Short communication

Symmetric redox supercapacitor with conducting polyaniline electrodes

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Abstract

Polyaniline doped with HCl (Pani-HCl) and $LiPF_6$ (Pani-$LiPF_6$) are prepared and used as the active electrode material of symmetric redox supercapacitors. The system using Et_4NBF_4 as an electrolyte solution has lower internal resistance and larger specific discharge capacitance, and thus, it is suitable for use in a polyaniline redox supercapacitor. The capacitance of Pani-HCl decreases during ~400 cycles and then becomes constant at ~40 F g^{-1}. On the other hand, the polyaniline electrode doped with lithium salt like $LiPF_6$ shows a specific discharge capacitance of ~107 F g^{-1} initially and ~84 F g^{-1} at 9000 cycles. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Supercapacitors provide higher specific power than batteries and higher specific energy, than conventional dielectric capacitors because of the high capacitance of the electrode materials. Recent interests in supercapacitors is stimulated by their potential applications such as power-storage devices operating in parallel with batteries in hybrid electric and electric vehicles. Many researchers are currently investigating two types of supercapacitors: the electric double-layer capacitor and the redox supercapacitor. The charge-storage mode is different in each type. The capacitance in the double-layer capacitor is electrostatic in origin, i.e. it arises from the separation of electron and ionic charges at the interface between high specific-area carbon electrodes and an aqueous or an organic electrolyte [1]. In the redox supercapacitor, fast Faradaic charge-transfer takes place at the electrode materials, as in a battery, and then produces the so-called redox or pseudo capacitance [2]. Generally, the redox supercapacitor has been proved to have a higher capacitance than the electric double layer capacitor.

Transition metal oxides or conducting polymers can be used as electrode materials for redox or pseudo capacitors. Ruthenium oxide is the best example of the inorganic class of pseudo capacitive materials, and its hydrous form has given a capacitance of ~720 F g^{-1} [3]. Conducting polymers have been regarded as other promising pseudo-capacitive materials. The use of conducting polymer materials for redox supercapacitors has several advantages over other systems. The materials have good intrinsic auto-conductivity and are relatively cheap, so the preparation and fabrication costs would be competitive. In addition, good specific capacitance can be obtained and existing battery-type technology for fabrication procedures may be used. Among them, polyaniline (Pani) has attracted much attention because of higher environmental stability, controllable electrical conductivity, and easy processability [4].

Pani synthesized by an electrochemical method was already investigated in terms of its performance as an electrode material for redox supercapacitors [5–7]. Pani synthesized by a chemical method, however, has been rarely studied and research about Pani doped with lithium ions salts has just started. Chen and Lin [8] have prepared Pani doped with ionic salts such as $LiClO_4$, $LiBF_4$, and $Zn(ClO_4)_2$, and have investigated the structure of materials by using various spectroscopic techniques. Recently, we reported [9] lithium salt-doped Pani samples prepared by immersion of the emeraldine base form of Pani film into electrolyte solutions containing lithium salts. The electrical conductivity, XPS, and EPR were investigated with respect to the doping level. The electrochemical characteristics of Li/Pani doped with lithium salt were also examined to study the electrochemical reaction mechanism during repeated charge–discharge processes [10]. From these results, we know that Pani doped with lithium salt is easily oxidized and reduced by the electrochemical potential in electrolyte solution. In addition, Pani doped with lithium salt has larger discharge capacitance than Pani doped with protonic acid and is suitable to

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use as the electrode material responsible for a redox reaction in a power source device.

In the present work, we have prepared, symmetric redox supercapacitors based on Pani-HCl (polyaniline doped with HCl) and Pani-LiPF$_6$ (polyaniline doped with LiPF$_6$), and have investigated their electrochemical properties associated with charge transfer and charge–discharge characteristics.

2. Experimental

The synthesis and doping with HCl of Pani powder have been reported elsewhere [11]. For the ionic salt doping of Pani powder, ethylene carbonate (EC) and dimethyl carbonate (DMC) (battery grade, Mitsubishi Chemical Co.) as solvents, and LiPF$_6$ (Aldrich) as lithium salt were used. The EB powder was immersed in 1 M LiPF$_6$ solution in EC/DMC (1:1 v/v) for 72 h in a dry room. After that, the doped powder was washed with ethyl ether and dried for 15 h at 60 °C under vacuum.

To identify the doping state of polyaniline, the electrical conductivity was measured at room temperature. To determine dc conductivity, a four-probe method was used. Four thin gold wires (0.1 mm thick and 99.95% pure gold) were attached in parallel on the sample surface by graphite glue (Acheson Electrodag 502) to eliminate contact resistance.

The electrochemical cell consisted of an electrode of Pani polymer powder, a separator of porous polyethylene film, and an electrolyte of 1 M Et$_4$NBF$_4$ or Et$_4$NCF$_3$SO$_3$ in acetonitnle. The powder electrode was prepared by mixing the synthesized Pani, carbon black (Super P, MMM Carbon Co.) as a conducting agent, and polytetrafluoroethylene (Aldrich) as a binder in a weight ratio of 50:40:10. The charge collector (Al foil), electrode, separator/electrolyte solution, electrode, and charge collector were assembled in
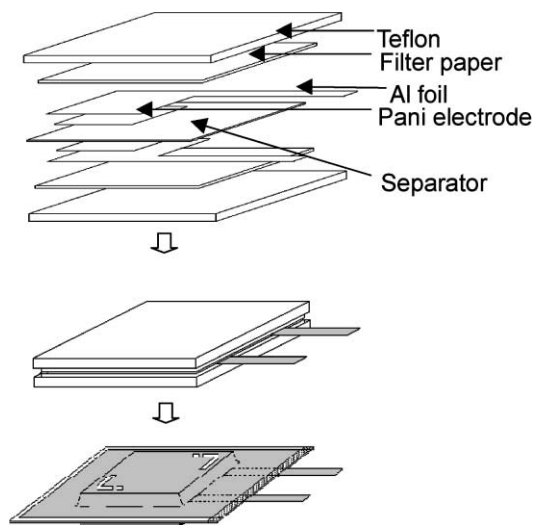
sequence as a sandwich and enveloped in a laminated-aluminum pauch in a dry room (see Fig. 1). A supercapacitor adopting the electrode of conductive carbon (Super P) solely was also prepared (Super P:binder = 90:10 in weight basis) for a blank test to investigate the effect of conductive carbon on the discharge capacitance characteristics. The redox supercapacitor was tested using a galvanostatic charge–discharge cycler in the potential range of 1.0–0.01 or 2.0–0.01 V with varing the current density (0.25 and 1.25 mA cm^{-2}).

Cyclic voltammograms were also obtained using a Mac-Pile-II potentiostat system at a constant scan rate of 1 mV s^{-1} in the range of −2 to 3 V. The electrochemical impedance spectroscopy was performed using a Solatron frequency response analyzer 1260 system in the range 1 MHz to 1 Hz.

3. Results and discussion

The capacitance of conductive carbon (Super P) was determined to investigate whether or not it has an effect on the total capacitance because a large quantity of Super P was measured in the electrode of the redox supercapacitor system examined in this study. Therefore, a conductive carbon electrode was composed of 90% of Super P carbon black and 10% of PTFE binder and 1 M Et$_4$NBF$_4$ in AN as electrolyte solution. The current density and cut-off range were 1.25 mA cm^{-2} and 2.0–0.01 V, respectively. The specific capacitance for the conductive carbon electrode as a function of cycle number is shown in Fig. 2. The capacitance of ∼1.9 F g^{-1} is too small to have any effect on the total capacitance.

The tetraalkylammonium salts have been widely used as supporting electrolyte salts in non-aqueous solvents because of their high solubility, electrolytic conductivity, electrochemical stability, and ease of preparation and purification. The capability of the electrolyte solution in a redox supercapacitor composed of Pani-HCl electrodes was also

Fig. 1. Components and assembling sequence of redox supercapacitor using conducting polymers as electrodes.
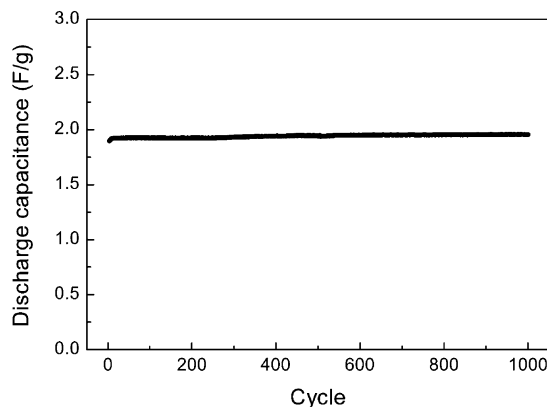

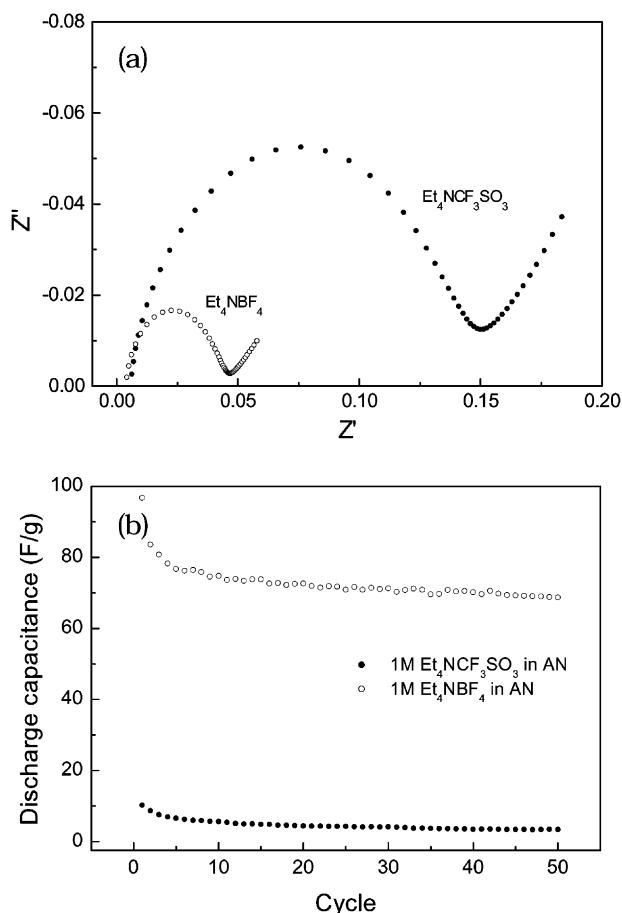Fig. 2. Specific capacitance of supercapacitor using conductive carbon (Super P) solely as electrode active-material.

Fig. 3. Results of (a) impedance spectroscopy and (b) charge–discharge when using two electrolyte salts of $Et_4NCF_3SO_3$ and Et_4NBF_4.

Fig. 4. Cycle-life characteristics of a redox supercapacitor using Pani-HCl (cut-off range of 1.0–0.01 V).

The state of polyaniline doped with lithium salt like $LiPF_6$ was checked with conductivity measurements. The pellet conductivity of Pani-LiPf$_6$ powder is $\sim10^{-2}$ S cm^{-1}, which confirms the formation of Polarons by doping. Next, in order to identify oxidation/reduction potentials and cell resistance, cyclic voltammetry and impedance spectroscopy were performed for a Pani-LiPF$_6$ powder cell. As shown in Fig. 5a,

evaluated. The electrolytic conductivity of these electrolytes was measured. Et_4NBF_4 ($\sim$50 mS cm^{-1}) dissolved in acetonitrile has a larger conductivity than $Et_4NCF_3SO_3$ ($\sim$10 mS cm^{-1}). As shown in Fig. 3a, the interfacial resistance between the electrodes and the separator is 4.3 mΩ (for Et_4NBF_4) and 3.3 mΩ (for $Et_4NCF_3SO_3$), and the total resistance is 147.7 and 44.54 mΩ, respectively. Also, the equivalent series resistance (ESR) values are 104.5 and 42.25 mΩ at 1 kHz. The specific capacitance of the Pani-HCl redox supercapacitor (current density 0.25 mA cm^{-2}, cut-off range 2.0–0.01 V) using Et_4NBF_4 is $\sim$70 F g^{-1}, which is higher than that when using $Et_4NCF_3SO_3$ ($\sim$5 F g^{-1}), as shown in Fig. 3b. Thus, the system with Et_4NBF_4 displays better performance in the Pani redox supercapacitor.

In Fig. 4, the specific discharge capacitance is given as a function of cycle number for a redox supercapacitor using Pani-HCl powder and 1 M Et_4NBF_4 in acetonitrile (current density 1.25 mA cm^{-2}, cut-off range 1.0–0.01 V). The specific capacitance is $\sim$70 F g^{-1} on the initial discharge and falls to $\sim$40 F g^{-1} after 1000 cycles. The discharge capacitance decreases continuously during $\sim$400 cycles and then remains constant.
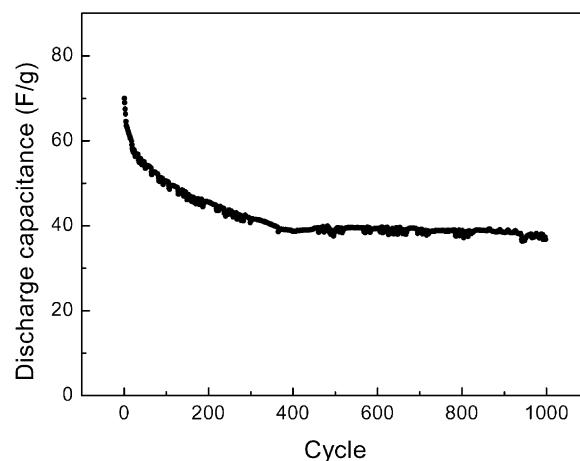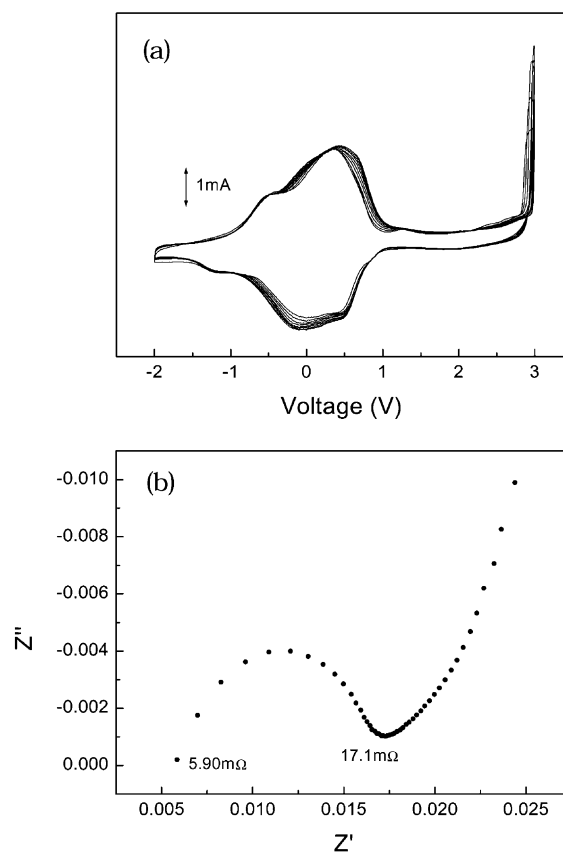

Fig. 5. Results of (a) cyclic voltammetry and (b) impedance of redox supercapacitor using Pani-LiPF$_6$ powder electrode.

the cyclic voltammogram for Pani-LiPF$_6$ in the redox type cell is different from that for a typical electrical double-layer capacitor. The oxidation and reduction peaks occur within −0.5 to 0.5 V and show approximately symmetric features. If the cut-off voltage exceeds ∼3 V, this capacitor suffers from the decomposition of electrolyte, electrode, and other compositions. In addition, if the range of the cut-off is 2.0–0.0 V, the small capacitance appears in the range 2.0–1.0 V and its contribution to the total capacitance becomes negligibly small. As shown in Fig. 5b, the interfacial characteristics between the electrodes and the separator appear as an internal resistance of ∼5.9 mΩ, a total resistance of 17.1 mΩ and an ESR value of 16.8 mΩ at 1 kHz. These values are remarkably smaller that those for the Pani-HCl system, which is expected to have large capacitance and good cycleability.

The discharge curves of a redox supercapacitor using a Pani-LiPF$_6$ electrode with different cut-off ranges and current densities are given in Fig. 6. The curve between 2.0 and 1.0 V decreases abruptly. That is, the capacitance between 2.0 and 1.0 V is negligibly small and does not contribute much to the total capacitance. This is confirmed by the results of cyclic voltammetry. The discharge curves are very similar irrespective of the quantity of electrode material. Discharge curves for different applied current densities are
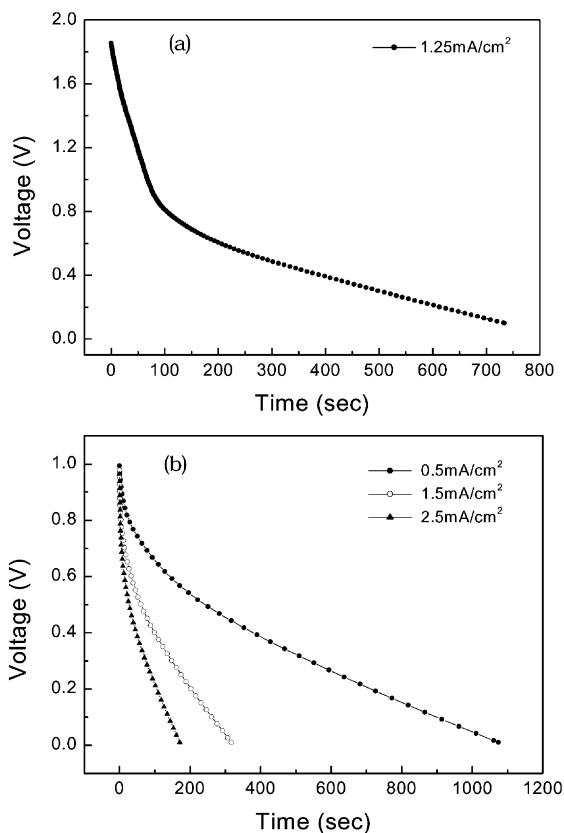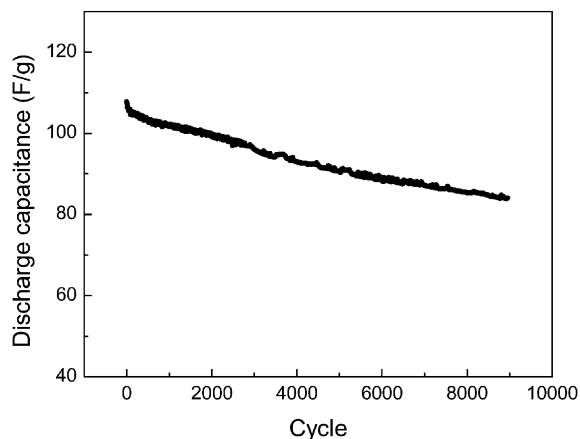

Fig. 7. Cycle-life characteristics of redox supercapacitor using Pani-LiPF$_6$ electrode (cut-off range 1.0–0.01 V).

presented in Fig. 6b. As the current density is increased, the voltage drop rapidly decrease, the discharge time decreases and, finally, the capacitance of the capacitor is decreased.

The cycle-life characteristics of a redox supercapacitor using Pani-LiFF$_6$ is shown in Fig. 7 (current density 1.25 mA cm^{-2}, cut-off range 1.0–0.01 V). The specific capacitance is ∼107 F g^{-1} on the initial discharge and falls to ∼84 F g^{-1} after 9000 cycles. The discharge capacitance continuously decreases with cycly-life. This value is larger than that of Pani-HCl redox supercapacitor. Therefore, Pani-LiPF$_6$ is a better electrode material for redox supercapacitors.

4. Conclusions

Polyaniline doped with HCl or Li salt has been used as an electrode and studies its electrochemical properties, impedance, charge and discharge characteristics, and cycle-life. To check the capability of the electrolyte solution in the redox supercapacitor, two kinds of electrolyte salt, such as Et$_4$NCF$_3$SO$_3$ and Et$_4$NBF$_4$ are tested. The system using Et$_4$NBF$_4$ has lower internal resistance and larger specific discharge capacitance. Thus, the system using Et$_4$NBF$_4$ is more suitable for polyaniline redox supercapacitors. The capacitance of Pani-HCl decreases until ∼400 cycles and then reaches at a constant value of ∼40 F g^{-1}. For the Pani-LiPF$_6$ cell, the oxidation or reduction of this system is occurred within −0.5 to 0.5 V with smaller internal resistance. As a result, the Pani-LiPF$_6$ system offers better capability than the Pani-HCl system, and shows a high initial discharge capacitance of ∼107 on the initial discharge and ∼84 F g^{-1} after 9000 cycles.

Fig. 6. Discharge curve of redox supercapacitor using Pani-LiPF$_6$ electrode within (a) cut-off range 2.0–0.01 V and (b) cut-off range 1.0–0.01 V with different current densities.

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