PERFORMANCE LIMITATIONS IN RESISTIVE-CAPACITIVE POROUS SUPERCAPACITOR ELECTRODES

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ABSTRACT

This work presents the first demonstration of a one-dimensional (1-D), “resistive-capacitive” porous electrode study both analytically and experimentally for faradaic (pseudo) supercapacitors, including an analysis of supercapacitor performance limitations. Resistive-capacitive model predictions for metal oxide pseudocapacitors (high and low conductivity oxides) and conducting polymer pseudocapacitors are compared with experimental results to determine the validity of model assumptions. Specific accomplishments compared to the state-of-the-art include: (1) a macroscale approach for ohmically-limited porous supercapacitor electrodes; (2) experimental validation for metal oxide- and conducting polymer-carbon nanotube (CNT) pseudocapacitors; and (3) identification of performance-limiting factors. As such, this work could open up a new methodology for guiding performance enhancements in the field of pseudocapacitor energy storage.

INTRODUCTION

Supercapacitors are electrochemical energy storage devices characterized by rapid charge-discharge speeds, high power densities, and long cycle lifetimes compared to batteries [1]. Supercapacitors have many promising applications in electric vehicles, renewable energy, and personal electronics [2]. Current research is focused on increasing supercapacitor energy density using pseudocapacitive materials that store charge by faradaic reactions [3]. To achieve high energy density pseudocapacitor electrodes, there is a need to develop analytical porous electrode models that can be used to identify pseudocapacitor performance limitations and optimize electrode design. The advantages of pseudocapacitor modeling include: 1) rapid prediction of performance without the need to fabricate and test a large number of different designs; 2) ability to identify the most significant variables affecting pseudocapacitor energy density; and 3) improved understanding of the fundamental processes and limiting factors governing pseudocapacitor charge storage [4].

Faradaic supercapacitors use high surface area, porous electrodes coated with pseudocapacitive materials to achieve high energy density [5]. Pseudocapacitor modeling therefore involves simulating electrochemical processes occurring in porous electrodes. There are two basic approaches to modeling porous electrodes: the microscale approach and the macroscale approach [6]. Macroscale models simulate electrochemical processes occurring in individual pores of supercapacitor electrodes. Due to the complexities of nanoporous electrode geometry, macroscale models require sophisticated numerical solutions [7]. Macroscale models use average physical parameters without considering individual pore geometries. Among the first macroscale models developed were those of Euler and Nonnenmacher [8], and Newman and Tobias [9]. Both models are one-dimensional (1-D), assume constant electrolyte properties, and neglect double layer capacitance. Despite these simplifying assumptions, these early 1-D models are mathematically complex: analytical solutions require solving eight nonlinear, dependent, partial differential equations. Since these early works, many variations of the 1-D, macroscale model have been developed to more accurately simulate ohmic resistance, reaction kinetics, and diffusion resistance in porous electrodes [10, 11]. These models are highly complex, and as a result, are not typically used in pseudocapacitor electrode design.

A promising approach to simplify analytical studies of porous pseudocapacitor electrodes is to consider performance-limiting factors. In their study of porous electrodes for electrochemical battery cells, Tiedemann and Newman considered the case of ohmically-limited charge storage [12]. Their model provides a simpler version of the full, macroscale model by neglecting diffusion and reaction kinetics. Using the ohmically-limited model, the authors determined the optimum electrode length and porosity for charge storage in electrochemical battery cells. Following on these promising results, this work considers for the first time the development of an ohmically-limited, macroscale, porous electrode model for pseudocapacitor electrodes.

Figure 1: Resistive-capacitive study for pseudocapacitor electrodes. (a) Conceptual illustration of a 1-D porous electrode described by the macroscale model. (b) Model equivalent circuit consisting of electrolyte resistance (R_s), matrix resistance (R_m), and faradaic capacitance (C_f). (c) SEM image of a VACNT-based pseudocapacitor electrode.
CONCEPT

Figure 1a provides a conceptual illustration of a porous electrode described by the 1-D resistive-capacitive model. The model consists of two parallel systems: matrix and electrolyte phase. The electrode is in contact with the free electrolyte solution at \( x = 0 \), and with a metal current collector at \( x = L \). Model assumptions include: internal losses due to reaction kinetics and diffusion are small compared to ohmic resistance; the external surface area of the electrode is small compared to the inner porous structure; and the electrode volume is large compared to individual pore dimensions [4].

The resistive-capacitive model simulates constant current discharge of pseudocapacitor electrodes. During pseudocapacitor discharge, electrode potential, \( \Delta V \), decreases due to resistive losses and capacitive discharging:

\[
\Delta V = iR + \Delta Q/C
\]

(1)

where \( i \) is the discharge current, \( R \) is electrode ohmic resistance, \( \Delta Q \) is the decrease in electrode charge, and \( C \) is the electrode capacitance. Re-writing equation 1 in terms of the discharge time, \( \Delta t \), the maximum pseudocapacitor electrode current can be calculated for a given cell voltage range and discharge time:

\[
i = C\Delta V/(RC + \Delta t)
\]

(2)

Electrode capacitance is assumed to be only faradaic capacitance, thereby neglecting double layer capacitance. For most pseudocapacitive materials, faradaic capacitance is 10-100x greater than double layer capacitance [13]. Total electrode resistance is calculated from the parallel contributions of matrix and solution phase resistances (Figure 1b):

\[
R = L/(A(\sigma + \kappa))
\]

(3)

where \( A \) is the electrode planar surface area, \( \sigma \) is the effective matrix conductivity, and \( \kappa \) is effective electrolyte conductivity. For porous electrodes, the parameters \( \sigma \) and \( \kappa \) are calculated according to equations 4 and 5, respectively:

\[
\sigma = \sigma_o(1-\varepsilon)^\alpha
\]

(4)

\[
\kappa = \kappa_o\varepsilon^\alpha
\]

(5)

where \( \varepsilon \) is electrode porosity, \( \alpha \) is the electrode tortuosity factor, \( \sigma_o \) is the matrix bulk conductivity, and \( \kappa_o \) is the electrolyte bulk conductivity [6]. The electrode tortuosity factor accounts for the complexity of the porous structure, with increasing values of \( \alpha \) corresponding to increasingly complex pore structures (1 \( \leq \alpha \leq 3 \)) [14].

RESULTS AND DISCUSSION

Resistive-capacitive model simulations described here are based on physical parameters for a vertically aligned carbon nanotube (VACNT) porous electrode structure. The 1-D model is well-suited for simulating VACNT-based pseudocapacitor electrodes because VACNT forests are uniform across large areas, and the porous structure is highly one dimensional (Figure 1c). Figure 2 summarizes resistive-capacitive model calculations for CNT-based pseudocapacitor electrodes. The porosity of a CNT electrode coated with pseudocapacitive material is calculated based on the CNT density, \( n_{CNT} \), CNT outer diameter, \( d_{CNT} \), and pseudocapacitive coating thickness, \( T \):

\[
\varepsilon = 1 - \pi(d_{CNT}/2 + T)n_{CNT}
\]

(6)

To validate resistive-capacitive model predictions, we compare analytical and experimental results for three types of pseudocapacitors: 1) “low conductivity metal oxide pseudocapacitors” using vanadium oxide (V\(_2\)O\(_5\)) on CNT electrodes [15] and manganese oxide (MnO\(_2\)) on VACNT electrodes [16]; 2) “conducting polymer pseudocapacitors” using the coating of polyppyrole (PPY) on VACNT electrodes [17]; and 3) “high conductivity metal oxide pseudocapacitors” using ruthenium oxide (RuO\(_2\)) on VACNT electrodes [18]. Figure 3a shows a typical experimental set-up for supercapacitor electrode performance testing. Figures 3b and 3c compare model predictions with experimental results for V\(_2\)O\(_5\)-CNT electrodes reported by Boukhalfa et al., and MnO\(_2\)-CNT electrodes reported by Liu et al., respectively [15, 16]. There is excellent agreement between model and experimental results (to within experimental error) for both low conductivity metal oxide pseudocapacitors.
In contrast to V_2O_5-CNT and MnO_2-CNT electrodes, the resistive-capacitive model greatly overestimates charge-discharge current for RuO_2-VACNT and PPY-VACNT electrodes. This result suggests that charge storage in highly conductive pseudocapacitor electrodes, such as RuO_2- and PPY-based electrodes, is limited by reaction kinetics and diffusion, rather than ohmic resistance. Table 1 summarizes performance-limiting factors for pseudocapacitor electrodes, as identified by the resistive-capacitive model.

Table 1: Pseudocapacitor performance limitations

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Performance limiting factor</th>
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<tbody>
<tr>
<td>RuO_2-VACNT</td>
<td>Reaction kinetics and diffusion</td>
</tr>
<tr>
<td>PPY-VACNT</td>
<td>Ohmic resistance</td>
</tr>
<tr>
<td>V_2O_5-CNT</td>
<td></td>
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<tr>
<td>MnO_2-VACNT</td>
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Figure 4 demonstrates the use of the resistive-capacitive model for charge storage optimization of low conductivity metal oxide-CNT pseudocapacitors. Figure 4a plots gravimetric current density for V_2O_5-CNT and MnO_2-CNT electrodes as a function of pseudocapacitive coating thickness using a CNT density of 1x10^13 CNTs/m^2. This CNT density corresponds to electrode porosities greater than 94% for V_2O_5 thicknesses up to 30 nm. As shown in Figure 4a, at low CNT density supercapacitor discharge current is a continuously increasing function of pseudocapacitive material coating thickness for MnO_2-VACNT and V_2O_5-CNT electrodes, irrespective of CNT height (Figure 4a remains unchanged for CNT heights of 10 µm, 100 µm, and 500 µm). This result is due to the high electrolyte effective conductivity at low CNT densities.

Figure 4b plots gravimetric current density as a function of V_2O_5 coating thickness using a CNT density of 5x10^14 CNTs/m^2. With a high CNT density, the results indicate that: 1) there is an optimum V_2O_5 thickness for maximizing gravimetric current, and 2) optimum thickness varies with CNT height. For low conductivity metal oxides, electrode conductivity is primarily via the electrolyte; decreasing electrode porosity therefore becomes a performance-limiting factor for high CNT densities. By decreasing CNT height, pseudocapacitive coating thickness can be increased, resulting in higher gravimetric current densities.

Figure 4c plots gravimetric current as a function of V_2O_5 thickness using the same model parameters as in Figure 4b, this time including the mass of the electrolyte in the gravimetric current calculation. The results in Figures 4b and 4c are based on 8 M LiCl electrolyte, as used in Boukhalfa et al. for V_2O_5-CNT electrodes [16]. Besides reducing overall gravimetric current density, including the mass of the electrolyte affects the optimum V_2O_5 coating thickness predicted by the resistive-capacitive model for a given CNT height. Most supercapacitor studies in the literature do not include electrolyte mass when designing pseudocapacitor electrodes or reporting gravimetric current density [19]. The results of Figure 4c highlight the importance of considering electrolyte mass in the design of supercapacitor electrodes to obtain maximum gravimetric current for the full supercapacitor cell.

Figure 5a illustrates the effects of electrode porosity and tortuosity on effective electrolyte conductivity by plotting equation 5. For a highly porous electrode (ε = 0.99), electrolyte conductivity is approximately equal to the free solution conductivity. Decreasing electrode porosity to ε = 0.5 reduces electrolyte conductivity to κ = 0.5k_0, 0.25k_0, and 0.125k_0 for electrode tortuosity factors of 1, 2, and 3, respectively. While reducing electrode porosity improves matrix conductivity (equation 4), high values of electrode tortuosity are detrimental to both electrolyte and matrix conductivities. For porous electrode supercapacitors, electrode tortuosity has a significant impact on optimum pseudocapacitive coating thickness and gravimetric current. Figure 5b plots optimum V_2O_5 coating thickness as a function of CNT height for tortuosity factors ranging from α = 1.5 to α = 3. For low values of electrode tortuosity factor, greater thicknesses of pseudocapacitor material can be used while still maintaining good electrolyte conductivity. With vertically aligned—as opposed to randomly oriented—CNTs, gravimetric current increases by 45% at a CNT height of 500 µm. These results demonstrate the importance of considering effective matrix and electrolyte conductivities when designing porous supercapacitor electrodes, and maintaining good alignment of CNT pores.

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Figure 4: Resistive-capacitive model results. (a) Electrode current vs. pseudocapacitive coating thickness for MnO_2-VACNT and V_2O_5-CNT electrodes. For low CNT densities (10^13 CNTs/m^2), electrode current is a continuously increasing function of pseudocapacitive thickness (experimental data points from [15], [16] shown for comparison). (b) For high CNT densities (5x10^14 CNTs/m^2), there is an optimum pseudocapacitive thickness for maximizing V_2O_5-CNT electrode current. The mass of the 8 M LiCl electrolyte is not included in gravimetric current. (c) Effect of including electrolyte mass on the optimum V_2O_5 pseudocapacitive coating thickness.
CONCLUSIONS

This work develops for the first time a simplified macroscale porous electrode model for faradaic (pseudo) supercapacitors. The resistive-capacitive model has good agreement with experimental results for low conductivity pseudocapacitive materials, in which ohmic losses are significant compared to reaction overpotential and diffusion resistance. For high conductivity pseudocapacitive materials, charge storage is limited by reaction kinetics and diffusion, rather than ohmic resistance. Preliminary demonstrations of model capability show that the simplified macroscale model can be used to predict optimum pseudocapacitor design parameters for porous electrodes of varying thickness, density, and material properties, as well as for different electrolytes. The model is an important tool for increasing understanding of performance-limiting factors in supercapacitor electrodes and identifying critical design parameters. To more accurately simulate charge storage in high conductivity materials, the resistive-capacitive model could be expanded in future work to include the effects of reaction kinetics and diffusion on pseudocapacitor performance.

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REFERENCES


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