25 mA/cm<sup>2</sup>,  $\approx 90$  seconds under the current density of 2.5 mA/cm<sup>2</sup> and  $\approx 60$  seconds under the current density of 3.75 mA/cm<sup>2</sup>. It is obvious that the capacitance is highly dependent on the current density. In addition, the features of the charge/discharge curve are different from those of electrical double layer capacitor (EDLC). The EDLC generally shows a straight-line, while the polymer redox supercapacitor exhibits a curved feature due to the redox reaction during the charge/discharge process.

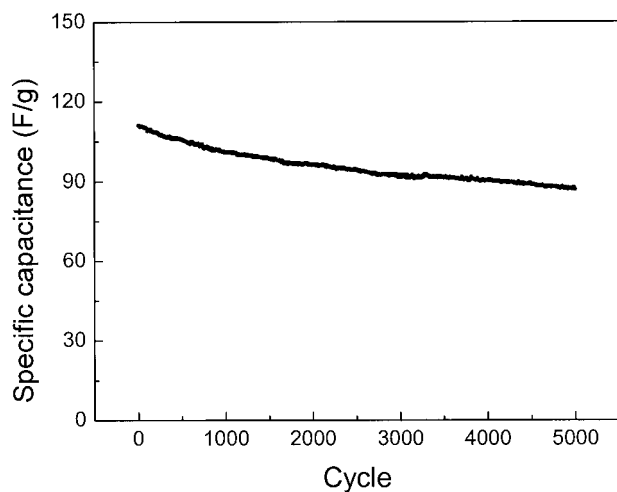
Figure 5 shows the specific discharge capacitance of the above redox supercapacitor after 5,000 cycles. The capacitor showed an initial specific capacitance of  $\approx 115$  F/g, and it retained  $\approx 90$  F/g even after 5000 cycles at a current density of 3.75 mA/cm<sup>2</sup>. The discharge capacitance was decreased gradually with cycling. This value is larger than that of the symmetrically coupled redox supercapacitor.<sup>16</sup>

## CONCLUSION

We prepared Pani-LiPF<sub>6</sub> and Pani-HCl powders chemically. Scanning electron microscope data show that the grain size of HCl doped Pani is smaller than that of LiPF<sub>6</sub> doped Pani. The supercapacitor consists of the Pani-LiPF<sub>6</sub> electrode, a polymer electrolyte membrane, a 1M Et<sub>4</sub>NBF<sub>4</sub> electrolyte solution, and a



**Figure 4** (a) 100<sup>th</sup> and (b) 1000<sup>th</sup> discharge curves for redox supercapacitor composed of Pani-LiPF<sub>6</sub> and Pani-HCl electrodes.



**Figure 5** Cycle life of redox supercapacitor composed of Pani-LiPF<sub>6</sub> and Pani-HCl electrodes at a current density of 3.75 mA/cm<sup>2</sup>.

Pani-HCl electrode. We investigated the performance of the asymmetrically coupled redox supercapacitor using various electrochemical methods. The electrical conductivity of the electrode was  $\approx 1.5$  S/cm, while the ionic conductivity of the polymer electrolyte membrane containing 20% silica was  $\approx 3 \times 10^{-3}$  S/cm. The oxidation and reduction peaks occurred in the range of  $-1.2$ – $0.8$  V with good reversibility. The internal resistances between electrodes and separator were 68 m $\Omega$ , 43 m $\Omega$ , and 53 m $\Omega$ . In addition, both the voltage and the discharge time decreased rapidly with the increase of current density. The initial specific capac-

itance was  $\approx 115$  F/g and it retained  $\approx 90$  F/g even after 5000 cycles.

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