EXAMINATION OF LINEAR POTENTIAL SWEEP METHODS FOR DETERMINING THE CAPACITANCE OF HYDROUS RUTHENIUM OXIDE MATERIALS

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Metal oxides and conducting polymer materials exhibit pseudo-capacitance behavior that involves faradaic reactions between the solid phase and the liquid electrolyte. Hydrous ruthenium oxides used with sulfuric acid electrolytes provide up to 750 F/g via the electrochemical intercalation of H^+ ions into the bulk of the material (1,2). These values are considerably higher than the capacitances for carbon or conducting polymer materials (1).

Cyclic voltammetry is the method generally selected for the determination of the capacitance of hydrous ruthenium oxide as well as for other materials (2-7). The effective capacitance (C) for the electrode is obtained from the simple relationship

$$C = i/v \qquad [1]$$

where i and v are the current response and the potential sweep rate, dE/dt, respectively. Cyclic voltammetric traces are generally shown only for the very slow potential sweep rate of 2 mV/s with no discussion of the effect of faster potential scan rates (2-5,7).

Studies of hydrous ruthenium oxide at our China Lake laboratory using cyclic voltammetry show that high specific capacitances are obtained by the use of Eq. [1] only at very slow potential sweep rates. Furthermore, the cyclic voltammograms collapse at the faster scan rates and lose their characteristic rectangular capacitance shapes. Especially noteworthy is the observation that the cyclic voltammograms become tilted and pointed at each end at faster potential sweep rates.

Our cyclic voltammetric results for hydrous ruthenium oxide can be readily explained by the correct equation

$$i = vC_d+(E_i/R_s-vC_d)exp(-t/R_sC_d) \qquad [2]$$

for a potential sweep involving an electrical circuit of a resistor, R_s, and a capacitor, C_d where E_i is the initial scan voltage at $t = 0$ (8). Furthermore, this equation involves the boundary condition that the charge (q) on the capacitor is zero at $t = 0$ (8). The use of Eq. [1] for the accurate determination of the capacitance of any material using either a single potential sweep or cyclic voltammetry requires that $t > 5\tau$ where the RC time constant is given by $\tau = R_sC_d$ (see Eq. [2]).

It is especially noteworthy that for systems with high capacitances where $R_sC_d >> t$, then Eq. [2] collapses approximately into Ohm's Law

$$i=E/R_s \qquad [3]$$

for potential sweep methods. This Ohm's Law equation is readily derived from Eq. [2] by the expansion $exp(-t/R_sC_d) = 1-t/R_sC_d$ for $R_sC_d >> t$ and by introducing the relationship $vt = E-E_i$ for a linear potential sweep. Thus, a system with a high capacitance, such as hydrous ruthenium oxide, can give Ohm's Law behavior when using a potential sweep method such as cyclic voltammetry and, therefore, a completely erroneous capacity measurement. This Ohm's Law behavior has been observed experimentally in cyclic voltammetric measurements at China Lake for hydrous ruthenium oxide electrodes with large RC time constants.

Figure 1 presents a computer simulation for an electrical circuit of a 1.00 ohm resistor and a 10 F capacitor at a potential scan rate of 500 mV/s. The expected capacity current of 5.00 A based on Eq. [1] would require 50 s (5τ) or 25 V and is never obtained. The actual behavior is approximated by Ohm's Law with $I = 0.9058E+0.0152$, $R^2 = 0.9993$. For cyclic voltammetric measurements the reversal of the potential sweep would re-set the time to zero. However, Eq. [2] is not strictly valid for the reverse scan because the charge on the capacitor is not zero at t=0. Nevertheless, the cyclic voltammograms become tilted, collapsed, and pointed at each end as the potential scan rate increases and the condition for Ohm's Law behavior ($R_sC_d >> t$) is approached.

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REFERENCES

1. A. Burke, *J. Power Sources*, **91**, 37 (2000).
2. J.P. Zheng and T.R. Jow, *J. Electrochem. Soc.*, **142**, L6 (1995).
3. J.P. Zheng, P.J. Cygan and T.R. Jow, *J. Electrochem. Soc.* **142**, 2699 (1995).
4. T.R. Jow and J.P. Zheng, *J. Electrochem. Soc.*, **145**, 49 (1998).
5. J.M. Miller, B. Dunn, T.D. Tran and R.W. Pekala, *J. Electrochem. Soc.*, **144**, L309 (1997).
6. J.P. Zheng, *Electrochem. Solid-State Letters*, **2**, 359 (1999).
7. Y. Sato, K. Yomogida, T. Nanaumi, K. Kobayakawa, J. Ohsawa and M. Kawai, *Electrochem. Solid-State Letters*, **3**, 113 (2000).
8. A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications," John Wiley and Sons, New York, pp. 10-15, 1980.

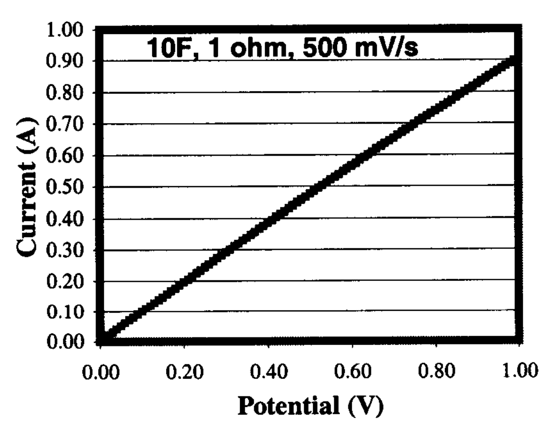

Fig. 1. Theoretical results for a potential scan rate of 500 mV/s involving an electrical circuit of a 1.00 ohm resistor and a 10 F capacitor. See Eq. [2] with $E_i = 0$ V.