TANTALUM OXIDE-RUTHENIUM OXIDE HYBRID\textsuperscript{®} CAPACITORS

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Electrochemical-electrolytic hybrid capacitors were first introduced by Evans Capacitor Company. The tantalum oxide or aluminum oxide cathode electrode of an electrolytic capacitor was replaced by a ruthenium oxide (RuO\textsubscript{2}) electrode for improving the energy density. Order-of-magnitude increases in volumetric energy density over electrolytic capacitor have been reported. 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 very high rate of charge and discharge with an RC product of just 0.1 sec. In contrast, the RC product of most electrochemical capacitor is > 0.1 sec.

This study characterized dynamic changes of the hybrid capacitor, anode and cathode electrodes inside the capacitor under different operational conditions. In this study, a 16 V hybrid capacitor was constructed with a pressed and sintered tantalum powder electrode and two RuO\textsubscript{2} films on Ta foil substrates as the cathode. A 38 wt.% H\textsubscript{2}SO\textsubscript{4} solution was used as the electrolyte. The cell had a diameter of 3.4 cm and a thickness of 0.2 cm. The hybrid capacitor was cycled under constant current. A capacitance of 34 mF was obtained from the discharge curves. In the current range of 0.5 mA to 1A, the capacitance value remained nearly constant. The internal resistance of the hybrid capacitor was measured by an ac impedance spectrometer in the frequency range from 1 to 20 kHz (as shown in Figure 1). It was found that at temperatures above 10 \degree C, the internal resistance was insensitive to the temperature; however, at temperatures below -10 \degree C, the internal resistance was increased with decreasing temperature. It indicated that at the low temperatures, the ionic resistance of the electrolyte dominated the internal resistance. From ac impedance spectra of the hybrid capacitor, it was also found that the phase angle of 45\degree at room temperature occurred at the frequency about 100 Hz, which is at least a order-of-magnitude higher than that from the best electrochemical capacitor.

The dynamic potentials of anode and cathode electrodes during constant current cycle or transient current were measured using a three-electrode configuration. The saturated calomel electrode (SCE) was used as the reference electrode. The potential change of about 0.39 V on RuO\textsubscript{2} cathode electrode was obtained during a low current cycle from 0 to 16 V biased on hybrid capacitor (as shown in Figure 2). The capacitance of RuO\textsubscript{2} electrode could be calculated based on the potential differences during the cycle and was about 1.3 F. The major voltage of the capacitor was biased on the anode electrode. However, a potential jump as high as 7.5 V was obtained from the RuO\textsubscript{2} electrode (as shown in Figure 3) when the hybrid capacitor was discharged to a short circuit at initial voltage of 16 V. A model for describing the transient behavior of the hybrid capacitor was established and was used to analyze the experimental results. It was found that internal resistances were distributed as 50%, 20%, and 30% from cathode, anode, and electrolyte, respectively. To reduce in the ratio of RuO\textsubscript{2} electrode resistance to the total resistance at high frequencies become an important issue in order to improve the performance and cycle life of the hybrid capacitors.

![Figure 1 Internal resistances in the frequency range of 1 to 20 kHz at different temperatures.](image1)

![Figure 2 Potentials of anode and cathode electrodes during a dc current cycle at 10 mA at 300 K. Time scale is 20 sec/div.](image2)

![Figure 3 Potentials of anode and cathode electrodes during a short circuit discharge at 300 K. Time scale is 20 ms/div.](image3)