Electrochemical capacitors are urgently needed as components in many advanced power systems requiring high power density, high energy density, and high cycleability.\textsuperscript{1,4} Energy storage mechanisms in an electrochemical capacitor include separation of charge at the interface between a solid electrode and a liquid electrolyte, leading to double-layer (DL) capacitance, and faradaic redox reactions occurring at or near a solid electrode surface, known as pseudocapacitance. Charge storage in DL capacitance is essentially electrostatic in nature, and so DL charge/discharge processes are usually highly reversible. Pseudocapacitance, originating from faradaic redox reactions of oxides like RuO\textsubscript{2}, IrO\textsubscript{2}, or Co\textsubscript{3}O\textsubscript{4} at or near the electrode surface, involves interfacial reaction as well as mass transfer of ionic charge across the double layer.\textsuperscript{5}

Capacitors employing both DL and pseudocapacitance generally perform better than those featuring just one kind of capacitance. Activated carbon has been frequently used because its porous structure and large internal surface area result in electrodes with high specific energy and specific power densities.\textsuperscript{6} The pore structure of activated carbon is a significant element in determining electrochemical capacitor performance. Shi\textsuperscript{7} argued that pores of different sizes (micro-, meso-, and macropores) play different roles in contributing to DL capacitance. Macropores make a small contribution to the total specific surface area and thus contribute little to the DL capacitance. At the other extreme, micropores are responsible for most of the specific surface area, but the smallest pores may not be accessible to the electrolyte and thus do not contribute to the DL capacitance. Nevertheless, Shi claims that much of the charge storage occurs in pores with diameters less than 2 nm.

The hydrous form of ruthenium oxide (RuO\textsubscript{2}·xH\textsubscript{2}O) has been identified as an excellent electrode material for electrochemical capacitors.\textsuperscript{8,9} Its redox reaction (shown later) produces significant pseudocapacitance as well as some contribution to DL capacitance. However, the low porosity of the native material leads to a sharp decrease in power density at high charge/discharge rates. Low power density combined with its high cost make pure RuO\textsubscript{2}·xH\textsubscript{2}O unsuitable for commercial electrochemical capacitor applications. To improve power density, high rate performance, and cost, recent electrochemical capacitor research has focused on developing nanostructured RuO\textsubscript{2}·xH\textsubscript{2}O-carbon composite materials.\textsuperscript{10,11} These materials have a high DL capacitance originating from high surface area of porous activated carbon, plus pseudocapacitance derived from the redox reactions of RuO\textsubscript{2} dispersed over the carbon surface. Dispersing the RuO\textsubscript{2} as nanoparticles improves the utilization of the redox active material. Thus the RuO\textsubscript{2} nanoparticle size and the efficiency of its dispersion on the carbon surface are variables that may affect electrochemical capacitor performance.

Various mathematical models have been developed to investigate the relationship between performance and material characteristics in the electrochemical capacitors. Johnson and Newman\textsuperscript{10} developed a model to describe DL charging in an electrochemical cell and to predict the specific energy and power densities of electrochemical capacitors.\textsuperscript{11} Srinivasan and Weidner\textsuperscript{12} presented an electrochemical capacitor model that assumed a uniform salt concentration profile and faradaic processes with features similar to those of capacitors. With these assumptions, their model yielded analytical solutions for discharge performance. Lin et al.\textsuperscript{13} developed a model to account for both DL capacitance and faradaic redox reactions in an electrochemical capacitor. Other simplified models in the literature have been reviewed previously.\textsuperscript{12,13}

All previous models have assumed a single value of electrode porosity and a uniform diameter for dispersed oxide particles. No previous models have considered the effect of varying pore structure, electrode composition (e.g., loading of RuO\textsubscript{2} in carbon), or size distribution of dispersed oxide particles on electrochemical capacitor performance. Related modeling work has considered the effects of the particle size distribution (PSD) and electrode composition for porous intercalation electrodes. Nagarajan et al.\textsuperscript{14} developed a model to study the effects of PSD on the galvanostatic discharge behavior of the lithium/seperator/intercalation electrode system. Packing theory was used to calculate the specific surface area and porosity of electrodes composed of materials having two characteristic particle sizes. The model was used to investigate capacity and utilization effects on the galvanostatic charge/discharge of electrodes composed of binary mixtures of spherical particles. Darling and Newman\textsuperscript{15} also modeled a porous intercalation electrode with two characteristic particle sizes and found that PSD had an even more pronounced influence on the open-circuit behavior. Heikonan et al.\textsuperscript{16} considered the effects of PSD on the discharge behavior of a nickel-metal hydride cell. Card et al.\textsuperscript{17} developed a model for an activated-carbon, packed-bed electrochemical reactor that considered the effects of both micropores and macropores.

In this paper, we extend our previous model\textsuperscript{11} by using packing theory\textsuperscript{18} to account for varying composition and particle size effects on electrochemical capacitor performance. The model is also used to investigate the salt concentration distribution in the electrolyte phase, although we are limited by the use of dilute solution theory.
The model can be used to optimize the electrode composition to lower costs and improve the electrochemical capacitor’s energy density, power density, and high rate performance.

**Model Description**

**Assumptions.**—The model presented here represents an extension of the general model of porous electrodes developed by Newman and Tiedemann.\(^1\) Here, we consider an electrochemical capacitor of the general model of porous electrodes developed by Newman, assuming that the specific surface area for DL charge/discharge, \(S_d\), is not the same as the specific surface area for the faradaic redox reactions, \(S_f\). One of the main objectives here is to develop expressions for \(S_d\), \(S_f\), and electrode porosity \(\varepsilon\) based on the specified composition of the electrode, the carbon pore size distribution, and the known RuO\(_2\) particle size.

The composite electrode consists of large, irregular particles of porous carbon-containing dispersed RuO\(_2\) nanoparticles. Shi, in his tabulation of the structural properties of many commercial activated carbons,\(^7\) divided the carbon specific surface area into internal and external contributions based on the pore size distribution. Only micropores (pore width less than 2 nm) contribute to the internal surface area (\(S_{C,int}\)). Meso- and macropores (pore width greater than 2 nm) are responsible for external surface area (\(S_{C,ext}\)). RuO\(_2\) particles of uniform diameter \(d_{Ru}\) are generally too large to fit inside micropores, but they do pack within the carbon’s meso- and macropores. To account for the effect of RuO\(_2\) particle packing on porosity, we define an effective spherical particle diameter for the activated carbon, \(d_C\), defined by

\[
d_C = \frac{6}{\hat{S}_{C,ext} \rho_C}
\]

based on the external surface area of the carbon that is accessible to the RuO\(_2\) nanoparticles. The RuO\(_2\) nanoparticles pack into the pores of the carbon as shown schematically in Fig. 1. Packing theory (detailed in the Appendix) provides the value of \(\varepsilon\) as a function of \(d_C\), \(d_{Ru}\), and the composition of the electrode.

Once \(\varepsilon\) has been determined, \(S_d\) and \(S_f\) may be expressed in terms of \(\hat{S}_{C,int}\), \(\hat{S}_{C,ext}\), and \(d_{Ru}\). We assume that all of the surface contributes to DL capacitance. Thus

\[
S_d = (\hat{S}_{C,int} + \hat{S}_{C,ext}) \rho_C x_C (1 - \varepsilon) + \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

However, only the RuO\(_2\) surface is redox-active and contributes to the pseudocapacitance, so

\[
S_f = \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

The volume fractions may be expressed in terms of mass fractions as shown in the Appendix.

The other governing equations are similar to those given previously.\(^{13}\) The conservation of charge and Ohm’s law in the matrix phase lead to

\[
\frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x} = 0 \tag{7}
\]

\[
i_1 = -\sigma \frac{\partial \Phi_1}{\partial x} \tag{8}
\]

Concentration polarization in the electrolyte, not considered previously, is considered here. In the context of concentrated solution theory,\(^{15}\) a mass balance on salt leads to

\[
\frac{\partial \tilde{i}_2}{\partial x} = \tilde{S}_d \frac{\partial (\tilde{\Phi}_1 - \tilde{\Phi}_2)}{\partial t} + \tilde{S}_f \tilde{j}_f \tag{3}
\]

where \(i_2\) is the superficial current density in the electrolyte phase. The first term on the right represents DL charge/discharge, and the second term represents charge production by the faradaic redox reactions, Eq. 1 and 2. Equation 3 differs from that used in previous work\(^{13}\) in that the specific surface area for DL charge/discharge, \(S_d\), is not the same as the specific surface area for the faradaic redox reactions, \(S_f\). One of the main objectives here is to develop expressions for \(S_d\), \(S_f\), and electrode porosity \(\varepsilon\) based on the specified composition of the electrode, the carbon pore size distribution, and the known RuO\(_2\) particle size.

The composite electrode consists of large, irregular particles of porous carbon-containing dispersed RuO\(_2\) nanoparticles. Shi, in his tabulation of the structural properties of many commercial activated carbons,\(^7\) divided the carbon specific surface area into internal and external contributions based on the pore size distribution. Only micropores (pore width less than 2 nm) contribute to the internal surface area (\(S_{C,int}\)). Meso- and macropores (pore width greater than 2 nm) are responsible for external surface area (\(S_{C,ext}\)). RuO\(_2\) particles of uniform diameter \(d_{Ru}\) are generally too large to fit inside micropores, but they do pack within the carbon’s meso- and macropores. To account for the effect of RuO\(_2\) particle packing on porosity, we define an effective spherical particle diameter for the activated carbon, \(d_C\), defined by

\[
d_C = \frac{6}{\hat{S}_{C,ext} \rho_C}
\]

Based on the external surface area of the carbon that is accessible to the RuO\(_2\) nanoparticles. The RuO\(_2\) nanoparticles pack into the pores of the carbon as shown schematically in Fig. 1. Packing theory (detailed in the Appendix) provides the value of \(\varepsilon\) as a function of \(d_C\), \(d_{Ru}\), and the composition of the electrode.

Once \(\varepsilon\) has been determined, \(S_d\) and \(S_f\) may be expressed in terms of \(\hat{S}_{C,int}\), \(\hat{S}_{C,ext}\), and \(d_{Ru}\). We assume that all of the surface contributes to DL capacitance. Thus

\[
S_d = (\hat{S}_{C,int} + \hat{S}_{C,ext}) \rho_C x_C (1 - \varepsilon) + \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

However, only the RuO\(_2\) surface is redox-active and contributes to the pseudocapacitance, so

\[
S_f = \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

The volume fractions may be expressed in terms of mass fractions as shown in the Appendix.

The other governing equations are similar to those given previously.\(^{13}\) The conservation of charge and Ohm’s law in the matrix phase lead to

\[
\frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x} = 0 \tag{7}
\]

\[
i_1 = -\sigma \frac{\partial \Phi_1}{\partial x} \tag{8}
\]

Concentration polarization in the electrolyte, not considered previously, is considered here. In the context of concentrated solution theory,\(^{15}\) a mass balance on salt leads to

\[
\frac{\partial \tilde{i}_2}{\partial x} = \tilde{S}_d \frac{\partial (\tilde{\Phi}_1 - \tilde{\Phi}_2)}{\partial t} + \tilde{S}_f \tilde{j}_f \tag{3}
\]

where \(i_2\) is the superficial current density in the electrolyte phase. The first term on the right represents DL charge/discharge, and the second term represents charge production by the faradaic redox reactions, Eq. 1 and 2. Equation 3 differs from that used in previous work\(^{13}\) in that the specific surface area for DL charge/discharge, \(S_d\), is not the same as the specific surface area for the faradaic redox reactions, \(S_f\). One of the main objectives here is to develop expressions for \(S_d\), \(S_f\), and electrode porosity \(\varepsilon\) based on the specified composition of the electrode, the carbon pore size distribution, and the known RuO\(_2\) particle size.

The composite electrode consists of large, irregular particles of porous carbon-containing dispersed RuO\(_2\) nanoparticles. Shi, in his tabulation of the structural properties of many commercial activated carbons,\(^7\) divided the carbon specific surface area into internal and external contributions based on the pore size distribution. Only micropores (pore width less than 2 nm) contribute to the internal surface area (\(S_{C,int}\)). Meso- and macropores (pore width greater than 2 nm) are responsible for external surface area (\(S_{C,ext}\)). RuO\(_2\) particles of uniform diameter \(d_{Ru}\) are generally too large to fit inside micropores, but they do pack within the carbon’s meso- and macropores. To account for the effect of RuO\(_2\) particle packing on porosity, we define an effective spherical particle diameter for the activated carbon, \(d_C\), defined by

\[
d_C = \frac{6}{\hat{S}_{C,ext} \rho_C}
\]

Based on the external surface area of the carbon that is accessible to the RuO\(_2\) nanoparticles. The RuO\(_2\) nanoparticles pack into the pores of the carbon as shown schematically in Fig. 1. Packing theory (detailed in the Appendix) provides the value of \(\varepsilon\) as a function of \(d_C\), \(d_{Ru}\), and the composition of the electrode.

Once \(\varepsilon\) has been determined, \(S_d\) and \(S_f\) may be expressed in terms of \(\hat{S}_{C,int}\), \(\hat{S}_{C,ext}\), and \(d_{Ru}\). We assume that all of the surface contributes to DL capacitance. Thus

\[
S_d = (\hat{S}_{C,int} + \hat{S}_{C,ext}) \rho_C x_C (1 - \varepsilon) + \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

However, only the RuO\(_2\) surface is redox-active and contributes to the pseudocapacitance, so

\[
S_f = \frac{6 x_{Ru}(1 - \varepsilon)}{d_{Ru}}
\]

The volume fractions may be expressed in terms of mass fractions as shown in the Appendix.

The other governing equations are similar to those given previously.\(^{13}\) The conservation of charge and Ohm’s law in the matrix phase lead to

\[
\frac{\partial i_1}{\partial x} + \frac{\partial i_2}{\partial x} = 0 \tag{7}
\]

\[
i_1 = -\sigma \frac{\partial \Phi_1}{\partial x} \tag{8}
\]

Concentration polarization in the electrolyte, not considered previously, is considered here. In the context of concentrated solution theory,\(^{15}\) a mass balance on salt leads to

\[
\frac{\partial \tilde{i}_2}{\partial x} = \tilde{S}_d \frac{\partial (\tilde{\Phi}_1 - \tilde{\Phi}_2)}{\partial t} + \tilde{S}_f \tilde{j}_f \tag{3}
\]
\[
\frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} \left[ \varepsilon D_e \left( 1 - \frac{d(\ln C_o)}{\partial (\ln C)} \right) \frac{\partial C_s}{\partial x} \right] + \frac{S_0 C_d (\Phi_1 - \Phi_2)}{2F} + \frac{S_0 j_f}{2F} (1 - \theta^*_n) - \frac{i_z}{\varepsilon n v_s + F} \frac{\partial \theta}{\partial x} \tag{9}
\]

The second term on the right accounts for the source/sink of ions due to electrode reactions as well as DL charging and discharging.

The current distribution in the electrolyte phase is

\[
i_z = -\kappa_p \frac{\partial \Phi_2}{\partial x} - \frac{\kappa_pRT}{F} \left[ 1 + \frac{\partial (\ln f_c)}{\partial (\ln C)} \right] \left( \frac{x_s}{n v_s^*} + \frac{\theta^*_n}{z_s^* v_s^*} \right) \frac{\partial (\ln C_o)}{\partial (\ln C)} \frac{\partial C_s}{\partial x} \tag{10}
\]

Equation 9 and 10 can account for variations of transference number and activity coefficient with salt concentration if appropriate activity coefficient data are available. Here, we ignore these corrections and work under the assumptions of dilute solution theory.\(^\text{18}\)

The molar fraction of oxidized species, \( \theta \), can be related to faradaic transfer current, \( j_f \), by\(^\text{13}\)

\[
\frac{\partial \theta}{\partial t} = \frac{S_0 j_f}{Q_{t,ox} - Q_{t,se}} \tag{11}
\]

where \( Q_{t,ox} \) and \( Q_{t,se} \) are the faradaic charge (per unit volume) of fully oxidized and reduced electrodes, respectively. If we assume Butler-Volmer kinetics for electrode reactions, we have

\[
j_f = i_o \exp \left[ \alpha_c (\Phi_1 - \Phi_2 - U_1) F/RT \right] - \exp \left[ -\alpha_c (\Phi_1 - \Phi_2 - U_1) F/RT \right] \tag{12}
\]

where \( U_1 \) is the equilibrium potential for the electrode reaction. Previous studies\(^\text{9,13}\) have assumed empirical expressions relating \( U_1 \) to \( \theta \) for the redox reactions of RuO\(_2\), namely

\[
U_1 = V_o (1 + \theta) \tag{13}
\]

\[
U_1 = V_o (1 - \theta) \tag{14}
\]

at the positive and negative electrodes, respectively, where \( V_o \) is initial equilibrium potential before charging, taken as 0.5 V. We follow previous studies in this regard by not accounting for the explicit dependence of kinetic expressions on local electrolyte concentration.

Defining the local potential as \( E = \Phi_1 - \Phi_2 \) and assuming transference numbers and activity coefficients that are independent of salt concentration, Eq. 3 and 7-10 can be combined to yield

\[
S_0 C_d \left( \frac{1}{\alpha} + \frac{1}{\kappa_p} \right) \frac{\partial \theta}{\partial t} = \frac{\partial^2 E}{\partial x^2} - \frac{RT}{F E_o} \left( \frac{x_s}{n v_s^*} + \frac{\theta^*_n}{z_s^* v_s^*} \right) \frac{\partial^2 (\ln C)}{\partial x^2} - \frac{S_0 j_f}{E_o S_0 C_d \tau_j} J \tag{15}
\]

\[
\frac{\partial C_s}{\partial t} = \frac{D_e}{\varepsilon^2} \frac{\partial^2 C_s}{\partial x^2} + \frac{S_0 C_d (1 - \theta^*_n)}{2eF} \frac{\partial E}{\partial t} + \frac{S_0 (1 - \theta^*_n)}{2eF} \frac{\partial C_s}{\partial t} \tag{16}
\]

Boundary conditions include\(^\text{13}\)

At \( x = 0, \ t > 0 \):

\[
\frac{\partial E}{\partial x} = \frac{I_{cell}}{\kappa_p} \tag{17}
\]

\[
\frac{\partial C_s}{\partial x} = 0 \tag{18}
\]

At \( x = L, \ t > 0 \):

\[
\frac{\partial E}{\partial x} = \frac{I_{cell}}{\kappa_p} \tag{19}
\]

\[
\frac{\partial C_s}{\partial x} = 0 \tag{20}
\]

In the above equation, \( \kappa_p \) is the separator porosity and \( D_s s_s \) is the salt diffusion coefficient in the pore of the separator. Equation 18 assumes that the concentration gradient, flux, and potential are continuous at the electrode-separator interface. Unlike the electrode phase, the effects of DL charging/discharge are neglected in the separator. Finally, Eq. 18 recognizes that the electrolyte phase carries all cell current at the electrode-separator interface, and that the anion flux is negligible compared to the cation flux there.

Initial conditions for discharge are

At \( t = 0 \):

\[
E = 2V_o = E_o \quad \theta = 1 \quad C_s = C_{so} \tag{21}
\]

Equation 11, 12, 15, and 16 can be solved together with these boundary and initial conditions.

**Dimensional analysis.**—First, we cast the equations in dimensionless form by defining the following dimensionless variables

\[
E = \frac{E}{E_o}, \quad C = \frac{C_s}{C_{so}}, \quad j = \frac{j_f}{i_o}, \quad U = \frac{U_1}{E_o}, \quad X = \frac{x}{L}, \quad \tau = \frac{t}{t_o} \tag{22}
\]

where

\[
t_o = \frac{S_0 C_d L^2}{\kappa_p} \left( 1 + \frac{\kappa_p}{\sigma} \right) \tag{23}
\]

and \( E_o = 2V_o \) was defined for convenience in Eq. 19. Thus, the time scale of the problem is scaled by a characteristic time for discharge of the DL. The system of equations has the dimensionless form

\[
\frac{\partial E}{\partial \tau} = \frac{\partial^2 E}{\partial X^2} - \frac{RT}{FE_o} \left( \frac{x_s}{n v_s^*} + \frac{\theta^*_n}{z_s^* v_s^*} \right) \frac{\partial^2 (\ln C)}{\partial X^2} - \frac{S_0 j_f}{E_o S_0 C_d \tau_j} J \tag{24}
\]

\[
\frac{\partial \theta}{\partial \tau} = \frac{S_0 j_f t_0}{Q_{t,ox} - Q_{t,se}} J \tag{25}
\]

\[
\frac{\partial C}{\partial \tau} = \frac{D_e L^2}{\varepsilon^2} \frac{\partial^2 C}{\partial X^2} + \frac{(1 - \theta^*_n) S_0 j_f t_0}{2eF C_{so}} J + \frac{S_0 C_d (1 - \theta^*_n)}{2eF C_{so}} \frac{\partial E}{\partial \tau} \tag{26}
\]

with the following boundary and initial conditions

At \( X = 0, \ \tau > 0 \):

\[
\frac{\partial E}{\partial X} = \frac{I_{cell}}{E_o \kappa_p} \frac{\partial C}{\partial X} = 0 \tag{27}
\]

At \( X = 1, \ \tau > 0 \):

\[
\frac{\partial E}{\partial X} = \frac{I_{cell}}{E_o \kappa_p} \frac{\partial C}{\partial X} = \frac{(1 - \theta^*_n) I_{cell}}{2eD_s C_{so} F} \tag{28}
\]
The solution of these equations provides the distributions of local potential difference and salt concentration in the electrode. The total dimensionless potential drop across the capacitor can be expressed as

$$\bar{\Phi}_{\text{cell}} = (\bar{\Phi}_1)_+ - (\bar{\Phi}_1)_- \quad [29]$$

where \((\bar{\Phi}_1)_+\) and \((\bar{\Phi}_1)_-\) denote the dimensionless potentials \(\bar{\Phi}_1 = \Phi_1 / E_0\) at the current collectors of the positive and negative electrodes, respectively. Equation 29 can be written as

$$\bar{\Phi}_{\text{cell}} = 2[E|_{x=0} - V_0] - 2[\bar{\Phi}_2|_{x=1} - \bar{\Phi}_2|_{x=0}] - \frac{I_{\text{cell}} L_s}{E_0 k_s}$$

where \((\bar{\Phi}_1)_+\) and \((\bar{\Phi}_1)_-\) denote the dimensionless potentials \(\bar{\Phi}_1 = \Phi_1 / E_0\) at the current collectors of the positive and negative electrodes, respectively. Equation 29 can be written as

$$\bar{\Phi}_{\text{cell}} = 2[E|_{x=0} - V_0] - 2[\bar{\Phi}_2|_{x=1} - \bar{\Phi}_2|_{x=0}] - \frac{I_{\text{cell}} L_s}{E_0 k_s}$$

in which the three terms represent the potential differences between the solid and the electrolyte, across the electrolyte phase within the electrodes, and across the separator. The third term assumes that Ohm’s law applies in the separator and ignores concentration polarization there. The second and third terms cannot be neglected if the discharge current density is high, because concentration polarization makes a significant contribution to cell potential in such cases.

The dimensionless potential in the electrolyte phase, \(\bar{\Phi}_2 = \Phi_2 / E_0\), may be determined after solving Eq. 22-25. The necessary governing equation, derived from Eq. 7, 8, and 10, is

$$\frac{\partial^2 \bar{\Phi}_2}{\partial X^2} + \left[1 + \frac{\kappa_p}{\sigma} \frac{\partial^2 \bar{\Phi}_2}{\partial X^2} + \frac{\kappa_p RT}{\sigma E_0} \left(\frac{\sigma}{n v_s} + \frac{I_0}{z_s v_s}\right) \frac{\partial^2 (\ln C)}{\partial X^2}\right] = 0 \quad [31]$$

with the boundary conditions

At \(X = 0, \tau > 0\): \(\bar{\Phi}_2 = 0 \quad [32]\)

At \(X = 1, \tau > 0\): \(\frac{\partial \bar{\Phi}_2}{\partial X} = \frac{I_{\text{cell}} L_s}{E_0 k_p} \quad [33]\)

Equations 22-25 and 31 can be solved numerically using the DASPK solver.\(^{20}\)

Model parameters.—Table I shows the base set of system parameters. The effective diffusion coefficients and ionic conductivity within the porous electrode are porosity-dependent functions given by\(^{18,21}\)

$$D_i = D_{i0} \bar{\varepsilon}_s^{0.5} \quad (i = +, -, s) \quad [34]$$

$$\kappa_p = \kappa_{p0} \bar{\varepsilon}_s^{1.5} \quad [35]$$

$${\gamma}_i = -\frac{2}{5}$$

Effect of concentration polarization.—The present model builds upon previous work\(^{12,13}\) by considering the effects of concentration polarization in the electrolyte phase. One might ask whether the improvement in the model’s physical realism justifies the additional computational burden (Eq. 9, etc.). Figure 2 addresses this issue by comparing theoretical discharge curves for pure RuO$_2$ electrodes computed with and without concentration polarization. As shown in Fig. 2, including concentration polarization in the model leads to a decrease of about 25% in the predicted value of RAC at the end of discharge, even for a relatively low current density. With increasing current density or decreasing porosity, the effects of concentration polarization should become even more significant. These effects are now considered in more detail.

Effect of activated carbon type.—Data tabulated by Shi\(^{7}\) show that the external surface areas of activated carbons vary widely. In
the context of the present model, this implies that the equivalent carbon particle size, electrode porosity, and surface area for double-layer capacitance also varies widely for different carbons. The model presented here can be used to compare the performance of various carbons in electrochemical capacitors. Parameters for three selected carbons are shown in Table II. For now, the mass fractions of RuO$_2$ and carbon are fixed at 0.32 and 0.68, respectively, leading to a carbon volume fraction of about 0.75. This value has been found previously$^{14}$ to maximize the specific surface area and minimize electrode porosity.

Figure 3 presents the galvanostatic discharge curves for capacitors employing various types of activated carbons. Parameters include $I_{\text{avg}} = 1.0$ A/cm$^2$, $C_{\text{el}} = 3.0$ M, and $x_C = 0.75$.

<table>
<thead>
<tr>
<th>Table II. Properties of selected carbons ($x_C = 0.75$) with electrode characteristics calculated from packing theory (Appendix).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
</tr>
<tr>
<td>$S_{C,\text{ext}}$ (m$^2$/g) (Ref. 7)</td>
</tr>
<tr>
<td>$S_{C,\text{int}}$ (m$^2$/g) (Ref. 7)</td>
</tr>
<tr>
<td>$d_e$ (nm)</td>
</tr>
<tr>
<td>$\gamma = a_{\text{Ru}}/a_{\text{C}}$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>$S_f$ (cm$^2$/cm$^3$)</td>
</tr>
<tr>
<td>$S_d$ (cm$^2$/cm$^3$)</td>
</tr>
</tbody>
</table>

Effect of carbon content.—The previous results show that electrodes containing mostly carbon can deliver a significant fraction of the charge that could be delivered by pure RuO$_2$ electrodes. Since activated carbon is much less expensive than RuO$_2$, it makes sense to explore the effect of carbon content on discharge performance. This, along with cost data, could be used to optimize the carbon type and parameters derived from packing theory calculations are given in Table III. As expected, the area under the discharge curve, proportional to total charge delivered, decreases as the volume fraction of carbon increases. Although the capacitance decreases with increasing carbon content, the RAC at the end of discharge remains relatively high. For example, when the electrodes contain 90% carbon by volume (only 13% RuO$_2$ by mass), the total delivered charge is still more than 30% of the theoretical maximum based on pure RuO$_2$.

Ragone plots provide a more comprehensive view of cell performance. We define energy and power densities as

\[
\text{Energy density} = \frac{I_{\text{avg}} \Phi_{\text{avg}} t_d}{2L + \Phi_{\text{avg}}} \tag{41}
\]

\[
\text{Power density} = \frac{I_{\text{avg}} \Phi_{\text{avg}}}{2L + \Phi_{\text{avg}}} \tag{42}
\]

where $t_d$ is the total discharge time and $\Phi_{\text{avg}}$ is the average cell potential during discharge. Since the discharge curves (Fig. 4) are nearly linear in time and the cell potential decreases from 1.0 to 0 V, $\Phi_{\text{avg}}$ is assumed to be constant and equal to 0.5 V.
Figure 5 shows Ragone plots for capacitors with electrodes containing varying volume fractions of M20B carbon. This kind of plot can be used to establish the mass fractions of RuO2 and carbon needed to achieve specified energy and power density requirements. As one might expect, energy density decreases with increasing carbon content and as power density increases. The power density is directly proportional to the cell current. The drop in energy density at high power density becomes less pronounced with increasing carbon content. The results suggest underutilization of the electrodes at high discharge rates. Results in the next section show that concentration polarization at high cell current density increases mass-transfer limitations for proton transport, leading to poorer discharge performance.

Current density and concentration polarization.—The results of Fig. 5 suggest a closer examination of performance as current density increases. Figure 6 presents galvanostatic discharge curves for capacitors with M20B carbon composite electrodes discharged at varying cell current densities. For discharge at relatively low current densities, the curves superimpose and are nearly linear. Such superposition is expected since RAC represents time made dimensionless using $I_{\text{cell}}$ (Eq. 39). For discharge current densities greater than 0.1 A/cm², the curve shifts to the left, indicating less delivered charge (area under the curve) and lower electrode utilization (lower RAC at full discharge). With increasing discharge current density, both the DL and faradaic contributions to RAC decrease, although the impact is much greater on the faradaic pseudocapacitance (results not shown).

Examination of potential drop and electrolyte concentration profiles (Fig. 7 and 8) shows that concentration polarization within the electrode becomes significant as $I_{\text{cell}}$ increases. With increasing $I_{\text{cell}}$, the potential drop in the electrolyte phase ($\Phi_2$, Fig. 7) becomes non-negligible. As shown by Eq. 30, increasing $\Phi_2$ leads to a lower overall cell potential at a given value of the “driving force” $E$. This shifts the dimensionless discharge curves downward relative to their location in the absence of concentration polarization. Significant concentration gradients (Fig. 8) that develop in the electrolyte phase suggest that mass-transfer limitations are detrimental to capacitor performance at high discharge rates.

Optimum porosity.—As discussed earlier, the carbon pore size distribution, quantified here by the internal and external specific surface areas ($S_{\text{C,int}}$ and $S_{\text{C,ext}}$, representing micropore and meso/macropores, respectively), has an important influence on electrode porosity and thus performance. Equation 4 shows that decreasing $S_{\text{C,ext}}$ increases the carbon equivalent diameter and thus decreases porosity (see Appendix). In effect, decreasing the diameter ratio

<table>
<thead>
<tr>
<th>$x_C$</th>
<th>$S_{\text{C,int}}$ (cm²/cm³)</th>
<th>$S_{\text{C,ext}}$ (cm²/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$0.375 \times 10^6$</td>
<td>$7.50 \times 10^6$</td>
</tr>
<tr>
<td>0.10</td>
<td>$0.357 \times 10^6$</td>
<td>$8.50 \times 10^6$</td>
</tr>
<tr>
<td>0.25</td>
<td>$0.327 \times 10^6$</td>
<td>$10.13 \times 10^6$</td>
</tr>
<tr>
<td>0.50</td>
<td>$0.271 \times 10^6$</td>
<td>$13.19 \times 10^6$</td>
</tr>
<tr>
<td>0.75</td>
<td>$0.205 \times 10^6$</td>
<td>$16.82 \times 10^6$</td>
</tr>
<tr>
<td>0.90</td>
<td>$0.316 \times 10^6$</td>
<td>$15.71 \times 10^6$</td>
</tr>
</tbody>
</table>

Figure 4. Galvanostatic discharge curves for capacitors with electrodes containing varying volume fractions of M20B carbon (values of carbon volume fraction shown on the lines). Parameters include $I_{\text{cell}} = 1.0$ A/cm², and $C_{\text{sol}} = 3.0$ M.

Figure 5. Ragone plot for capacitors with electrodes containing varying volume fractions of M20B carbon (values of carbon volume fraction shown on the lines). Parameters include $C_{\text{sol}} = 3.0$ M.

Figure 6. Galvanostatic discharge curves for capacitors discharged at varying cell current densities (values of discharging current density, in A/cm², shown on the lines). Parameters include $I_{\text{cell}} = 1.0$ A/cm², $C_{\text{sol}} = 3.0$ M, and $x_C = 0.75$ (M20B carbon).
makes it possible to achieve a higher packing fraction through more efficient packing of small particles into the voids between larger particles (see Fig. 3 of Ref. 14). As porosity decreases, the DL and faradaic surface areas per unit volume of electrode both increase (Eq. 5 and 6). This should increase the total delivered charge (i.e., the area under the discharge curve). Equation 35 shows that decreasing porosity sharply reduces the effective ionic conductivity of the electrolyte in the porous electrode. Ultimately, concentration polarization should become important and limit performance. Thus an optimum porosity may exist.

We investigate this hypothesis by studying a hypothetical carbon with constant total surface area, \( r_C (S_{C,int} + S_{C,ext}) \), but varying amounts of internal and external surface area, \( S_{C,int} \) and \( S_{C,ext} \). Varying the latter changes the porosity. The sum \( r_C (S_{C,int} + S_{C,ext}) \) remains constant in Eq. 5, so the DL and faradaic specific areas only change with \( \varepsilon \). Figure 9 shows discharge curves for selected porosities. Upon decreasing the porosity from 0.375 to 0.25, the discharge curve moves up, implying increases in the total delivered charge and electrode utilization. However, further decrease in porosity to 0.15 impacts the performance of the system due to the effects of concentration polarization. Thus, discharge performance depends not only on the total specific surface area, but also on the distribution of that surface area as represented by porosity. Further quantification should lead to identification of the optimal porosity that maximizes discharge current density as a function of cell voltage and other design parameters.

Conclusion

The effects of composition variations, particle packing, and concentration polarization have been incorporated in an extension of the previous model by Lin et al.\textsuperscript{13} We have used this model to investigate the effects of varying carbon type, carbon mass/volume fraction, and discharge current density on the performance of RuO\textsubscript{2}/C electrochemical capacitors. Under all conditions, polarization of the electrolyte has a significant effect on discharge performance and must be incorporated in realistic models of electrochemical capacitor charge/discharge. Among the many available activated carbons,\textsuperscript{7} ones with relatively large internal surface areas (micropores) but low external surface areas should be most useful for maximizing both DL capacitance and faradaic pseudocapacitance. These characteristics increase the specific surface area for DLs as well as favor better packing of RuO\textsubscript{2} within the carbon. At high discharge current densities, one may use electrodes containing substantial amounts of carbon without greatly sacrificing performance, particularly energy density (Fig. 5). Because the carbon provides significant DL capacitance but costs much less than RuO\textsubscript{2}, one should be able to find an optimum composition that provides acceptable performance and minimum cost under specified discharge conditions.

Acknowledgments

We acknowledge the financial support of this work by the South Carolina Commission on Higher Education and the U.S. Army Research Office under grant no. DAAH04-96-1-0422.

The University of South Carolina assisted in meeting the publication costs of this article.
Appendix
Theory of Electrochemical Processes

The composition of the electrode may be expressed in terms of the mass fractions $f_i (i = C, RuO_2)$ or volume fractions based on solid volume given by

$$x_i = \frac{f_i}{\sum_j f_j}$$

in which the sum runs over the two solid components. The porosity $\varepsilon$ may be calculated in terms of the particle size ratio $\gamma = d_g / d_c$ and the component volume fractions using the packing theory developed by Yu et al.\(^\text{22}\). Starting with a matrix of large particles (carbon), filling the voids with small particles (RuO$_2$) produces a composite with specific volume $V_L$ given by

$$V_L = V_{xc} + \hat{V}_S x_{Ru}$$

where $V = 1.6$ is the specific volume for random packed spheres and $\hat{V}_S$ is the partial specific volume of the small particles, given by

$$\hat{V}_S = V [1 - (1 - \gamma)^{3.3} - 2.8(1 - \gamma)^{2.7}]$$

Alternately, starting with a matrix of small particles and replacing portions of the matrix with large particles, the specific volume $V_S$ is

$$V_S = V_{Ru} + \hat{V}_L x_{xc}$$

Here $\hat{V}_L$ is the partial specific volume of the large particles, calculated as

$$\hat{V}_L = V - (V - 1) [(1 - \gamma)^{2.0} + 0.4\gamma (1 - \gamma)^{3.7}]$$

The specific volume of the mixture, $V_m$, and electrode porosity, $\varepsilon$, are given by

$$V_m = \max \{V_S, V_L\}$$

and

$$\varepsilon = 1 - 1/V_m$$

List of Symbols

- $C$ dimensionless electrolyte concentration
- $C_d$ double-layer capacitance per area of electrode, F/cm$^2$
- $C_e$ electrolyte concentration, mol/cm$^3$
- $C_{int}$ internal electrolyte salt concentration, mol/cm$^3$
- $C_{total}$ total available charge per electrode area in pure RuO$_2$, C/cm$^2$
- $D_4$ diffusion coefficient (i = c, anion, and electrolyte salt in the bulk solution (i = c, anion, and electrolyte salt)
- $D_{4s}$ salt diffusion coefficient in the separator, cm$^2$/s
- $d_{ec}$ effective carbon particle diameter, cm
- $d_{RuO_2}$ RuO$_2$ particle diameter, cm
- $E_e$ local potential difference between matrix phase and electrolyte phase, V
- $E_0$ initial local potential difference between matrix and electrolyte phases ($\approx V_0$), V
- $f_{zc}$ electrolyte activity coefficient
- $f_{xc}$ carbon mass fraction in composite electrode
- $f_{RuO_2}$ RuO$_2$ mass fraction in composite electrode
- $h$ edge length of crystal lattice unit cell for RuO$_2$, cm
- $i_{ox}$ exchange current density for the electrode reaction, A/cm$^2$
- $i_{sc}$ superficial current density in the matrix phase, A/cm$^2$
- $i_{s}$ superficial current density in the electrolyte phase, A/cm$^2$
- $i_{dc}$ double-layer capacitance per area of electrode, F/cm$^2$
- $j_1$ faradaic transfer current density for the RuO$_2$ redox reaction, A/cm$^2$
- $j_2$ dimensionless faradaic transfer current density for the RuO$_2$ redox reaction
- $L$ thickness of the electrode, cm
- $L_0$ length of the separator, cm
- $L_A$ Avogadro’s number, $6.0226 \times 10^{23}$/mol
- $n$ number of electrons transferred in electrode reaction
- $Q_{Far}$ faradaic charge per unit volume of the fully oxidized electrode, C/cm$^3$

Greek

- $\alpha$ anodic transfer coefficient of the electrode reaction
- $\alpha_c$ cathodic transfer coefficient of the electrode reaction
- $\gamma$ RuO$_2$/carbon particle diameter ratio
- $\varepsilon$ electrode porosity
- $\varepsilon_c$ separator porosity
- $E$ dimensionless local potential difference between matrix phase and electrolyte phrase
- $\theta$ local molar fraction of oxidized RuO$_2$
- $\sigma$ electronic conductivity in the electrolyte phase, S/cm
- $\tau$ dimensionless time
- $\Phi_1$ potential in the matrix phase, V
- $\Phi_2$ potential in the electrolyte phase, V
- $\Phi_{cell}$ dimensionless cell potential drop
- $\Phi_{avg}$ average cell potential during discharge, V

References