Short communication

Anthraquinone modified carbon fabric supercapacitors with improved energy and power densities

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ABSTRACT

Supercapacitors with improved energy and power densities have been constructed with anthraquinone modified carbon fabric (Spectracarb 2225) as the negative electrode and unmodified carbon fabric as the positive electrode. A Nafion separator and 1 M sulfuric acid electrolyte were employed. The performances of the supercapacitors were characterized by cyclic voltammetry and constant current discharging. Use of the anthraquinone modified electrode as the negative electrode (anode during discharge) in the supercapacitor provides 40% higher average capacitance, 56–86% higher energy density, and improved power duration.

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1. Introduction

Electrochemical capacitors (supercapacitors) are attracting increasing interest for use in high power electronic devices and electric vehicles [1–5]. High surface-area carbons are generally used as the capacitive material because of their low cost, excellent cycle life, and wide potential window in non-aqueous solvents [6–9]. Carbon supercapacitors store charge primarily by non-Faradaic charging of the carbon/electrolyte double-layer, although there can be substantial contributions from Faradaic processes such as the redox of surface quinone groups. Faradaic processes offer much higher potential energy densities and so form the basis for energy storage in batteries and redox supercapacitors based on the Faradiac pseudo-capacitance of metal oxides and conducting polymers. There have been many examples of the use of hybrid systems involving both carbon and materials with redox capacitance [8].

Leitner al el. [10] have reported the modification of high surface-area carbon with 1,2-naphthahydroquinone (from 2-nitro-1-naphthol) in order to enhance its capacitance with a redox pseudo-capacitance. In H_2SO_4 (aq), the naphthaquinone/naphthahydroquinone couple produced a pseudo-capacitance peak at ca. +0.3 V vs. SCE that was super-imposed on the almost constant (i.e. independent of potential) double-layer capacitance of the carbon. Voltammetric and impedance data obtained in a conventional three-electrode cell were reported, but the modified carbon was not evaluated in a supercapacitor. In fact, the added redox capacitance would be of limited value in a supercapacitor because it occurs in a potential region (ca. 0.2–0.35 V vs. SCE) over which the capacitor would have a very low voltage.

The addition of redox capacitance to high surface-area carbons by immobilization of redox species does have considerable potential to increase energy and power densities, but the formal potentials of these species should be carefully chosen to provide additional charge at the beginning of discharge of the supercapacitor, when its voltage is high. Thus the negative electrode should be modified with a redox species with a formal potential close to the cathodic limit of the carbon in the electrolyte employed. For an aqueous acid electrolyte, this is ca. −0.3 V vs. SCE. Conversely, the modifier on the positive electrode should have a potential close to the anodic limit of ca. +0.9 V.

We report here on the use of anthraquinone (AQ) as a redox modifier for the negative electrode of a carbon supercapacitor with an aqueous acid electrolyte, and demonstrate that enhanced energy and power densities can indeed be achieved. The formal potential of the immobilised AQ is −0.1 V vs. SCE, which is well suited for the negative electrode in aqueous acid. It was immobilised by using a diazonium coupling method reported by Compton and co-workers

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[11]. The use of similarly modified carbons in supercapacitors has been patented by Cabot Corp. [12].

2. Experimental

2.1. Immobilization of AQ

Fast Red Al salt (Acros; anthraquinone-1-diazonium chloride $0.5ZnCl_2$; 10 ml; 50 mM) was mixed with a 10 ml solution of 50 wt.% hypophosporous acid (Aldrich) with sonication. This mixture was then placed in an ice bath and two pieces (22.9 mg and 14.1 mg) of Spectracarb 2225 carbon fabric (Engineered Fibers Technology) were added. After 30 min with occasional stirring the Spectrcarb discs were collected by filtration, washed well with de-ionized water and then acetonitrile, air dried, and weighed. The masses of the two samples increased by 7.1% and 9.8%. In subsequent work, we have only been able to obtain comparable AQ loadings by adding acetone to increase the solubility of the Fast Red salt.

2.2. Supercapacitors

Prototype supercapacitors (2-electrode sandwich cells) were constructed by sandwiching an electrolyte separator (Nafion^{TM} 115) between an AQ-modified Spectracarb electrode ($\sim$1 cm^2; 14.2 mg or 15.1 mg) and an unmodified Spectracarb electrode ($\sim$1 cm^2; 14.1 mg). Ti plates in polycarbonate blocks were used to make electrical contact, and the whole cell was immersed in 1 M H$_2$SO$_4$ (aq) containing an Ag/AgCl reference electrode. Initially, the two Spectracarb discs were placed in direct contact with the Ti current collector plates. However, impedance measurements revealed the presence of large interfacial resistances that were traced to the Ti/Spectracarb interfaces. These resistances were eliminated by placing a carbon fibre paper disc (Toray^{TM} TGP-H-090) between each Spectracarb electrode and its Ti current collector. Air was not excluded from the cell.

Cyclic voltammetry (Pine RDE4 Potentiostat/Galvanostat) was obtained for the AQ-modified electrode in three-electrode mode, by using the reference electrode and with the unmodified electrode acting as the counter electrode. Voltammograms were also obtained in two-electrode mode (i.e. with the cell acting as a supercapacitor) by connecting the reference lead of the potentiostat to the Specracarb disc being used as the counter electrode. For constant current discharging experiments (EG&G 273A Potentiostat/Galvanostat), also in two-electrode mode, the supercapacitor was charged for a period of ca. 5 min at a cell voltage of 1 V. For all experiments in two-electrode mode, a +ve cell voltage means that the working electrode was the anode (i.e. +ve) during charging of the supercapacitor.

3. Results

3.1. Cyclic voltammetry of AQ-modified Spectrcarb 2225

Fig. 1 shows cyclic voltammograms of two different AQ-modified electrodes in the sandwich cell, in pressure contact with a Nafion membrane and flooded with H$_2$SO$_4$ containing a reference electrode. In these voltammograms, the current has been normalized with respect to the scan rate and electrode mass to provide a specific capacitance (F g^{-1}) scale. Redox peaks due to the AQ can be seen at a formal potential of ca. −0.11 V. These peaks were very stable, actually increasing slightly with scanning in these experiments and over 2000 cycles for another electrode. The AQ peaks are much sharper at 1 mV s^{-1} because of the decreased influence of the uncompensated resistance. At this speed they exhibit symmetric
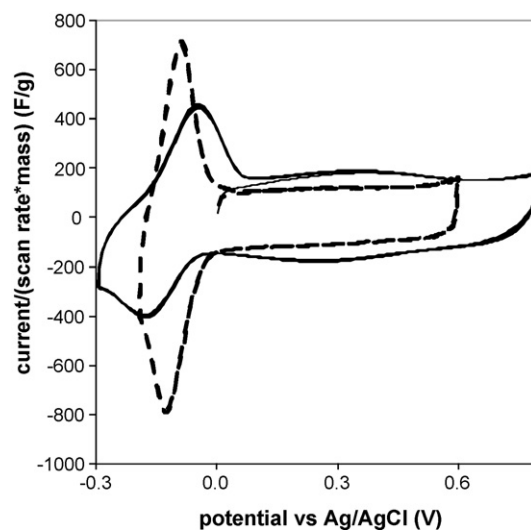

Fig. 1. Cyclic voltammetry of AQ-modified Spectracarb electrodes in 1 M H$_2$SO$_4$ (aq). Solid line: 14.2 mg electrode at 10 mV s^{-1}; dashed line: 15.1 mg electrode at 1 mV s^{-1}.

wave-shapes with little peak separation, as expected for a surface confined redox species, and an average peak specific capacitance of 727 F g^{-1}. The carbon background specific capacitance was ca. 110 F g^{-1}. Subtraction of this value from the peak capacitance yields a peak specific capacitance of ca. 9500 F g^{-1} for the AQ component which was 7.1% of the total mass.

At 10 mV s^{-1}, the AQ peaks were highly distorted by the uncompensated resistance, with lower peak capacitances and the peak separation rising to 139 mV, from 23 mV at 1 mV s^{-1}. The carbon background capacitance was higher (average of ca. 150 F g^{-1}), however, because the wider potential range used in this experiment generates redox active surface functionality [13] with an average formal potential of ca. 0.3 V.

3.2. Cyclic voltammetry of the supercapacitor

The redox peaks of the AQ seen in Fig. 1 are well suited for enhancing the charge and power of the carbon when used as the
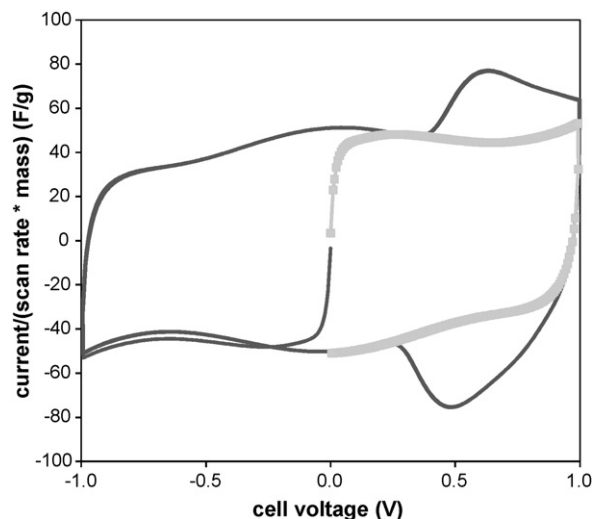

Fig. 2. Cyclic voltammograms (two-electrode mode) at 10 mV s^{-1} of a supercapacitor with an unmodified Spectracarb working electrode and an AQ-modified Spectracarb counter/reference electrode (black line), and with the polarity reversed (grey squares; obtained simply by reversing the polarity of the −ve cell voltage data).
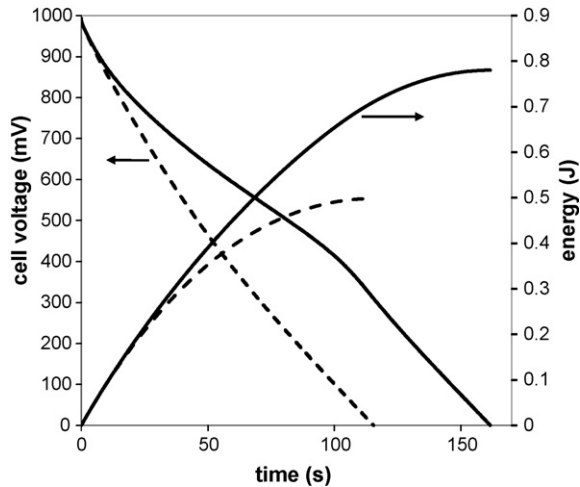
Fig. 3. Discharge curves at 10 mA for a supercapacitor with an unmodified Spectracarb working electrode and an AQ-modified Spectracarb counter electrode (modified −ve; solid lines) and for the same device under reverse polarity (modified +ve; dashed lines).

Fig. 4. Discharge curves at 1 A for a supercapacitor with an unmodified Spectracarb working electrode and an AQ-modified Spectracarb counter electrode (modified −ve; solid line) and for the same device under reverse polarity (modified +ve; dashed line).

Fig. 5. Power density as a function of the energy density drawn during 1 A discharge of a supercapacitor with an unmodified Spectracarb working electrode and an AQ-modified Spectracarb counter electrode (modified −ve; solid line) and for the same device under reverse polarity (modified +ve; dashed line).

negative electrode in a supercapacitor. This is illustrated in Fig. 2, where the cell was operated in two-electrode mode. In this experiment the modified electrode was driven negative as the cell voltage was scanned positively. The capacitance waves in the +0.3 to +1.0 V range are due to reduction and then reoxidation of the AQ groups. During discharge (−ve scan from +1 V to 0 V), these groups provide extra energy and power. When the cell voltage is in the −ve region in Fig. 2, the AQ groups remain oxidized and do not contribute to the capacitance. The behaviour of the capacitor is then as if both electrodes were unmodified. Thus the enhancement of the capacitance of the supercapacitor due to the redox activity of the AQ groups can unambiguously be seen by comparing the +ve and −ve cell voltage regions in Fig. 2. This comparison is aided visually by re-plotting of the −ve voltage data with reversed polarity as the grey squares in Fig. 2. For discharging from +1.0 V to 0 V (i.e. with the AQ active), the average capacitance was 1.51 F, while it was only 1.06 F for discharging from −1.0 V to 0 V (AQ inactive). This represents an enhancement of 42%. Furthermore, the additional charge is concentrated at high cell voltages (peaking at +0.48 V) and so pro-
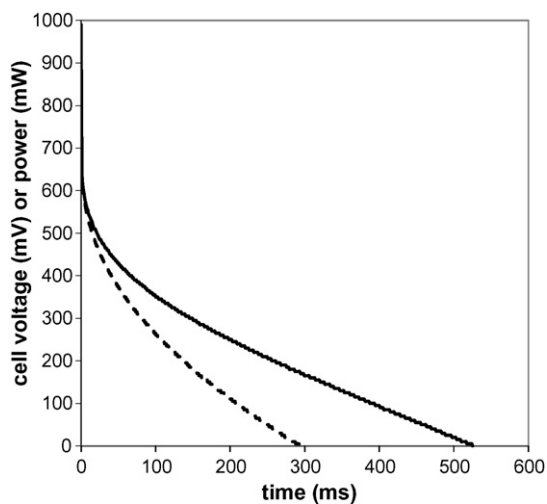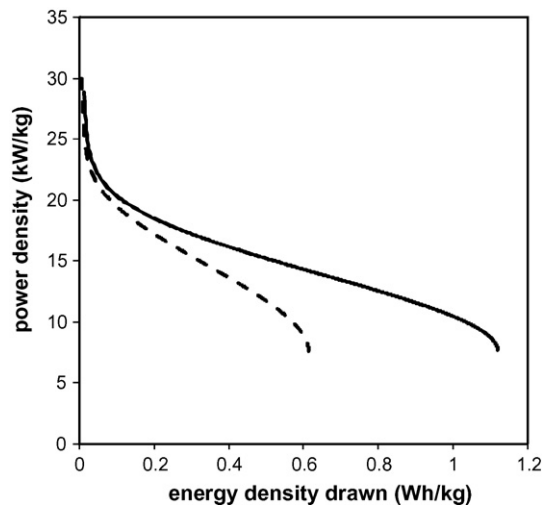
vides an even greater enhancement of energy and power densities (see below).

It should be noted that the specific capacitances plotted in Fig. 2 represent values for the two-electrode device, while those in Fig. 1 are single electrode values. They differ by a factor of approximately four (exactly four only for two identical electrodes) because the mass of the two electrodes is double that of one electrode and the capacitance of two electrodes in series is half that of a single electrode.

3.3. Constant current discharging

In order to further assess the benefits of using the modified electrode as the −ve electrode of the supercapacitor, constant current discharge experiments were run from 1 V, first with the modified electrode as the −ve electrode and then as the +ve electrode (where it behaves as if unmodified). Results at 10 mA and 1 A discharge rates are shown in Figs. 3 and 4, respectively.

The 10 mA data (Fig. 3) show the benefits of the AQ-modified −ve electrode in terms of improved total capacitance and energy. The total capacitance (proportional to the discharge time) increased by 41% from 1.15 F to 1.62 F, with most of the extra charge being obtained at voltages above 0.4 V. The energy obtained increased by 56% from 0.498 J (4.79 Wh kg^{-1}) to 0.780 J (7.96 Wh kg^{-1}).

The 1 A data (Fig. 4) show that the AQ-modified −ve electrode greatly improved the high power performance and the energy available at high power. With the AQ electrode −ve, the capacitor was still delivering 0.175 W (6.18 W g^{-1}) when the power had dropped to zero when operated in the reverse polarity. The available energy density at 1 A increased by 86% from 0.605 Wh kg^{-1} to 1.13 Wh kg^{-1}.

4. Discussion

The use of AQ as a redox modifier for the negative electrode (anode during discharge) of a carbon supercapacitor has been shown to provide a ca. 40% enhancement in average capacitance and 56–86% increase in energy density. The additional redox capacitance occurs as a peak close to the negative limit of the anode and this provides the capacitor with battery-like characteristics in that the cell voltage is maintained at higher values

for a longer fraction of the discharge (see Fig. 3). This results in higher energy densities than would be obtained for a pure capacitor with the same capacitance. It also allows high power densities to be maintained for longer (Fig. 4). This is illustrated in Fig. 5, where the power density is plotted as a function of the energy density drawn from the capacitor during discharge at 1 A.

The theoretical peak specific capacitance for AQ is $18 \, \text{kF} \, \text{g}^{-1}$, based on ideal Nernstian behaviour and a molar mass of $208 \, \text{g} \, \text{mol}^{-1}$. The experimental value of ca. $9500 \, \text{F} \, \text{g}^{-1}$ is much less than this due to the ubiquitous peak broadening observed for surface confined redox species [14]. It is therefore more meaningful to compare average capacitances over the redox wave. The theoretical specific capacitance for AQ with the charge averaged over a 0.5 V potential range (as for one side of a 1 V supercapacitor) is $1856 \, \text{F} \, \text{g}^{-1}$, while the experimental value at $1 \, \text{mV} \, \text{s}^{-1}$ from Fig. 1 is $1470 \, \text{F} \, \text{g}^{-1}$.

Further improvements in the performance of the supercapacitor could be made by use of a suitable redox modifier on the +ve electrode. For this, a couple with a formal potential of +0.6 V to 0.7 V or slightly higher would be required for optimum performance. A number of possible candidates are currently being assessed.

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