



Enhancing Faradaic Charge Storage Contribution in Hybrid Pseudocapacitors



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ARTICLE INFO

Article history:

Received 1 July 2015

Received in revised form 6 September 2015

Accepted 13 September 2015

Available online 18 September 2015

Keywords:

Hybrid pseudocapacitor
Faradaic potential window
Electrode Thickness
Dimensional analysis

ABSTRACT

This study aims to provide metrics and design rules for hybrid pseudocapacitors consisting of a transition metal oxide pseudocapacitive electrode and an inert carbon electrode with asymmetric and binary electrolyte. Hybrid pseudocapacitors are often limited by intercalation of Li^+ ions in the pseudocapacitive electrode. Then, during cyclic voltammetry, only a portion of the potential window is dominated by faradaic current while the electric double layer (EDL) formation and dissolution dominate the rest. However, faradaic reactions result in a significantly larger current magnitude and capacitance than EDL charge storage. Hence, it is beneficial to extend the fraction of the potential window dominated by the faradaic current. This fraction increases with a combination of thinner pseudocapacitive electrode, faster intercalation, and slower scan rate. To study the interplay between these variables, a scaling analysis was performed to identify the relevant dimensionless similarity parameters governing Li^+ transport and intercalation in the pseudocapacitive electrode. The fraction of the potential window dominated by faradaic reactions was a unique function of a dimensionless parameter Π_f accounting for the respective contributions of the electrode thickness, Li^+ diffusion coefficient, and scan rate. Above a critical value of Π_f , the faradaic current dominated the entire potential window. Then, the device was no longer limited by intercalation in the electrode and the performance of the electrode was maximal.

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1. Introduction

Electrochemical capacitors are promising devices for electrical energy storage in particular for high power application because of their very large power density compared with batteries [1–3]. They are usually classified as either electric double layer capacitors (EDLCs) or pseudocapacitors. EDLCs store charge physically via the formation of an electric double layer (EDL) at the interface between the electrode and the electrolyte [1–3]. This phenomenon involves the fast diffusion of ions in the electrolyte responsible for their high power density. However, EDLCs have relatively low energy density compared with batteries. By contrast, pseudocapacitors can store charge not only via the formation of an EDL but also via reversible oxidation–reduction (redox) reactions with fast insertion of the reaction products in the electrode [1,3–6]. Because the electrical energy is stored chemically in the volume of the electrode, pseudocapacitors tend to feature larger energy density than EDLCs. They also maintain high power density as the behavior of the cell

is typically capacitive even though the charge storage mechanism is faradaic [6]. Finally, hybrid pseudocapacitors combine a pseudocapacitive electrode, typically made of transition metal oxide, providing high energy density, and an EDLC-type electrode, made of carbon, enabling large power density [2,7–11]. For this reason, hybrid pseudocapacitors have been extensively studied both experimentally [2,7–11,6] and numerically [12–21].

Optimizing the pseudocapacitive electrode in hybrid pseudocapacitors is made difficult by the numerous interdependent physical phenomena involved. Indeed, thicker electrodes offer more volume to store charge but the typically low electrical conductivity of transition metal oxides is responsible for a potential drop across the electrode that limits the thickness that can be used in practice. In addition, the relatively small solid-state diffusion coefficient associated with intercalation inside the electrode also limits the performance of the electrode, in particular for fast cycling or high power applications. Moreover, it is very challenging to discriminate experimentally the contribution to charge storage of the faradaic reactions from that of the EDL formation. However, this can be achieved through numerical simulations [22]. In fact, it has been established numerically that hybrid pseudocapacitors feature two asymptotic regimes: a faradaic and a capacitive regime.

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Nomenclature

a	effective ion diameter (nm)
c_i	concentration of ion species i (mol/L)
$c_{i,max}$	maximum ion concentration, $c_{i,max} = 1/N_A a_i^3$ (mol/L)
$c_{1,P}$	concentration of intercalated Li^+ (mol/L)
$c_{1,P,max}$	maximum concentration of intercalated Li^+ , $c_{1,C,max} = m \rho/M$ (mol/L)
D_i	diffusion coefficient of ion species i in the electrolyte (m^2/s)
$D_{1,P}$	diffusion coefficient of intercalated Li^+ (m^2/s)
e	elementary charge, $e = 1.602 \times 10^{-19}$ C
F	faraday constant, $F = eN_A = 9.648 \times 10^4$ C mol $^{-1}$
H	stern layer thickness (nm)
j_C	capacitive current density (A/m^2)
j_F	faradaic current density (A/m^2)
j_T	total current density (A/m^2)
k_0	reaction rate in Equation (20) ($\text{m}^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$)
L	half of interelectrode distance (nm)
L_C	thickness of the carbon electrode (nm)
L_P	thickness of the pseudocapacitive electrode (nm)
m	stoichiometric number of intercalated lithium, $\text{Li}_m\text{M}_p\text{O}_q$
M	molecular weight of the fully intercalated pseudocapacitive electrode (g/mol)
n	cycle number
N_A	Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol $^{-1}$
N_i	ion flux of species i (mol m $^{-2}\text{s}^{-1}$)
R_f	faradaic fraction defined as $\Delta\psi_f/\Delta\psi_s$
R_u	universal gas constant, $R_u = 8.314$ J mol $^{-1}\text{K}^{-1}$
T	local temperature (K)
t	time (s)
ν	scan rate of the cyclic voltammetry (V/s)
x	location in one-dimensional space (μm)
z_i	ion valency

Greek symbols

α	transfer coefficient in Equation (20)
ϵ_0	vacuum permittivity, $\epsilon_0 = 8.854 \times 10^{-12}$ F m $^{-1}$
ϵ_r	relative permittivity of electrolyte
$\Delta\psi_{eq}$	equilibrium potential difference (V)
$\Delta\psi_f$	faradaic potential window defined as $\psi_f - \psi_{min}$ (V)
$\Delta\psi_H$	potential drop across the Stern layer (V)
$\Delta\psi_s$	potential window (V)
λ_D	Debye length (m)
η	overpotential, $\eta = \Delta\psi_H - \Delta\psi_{eq}$ (V)
ρ	density of the fully intercalated pseudocapacitive electrode (kg/m^3)
σ_C	electrical conductivity of the carbon electrode (S/m)
σ_P	electrical conductivity of the pseudocapacitive electrode (S/m)
τ_{CV}	cycle period (s)
τ_d	diffusion time scale across the EDL, $\tau_d = \lambda_D^2/D_1$ (s)
τ_{th}	thermal potential, $\tau_{th} = R_u T/z_1 F$ (s)
ψ	local electric potential (V)
ψ_f	potential associated with the Li^+ starvation (V)
ψ_s	imposed cell potential (V)

Superscripts and subscripts

*	refers to dimensionless variable
∞	refers to bulk electrolyte
i	refers to ion species i
C	refers to the carbon electrode
P	refers to the pseudocapacitive electrode

The first is dominated by charge storage via faradaic reactions while the second is dominated by EDL formation albeit with smaller current density.

Numerical simulations can also be used to identify the conditions that maximize the faradaic contribution leading to larger total current densities and areal capacitance. Several models for pseudocapacitors have been developed based on equivalent RC circuit models [23–25], molecular dynamics simulations [26–30], and continuum modeling [12–21]. In particular, the Generalized Modified Poisson-Nernst-Planck (GMPNP) model accounts simultaneously for EDL formation by electromigration of an arbitrary number of ions with different finite sizes, valencies and diffusion coefficients. It has been used along with models for redox reactions and insertion of the reaction product to predict trends and to provide physical interpretation in hybrid pseudocapacitors [22]. In particular, Li^+ starvation at the electrode/electrolyte interface was shown to be responsible for the transition from the faradaic to the capacitive regime. This transition also corresponded to the drop in b -value often observed experimentally [31–33]. Indeed, up to that point, the faradaic reaction consumed Li^+ accumulated at the surface and was therefore diffusion-independent. In this case, the device had a capacitive behavior and the b -value was unity. After Li^+ starvation, however, Li^+ ions had to diffuse from the inner electrode to reach the reaction front at the electrode/electrolyte interface. Then, the faradaic reaction was diffusion-controlled and the b -value was less than one [22].

Scaling analysis is a powerful tool used to simplify complex models and to reduce the number of variables by non-dimensionalizing the governing equations and the initial and boundary conditions. This process typically leads to the introduction of dimensionless numbers or similarity parameters comparing competing physical phenomena. It can also be used to identify different regimes of operation and to uncover scaling laws or correlations governing the evolution of various parameters of interest. These correlations can then be used to design or to operate a device in the most favorable regime. For example, Wang and co-workers [34,35] identified a criteria for the transition between diffusion-limited and diffusion-independent regimes in cyclic voltammetry for EDLCs with binary symmetric [34] and asymmetric electrolyte [35]. They also performed scaling analysis to identify a self-similar behavior for the EDL capacitance for EDLCs with binary and symmetric electrolytes under equilibrium conditions [34]. They then derived a correlation relating the electrode capacitance to the average pore size and electrolyte properties from experimental data for a wide range of porous carbon electrode morphologies [34].

The objective of this study is to derive design rules for pseudocapacitive electrodes in order to ensure that the hybrid pseudocapacitor operates exclusively in the faradaic regime. To do so, dimensional analysis of the continuum model recently developed - to simulate hybrid pseudocapacitors subjected to cyclic voltammetry [22] - was performed to capture the combined effects of electrode thickness, diffusion coefficient for intercalation, and scan rate.

2. Analysis

2.1. Schematics and Assumptions

Figure 1 shows the schematic of the one-dimensional (1D) hybrid pseudocapacitor simulated as well as the computational domain and the associated coordinate system. The origin was located at the midplane of the cell. The device consisted of two planar electrodes separated by an electrolyte. The pseudocapacitive electrode had a thickness L_P and was made of transition metal oxide M_pO_q . The carbon electrode thickness was L_C . The electrolyte, of thickness $2L$, consisted of LiClO_4 salt in propylene carbonate (PC)

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