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http://scholarcommons.sc.edu/
Publisher’s link: http://dx.doi.org/10.1149/1.1392450
DOI: 10.1149/1.1392450

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A Mathematical Model of an Electrochemical Capacitor with Double-Layer and Faradaic Processes

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A mathematical model of an electrochemical capacitor with hydrous ruthenium oxide (RuO₂·xH₂O) electrodes including both double-layer and surface faradaic processes is developed to predict the behavior of the capacitor under conditions of galvanostatic charge and discharge. The effect of RuO₂·xH₂O particle size is studied and shows that the smaller the particles the better the performance because of the increased surface area per unit volume or mass. The model also predicts that the faradaic process increases significantly the energy per unit volume of the capacitor for power densities of 100 kW/L or less.

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Manuscript submitted November 16, 1998; revised manuscript received April 28, 1999.

Electrochemical capacitors have been receiving increased attention during recent years1-5 as high-power devices in energy-storage systems. There are two mechanisms of energy storage in electrochemical capacitors: (i) a double-layer (DL) charging process due to charge separation, and (ii) a faradaic process due to redox reactions. Devices based on the DL phenomenon are referred to as electrochemical DL capacitors, and those based on faradaic reactions are termed pseudocapacitors. Very high-surface-area carbon materials,6-9 which are widely used for DL capacitors. On the other hand, relatively high-surface-area transition metal oxides, such as amorphous RuO₂·xH₂O,10 porous NiO,11,12 and CoO,12,13 have been identified as possible electrode materials for pseudocapacitors.

A number of models have been developed for analyzing the behavior of DL capacitors. Posey and Morozumi14 developed a model for potentiostatic and galvanostatic charging of the DL in porous electrodes. Johnson and Newman15 also developed a model for a porous electrode to analyze desalting processes in terms of ionic adsorption on porous carbon, and Tiedemann and Newman16 used the results from that model to evaluate the DL capacity of porous electrodes. Recently, Srinivasan et al.17 developed an analytic model and used it to study constant-current discharging, cyclic voltage sweeping, and the ac impedance of carbon xerogel DL capacitors. Also, an analytic model was developed by Farahmandi18 and used to study the effects of both ionic and solid-phase conductivities on the behavior of an electrochemical capacitor. More recently, Fillay and Newman19 modeled the influence of side reactions on the performance of electrochemical capacitors. However, none of these capacitor models accounted for both pseudocapacitance and DL capacitance. In fact, few capacitor models have considered faradaic reactions, and for those that did,20,21 only the approximation of linear faradaic kinetics was considered.

Therefore, the objective of this work is to develop a mathematical model of an electrochemical capacitor with both DL and faradaic processes. These two capacitive processes can occur simultaneously with both contributing to the overall capacitance of the material. This is especially true in the relatively high-surface area transition metal oxide pseudocapacitor materials.5 The specific system used to illustrate the complementary effects of DL and faradaic processes is a symmetric capacitor comprised of uniformly sized spherical hydrous ruthenium oxide (RuO₂·xH₂O) particles with 30 wt % sulfuric acid as the electrolyte. In the model, the diffusion of protons into the solid RuO₂·xH₂O particles is ignored for simplicity; consequently, the DL and faradaic processes take place only on the external surface of the particles. This simplification can be removed, however, by following the procedure presented by Doyle et al.22 for ionic diffusion in the particles. The effects of particle size and cell current density on the charge/discharge behavior are studied, and the roles of the DL and Faradaic processes are delineated with specific reference to Ragone plots.

Model Description

Figure 1 displays a schematic of a typical capacitor cell. Two identical RuO₂·xH₂O electrodes are separated by an ionically conductive glass fiber and are contacted on one side, as shown in Fig. 1, with tantalum current collectors. A solution of 30 wt % H₂SO₄ is used as the electrolyte, which completely fills the pores in the electrodes and the separator. A one-dimensional model is developed using the macrohomogeneous theory of porous electrodes, reviewed by Newman and Tiedemann,23 and De Vidts and White.24 In the model presented here, the electrolyte concentration is assumed to be invariant and side reactions and thermal effects are ignored, along with the variation of the DL capacitance with potential.

Figure 1. Schematic of an electrochemical capacitor cell upon which the model is based.

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The faradaic reactions occurring in the electrodes during charge/discharge are expressed as
\[ \text{charge} \quad \text{discharge} \]
\[ H_{0.8}\text{RuO}_2\cdot xH_2O \quad \leftrightarrow \quad H_{0.8}\text{RuO}_2\cdot xH_2O + \delta H^+ + \delta e^- \quad [1] \]
for the positive electrode, and as
\[ \text{charge} \quad \text{discharge} \]
\[ H_{0.8}\text{RuO}_2\cdot xH_2O + \delta H^+ + \delta e^- \quad \leftrightarrow \quad H_{0.8}\text{RuO}_2\cdot xH_2O \quad [2] \]
for the negative electrode, where the state of charge, \( \delta \), is 0.5 for a cell to be charged to 1 V. These reactions show that initially the active materials in both electrodes are \( H_{0.8}\text{RuO}_2\cdot xH_2O \), which may be obtained by discharging each \( \text{RuO}_2\cdot xH_2O \) electrode separately using external electrodes. Then, during charge, the oxidation reaction (Eq. 1) takes place in the positive electrode and the reduction reaction (Eq. 2) occurs in the negative electrode. Finally, during discharge, the opposite reactions take place in both electrodes, which brings both electrodes to their original states after full discharge, thereby completing a charge/discharge cycle. Thus, during charge, the oxidation state of \( \text{Ru} \) changes from 3.2 to 3.7 in the positive electrode and from 3.2 to 2.7 in the negative electrode. During discharge, it changes back from 3.7 to 3.2 in the positive electrode and from 2.7 to 3.2 in the negative electrode.

In an electrode, the total current transferred from the matrix phase to the electrolyte phase is expressed in terms of the DL current and the faradaic current as
\[ \frac{\partial j_t}{\partial x} = s_C j_d \frac{\partial (\Phi_1 - \Phi_2)}{\partial t} + s_v j_f \quad [3] \]
where \( j_t \) is the superficial current density based on the projected electrode area in the electrolyte phase, \( x \) is the position coordinate, \( s_C \) is the specific surface area per unit volume of the electrode, \( C_d \) is the DL capacitance, \( \Phi_1 \) and \( \Phi_2 \) are the potentials in the matrix and electrolyte phases, respectively, and \( j_f \) is the faradaic transfer current density. \( \Phi_1 \) is defined as the potential of a saturated calomel reference electrode (SCE) connected to the electrolyte phase at the position of interest relative to an identical electrode connected to the electrolyte phase just inside the left current collector \( (x = 0) \). Thus, \( \Phi_2 \) is zero at \( x = 0 \). The faradaic transfer current, \( j_f \), is taken in the form of the Butler-Volmer equation
\[ j_f = j_{i0} \exp(\alpha_f (\Phi_1 - \Phi_2 - U_t)) \quad [4] \]
where \( j_{i0} \) is the exchange current density of the faradaic reaction, \( f \) is equal to \( F/R_T \), \( F \) is Faraday’s constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( \alpha_f \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients for the reactions, respectively, and \( U_t \) is the equilibrium potential of the faradaic reaction. \( U_t \) is a function of the state of charge, \ref{25}, which can be expressed by \( \delta \), the fraction of oxidized species in the electrode. By introducing another variable, \( Q_t \), the faradaic charge of the electrode, \( \delta, \theta, \phi \), and \( j_f \) are related by the following equations
\[ \frac{\partial Q_t}{\partial t} = s_v j_f \quad [7] \]
where \( Q_{t,\text{red}} \) is the faradaic charge of a fully reduced electrode, and \( Q_{t,\text{oxd}} \) is the faradaic charge of a fully oxidized electrode. Equation 7 relates the rate of accumulation of the faradaic charge within the electrode to the faradaic transfer current. For simplicity, Eq. 4, 5, and 7 are combined into a single equation
\[ \frac{\partial \theta}{\partial t} = \frac{s_v j_{i0}}{Q_{t,\text{oxd}} - Q_{t,\text{red}}} \left[ \exp(\alpha_f (\Phi_1 - \Phi_2 - U_t)) \right] - \left[ \exp(-\alpha_f (\Phi_1 - \Phi_2 - U_t)) \right] \quad [8] \]
Conservation of charge leads to
\[ \frac{\partial i_1}{\partial t} + \frac{\partial i_2}{\partial x} = 0 \quad [9] \]
where \( i_1 \) is the superficial current density based on the projected electrode area in the matrix phase of the porous electrode. With the assumption of no concentration gradients in the electrodes, Ohm’s law applies in both the matrix and electrolyte phases as
\[ \begin{align*}
  i_1 &= -\sigma \frac{\partial \Phi_1}{\partial x} \\
i_2 &= -\kappa_p \frac{\partial \Phi_2}{\partial x}
\end{align*} \quad [10],[11] \]
where \( \sigma \) is the electronic conductivity of the matrix, and \( \kappa_p \) is the ionic conductivity of the electrolyte inside the pores of the electrodes. In order to solve the system of equations more efficiently, Eq. 3, 4, 9, 10, and 11 are combined into a single equation
\[ \frac{\partial^2 E}{\partial x^2} = \tau \frac{\partial E}{\partial t} + \frac{\tau_0}{C_d} \left[ \exp(\alpha_f (E - U_t)) \right] - \left[ \exp(-\alpha_f (E - U_t)) \right] \quad [12] \]
with the local electrode potential, \( E \), defined as
\[ E = \Phi_1 - \Phi_2 \quad [13] \]
and the DL time constant as
\[ \tau = s_C L^2 \left( \frac{1}{\sigma} + \frac{1}{\kappa_p} \right) \quad [14] \]
where \( L \) is the thickness of one electrode \( (L = L_+ = L_-) \), and the dimensionless distance \( \xi \) is defined as \( x/L \). In the separator, because the electronic conductivity in the glass fiber is zero
\[ i_1 = 0 \quad [15] \]
and thus the total transfer current is zero
\[ \frac{\partial j_2}{\partial x} = 0 \quad [16] \]
However, Ohm’s law still applies to the current in the electrolyte within the pores of the separator, as
\[ i_2 = -\kappa_s \frac{\partial \Phi_2}{\partial x} \quad [17] \]
where \( \kappa_s \) is the ionic conductivity in the pores of the separator.

To solve this system of partial differential and algebraic equations, the following boundary and initial conditions are used. For the case of a constant-current charge/discharge between 0 and 1 V, the boundary conditions for the positive electrode are
\[ \begin{align*}
  &\text{at } \xi = 0, \ t > 0 \quad \frac{\partial E}{\partial \xi} = -\frac{i_{\text{cell}} L}{\sigma} \\
\end{align*} \quad [18] \]
\[ \begin{align*}
  &\frac{\partial \theta}{\partial t} = \frac{s_v j_{i0}}{Q_{t,\text{oxd}} - Q_{t,\text{red}}} \left[ \exp(\alpha_f (E - U_t)) \right] - \left[ \exp(-\alpha_f (E - U_t)) \right] \quad [19] \]
\[ \begin{align*}
  &\text{at } \xi = 1, \ t > 0 \quad \frac{\partial E}{\partial \xi} = -\frac{i_{\text{cell}} L}{\kappa_p} \quad [20] \]
\]
\[
\frac{\partial \theta}{\partial t} = 0 \quad \text{[21]}
\]

The boundary conditions are set such that at the interface between the current collector and the electrode \((\xi = 0)\), the current arises from the matrix phase, and at the interface between the electrode and separator \((\xi = 1)\), the current arises from the solution phase. The initial conditions are

\[
\begin{align*}
&\text{at } t = 0 \text{ for charge } E = V_o \text{ and } \theta = 0 \quad \text{[22]} \\
&\text{at } t = 0 \text{ for discharge } E = 2V_o \text{ and } \theta = 1 \quad \text{[23]}
\end{align*}
\]

where \(V_o\) is the initial potential before charge and is taken as 0.5 V (SCE) for a cell charge/discharge between 0 and 1 V. Similar boundary and initial conditions can be set for the negative electrode. However, in this model only the positive electrode is simulated; because of the symmetrical feature of the two electrodes, results for the negative electrode are calculated based on the simulation results for the positive electrode.

The entire system of equations to be solved is comprised of two equations and two unknowns, which are Eq. 8 and 12, and \(E\) and \(\theta\), respectively. The system of equations for the potential charges is solved using a backward finite difference method with Newman’s BAND(J) algorithm. It is noteworthy that Eq. 17 is used to evaluate the potential in the solution phase of the separator, which is also solved simultaneously with the system of equations for the positive electrode. Once \(E\) and \(\theta\) are obtained, the other unknowns are calculated using these above equations; for example, Eq. 11, 13, and 4 are used to calculate \(\Phi_f\), \(\Phi_y\), and \(j_r\) respectively. The DL capacitance in each electrode is defined by and obtained from the following two equations, respectively

\[
\begin{align*}
&i_c = -\sigma_C \frac{\partial E}{\partial t} \quad \text{[24]} \\
&i_l = -\nu_L j_l \quad \text{[25]}
\end{align*}
\]

### Model Parameters

In this study, the RuO$_2$:H$_2$O particles are assumed to be non-porous spheres with a uniform size; thus, the pores in the electrodes are composed of the spaces between the particles, and the surface area per unit volume, \(s_v\), of the electrode is expressed as

\[
s_v = \frac{6(1 - \epsilon)}{D} \quad \text{[26]}
\]

where \(D\) is the diameter of the particles and \(\epsilon\) is the electrode porosity (taken as 0.25). Many of the other parameters associated with the RuO$_2$:H$_2$O are unavailable in the literature; therefore, the following reasonable assumptions are made. The DL capacitance on the RuO$_2$:H$_2$O surface is assumed to be \(2 \times 10^{-5} \, \text{F/cm}^2\), which is the same for carbon materials. Both of the anodic and cathodic transfer coefficients, \(\alpha_a\) and \(\alpha_c\), are taken as 0.5; and the exchange current density, \(i_0\), is taken as 10$^{-5}$ A/cm$^2$ from Ref. 27. At \(\delta = 0\), \(U_1\) is equal to 0.5 V for both the electrodes, and at \(\delta = 0.5\), \(U_1\) is equal to 1 and 0 V for the positive and negative electrodes, respectively. Also, according to the relationship between \(\delta\) and \(\theta\) (Eq. 6), \(U_1\) is equal to 0.5(1 + \theta) and 0.5 for the reactions in the positive (Eq. 1) and negative electrodes (Eq. 2), respectively. Here \(\theta\) is the fraction of oxidized species in the Faradaic reaction.

In addition, it is assumed that the Faradaic reactions take place only on the surface of the RuO$_2$:H$_2$O particles inside the electrodes. As a result, the Faradaic charge of a fully oxidized electrode, \(Q_{\text{F,oxd}}\), is estimated from

\[
Q_{\text{F,oxd}} = \frac{s_v \delta F}{h^2 L_A} \quad \text{[27]}
\]

where \(s_v\) is obtained from Eq. 26, \(\delta\) is equal to 0.5 for the fully charged cell, \(h\) is the length of the crystal lattice on the surface and taken approximately as 4 Å,\textsuperscript{31} and \(L_A\) is Avogadro’s number. Equation 27 implies that there is only one Ru atom in the area of $h^2$ on the surface of the RuO$_2$:H$_2$O particles and that $Q_{\text{F,oxd}}$ is a function of the particle size. The Faradaic charge of a fully reduced electrode, $Q_{\text{F,red}}$, is taken as zero.

The electronic conductivity of the matrix, \(\sigma\), is taken as 10$^3$ S/cm,\textsuperscript{32} and the ionic conductivity of bulk 30 wt % H$_2$SO$_4$, \(\kappa_0\), is 0.8 S/cm.\textsuperscript{33} The ionic conductivity of the electrolyte inside the pores of the electrode is frequently expressed as

\[
\kappa_p = \kappa_0 \epsilon^{1.5} \quad \text{[28]}
\]

Similarly, the ionic conductivity of the electrolyte inside the pores of the separator is given by

\[
\kappa_s = \kappa_0 \epsilon^{1.5} \quad \text{[29]}
\]

where the separator porosity, \(\epsilon_s\), is taken as 0.7. The electrode thickness for both the positive and negative electrodes is 50 μm, the separator thickness is 25 μm, and the temperature is 25°C. All these values are summarized in Tables I and II, along with the values of other parameters used in this model.

### Results

At the outset, it is useful to verify the accuracy of the numerical method, which is done by comparing the numerical results for the

### Table I. Model parameters that describe the Faradaic kinetics and open-circuit potentials of the electrodes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_0$</td>
<td>$10^{-5}$ A/cm$^2$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\alpha_a$</td>
<td>0.5</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>0.5</td>
<td>Assumed</td>
</tr>
<tr>
<td>$U_1$ (positive electrode)</td>
<td>0.5(1 + \theta) V (vs. SCE)</td>
<td>Jow and Zhang\textsuperscript{25}</td>
</tr>
<tr>
<td>$U_1$ (negative electrode)</td>
<td>0.5 V (vs. SCE)</td>
<td>Jow and Zhang\textsuperscript{25}</td>
</tr>
</tbody>
</table>

### Table II. Model parameters that describe the electrodes and separator.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>5, 10, 30 nm</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.25</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\epsilon_s$</td>
<td>0.7</td>
<td>Assumed</td>
</tr>
<tr>
<td>$L = L_+$</td>
<td>$5 \times 10^{-3} , \text{cm}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$L_-$</td>
<td>$5 \times 10^{-3} , \text{cm}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$L_m$</td>
<td>$2.5 \times 10^{-3} , \text{cm}$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$C_\text{eq}$</td>
<td>$2 \times 10^{-5} , \text{F/cm}^2$</td>
<td>Assumed</td>
</tr>
<tr>
<td>$s_v$</td>
<td>$1.5 \times 10^4$, $4.5 \times 10^4$, and $9.0 \times 10^4 , \mu\text{F/cm}^2$ for the particle sizes of $D = 30$, $10$, and $5 , \text{nm}$, respectively</td>
<td>From Eq. 26</td>
</tr>
<tr>
<td>$h$</td>
<td>$4.0 \times 10^{-8} , \text{cm}$</td>
<td>Pollak and O’Grady\textsuperscript{31}</td>
</tr>
<tr>
<td>$Q_{\text{F,oxd}}$</td>
<td>150.2, 450.6, and 901.2 C/cm$^2$ for the particle sizes of $D = 30$, $10$, and $5 , \text{nm}$, respectively</td>
<td>From Eq. 27</td>
</tr>
<tr>
<td>$Q_{\text{F,red}}$</td>
<td>0</td>
<td>Assumed</td>
</tr>
<tr>
<td>$\kappa_0$</td>
<td>$10^3$ S/cm</td>
<td>Trasatti and Lodji\textsuperscript{32}</td>
</tr>
<tr>
<td>$\kappa_p$</td>
<td>0.8 S/cm</td>
<td>Darling\textsuperscript{33}</td>
</tr>
<tr>
<td>$\kappa_s$</td>
<td>0.1 S/cm</td>
<td>From Eq. 28</td>
</tr>
<tr>
<td>$s_v$</td>
<td>0.469 S/cm</td>
<td>From Eq. 29</td>
</tr>
<tr>
<td>$T$</td>
<td>298.15 K</td>
<td>Assumed</td>
</tr>
<tr>
<td>$V_o$</td>
<td>0.5 V (vs. SCE)</td>
<td>Assumed</td>
</tr>
</tbody>
</table>
DL process alone (i.e., faradaic process is shut off) with those generated from a completely analytical model for DL capacitors developed by Srinivasan et al. Some dimensionless variables are also introduced, such as dimensionless cell potential, $\Phi^*_{cell}$, dimensionless local potential, $E^*$, dimensionless time, $\tau^*$, dimensionless cell current, $i^*_{cell}$, etc. The definitions of these dimensionless variables are given in the List of Symbols. Finally, the results presented here are for discharge only, because the results for charge are simply the mirror image of those for discharge.

Figure 2A, B, and C compares the results for the change in the dimensionless cell potential with time at two different cell currents, the dimensionless potential distribution at different discharge times, and the dimensionless DL current distribution at different discharge times, respectively. In Fig. 2A, the dimensionless cell potential, $\Phi^*_{cell}$, is defined as $\Phi_{cell}/2V_o$, where $\Phi_{cell}$ represents the matrix potential difference between the two current collectors. Also, the relative utilization, $\tau^*/i^*_{cell}$, represents the fraction of the available capacity extracted from the cell. The RuO$_2$–xH$_2$O particles are 5 nm in diameter. The results show that the numerical solutions agree very well with the analytical solutions up to the fourth digit, which is sufficient for numerical simulations. It is noteworthy that this numerical accuracy is achieved by taking 101 space node points and a time step of $10^{-6}$ s up to 2 s and $10^{-4}$ s thereafter. All of the results presented were obtained from the numerical model using these discretization grid sizes.

Figure 3A shows discharge curves for the combined DL and faradaic processes at a constant cell current of $i^*_{cell} = 0.001$ for three different RuO$_2$–xH$_2$O particle sizes, and Fig. 3B compares the discharge behavior of each of their contributions for a capacitor with 5 nm diam RuO$_2$–xH$_2$O particles at a constant cell current of $i^*_{cell} = 0.001$ to examine how the DL and faradaic processes separately affect the cell potential. Linear relationships of the cell potential with discharge time are observed in Fig. 3A for all three particle sizes.
sizes, and the discharge time increases with a decrease in the particle size. The actual discharge time is used here instead of relative utilization \( (\tau_i i_{\text{cell}}) \), because the DL time constant \( \tau \) depends on the particle size, which makes the discharge curves incomparable in terms of relative utilization. Linear relationships are again observed in Fig. 3B for the DL process alone, faradaic process alone, and the combined DL and faradaic processes; and the DL process alone has the shortest discharge time, the faradaic process alone has a discharge time five times longer than the DL process alone, and the combined DL and faradaic processes has the longest discharge time, appearing as a linear combination of the two individual processes. The linear behavior of the change in cell potential with time is characteristic of a DL capacitor when the DL capacitance is independent of the potential. As for the faradaic process simulated here, the linear behavior is most likely due to the linear relationship between the equilibrium potential and the state of charge, which makes this faradaic material of \( \text{RuO}_2 \cdot x \text{H}_2 \text{O} \) behave like a simple DL capacitor.

Figure 4A and B illustrates the effect of cell current on the cell potential for the combined DL and faradaic processes and for the faradaic process alone, respectively. The \( \text{RuO}_2 \cdot x \text{H}_2 \text{O} \) particles are 5 nm in diam. For the combined DL and faradaic processes (Fig. 4A), at the smaller current \( i_{\text{cell}} = 0.001 \), the cell potential decreases linearly with time. However, at the larger current \( i_{\text{cell}} = 0.5 \), a sharp drop in potential at the start of discharge is observed, which is followed by a linear decrease in potential for the remainder of the discharge. These discharge curves are similar in shape to those for the DL process alone, as shown in Fig. 2A, but the potential drop is larger for the combined DL and faradaic processes.

For the faradaic process alone (Fig. 4B), at the smaller current, the cell potential also decreases linearly as those observed for the combined DL and faradaic processes (Fig. 4A) and for the DL process alone (Fig. 2A). At the larger current, however, the cell potential behaves differently from that for the DL process alone. The potential decreases almost linearly with time but with a marked drop at the start of discharge, unlike the initial potential drops for the DL process alone that exhibit curvature. This marked potential drop is believed to be associated with the faradaic kinetic resistance; the result is consistent with a larger drop in potential for the combined DL and faradaic processes than that for the DL process alone.

To examine how potentials and currents inside the electrode change during discharge, the distributions of the potential throughout the positive electrode at different discharge times at a cell current of \( i_{\text{cell}} = 0.5 \) are shown in Fig. 5A and B for the combined DL and faradaic processes and for the faradaic process alone, respectively. The corresponding distributions of the currents are illustrated in Fig. 6A and B for the combined DL and faradaic processes and in Fig. 6C for the faradaic process alone. For the combined DL and faradaic processes (Fig. 5A), the potential distribution changes gradually from the initial uniform distribution at the start of discharge to a steady-state nonuniform profile at about \( \tau i_{\text{cell}} = 0.222 \). Then the cell potential decreases with this steady-state profile until the cell is totally discharged. The nonuniform potential distribution is due mainly to the ohmic potential drop in the solution phase (the conductivity in the matrix phase is much greater than that in the solution phase in this modeling simulation), and the transition time to reach the steady-state profile is determined by the DL time constant.

![Figure 4](image1.png)

**Figure 4.** Constant-current discharge curves at two dimensionless currents: (A) for the combined DL and faradaic processes and (B) for the faradaic process alone.

![Figure 5](image2.png)

**Figure 5.** Potential distributions throughout the positive electrode at different times during discharge at a constant current of \( i_{\text{cell}} = 0.5 \): (A) for the combined DL and faradaic processes and (B) for the faradaic process alone.
Again, these distributions are similar in shape to those at the same discharge times for the DL process alone, as shown in Fig. 2B, but the decrease in potential is slower for the combined DL and faradaic processes because it holds more energy compared with the DL process alone. For the faradaic process alone (Fig. 5B), the potential distribution changes immediately to a steady-state nonuniform profile after the start of the discharge, then the potential decreases with this profile until the cell is fully discharged. The reason for this immediate change in potential distribution is that in this case there is no DL time constant that controls the transition of the potential distribution to gradually reach a steady-state profile. Again, the nonuniform potential distribution is largely due to the ohmic resistance in the solution phase.

For the combined DL and faradaic processes, the DL current distribution throughout the electrode (Fig. 6A) is very nonuniform at short times, and the degree of this nonuniformity decreases with time. The DL current attains a uniform profile at about \( \tau_{\text{ave}}^{i_{\text{DL}}} = 0.222 \), and then decreases continuously with this uniform profile until the cell is totally discharged at \( \tau_{\text{ave}}^{i_{\text{DL}}} = 3.7 \) and it reaches 0.2. These distributions are also similarly shaped to those for the DL process alone, as shown in Fig. 2C. Meanwhile, the faradaic current (Fig. 6B) increases with time and its distribution reaches a maximum of nonuniformity at about \( \tau_{\text{ave}}^{i_{\text{DL}}} = 0.222 \). Finally, a uniform distribution is attained and the faradaic current reaches 0.8 at \( \tau_{\text{ave}}^{i_{\text{DL}}} = 3.7 \), which is four times greater than the final current for the DL process alone, as shown in Fig. 6A. For the faradaic process alone (Fig. 6C), the faradaic current distribution is at a maximum of nonuniformity at the start of discharge, then the degree of this nonuniformity decreases with time, and finally it reaches a uniform profile at \( \tau_{\text{ave}}^{i_{\text{DL}}} = 2.8 \).

Because local potentials are related to local currents, a change in local potential must result in a change in local current. However, for the DL and faradaic processes alone, they are related in different ways. The DL current is proportional to the derivative of the local potential with respect to time (Eq. 24), but the faradaic current is nonlinearly related to the local potential with an exponential dependence (Eq. 25 and 4). These different features for the two processes determine their different current distributions in response to a change in local potential. For the DL process alone (Fig. 2B and C), the change in local potential is the greatest at the start of discharge; as a result, the DL current distribution reaches a maximum of nonuniformity. As the change in local potential becomes smaller with time, the DL current distributions become more uniform. Finally, as the potential distribution attains a steady-state profile, the change in local potential with time is the same throughout the electrode, which leads to a uniform DL current distribution. For the faradaic process alone (Fig. 5B and 6C), the change in local potential is also the greatest at the start of discharge, which leads to a very nonuniform, faradaic current distribution; meanwhile, the potential distribution reaches a steady-state profile instantly. This steady-state potential profile does not translate into a uniform faradaic current distribution because of the nonlinear relationship between the local potential and the local current as shown in Eq. 4. The final uniform faradaic current distribution is likely reached because the difference between the two exponential terms approaches a constant. For the combined DL and faradaic processes, the potential and the DL current distributions are similar to those for the DL process alone; its faradaic current distributions are similar to those for the faradaic process alone. However, the relative magnitudes of the DL and faradaic currents are determined by how they are related in the governing equations (Eq. 4, 24, and 25).

The results in Fig. 3A show that the particle size is extremely important to the discharge behavior of the capacitor. It is therefore of interest to investigate the performance of this model capacitor in terms of Ragone plots, *i.e.*, in terms of the energy and power densities. The energy and power densities are calculated as follows:

\[
\text{Energy density} = \frac{I_{\text{ave}} \Phi_{\text{ave}} d}{V_{\text{cell}}} \tag{30}
\]

\[
\text{Power density} = \frac{I_{\text{ave}} \Phi_{\text{ave}}}{V_{\text{cell}}} \tag{31}
\]

where \( I_{\text{ave}} \) is the total cell current, which is obtained by multiplying the cell current density \( i_{\text{ave}} \) by the cross-sectional area of the electrode, \( A \). \( \Phi_{\text{ave}} \) is the average cell potential, \( t_{\text{d}} \) is the discharge time, and \( V_{\text{cell}} \) is the volume of the cell including the electrodes, electrolyte, and separator. The average cell potential is given by...
Figure 7A shows Ragone plots for the combined DL and faradaic processes and for three different particle sizes. The curves are all similarly shaped, but the energy density decreases with an increase in particle size over the entire range of power densities, and it begins to drop off sooner but more slowly as the power density increases.

Image 7A: Ragone plots for the combined DL and faradaic processes for three different particle sizes.

Figure 7A: Ragone plots: (A) for the combined DL and faradaic processes for three different sizes of RuO$_2$·xH$_2$O particles and (B) for the DL process alone, faradaic process alone, and combined DL and faradaic processes with 5 nm diam RuO$_2$·xH$_2$O particles.

Discussion

Both of the DL and faradaic processes studied here are surface phenomena which take place at the interface between the electrode and electrolyte. For the DL process, more surface area and a higher specific capacitance both give rise to more energy storage at the interface. Also, for the surface faradaic process, more surface area gives rise to more energy storage at the interface. Moreover, the more active the surface material is toward reversible redox reactions (determined by the value of the exchange current density, $i_0$), the higher the power density. In this study, however, the specific capacitance of the DL process and the exchange current density of the faradaic process are all fixed; so the only variable is the surface area, which is changed by varying the size of the RuO$_2$·xH$_2$O particles in the electrode. In fact, some researchers$^{34}$ reported much higher DL capacitance of 60 mF/cm$^2$ for oxide electrode systems based on a proton-exchange mechanism. In this case, the calculated DL current would be expected to be tripled, which in turn would result in a threefold increase in the energy density contributed from the DL process.

According to Eq. 26, the surface area is inversely proportional to the particle size. As the particle size decreases from 30 to 10 to 5 nm, the surface area increases three times and six times, respectively, which is proportionally the same as the increase in the discharge times shown in Fig. 3A. In addition, the results in Fig. 3B show clearly that the discharge time for the faradaic process alone is five times higher than that for the DL process alone, indicating the importance of the faradaic process for increasing the energy density of a capacitor. Furthermore, Eq. 30 and 31 state that the energy density is proportional to the total cell current, $I_{cell}$ average cell potential, $\Phi_{ave}$, and discharge time, $t_d$, but it is inversely proportional to the cell volume, $V_{cell}$. The power density is the same as the energy density except that it is independent of $i_d$ (which may not be true because $\Phi_{ave}$ is a function of $i_0$). Although a first glance at these equations suggests that an increase in cell current results in an increase in energy density, actually this is not true because the discharge time decreases with an increase in cell current. The overall effect is that the energy density decreases with an increase in power density. The results in Fig. 7A show that the ratio of the increase in energy density at the same power density is roughly the same as the ratio of the increase in surface area for the different sizes of RuO$_2$·xH$_2$O particles.

In addition, in order to increase the power density, the cell current density must be increased, as shown in Fig. 7A and B. However, the resulting increase in power density is obtained at the expense of decreasing energy density, mainly because of the ohmic resistance in the solution phase for the DL process alone. For the faradaic process alone, the energy loss at higher power densities is due to the ohmic resistance in the solution phase as well as the faradaic kinetic resistance. The faradaic kinetic resistance even makes the faradaic process alone fail, because the cell potential cannot hold at the working potential range. What is even more interesting, however, is that for the combined DL and faradaic processes, the energy loss is less compared with that for the faradaic process alone at the same power density. The reason is that the DL process has the ability to hold the cell potential, which allows the faradaic process to deliver some energy even beyond the power at which the faradaic process alone would fail. These results are consistent with those shown in Fig. 2A, 4A, and 4B, which indicate that the energy loss at the larger current (based on relative utilization) is 20, 44, and 37% for the DL process alone, faradaic process alone, and combined DL and faradaic processes, respectively. Although there is always a trade-off between the energy and power densities, a capacitor with both DL and faradaic processes can store more energy and deliver more power compared with that obtained from either the DL or faradaic processes alone.

\[
\Phi_{ave} = \frac{1}{i_d} \int_0^{t_d} \Phi_{cell} dt \tag{32}
\]
In this study, it is also assumed that the faradaic reaction takes place only at the surface of the particle with one-electron exchange between 0 and 1 V (SCE). In practice, however, the inner layers within a particle may also participate in the redox reaction through a proton diffusion mechanism.\cite{37,38} Other authors\cite{39} have suggested a faradaic reaction of RuO$_2$ with a two-electron exchange. As a result, the faradaic charge of a fully oxidized electrode can double according to Eq. 27, which means that the energy density from the faradaic process can also double. Nevertheless, the power density may decrease because of slow proton diffusion in the innerlayers of the solid phase. In addition, in this study the electronic conductivity of the matrix is taken as 105 S/cm, which is 3-4 orders of magnitude higher than the value suggested by some researchers\cite{40} based on boundary effects associated with powder materials\cite{41} and less crystallinity\cite{42} in hydrous RuO$_2$. However, if the conductivity is taken as this lower value, the simulated results will not be affected much because the limiting conductivity is in the solution.

Conclusions

A mathematical model of an electrochemical capacitor comprised of hydrous ruthenium oxide (RuO$_2$-H$_2$O) electrodes, including both DL and surface faradaic processes, was developed to predict the behavior of the capacitor under the conditions of galvanostatic charge and discharge. A comparison of various numerical solutions from the model with analytical ones for the DL process alone revealed that the numerical simulations were accurate up to the fourth digit. The results show that the energy density can be increased by increasing the particle size, whereas the power density can only be increased by increasing the cell current density. However, there is always a trade-off between the energy and power densities. The results also indicate that a capacitor with both DL and faradaic processes has higher energy densities compared with the DL process alone and higher power densities compared with the faradaic process alone. The model predicts that the faradaic process increases significantly the energy per unit volume of the capacitor for power densities of 100 kW/L or less.

Acknowledgments

The authors are grateful for the financial support provided in part by the U.S. Army Research Office under grant no. DAAH04-96-1-0421 and in part by the U.S. Department of Energy under Cooperative Agreement no. DE-FC02-91ER75666. The University of South Carolina assisted in meeting the publication costs of this article.

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>cross-sectional area of the electrode, cm$^2$</td>
</tr>
<tr>
<td>$C_d$</td>
<td>DL capacitance per unit surface area, F/cm$^2$</td>
</tr>
<tr>
<td>$D$</td>
<td>diameter of the RuO$_2$-H$_2$O particles, cm</td>
</tr>
<tr>
<td>$E$</td>
<td>local electrode potential, $\Phi - \Phi_r$, V</td>
</tr>
<tr>
<td>$E_0$</td>
<td>dimensionless local potential, $E_0/V_o$</td>
</tr>
<tr>
<td>$f$</td>
<td>$F/RT$, $V^{-1}$</td>
</tr>
<tr>
<td>$F_{\text{Faraday's constant}}$</td>
<td>96487 C/equiv</td>
</tr>
<tr>
<td>$h$</td>
<td>length of the crystal lattice on the RuO$_2$-H$_2$O surface, cm</td>
</tr>
<tr>
<td>$i_b$</td>
<td>exchange current density for the faradaic reaction, A/cm$^2$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>superficial current density in the matrix phase, A/cm$^2$</td>
</tr>
<tr>
<td>$i_1$</td>
<td>superficial current density in the electrolyte phase, A/cm$^2$</td>
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<tr>
<td>$i_{\text{cell}}$</td>
<td>DL current per unit volume of the electrode, A/cm$^3$</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{applied}}$</td>
<td>cell current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{total}}$</td>
<td>total cell current, A</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{f}}$</td>
<td>dimensionless faradaic current, $i_{\text{cell}}^{\text{f}} / L_{\text{cell}}$</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{f,red}}$</td>
<td>faradaic current per unit volume of the electrode, A/cm$^3$</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{f,trans}}$</td>
<td>faradaic transfer current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_{\text{cell}}^{\text{f,trans}}$</td>
<td>dimensionless faradaic current, $i_{\text{cell}}^{\text{f,trans}} / L_{\text{cell}}$</td>
</tr>
<tr>
<td>$L$</td>
<td>thickness of the electrode, $L = L_1 = L_2 = L$, cm</td>
</tr>
<tr>
<td>$L_A$</td>
<td>Avogadro's number, 6.022 $\times$ 10$^{23}$ mol$^{-1}$</td>
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<td>$L_{\text{eff}}$</td>
<td>thickness of the separator, cm</td>
</tr>
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<td>$Q_{\text{f,red}}$</td>
<td>faradaic charge per unit volume of the fully reduced electrode, C/cm$^3$</td>
</tr>
<tr>
<td>$Q_{\text{f,red}}$</td>
<td>faradaic charge per unit volume of the fully oxidized electrode, C/cm$^3$</td>
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<td>$R$</td>
<td>universal gas constant, 8.3143 J/mol K</td>
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<td>$s_0$</td>
<td>specific surface area per unit volume of the electrode, cm$^2$/cm$^3$</td>
</tr>
<tr>
<td>$t$</td>
<td>time, s</td>
</tr>
</tbody>
</table>

References