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Tantalum oxide–ruthenium oxide hybrid(R) capacitors

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Abstract

A hybrid capacitor consisting of porous tantalum oxide anode electrode and ruthenium oxide cathode electrode was examined and characterized. The capacitor has a capacitance of 35 mF and an internal resistance of 45 mΩ. It was found that the capacitance was insensitive to current density up to 110 mA/cm^2, and temperature ranging from −70 to 50 °C. During dc charge and discharge cycles, the potential of the cathode electrode was within the electrochemical stability window. However, a sudden voltage-jump as high as 7.5 V could occur at the cathode electrode during a short circuit discharge. A simple model was established to describe the transient behavior of cathode and anode electrodes. It was found that the voltage-jump was proportional to the ratio of the internal resistance of the cathode electrode to the total resistance of the capacitor. The resistance distribution inside the capacitor was also determined to be 47, 28, and 25% from the cathode, anode, and electrolyte, respectively.

Keywords: Hybrid capacitors; Ruthenium oxide; Tantalum oxide

1. Introduction

Electrochemical–electrolytic hybrid capacitors were first introduced by the Evans Capacitor Company. The tantalum oxide or aluminum oxide cathode electrode in an electrolytic capacitor was replaced by a ruthenium oxide (RuO_2) electrode for improving the energy density. Order-of-magnitude increases in volumetric energy density over electrolytic capacitors have been reported [1]. Also in contrast to electrochemical capacitors, where cell voltage is limited to the stable potential window of the electrolyte, the hybrid capacitor cell voltage depends on the breakdown voltage of the anode dielectric, which is orders-of-magnitude higher than that of electrochemical capacitors. An advantage of the hybrid capacitor is its ability to handle a very high rate of charge and discharge with an *RC* product of just 10^{-3} to 10^{-4} s [1,2]. In contrast, the *RC* product of most electrochemical capacitor is >0.1 s [3]. The present study characterizes dynamic changes of the hybrid capacitor, anode and cathode electrodes inside the capacitor under different operational conditions.

2. Devices

A 16 V hybrid capacitor was constructed with a pressed and sintered tantalum powder electrode as the anode and two RuO_2 films on Ta foil substrates as the cathode. The detailed configuration of the capacitor and the method for fabrication of electrodes can be found from [2,4]. A 38 wt.% H_2SO_4 solution was used as the electrolyte. The anode electrode had a diameter of 3.4 cm and a thickness of 0.2 cm. The cathode electrode had a diameter of 3.4 cm and a thickness of 50 μm. Fig. 1 shows a picture of the final packed cell with weight of about 25 g. The cell is rated at 36 mF and 16 V.

3. Experimental

A Solartron electrochemical measurement unit (model 1280B) was used for dc charge and discharge cycle testing. The capacitor was charged and discharged at a constant current ranging from 0.5 mA to 1 A. The voltage as a function of time was recorded by the measurement unit. The Solartron unit was also used to measure the ac impedance spectra in the frequency range from 1 Hz to 20 kHz. During the ac impedance measurement, a sinusoidal source with an amplitude of 10 mV was applied to the capacitor,

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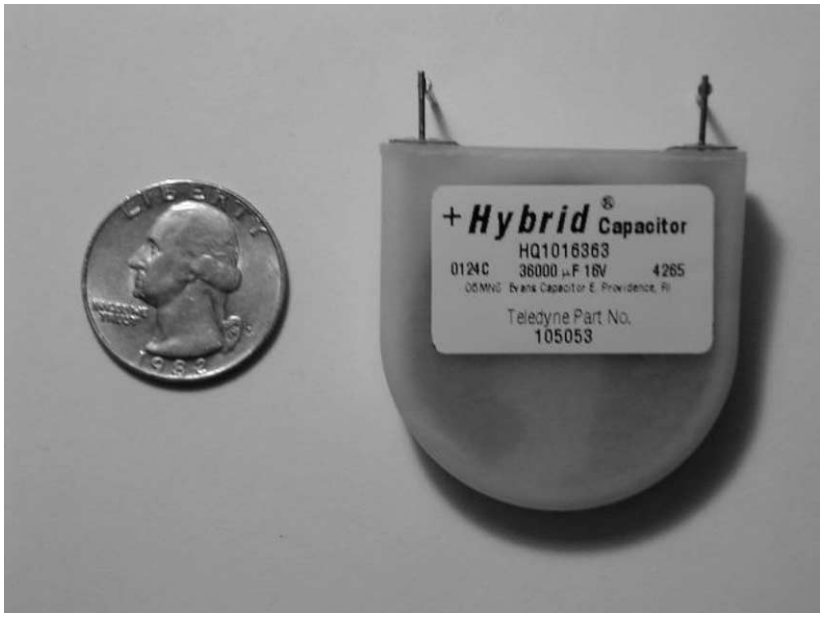

Fig. 1. The picture of a tantalum oxide–ruthenium oxide hybrid capacitor made by Evans Capacitor Company. The capacitor is rated as 36 mF and 16 V.

and the ambient temperature for the capacitor was varied from −70 to 50 °C using an environmental chamber.

Fig. 2 shows the dc discharge characteristics of the hybrid capacitor at different currents. The average capacitance was calculated by multiplying the current by the time duration of the discharge process and then dividing by the maximum applied voltage. It was found that the capacitance was about 35 mF and was insensitive to the current in the range of 0.5 mA–1 A. In Contrast to this observation with electrochemical capacitors, the capacitance of electrochemical capacitors decreased with increasing current [3,5]. This result indicated that hybrid capacitors are capable of high current and high power performance.

The internal resistance and capacitance of the hybrid capacitor as a function of frequency were measured in the range of 1 Hz–20 kHz and are shown in Fig. 3. It was found that the internal resistance (ESR) decreased with increasing frequency and a phase angle of −45° occurred at a frequency of about 100 Hz at room temperature. This is at least an order-of-magnitude higher than that for electrochemical capacitors [6]. Fig. 4 shows the ESR and capacitance as a function of temperature. The ESR was measured at a frequency of 1 kHz and capacitance was measured from the dc discharge curve at a current of 10 mA. It can be seen that the capacitance increased slowly with increasing temperature from about 31 mF at −70 °C to 35 mF at 50 °C. It can also be seen that at temperatures above 10 °C, the internal resistance was about 45 mΩ and was insensitive to the temperature change, however, at temperatures below −10 °C, the ESR increased with decreasing temperature. It is believed that at low temperatures, the ionic resistance of the electrolyte dominated the ESR of the capacitor.

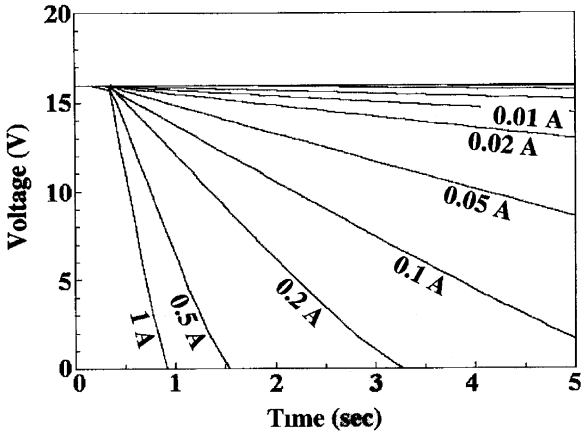

Fig. 2. The dc discharge curves of hybrid capacitor at different currents at 300 K.

The dynamic potentials of anode and cathode electrodes during constant or transient current were measured using an experimental cell with a three electrode configuration. The experimental cell has a similar configuration to the packed cell; however, the capacitor was removed from the container and placed in a beaker filled with 38 wt.% H_2SO_4 solution. The tantalum oxide anode and ruthenium oxide cathode were connected to the working and counter electrodes of the measurement unit, respectively. A saturated calomel electrode (SCE) was used as the reference electrode. Since, the anode and cathode electrodes were not packed as tightly as those in the container, it was found that the ESR of the cell was increased to 125 mΩ at 1 kHz at room temperature. The ESR was almost three times that obtained from the packed capacitor.

The experimental cell was charged and discharged under constant current by the measurement unit, and potentials of

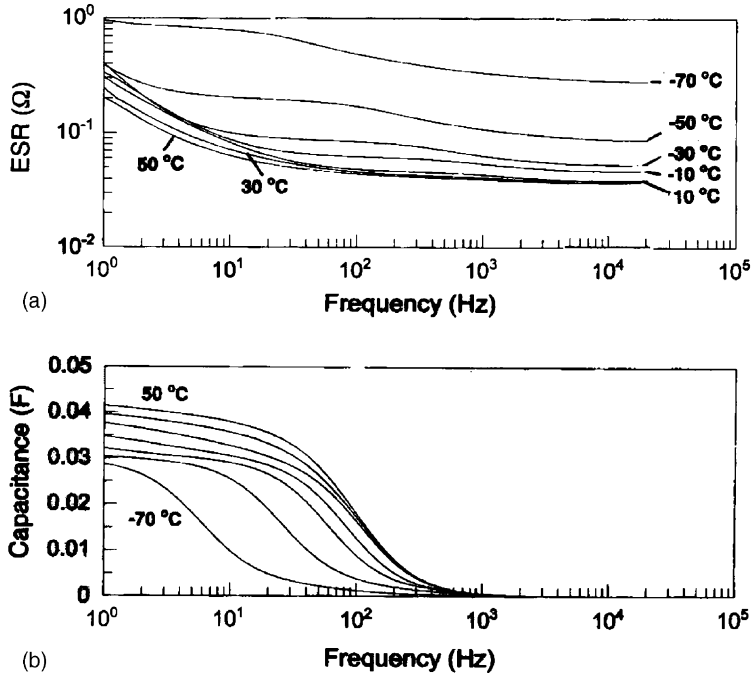

Fig. 3. (a) ESR, and (b) capacitance in the frequency range of 1 Hz–20 kHz at different temperatures.

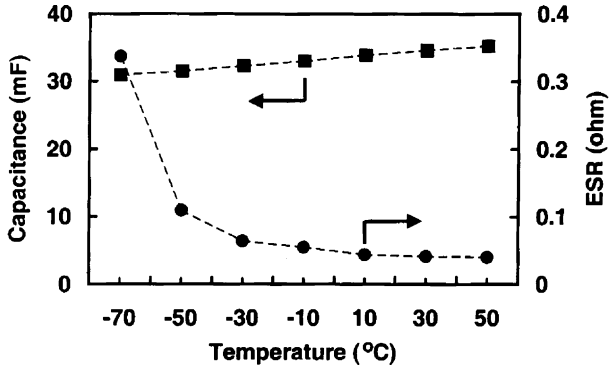

Fig. 4. ESR and capacitance as a function of ambient temperature. The ESR was measured at 1 kHz and capacitance was measured by dc discharge.

both electrodes versus the reference electrode were recorded by a digital oscilloscope. Fig. 5 shows potential changes for both anode and cathode electrodes under a low constant current (10 mA) cycle from 0 to 16 V biased on the cell. A potential change of about 0.39 V on ruthenium oxide cathode electrode was obtained. The majority of the voltage of the capacitor was on the anode electrode. From the potential change of the cathode during the cycle, the capacitance of the ruthenium oxide cathode electrode was calculated, and was about 1.3 F. This was about 36 times greater than the capacitance of the tantalum oxide anode electrode. The high value of capacitance for the cathode electrode is required in order to guarantee that the cathode electrode would be operating within the electrochemical stability window.

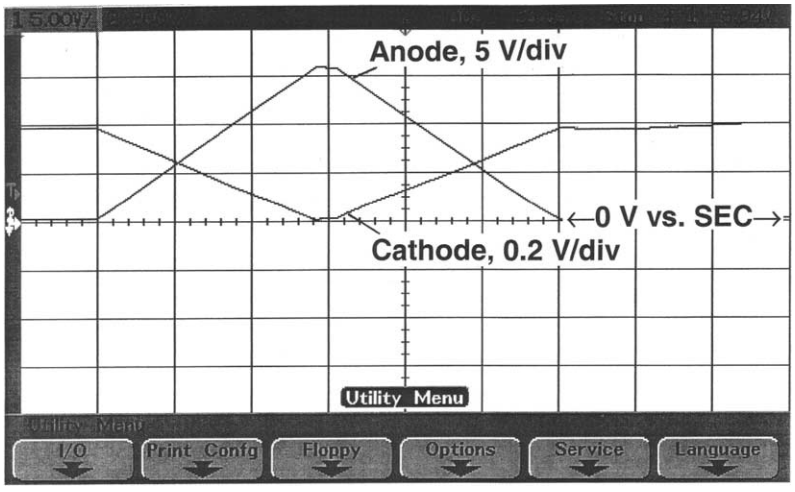

Fig. 5. Potentials of cathode and anode electrodes during a dc current cycle at 10 mA at 300 K. Time scale is 20 s per division.

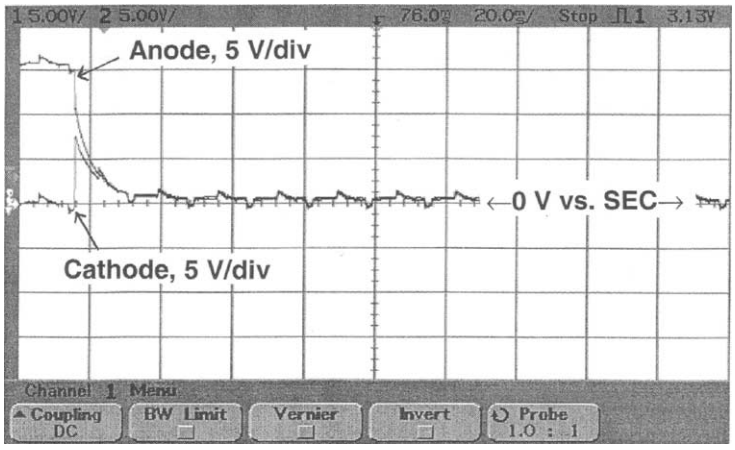

Fig. 6. Potentials of cathode and anode electrodes during a short circuit discharge at 300 K. Time scale is 20 ms per division. The signals at 60 Hz are noise.

The potential changes of both anode and cathode during the transient discharge through a low resistor were also studied. Fig. 6 shows the potential as a function of time, while the cell was discharged through a short circuit with an initial voltage of 16 V. It can be seen that a voltage-jump as high as 7.5 V was obtained from the ruthenium oxide cathode electrode at the initial time of the discharge. This value is well in excess of the stability window (e.g. 1.4 V) of ruthenium oxide in aqueous electrolyte. A sudden drop in potential of about 4.5 V was also obtained from the tantalum oxide anode electrode. The cell was also discharged through resistor loads. The load was made with different combinations of three resistors (0.47 Ω, 10 W) to obtain a total resistance of 0.16, 0.24, 0.47, 0.94, and 1.41 Ω. Fig. 7 shows the initial potential changes for the cathode and anode electrodes due to discharging through loads with different resistances. It can be seen that the voltage-jump at the cathode electrode and voltage-drop at the anode electrode decreased with increasing the resistance of the load.

4. Transient model

A model for describing the transient behavior of the hybrid capacitor was established in order to analyze the experimental results. Fig. 8 shows an equivalent circuit of the hybrid capacitor to be discharged through a load with resistance, R_E. In the circuit, both cathode and anode

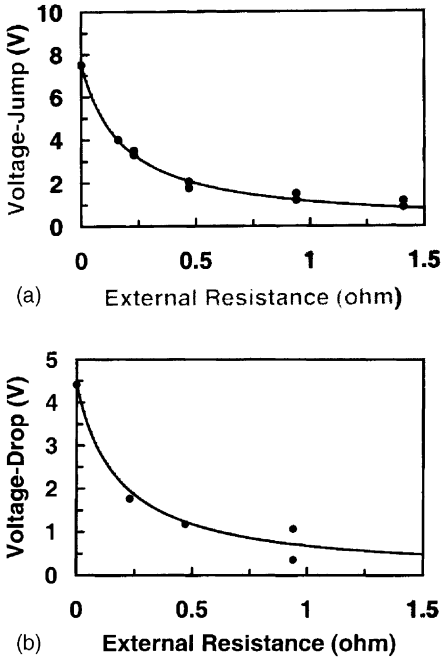

Fig. 7. The initial potential changes from (a) cathode and (b) anode electrodes during transient discharge as a function of resistance value of the load.

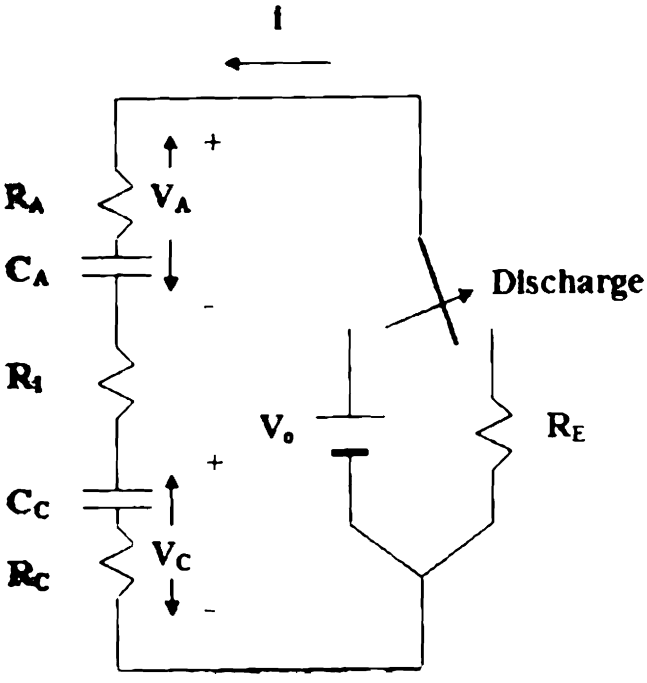

Fig. 8. A simplified equivalent circuit of a hybrid capacitor during the discharge process.

electrodes were represented as a capacitance and resistance in series. C_C and R_C represent the capacitance and resistance of the cathode electrode, respectively; C_A and R_A represent the capacitance and resistance of the anode electrode, respectively; R_I represents the ionic resistance of the electrolyte; and V_C and V_A represent the voltage across the cathode and anode electrodes, respectively. Before discharge, the hybrid cell was charged to a high voltage (e.g. $V_0 = 16$ V). The voltage across each electrode can be expressed as:

$$V_C(0^-) = \frac{C_A}{C_A + C_C} V_0 \quad (1)$$

$$V_A(0^-) = \frac{C_C}{C_A + C_C} V_0 \quad (2)$$

When the hybrid cell was discharged through a resistor, the current is easily expressed as:

$$i(t) = -\frac{V_0}{R} e^{-t/RC} \quad (3)$$

where the total resistance is $R = R_A + R_C + R_I + R_E$, and total capacitance is $C = (C_A C_C)/(C_A + C_C)$. The voltage across the cathode electrode will decay with time and can be expressed as:

$$V_C(t) = \left(\frac{C}{C_C} - \frac{R_C}{R}\right) V_0 e^{-t/RC} \quad (4)$$

The voltage change at the time of discharge can be obtained by subtracting the voltage described by Eq. (1) from the voltage (at $t = 0$) described by Eq. (4), and can be expressed as:

$$\Delta V_C(0) = V_C(0^+) - V_C(0^-) = -\frac{R_C}{R} V_0 \quad (5)$$

Since, the voltage of cathode electrode displayed in Fig. 6 was measured as the potential difference from the cathode electrode to the reference electrode, the polarity of the voltage should be opposite to that of V_C, which is defined in Fig. 8. A voltage-jump at $t = 0$ was observed from the experiment as shown in Fig. 6. Eq. (5) along with Eq. (1) provide important information about the maximum voltage on the cathode electrode. For a hybrid capacitor, it is important that the ruthenium cathode electrode should be always operated within the electrochemical stability window, and both voltage $V_C(0^-)$ and $\Delta V_C(0)$ should be less than 1.4 V [7]. From Eqs. (1) and (5), the minimum capacitance and the maximum resistance of the cathode electrode can be found. From Eq. (5), it can also be seen that the maximum voltage-jump at the cathode electrode increased with increasing internal resistance of the cathode electrode itself. From the voltage-jump in Fig. 6, it can be determined that the internal resistance of the cathode electrode is about 47% of the total resistance of the hybrid cell. Combining Eqs. (1), (2), and (5), it can be concluded that in order to prevent the potential of the cathode electrode from going out of the stability window, not only the capacitance of the cathode electrode should be much greater than that of the anode electrode but also the internal resistance of cathode electrode should be much less than the total resistance of the hybrid capacitor.

Similarly, it can be proved that the voltage-drop at the anode electrode also increased with increasing the internal resistance of the anode electrode itself and can be expressed as:

$$\Delta V_A(0) = -\frac{R_A}{R} V_0 \quad (6)$$

From the initial voltage-drop while discharging through a short circuit, it was found that internal resistances of anode electrode was about 28% of the total resistance of the hybrid cell; therefore, the resistance distributed in the hybrid cell was 47, 28, and 25 from cathode, anode, and electrolyte, respectively. From Eqs. (5) and (6), it can also be seen that the voltage changes at initial discharge were not only dependent on the internal resistance of the cathode and anode electrodes, but also dependent on the total resistance of the entire circuit including the external resistance. The dependence of the voltage-jump or voltage-drop at cathode and anode electrodes on the external resistance was observed experimentally as shown in Fig. 7. The lines in Fig. 7(a) and (b) were the theoretical fitting from Eqs. (5) and (6) using resistance values of 0.085, 0.050, and 0.046 Ω for R_C, R_A, and R_I, respectively. The total internal resistance will be the sum of three resistances which is 0.181 Ω. This is about 45% greater than that measured by ac impedance spectra at high frequency (e.g. at 1 kHz). It can be understood by the fact that during the rapid discharge, the local ions would be depleted in a short period of time [8,9]; therefore, the effective resistance of the cell would increase. The maximum current due to a short circuit discharge can be estimated from Eq. (3) at $t = 0$ and is about 88 A for the experimental cell and will be as high as 350 A for the packed cell.

It must be noted that in the transient model, resistances of R_C and R_A are contributed by the cathode and anode electrodes, respectively, which are impregnated with electrolyte; however, during the transient discharge experiment, beside resistances of R_C and R_A, other resistances such as the contact of the metal wire to the current collector of the electrode and the resistance of the metal wire itself will also contribute to the voltage-jump and voltage-drop on the cathode and anode electrodes, respectively. In the transient model, resistances of the contact and metal wire are part of the internal resistance, R_I. Therefore, actual potential changes at the electrode surface during the transient discharge are smaller than obtained experimentally. However, it was also found that for packed and experimental cells, resistances from the wire and contact were the same, but the internal resistances were different. This result demon-

strated that the internal resistance from electrodes is a significant factor in determining the total internal resistance.

5. Conclusion

It has been demonstrated that the hybrid capacitor has a low internal resistance and is capable of high current or high power charge and discharge. The *RC* product of the hybrid capacitor is about 1×10^{-3} s, which is orders-of-magnitude lower than that of an electrochemical capacitor. The hybrid capacitor can be operated in a wide temperature range from -70 to 50 °C. At low current charge and discharge processes, the ruthenium oxide electrode operates within the electrochemical stability window; however, during high current transient charge or discharge, the potential of the ruthenium oxide electrode exceeds the stability window due to the internal resistance of the cathode electrode. If the high ratio of the capacitance of the cathode electrode to the capacitance of the anode electrode is important to keep the cathode electrode within the stability window in steady state, then the low ratio of the resistance of the cathode electrode to the total resistance of the capacitor is important to keep the cathode electrode within the stability window during the transient mode. Therefore, reduction in the ratio of ruthenium oxide electrode resistance to the total resistance at high frequencies becomes an important issue in order to improve the performance and cycle life of the hybrid capacitors.

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