Short communication

An asymmetric anthraquinone-modified carbon/ruthenium oxide supercapacitor

Zaher Algharaibeh, Xiaorong Liu, Peter G. Pickup*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7

ABSTRACT

An asymmetric supercapacitor with improved energy and power density, relative to a symmetric Ru oxide device, has been constructed with anthraquinone-modified carbon fabric (Spectracarb 2225) as the negative electrode and Ru oxide as the positive electrode. The performance of the supercapacitor was characterized by cyclic voltammetry and constant current discharging. Use of the anthraquinone-modified electrode extends the negative potential limit that can be used, relative to Ru oxide, and allows higher cell voltages to be used. The maximum energy density obtained was $26.7\,Wh\,kg^{-1}$ and an energy density of $12.7\,Wh\,kg^{-1}$ was obtained at a $0.8\,A\,cm^{-2}$ discharge rate and average power density of $17.3\,kW\,kg^{-1}$. The C-AQ/Ru oxide supercapacitor requires 64% less Ru relative to a symmetric Ru oxide supercapacitor.

1. Introduction

Electrochemical capacitors (supercapacitors) are being developed for use in high power electronic devices and electric vehicles [1–5]. Asymmetric or hybrid supercapacitors in which the two electrodes are constructed with different materials are attracting increasing interest because each electrode can be designed and optimized for potential excursions in only one direction [6,7]. This can significantly extend the operating voltage of the device.

We report here on an asymmetric device with an anthraquinone-modified carbon fabric (C-AQ) negative electrode (cathode during charging) and a Ru oxide positive electrode. We have previously shown [8] that anthraquinone-modified carbon fabric is an attractive electrode material for the negative electrode of high power supercapacitors with an aqueous sulphuric acid electrolyte. The redox activity of the AQ provides extra charge at high cell voltages, increasing the energy and power density of the device. Ru oxide is also an excellent electrode material for high power supercapacitors, due to its very high specific capacitance and low resistance [1,9–17]. However, the inferior low potential limit of Ru oxide relative to C-AQ makes AQ-C/Ru oxide asymmetric devices potentially superior to symmetric Ru oxide/Ru oxide devices. The C-AQ/Ru oxide device also has the advantage of lower cost because of the lower mass of Ru required.

2. Experimental

2.1. AQ-modified carbon fabric electrodes (C-AQ)

AQ-modified Spectracarb 2225 carbon fabric was prepared following a slightly modified version of our previously reported method [8]. Two $1\text{-}cm^2$ discs (ca. 14 mg each) of Spectracarb 2225 carbon fabric (Engineered Fibers Technology) were added to FastRed Al salt (0.135 g; Acros; anthraquinone-1-diazonium chloride $0.5\ ZnCl_2$) in acetone (15 mL). Water (3 mL) and 50 wt.% hypophosporous acid (2 mL; Aldrich) that had been cooled in an ice bath were then added. After 30 min in the ice bath with occasional stirring, the Spectrcarb discs were collected by filtration, washed well with de-ionized water and then dried at 110 °C for 20 min, and weighed.

Cyclic voltammetry (Pine RDE4 Potentiostat/Galvanostat) was obtained for an AQ-modified electrode in a supercapacitor (see below) by using an Ag/AgCl reference electrode and an unmodified carbon fabric counter electrode.

2.2. Ru oxide electrodes

Ru oxide electrodes with a carbon fibre paper support and 5% Nafion binder were prepared as previously described [16]. Cyclic voltammetry of the Ru oxide on carbon fibre paper was recorded in a conventional glass cell with an EG&G 237A Potentiostat/Galvanostat.

* Corresponding author. Tel.: +1 709 737 8657; fax: +1 709 737 3702.
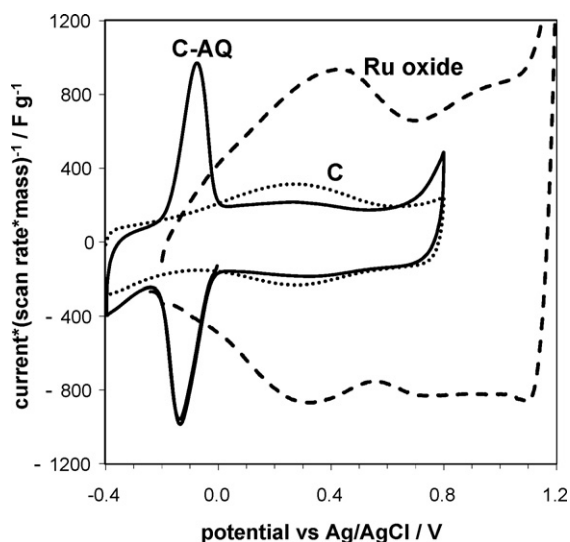 *E-mail address:* ppickup@mun.ca (P.G. Pickup).

Fig. 1. Cyclic voltammetry of an AQ-modified Spectracarb electrode (solid line; 14.8 mg; 2 mV s^{-1}), and unmodified Spectracarb electrode (dotted line; 14.3 mg; 20 mV s^{-1}) and a Ru oxide electrode (dashed line; 5.1 mg, 20 mV s^{-1}) in 1 M H$_2$SO$_4$ (aq).

2.3. Supercapacitors

Supercapacitors were constructed by sandwiching an electrolyte separator (Nafion^{TM} 112) between a C-AQ electrode (1 cm^2; 15.1 mg) and a Ru oxide electrode (1 cm^2; 8.5 mg Ru oxide + 5% Nafion). 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. A carbon fibre paper disc (Toray^{TM} TGP-H-090) was placed between the C-AQ electrode and its Ti current collector. Air was not excluded from the cell.

Voltammograms of the C-AQ/Nafion 112/Ru oxide supercapacitor were obtained in two electrode mode (i.e. with the cell acting as a supercapacitor) by connecting the reference lead of the potentiostat (EG&G 273A) to the counter electrode lead. For constant current discharging experiments (EG&G 273A), also in two electrode mode, the supercapacitor was charged for a period of ca. 5 min at a cell voltage of 1.3 V.

3. Results

3.1. Cyclic voltammetry of the individual electrode materials

Fig. 1 shows cyclic voltammograms of an AQ-modified carbon fabric electrode, an unmodified carbon fabric electrode, and a Ru oxide electrode in 1 M H$_2$SO$_4$ (aq). These voltammograms have 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, which are absent in the voltammogram of the unmodified carbon, can be seen at a formal potential of ca. −0.11 V. The average specific capacitance due to the carbon fabric, measured between −0.25 and 0.8 V, was 199 F g^{-1}, while an average of 482 F g^{-1} was obtained between 0 and −0.25 V for the C-AQ due to enhancement by the redox capacitance of the AQ. Even though this enhanced capacitance occurs over only a narrow potential range, it can provide a disproportionate increase in power and energy density when the C-AQ is used as a negative electrode [8].

Ru oxide provides a much higher specific capacitance than carbon between 0 and +1 V, with an average of 770 F g^{-1} seen in Fig. 1. However, its electrochemistry becomes slow and its capacitance decreases at potentials below 0 V. It can be seen from Fig. 1 that the

C-AQ electrode complements the Ru oxide electrode, when used as the negative electrode, by extending the negative potential range and by providing enhanced capacitance at potentials below 0 V vs. Ag/AgCl.

3.2. Cyclic voltammetry of the supercapacitor

Fig. 2 shows a cyclic voltammogram of an AQ-C/Ru oxide supercapacitor with the Ru oxide as the working (positive) electrode. Since this voltammogram was recorded in staircase mode, with a long step-time (1 s) determined by the instrument, the currents do not provide an accurate measure of the true specific capacitance. However, the voltammogram does accurately reflect the voltage dependence of the capacitance. The broad peaks centred at ca. 0.8 V are due to the reduction (positive scan) and reoxidation (negative scan) of the AQ groups on the surface of the C-AQ electrode that is driven to negative potentials as the supercapacitor is charged. The positions of these peaks can be changed by pre-setting the initial potentials of the electrodes relative to a reference electrode by employing an external counter electrode. For the experiment reported here, both electrodes were initially set at ca. +0.3 V vs. Ag/AgCl.

3.3. Constant current discharging

The additional charge storage and release represented by the broad peaks in Fig. 2 improves the discharge characteristics of the supercapacitor at high cell voltages as shown in Fig. 3, which compares 10 mA discharge data for an AQ-C/Ru oxide supercapacitor and a symmetric Ru oxide supercapacitor. The slopes of these curves are proportional to the capacitance of the device, and the initial slope is larger for the AQ-C/Ru oxide device than the symmetric Ru oxide device because of the greater electrode masses employed. This is addressed below in a comparison of the specific capacitances of the two devices.

The effect of the AQ groups is seen in Fig. 3 as a lower slope in the discharge curve at high voltages where the AQ groups are being oxidized. The higher slope at potentials below ca. 900 mV approximates the slope that would be seen over the full discharge for an asymmetric supercapacitor with an unmodified carbon electrode and a Ru oxide electrode. A key advantage of the AQ-C is that the enhanced capacitance due to the AQ groups maintains a higher
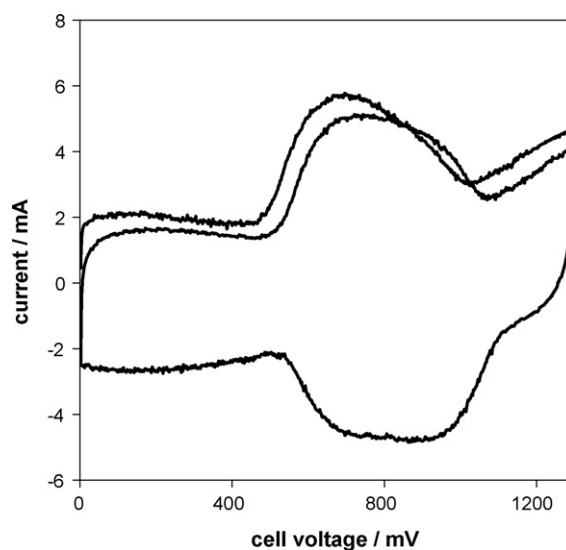

Fig. 2. Cyclic voltammogram at 2 mV s^{-1} for an AQ-C (15.1 mg)/Nafion 112/Ru oxide (8.5 mg) supercapacitor in 1 M H$_2$SO$_4$ (aq).
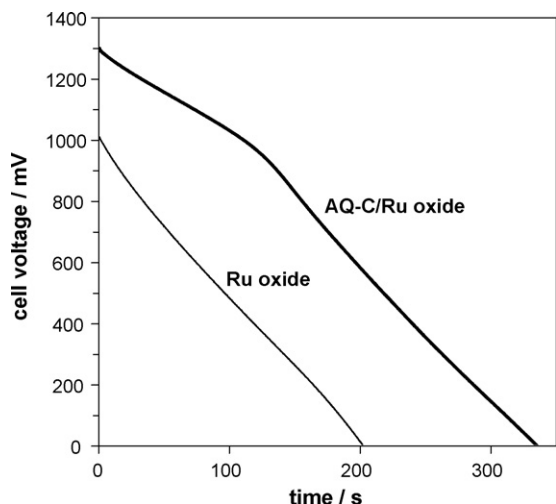
Fig. 3. Constant current discharge curves at 10 mA for an AQ-C (15.1 mg)/Nafion 112/Ru oxide (8.5 mg) supercapacitor ($V_{initial}$ = 1.3 V) and a Ru oxide (5 mg)/Nafion 112/Ru oxide (5 mg) supercapacitor ($V_{initial}$ = 1.0 V), both in 1 M H_2SO_4 (aq).

Fig. 5. Ragone plots for an AQ-C (15.1 mg)/Nafion 112/Ru oxide (8.5 mg) supercapacitor (solid points; $V_{initial}$ = 1.3 V) and a Ru oxide (5 mg)/Nafion 112/Ru oxide (5 mg) supercapacitor (open circles; $V_{initial}$ = 1.0 V; data from Ref. [17]), both in 1 M H_2SO_4 (aq). The open triangles show the data for the symmetric Ru oxide device with the power values divided by a mass of 23.6 mg. All values were calculated for discharge to 0 V.

cell potential during the first 30% of the discharge and so provides maximum benefit in terms of energy and power density.

The specific capacitance obtained for the C-AQ/Ru oxide supercapacitor from the initial slope (0–100 s) of the 10 mA discharge curve (Fig. 3) was 159 F g^{-1}, while the average specific capacitance for discharge to 0 V was 109 F g^{-1}. These values are based on the mass of active materials on both electrodes (i.e. the combined masses of Ru oxide, carbon fabric, and AQ). The symmetric Ru oxide supercapacitor (Fig. 3) had an average specific capacitance for full discharge of 193 F g^{-1}. A symmetric carbon fabric device would have a specific capacitance of ca. 50 F g^{-1}, based on a specific capacitance of ca. 199 F g^{-1} per electrode. An asymmetric unmodified-C/Ru oxide device would have a specific capacitance of ca. 95 F g^{-1} based on the slope below 900 mV in Fig. 3 for the C-AQ/Ru oxide device. It is clear from the comparison of these capacitances that the C-AQ electrode offers an attractive high voltage performance, particularly in light of its much lower cost relative to Ru oxide, and is much better than unmodified carbon.

Discharge curves at higher currents are shown for the C-AQ/Ru oxide supercapacitor in Fig. 4. The influence of the AQ electrochemistry on the initial slope is still pronounced at 0.1 A and is clear, although less distinct, at 0.8 A. This indicates that the AQ electro-
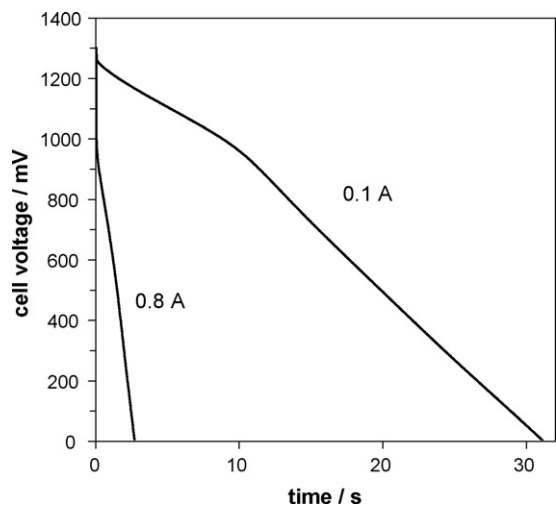

Fig. 4. Constant current discharge curves for an AQ-C (15.1 mg)/Nafion 112/Ru oxide (8.5 mg) supercapacitor in 1 M H_2SO_4 (aq).
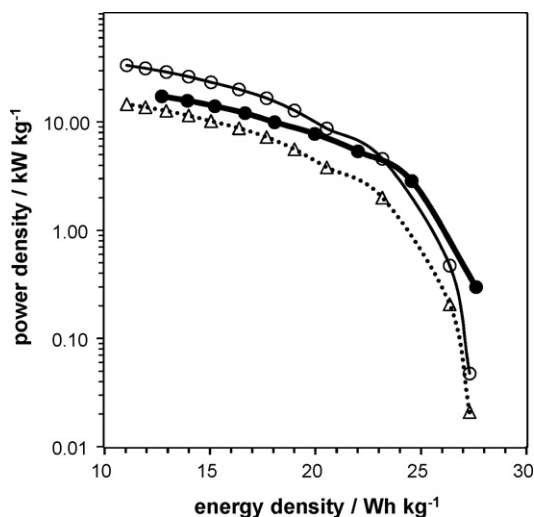
chemistry is sufficiently fast to significantly increase the energy density of the device at high discharge rates.

Ragone plots for the AQ-C/Ru oxide supercapacitor are shown in Fig. 4, together with data from Ref. [17] (over a slightly larger range of currents) for a symmetric Ru oxide (10 mg total) device with a Nafion 112 separator. The maximum energy density for the AQ-C/Ru oxide supercapacitor was 26.7 Wh kg^{-1} and an energy density of 12.7 Wh kg^{-1} was obtained at a 0.8 A discharge rate and average power density of 17.3 kW kg^{-1}. The AQ-C/Ru oxide device provided slightly higher energy densities than the Ru oxide device at currents below 0.7 A. It also provided higher power at all currents used.

To properly compare the power densities of the two devices, the results should be scaled to the same mass, since power is theoretically independent of the electrode mass. In practice, the increasing resistance of the electrodes causes the power (and energy density) to drop as the electrode mass is increased, so scaling of the results for the symmetric Ru oxide device to a mass of 23.6 mg, as shown in Fig. 5, will overestimate the performance of a 23.6 mg device. However, it is clear from doing this, that both the energy and power densities are higher for the AQ-C/Ru oxide device than they would be for a 23.6 mg symmetric Ru oxide device. Importantly, there would also be a 64% reduction in the mass of Ru required (i.e. 8.5 mg vs. 23.6 mg of Ru oxide).

The better performance of the AQ-C/Ru oxide supercapacitor is largely due to its higher operating voltage of 1.3 V relative to 1.0 V for the symmetric Ru oxide supercapacitor. Although it may be possible to operate the symmetric device at higher voltages [17], the reduced Ru requirement will still make the AQ-C/Ru oxide an attractive alternative. There is also significant scope for improving its performance by use of larger area electrodes, minimizing contact resistances [17], and increasing the loading of AQ on the carbon support.

4. Conclusions

The AQ-C/Ru oxide supercapacitor described here provides higher energy and power densities than a symmetric Ru oxide device with the same mass, and requires 64% less Ru. In part, the better performance is due to the higher operating voltage. However, the peak shaped redox capacitance of the AQ is also a crucial factor, as is the fact that this capacitance occurs in a potential region close

to and beyond the negative potential limit of Ru oxide. Thus the AQ-C electrode has an inherent advantage over Ru oxide as a negative electrode since its negative limit of ca. −0.4 V is lower than that of ca. −0.2 V for Ru oxide.

Acknowledgements

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