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Short communication

Hybrid electrochemical capacitors based on polyaniline and activated carbon electrodes

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Abstract

The performance of a newly designed, polyaniline–activated carbon, hybrid electrochemical capacitor is evaluated. The capacitor is prepared by using polyaniline as a positive electrode and activated carbon as a negative electrode. From a constant charge–discharge test, a specific capacitance of 380 F g^{-1} is obtained. The cycling behaviour of the hybrid electrochemical capacitor is examined in a two-electrode cell by means of cyclic voltammetry. The cycle-life is 4000 cycles. Values for the specific energy and specific power of 18 Wh kg^{-1} and 1.25 kW kg^{-1}, respectively, are demonstrated for a cell voltage between 1 and 1.6 V.

Keywords: Supercapacitor; Electrochemical capacitor; Hybrid capacitor; Energy storage

1. Introduction

The π-conjugated conducting polymers have been investigated for use as electrode materials for secondary batteries [1–3] and, more recently, for electrochemical capacitors [4–6]. The conducting polymers can be positively or negatively charged with ion insertion in the polymer matrix to balance the injected charge. This behaviour is called p- or n-doping, respectively.

Electrochemical (EC) capacitors based on p- and n-dopable polymers are very attractive for delivering high energy with high power in various electric devices, which include electric vehicle (EV) applications. Because this type of polymer-based EC capacitor (type III) has a p-dopable polymer as the positive electrode and a n-dopable polymer as the negative electrode, it has high specific energy and power performance which results from the high working voltage [7–9].

Very negative potentials are necessary, however, for making the n-doped state of conventional polymers such as poly(thiophene) and poly(thiophene) derivatives [10–12]. Though newly designed poly(thiophene) derivatives can be n-doped at less negative potentials, higher doping level values are required for materials with almost the same specific capacitance due to the high molecular weight of their monomer unit [13,14]. This is a defect of conducting polymer-based electrochemical capacitors because the need for very high doping levels concomitantly requires insertion/de-insertion of counter ions that causes a volume change of the polymer. The consequent mechanical stress in the polymer chain relates directly to the cycle-life.

In this study, an investigation is made of the performance of a hybrid type EC capacitor which has electronically conducting p-dopable polyaniline (PANI) as the positive electrode material, and activated carbon (AC) with high specific surface-area as the negative electrode material instead of n-dopable conducting polymers. The idea is based on a novel design of electrodes for improving the performance of a EC capacitor [15]. These components have already been shown to have good cycle characteristics due to the electrostatic charge–discharge mechanism (AC) and very reversible doping–de-doping process (PANI), respectively. The charge–discharge property of the hybrid EC capacitor is examined for its feasibility and its specific energy and power are compared with those of a general type III EC capacitor composed of p- and n-dopable conducting polymers.

2. Experimental

The PANI was chemically synthesised from aniline monomer (Aldrich Chem.) [15]. Activated carbon (MSC-30, KANCEI Coke) was used without further purification.

The positive and negative electrodes were prepared by addition of 90 wt.% active material (PANI or activated

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carbon) and 5 wt.% conducting powder (super-p) in 5 wt.%. PTFE (polytetrafluroethylene, Aldrich) dispersed in IPA (isopropyl alcohol, JUNSEI) to yield a homogeneous paste. The paste was spread on a glass substrate and flexible films were prepared by rolling. The prepared films were then cut into 2 cm × 2 cm sections and the resulting electrode films were pressed on a Ni-foam current-collector and dried at 100 °C under vacuum for 12 h. The positive and negative electrodes were tested by cyclic voltammetry (CV) at various potential sweep rates in 6 M KOH in an aqueous medium using a conventional three-electrode cell (EG&G 273A).

Unit cells were assembled from two different positive and negative electrodes (4 cm^2) that were kept apart by a polypropylene separator (Cellgard 3501, 25 μm). They were immersed in a 6 M KOH electrolyte solution and galvanostatic charge–discharge tests were performed by means of an Toyo Toscat 300 u. The cycleability performance of the electrochemical capacitor was tested by repeated potentiostatic cycles at a 50 mV s^{-1} sweep rate. All experiments were conducted at room temperature.

The integral capacitance of the prepared unit cell was measured by charge–discharge experiments using a constant current density. Due to problems in previous experimental methods used to determine capacitance, the specific capacitances reported in literature are not consistent.

Consequently, calculate the specific capacitance as follows.

Assuming the total weight of both positive and negative electrodes except for the current-collectors is M, the capacitance, C, for a two-electrode system is:

$$C = \frac{\int i\Delta t}{\Delta V} \tag{1}$$

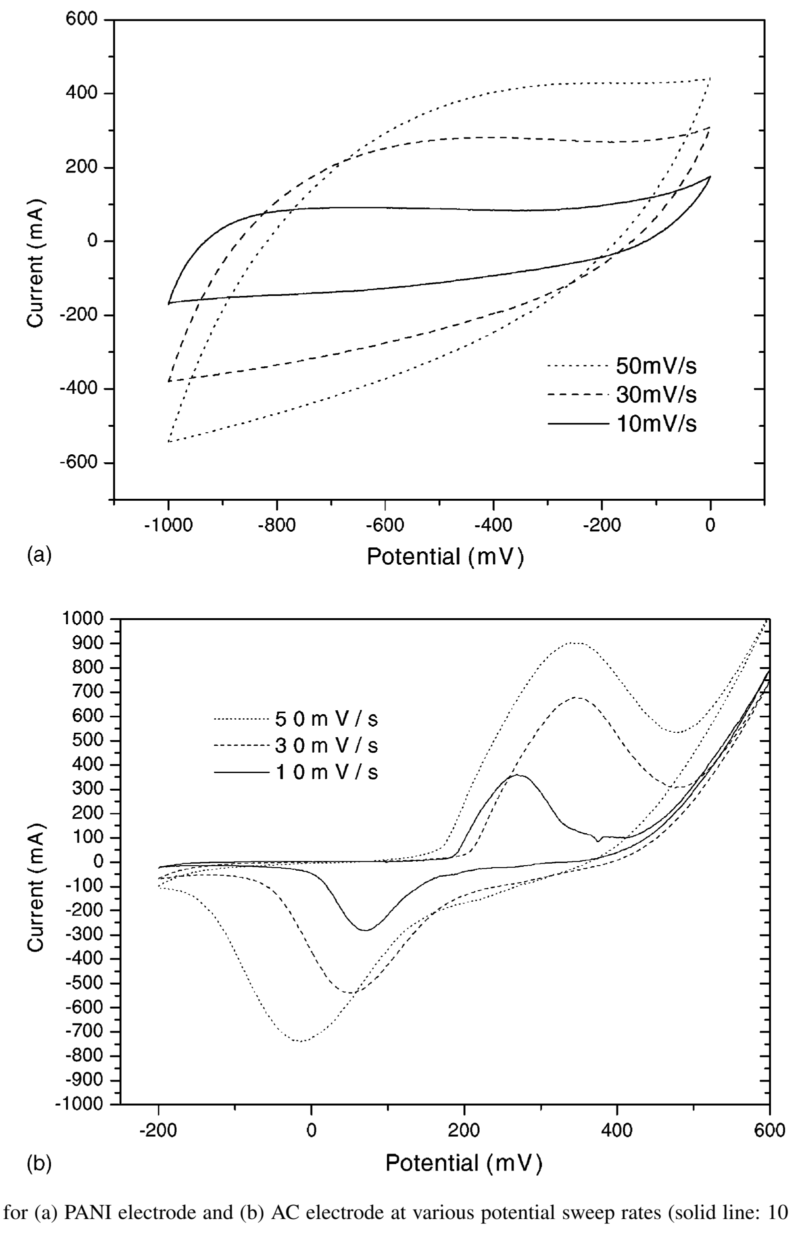

Fig. 1. Cyclic voltammogram for (a) PANI electrode and (b) AC electrode at various potential sweep rates (solid line: 10 mV s^{-1}, broken line: 30 mV s^{-1}, dotted line: 50 mV s^{-1}).

where i is the current density, t the time and V is the voltage.

The specific capacitance is:

$$C_{spec} = \frac{4C}{M} \quad (2)$$

The specific energy and power was also obtained from charge–discharge curves using the general method.

3. Results and discussion

Cyclic voltammograms (CV) for the PANI and AC electrodes at various potential sweep rates are shown in Fig. 1. For the AC-based electrodes, nearly rectangular CV curves are obtained due to a charge separation with the same magnitude between the electrode | electrolyte interfaces. The capacitances are obtained from the CV curves with the equation $C = i/s$ where i is the average current and s is the potential sweep rate. An average specific capacitance of about 260 F g^{-1} is obtained by integrating positive and negative currents in the CV curve. This value is in good agreement with that obtained by Kim et al. [16]. The CV curves of the PANI-based electrode show a pseudocapacitive current which arises mainly from the redox transitions of the PANI molecular chain. The CV shape for the PANI electrode resembles that for electroactive PANI in neutral aqueous solution [17]. Though the conductivity of PANI is well recognised to be poor in base media, it is seen that the CV curve for the PANI electrode shows higher specific capacity than that for the AC electrode due to the reducing contact resistance between the PANI electrode and the foam-type current-collector. The contact resistance between the electrode and the collector is known to be an important factor in determining the performance of EC capacitors [18].

Two-electrode CV curves of a unit cell prepared by using PANI as the positive electrode and AC as the negative electrode are shown in Fig. 2 as a function of cycle number. The voltage for this two-electrode system is based on the negative AC-based electrode. The unit cell is charged between 1.25 and 1.5 V and discharged between 1.0 and 1.4 V. This can be predicted by the three-electrode CV curves, as shown in Fig. 1. At a fully oxidised state, PANI gives about 0.6 V (vs. Ag/AgCl) but the AC-based electrode gives about −1 V (vs. Ag/AgCl) at a fully-reduced state. Thus, in the fully-charged state, the PANI electrode is in a fully p-doped state and the AC electrode is in a fully cathodic polarised state, whereas the discharge process proceeds until the potential of both electrodes is the same. Thus, the potential of the unit cell can reach 1.5–1.6 V in the fully-charged state.

The cycle characteristics of a PANI | AC hybrid EC capacitor were evaluated using CV cycling over about 4000 cycles. From Fig. 2, a total loss of about 20% of the initial discharge capacity is found after 300 cycles, but a fairly steady capacity is maintained thereafter. The CV cycling curves of the hybrid EC capacitor between 1 and 4000 cycles reveal that the decrease of performance can be linked mainly to a shifting in the positive potential direction of the equilibrium potentials of both electrodes. As a result, the charge capacity decreases with increasing cycle number and results in a decrease of discharge capacity within the cut-off potential range. Though the potential window employed in the hybrid EC capacitor is wider than that for a general aqueous electrolyte system, no serious gas formation from water decomposition occurs.

In order to obtain information concerning the capability of a unit cell of the PANI | AC hybrid EC capacitor, constant-current charge–discharge cycles were obtained galvanostatically at 0.5–20 mA cm^{-2} with 0.8 and 1.6 V cut-off

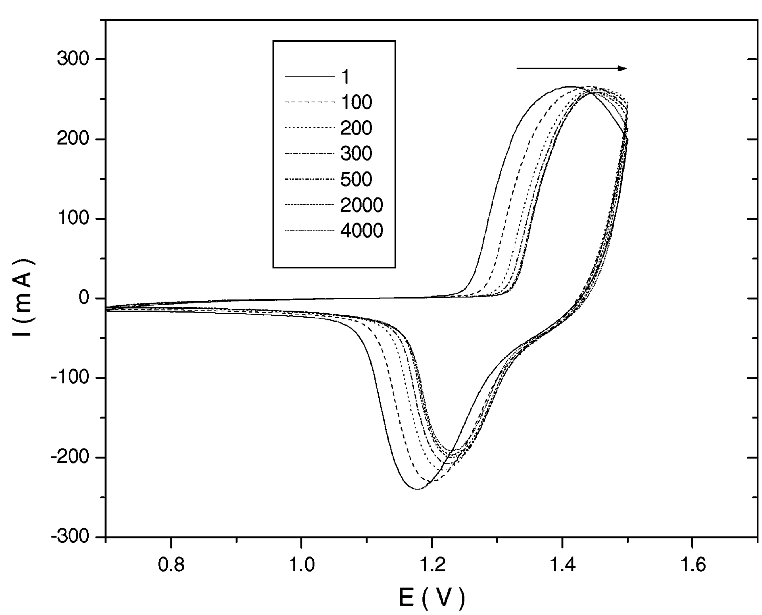

Fig. 2. Cyclic voltammograms for PANI–AC hybrid EC capacitor as function of cycle number.

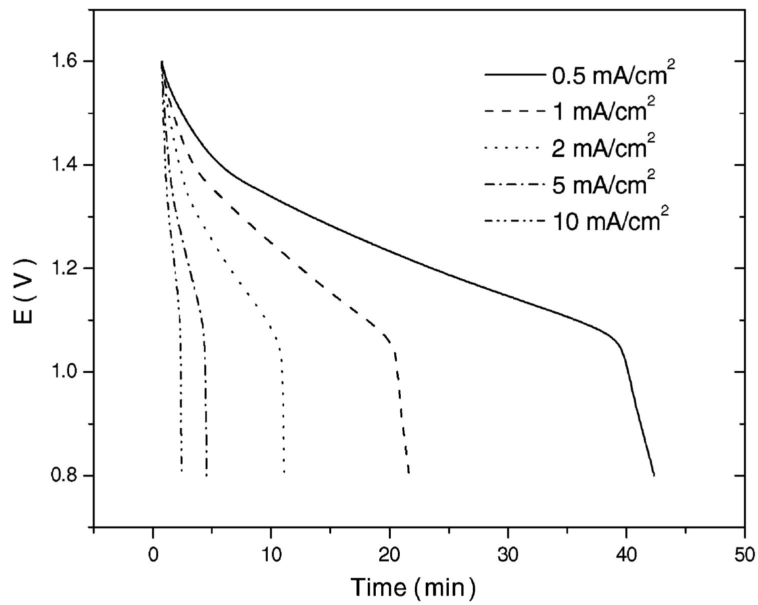

Fig. 3. Galvanostatic discharge curves for PANI–AC hybrid EC capacitor at various discharge current densities.

potentials (positive electrode: 36.6 mg/4 cm^2; negative electrode: 46.6 mg/4 cm^2). Typical potential profiles of the discharge process are shown in Fig. 3 as a function of discharge current density. During the charge and the discharge steps, non-linear behaviour of the cell potential is observed, as expected from the CV curves. The results shown in Fig. 3 demonstrates that this device exhibits the typical response of hybrid-type EC capacitor [19].

Potential profiles of the average discharge specific capacitance of the hybrid EC capacitor calculated between 1 and 1.6 V are shown in Fig. 4 as a function of the charge–discharge current density. The slightly decreased slope of the specific capacitance indicates good power characteristics of the hybrid EC.

The specific power P, and energy E for the hybrid EC capacitor are shown in Fig. 5. The energy and power data are calculated taking into account only the weight of the electrode material (active material + conducting agent+ binder). The energy and power densities reach values of 18 Wh kg^{-1} and 1.25 kW kg^{-1}, respectively. The specific energy increases by more than 5 times compared with that of a symmetric PANI-based EC capacitor using an aqueous acid electrolyte, or a non-aqueous electrolyte [19,20]. In addition, the specific energy of the PANI–AC, aqueous base,

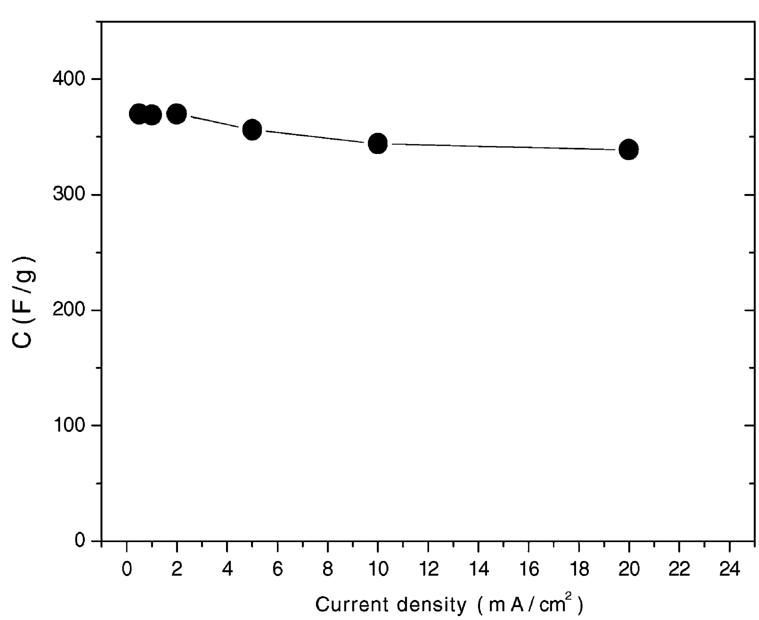

Fig. 4. Specific capacitances of PANI–AC hybrid EC capacitor as function of charge–discharge current density.

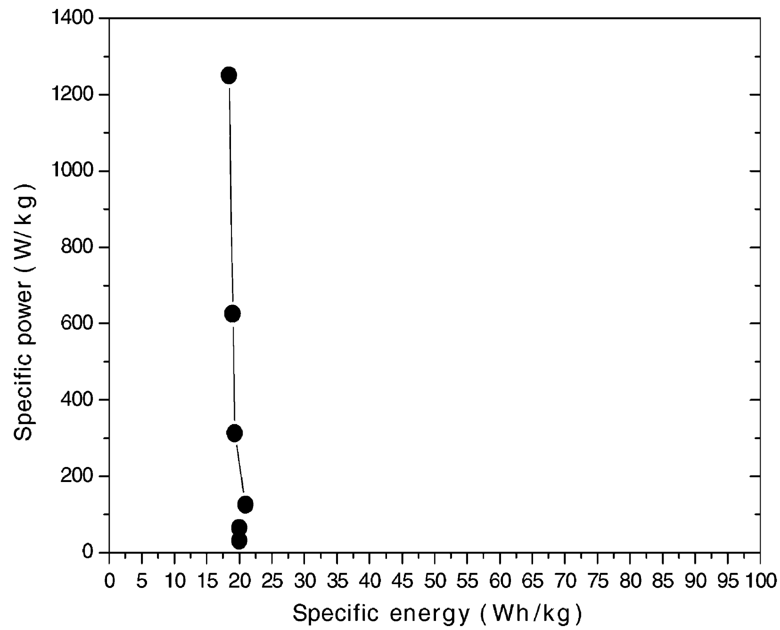

Fig. 5. Ragone plot of PANI–AC hybrid EC capacitor.

hybrid type EC capacitor shows similar or higher values than those recently reported for a polythiophene derivative based EC capacitor (type III) [10].

The technique of ac impedance spectroscopy can be used to obtain a measure of the resistance associated with the potential specific power of the hybrid EC capacitor [21]. Impedance spectra for the hybrid EC, at various potentials which correspond to a working potential range, are shown in Fig. 6. The 0.4 Ω cm^2, high frequency impedance intercept reflects the total resistance of the bulk electrolyte. The most important point in the impedance spectra is the resistances associated with the transport process within both electrodes. These resistances were evaluated from the difference in the real part of the impedance between the low and high frequencies [11].

For a hybrid EC at working potential (1.3–1.5 V), about 1.9 Ω cm^2 is obtained. This value is very low, given that the EC capacitor is composed of a bulk-type electrode rather than a thin-film type electrode. Therefore, this demonstrates the good power characteristics of the newly designed hybrid EC capacitor which is consistent with the Ragone plot shown in Fig. 5.

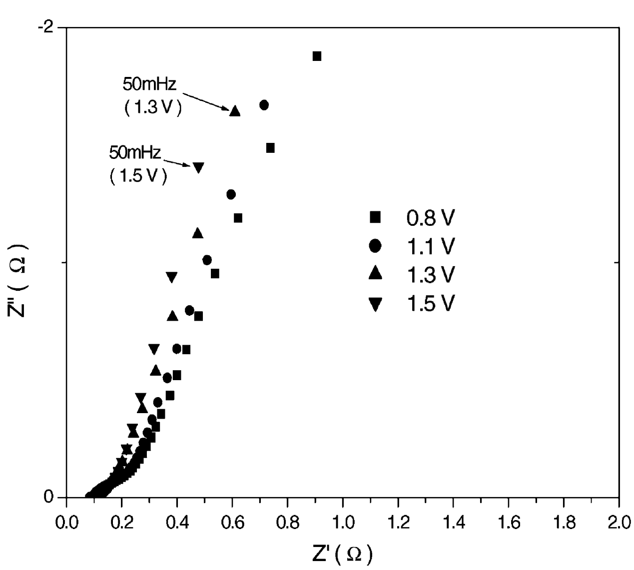

Fig. 6. Impedance diagram for PANI–AC hybrid EC capacitor with potential stepped in range between 0.8 and 1.5 V.

4. Conclusions

The electrochemical properties, especially the capacitance, specific energy, specific power and resistance, of a hybrid type EC capacitor composed of a PANI electrode (positive) and an AC (negative) electrode are studied by the cyclic voltammetric responses, charge–discharge tests, and ac impedance analysis. In the base electrolyte, the hybrid EC capacitor provides about 380 F g^{-1} specific capacitance based on the electrode active-material. The specific energy and specific power (1.8 Wh kg^{-1}, 1.25 kW kg^{-1}) of a PANI | AC hybrid EC are improved compared with those of a p-dopable, polymer-based and general AC–based EC capacitor. From cycling curves, the hybrid EC capacitor shows an initial loss in its capacity during the first 300 cycles (less than 20% of initial value), but a fairly steady capacity is maintained over 4000 cycles.

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