



Enhancing Faradaic Charge Storage Contribution in Hybrid Pseudocapacitors



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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^+ , $c_{1,P,max} = m \rho / M$ (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, $e = 1.602 \times 10^{-19} \text{ C}$
F	faraday constant, $F = e N_A = 9.648 \times 10^4 \text{ C mol}^{-1}$
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, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
N_i	ion flux of species i ($\text{mol m}^{-2} \text{s}^{-1}$)
R_f	faradaic fraction defined as $\Delta \psi_f / \Delta \psi_s$
R_u	universal gas constant, $R_u = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$
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, $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$
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 $\text{M}_p \text{O}_q$. The carbon electrode thickness was L_C . The electrolyte, of thickness $2L$, consisted of LiClO_4 salt in propylene carbonate (PC)

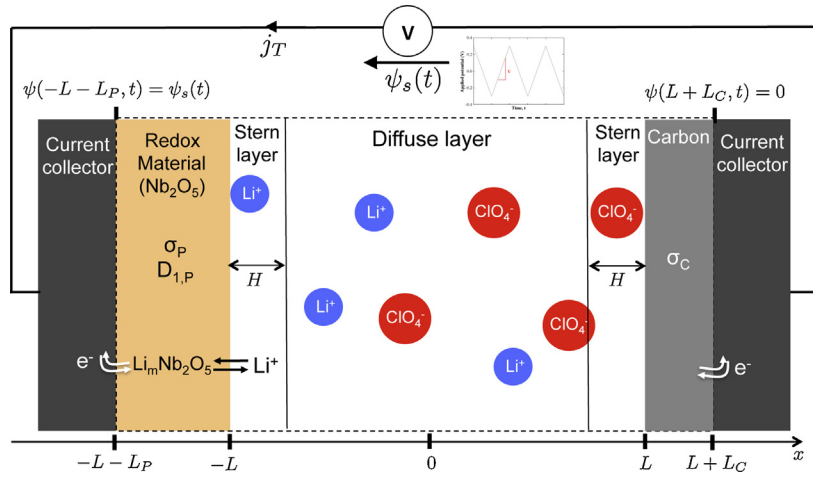
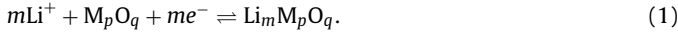


Fig. 1. Schematic of one-dimensional hybrid supercapacitor consisting of a pseudocapacitive electrode and a carbon electrode with LiClO_4 electrolyte in PC. The dotted line encloses the computational domain considered.

solvent. It was further divided in three domains: a Stern layer of thickness H near each electrode and a diffuse layer. There was no free charge in the Stern layer and its thickness corresponded to the distance of closest approach of the ions to the electrode. In the diffuse layer, ions were mobile under the effects of electrodiffusion and steric repulsion. At the interface between the pseudocapacitive electrode and the electrolyte, the following reaction was assumed to take place [32,6]



To make the problem mathematically tractable, the following assumptions were made: (1) the electrodiffusion of all species was treated as one-dimensional. (2) The Stern layer thickness was approximated as the radius of the largest solvated ion [35–37]. In practice, the ions may lose part of their solvation shell near the electrode. However, to the best of our knowledge, no quantitative model exists to account for this phenomenon. (3) The diffusion coefficients of all ion species in the electrolyte were independent of their respective concentrations. Their values corresponded to those of dilute solutions. Note that in reality the diffusion coefficient of ions varies with concentration. However, when reported, this variation did not exceed 40% and the effect on the current response was found to be negligible [22,38]. (4) The temperature was constant and uniform throughout the device. (5) Advection of the electrolyte was negligible. (6) The redox reaction was heterogeneous and occurred at the pseudocapacitive electrode/electrolyte interface [37]. (7) Li^+ ion insertion (or intercalation) in the pseudocapacitive electrode was treated as a diffusion process. (8) The redox material did not undergo any phase transition. This assumption is consistent with experimental observations even for thick Nb_2O_5 electrodes [39]. (9) Ion adsorption due to non-electrostatic forces was assumed to be negligible. (10) The current collectors were assumed to be perfect conductors such that the potential drop across them was negligible. (11) The relative permittivity of the electrolyte ϵ_r was taken as constant and independent of the electric field. This simplification was necessary to be able to perform dimensional analysis of the governing equations.

2.2. Generalized Modified Poisson-Nernst-Planck (GMPNP) Model with Faradaic Reactions

The model used in this study was described in Equations (4) to (22) of Ref. [22] and need not be repeated. It accounts simultaneously for (i) charge transport in the electrodes and electrolyte, (ii) formation and dissolution of the electric double layer (EDL)

at the electrode/electrolyte interface, (iii) steric repulsions due to finite ion size, (iv) redox reactions at the pseudocapacitive electrode/electrolyte interface, and (v) insertion and deinsertion of the reaction product in the pseudocapacitive electrode. Mathematically, this model consists of the 1D Poisson equation for the local electrical potential $\psi(x, t)$ in both electrodes and in the electrolyte coupled to the time-dependent 1D mass conservation equations for the ion concentrations $c_1(x, t)$ and $c_2(x, t)$ in the electrolyte, and for the concentration of lithium $c_{1,p}(x, t)$ in the pseudocapacitive electrode. Here, ions species $i = 1$ refers to cations Li^+ of valency $z_1 = 1$ while $i = 2$ refers to anions ClO_4^- of valency $z_2 = -1$ while subscript “1,p” refers to intercalated lithium. The initial conditions impose (a) a uniform potential, $\psi(x, 0) = 0\text{ V}$ throughout the device, (b) uniform bulk concentrations $c_1(x, 0) = c_2(x, 0) = c_{i,\infty} = 1\text{ mol/L}$ in the electrolyte, and (c) a non-zero uniform lithium concentration in the pseudocapacitive electrode $c_{1,p}(x, 0) = c_{1,p,0}$. Finally, in order to simulate cyclic voltammetry experiments, a triangular potential waveform was imposed at the current collector of the pseudocapacitive electrode with a potential window between $\psi_{\min}$ and $\psi_{\max}$ with respect to the carbon electrode treated as grounded. The ion fluxes vanished at the electrode surfaces except for the reacting species at the pseudocapacitive electrode/electrolyte interface. The rate of the faradaic reaction at this interface was governed by the Frumkin-Butler-Volmer equation [37].

2.3. Dimensional Analysis

2.3.1. Dimensionless Variables

Based on our previous studies [40,35], the following scaling parameters were used to scale the governing equations for the potential $\psi(x, t)$, the ion concentrations $c_i(x, t)$, and the concentration of intercalated lithium in the pseudocapacitive electrode $c_{1,p}(x, t)$ as well as the associated boundary and initial conditions

$$x^* = \frac{x}{\lambda_D}, \quad t^* = \frac{t}{\lambda_D^2/D_1}, \quad \psi^* = \frac{\psi(x, t)}{R_u T/z_1 F}, \quad c_i^* = \frac{c_i(x, t)}{c_{i,\infty}}, \quad \text{and} \quad c_{1,p}^* = \frac{c_{1,p}(x, t)}{c_{1,p,\max}} \quad (2)$$

where λ_D is the Debye length for binary and asymmetric electrolytes defined as [36]

$$\lambda_D = \sqrt{\epsilon_0 \epsilon_r R_u T / F^2 \sum_{i=1}^2 z_i^2 c_{i,\infty}}. \quad (3)$$

It represents an estimate of the electric double layer thickness [41]. The time t was scaled by the timescale for ion diffusion across the EDL given by $\tau_d = \lambda_D^2/D_1$ where D_1 is the diffusion coefficient of the cation Li^+ in the electrolyte. The potential $\psi(x, t)$ was scaled by the thermal potential $\tau_{th} = R_u T/z_1 F$ representing the electric potential at which the electrical potential energy of one mole of Li^+ ions is equal to its thermal energy $R_u T$. $R_u = 8.3145 \text{ J/mol K}$ is the universal gas constant and $F = 96485 \text{ s A/mol}$ is the Faraday constant. The ion concentrations $c_i(x, t)$ were scaled by the bulk concentration $c_{1,\infty}$ of Li^+ in the electrolyte. The lithium concentration in the pseudocapacitive electrode $c_{1,p}(x, t)$ was scaled by the maximum lithium concentration $c_{1,p,\max}$ corresponding to the fully intercalated metal oxide electrode.

2.3.2. Dimensionless Governing Equations

The Poisson equations governing the electric potential in the pseudocapacitive and carbon electrodes assuming constant electrical conductivities, respectively denoted by σ_P and σ_C , can be expressed in dimensionless form as

$$\frac{\partial}{\partial x^*} \left(\sigma_P^* \frac{\partial \psi^*}{\partial x^*} \right) = 0 \quad \text{for} \quad -(L^* + L_P^*) \leq x^* < -L^* \quad (4)$$

$$\frac{\partial}{\partial x^*} \left(\sigma_C^* \frac{\partial \psi^*}{\partial x^*} \right) = 0 \quad \text{for} \quad L^* < x^* \leq L^* + L_C^* \quad (5)$$

where the dimensionless electrode conductivities are given by

$$\sigma_{P/C}^* = [\sigma_{P/C}(\psi_{\max} - \psi_{\min})/L_{P/C}]/(F z_1 c_{1,\infty} D_1/L) \quad (6)$$

where subscript P and C refers to the pseudocapacitive and to the carbon electrode, respectively. They represent the ratios of the characteristic electric current density in the pseudocapacitive or carbon electrode to the ionic current density in the electrolyte. Here, $L^* = L/\lambda_D$ represents the dimensionless electrolyte thickness while $L_P^* = L_P/\lambda_D$ and $L_C^* = L_C/\lambda_D$ are the dimensionless pseudocapacitive and carbon electrode thicknesses, respectively.

Similarly, the mass conservation equation in the pseudocapacitive electrode was non-dimensionalized as

$$\frac{\partial c_{1,p}^*}{\partial t^*} = \frac{\partial}{\partial x^*} \left(D_{1,p}^* \frac{\partial c_{1,p}^*}{\partial x^*} \right) \quad \text{for} \quad -(L^* + L_P^*) \leq x^* \leq -L^* \quad (7)$$

where $D_{1,p}^* = D_{1,p}/D_1$ is the ratio of lithium atom diffusion coefficient in the pseudocapacitive electrode $D_{1,p}$ to that of Li^+ ions in the electrolyte D_1 .

Moreover, the GMPNP model in the diffuse layer of the binary and asymmetric electrolyte, between $-L^* + H^*$ and $L^* - H^*$, has already been written in dimensionless form as [35]

$$\left\{ \frac{\partial^2 \psi^*}{\partial x^{*2}} = -\frac{c_1^* + z_2^* c_2^*}{1 - z_2^*} \right. \quad (8a)$$

$$\left. \frac{\partial c_i^*}{\partial t^*} = -\frac{\partial N_i^*}{\partial x^*} \quad \text{for } i = 1 \text{ or } 2. \right. \quad (8b)$$

Here, $H^* = H/\lambda_D = a_2^*/2$ where $a_2^* = a_2/\lambda_D$ is the effective ion diameter a_2 of the largest ion (ClO_4^- with $i = 2$) scaled by the Debye length λ_D . Additionally, $z_i^* = z_i/z_1$ is the ratio of the valency of the ion considered to that of the cation Li^+ ($i = 1$). The dimensionless mass flux N_i^* of ion species i was given by [35]

$$N_i^*(x^*, t^*) = -D_i^* \frac{\partial c_i^*}{\partial x^*} - D_i^* z_i^* c_i^* \frac{\partial \psi^*}{\partial x^*} - \frac{D_i^* c_i^*}{2 - \sum_{j=1}^2 \nu_{pj} c_j^*} \frac{\partial}{\partial x^*} \left(\sum_{j=1}^2 \nu_{pj} c_j^* \right) \quad (9)$$

for $i = 1 \text{ or } 2$

where $D_i^* = D_i/D_1$ is the ratio of the diffusion coefficient of the ion species i and that of the cation Li^+ . Here, the packing parameter for ion species i is also a dimensionless number defined as

$\nu_{pi} = 2c_{i,\infty}/c_{i,\max}$. It represents the ratio of the total bulk ion concentration to the maximum ion concentration $c_{i,\max} = 1/a_i^3 N_A$ assuming a simple cubic packing of ions of diameter a_i [42].

2.3.3. Dimensionless Initial and Boundary Conditions

The initial dimensionless electric potential was uniformly zero across the device, i.e.,

$$\psi^*(x^*, 0) = 0 \quad \text{for} \quad -L^* - L_P^* \leq x^* \leq L^* + L_C^* \quad (10)$$

The initial dimensionless concentration of lithium was uniform in the pseudocapacitive electrode such that

$$c_{1,p}^*(x^*, 0) = c_{1,p,0}^* = c_{1,p,0}/c_{1,p,\max} \quad \text{for} \quad -L^* - L_P^* \leq x^* \leq -L^* \quad (11)$$

where $c_{1,p,0}$ is the concentration of Li^+ initially intercalated in the pseudocapacitive electrode.

The concentrations of Li^+ and ClO_4^- in the electrolyte were also initially uniform and satisfied electroneutrality so that [35]

$$c_1^*(x^*, 0) = 1, \text{ and } c_2^*(x^*, 0) = -1/z_2^* \quad \text{for} \quad -L^* + a_2^*/2 \leq x^* \leq L^* - a_2^*/2. \quad (12)$$

The dimensionless electric potentials imposed at the current collector/electrode interfaces were given by [35],

$$\psi^*(L^* + L_C^*, t^*) = 0 \quad \text{and} \quad \psi^*(-L^* - L_P^*, t^*) = \psi_s^*(t^*) \quad (13)$$

where $\psi_s^*(t^*)$ is the dimensionless surface potential. For cyclic voltammetry, it is given by [35]

$$\psi_s^*(t^*) = \begin{cases} \psi_{\max}^* - \nu^*[t^* - (n_C - 1)\tau_{CV}^*] & \text{for } (n_C - 1)\tau_{CV}^* \leq t^* \leq (n_C - 1/2)\tau_{CV}^* \\ \psi_{\min}^* + \nu^*[t^* - (n_C - 1/2)\tau_{CV}^*] & \text{for } (n_C - 1/2)\tau_{CV}^* \leq t^* \leq n_C \tau_{CV}^* \end{cases} \quad (14)$$

where n_C is the cycle number and $\psi_{\max}^* = \psi_{\max}/(R_u T/z_1 F)$ and $\psi_{\min}^* = \psi_{\min}/(R_u T/z_1 F)$ are the maximum and minimum dimensionless surface potentials, respectively. Here, the dimensionless scan rate $\nu^* = (\lambda_D^2/D_1)/[(R_u T/z_1 F)/v]$ can be interpreted as the ratio of the timescale for ion diffusion across the EDL $\tau_d = \lambda_D^2/D_1$ and the characteristic time $\tau_{th} = (R_u T/z_1 F)/v$ necessary to reach the thermal potential at scan rate v , i.e., $\nu^* = \tau_d/\tau_{th}$ [35]. Finally, $\tau_{CV}^* = \tau_{CV}/\tau_d = (\psi_{\max}^* - \psi_{\min}^*)/\nu^*$ represents the dimensionless cycle period.

Moreover, the boundary conditions accounting for the Stern layer at both electrodes can be written in dimensionless form as [35],

$$\begin{aligned} \frac{\partial \psi^*}{\partial x^*}(L^* - a_2^*/2, t^*) &= \frac{2}{a_2^*} [\psi^*(L^*, t^*) - \psi^*(L^* - a_2^*/2, t^*)] \\ -\frac{\partial \psi^*}{\partial x^*}(-L^* + a_2^*/2, t^*) &= \frac{2}{a_2^*} [\psi^*(-L^*, t^*) - \psi^*(-L^* + a_2^*/2, t^*)] \end{aligned} \quad (15)$$

The boundary conditions ensuring the continuity of the current density across the pseudocapacitive electrode/electrolyte interface can be written in dimensionless form as

$$-\frac{\sigma_P^*}{\psi_{\max}^* - \psi_{\min}^*} \frac{L_P^*}{L^*} \frac{\partial \psi^*}{\partial x^*}(-L^*, t^*) = j_C^*(-L^* + a_2^*/2, t^*) + j_F^*(t^*) \quad (16)$$

Similarly, across the carbon electrode/electrolyte interface [35]

$$-\frac{\sigma_C^*}{\psi_{\max}^* - \psi_{\min}^*} \frac{L_C^*}{L^*} \frac{\partial \psi^*}{\partial x^*}(L^*, t^*) = j_C^*(L^* - a_2^*/2, t^*). \quad (17)$$

Here, the capacitive $j_C(x, t)$ and faradaic $j_F(t)$ current densities are given by [22]

$$j_C(\pm(L-H), t) = -\epsilon_0 \epsilon_r \frac{\partial^2 \psi}{\partial x \partial t}(\pm(L-H), t) \quad (18)$$

$$j_F(t) = j_{F,0}(t) \left[\exp\left(\frac{(1-\alpha)z_1 F \eta}{R_u T}\right) - \exp\left(\frac{-\alpha z_1 F \eta}{R_u T}\right) \right] \quad (19)$$

where α is the transfer coefficient. The surface overpotential $\eta(t)$ is defined as $\eta(t) = \Delta\psi_H(t) - \Delta\psi_{eq}$ where $\Delta\psi_H(t) = \psi(-L, t) - \psi(-L+H, t)$ is the electrical potential drop across the Stern layer near the pseudocapacitive electrode and $\Delta\psi_{eq}$ is the equilibrium potential difference associated with the redox reaction [37]. Finally, the exchange current density $j_{F,0}(t)$ is expressed as [22]

$$j_{F,0}(t) = F z_1 k_0 [c_1(-L+H, t)]^{1-\alpha} [c_{1,P,\max} - c_{1,P}(-L, t)]^\alpha [c_{1,P}(-L, t)]^\alpha \quad (20)$$

where k_0 is the reaction rate constant expressed in $\text{m}^{1+3\alpha} \text{mol}^{-\alpha} \text{s}^{-1}$.

Both current densities $j_C(x, t)$ and $j_F(t)$ can be scaled by a characteristic ionic current density $F z_1 D_1 c_{1,\infty} / \lambda_D$ corresponding to diffusion of Li^+ ($i=1$) over the characteristic concentration gradient $c_{1,\infty} / \lambda_D$ to yield the dimensionless current densities

$$j_C^*(x^*, t^*) = \frac{j_C(t)}{F z_1 D_1 c_{1,\infty} / \lambda_D} \quad \text{and} \quad j_F^*(t^*) = \frac{j_F(t)}{F z_1 D_1 c_{1,\infty} / \lambda_D}. \quad (21)$$

These dimensionless current densities can be expressed as

$$j_C^*(\pm(L^* - a_2^*/2), t^*) = -(1 - z_2^*) \frac{\partial^2 \psi^*}{\partial x^* \partial t^*}(\pm(L^* - a_2^*/2), t^*) \quad (22)$$

$$\text{and} \quad j_F^*(t^*) = j_{F,0}^*(t^*) [\exp((1-\alpha)\eta^*) - \exp(-\alpha\eta^*)]. \quad (23)$$

Here, η^* is the dimensionless surface overpotential defined as $\eta^* = \Delta\psi_H^*(t^*) - \Delta\psi_{eq}^*$ and the dimensionless exchange current density $j_{F,0}^*$ can be expressed as

$$j_{F,0}^*(t^*) = k_0^* c_{1,P,\max}^* c_1^*(-L^* + H^*, t^*)^{1-\alpha} [1 - c_{1,P}^*(-L^*, t^*)]^\alpha \times (c_{1,P}^*(-L^*, t^*))^\alpha \quad (24)$$

where the dimensionless reaction rate constant is expressed as $k_0^* = k_0 c_{1,\infty}^\alpha \lambda_D / D_1$ and can be interpreted as the ratio of the timescale for ion diffusion across the EDL $\tau_d = \lambda_D^2 / D_1$ to the redox reaction timescale given by $\tau_f = \lambda_D / k_0 c_{1,\infty}^\alpha$.

In addition, the dimensionless mass fluxes of Li^+ ($i=1$) and ClO_4^- ($i=2$) at the Stern/diffuse layer interface near the pseudocapacitive electrode satisfied

$$N_1^*(-L^* + a_2^*/2, t^*) = j_F^*(t^*) \quad \text{and} \quad N_2^*(-L^* + a_2^*/2, t^*) = 0. \quad (25)$$

However, at the carbon electrode Stern/diffuse layer interface both ion fluxes vanish so that

$$N_1^*(L^* - a_2^*/2, t^*) = N_2^*(L^* - a_2^*/2, t^*) = 0. \quad (26)$$

Overall, the scaling analysis indicates that the dimensionless governing equations and associated boundary and initial conditions

are governed by seventeen dimensionless similarity parameters expressed as

$$\begin{aligned} v^* &= \frac{\lambda_D^2 / D_1}{(R_u T / z_1 F) / v}, \quad \psi_{\min}^* = \frac{\psi_{\min}}{R_u T / z_1 F}, \quad \psi_{\max}^* = \frac{\psi_{\max}}{R_u T / z_1 F}, \quad L^* = \frac{L}{\lambda_D}, \\ a_2^* &= \frac{a_2}{\lambda_D}, \quad \nu_{p1} = 2a_1^3 N_A c_{1,\infty}, \quad \nu_{p2} = 2a_2^3 N_A c_{1,\infty}, \quad D_2^* = \frac{D_2}{D_1}, \quad z_2^* = \frac{z_2}{z_1}, \\ \sigma_p^* &= \frac{\sigma_p (\psi_{\max} - \psi_{\min}) / L_p}{F z_1 c_{1,\infty} D_1 / L}, \quad \sigma_c^* = \frac{\sigma_c (\psi_{\max} - \psi_{\min}) / L_c}{F z_1 c_{1,\infty} D_1 / L}, \\ L_p^* &= \frac{L_p}{\lambda_D}, \quad L_c^* = \frac{L_c}{\lambda_D}, \quad D_{1,P}^* = \frac{D_{1,P}}{D_1}, \quad c_{1,P,\max}^* = \frac{c_{1,P,\max}}{c_{1,\infty}}, \\ k_0^* &= \frac{k_0 c_{1,\infty}^\alpha \lambda_D}{D_1}, \quad \text{and} \quad \Delta\psi_{eq}^* = \frac{\Delta\psi_{eq}}{R_u T / z_1 F}. \end{aligned} \quad (27)$$

Note that v^* , $\psi_{\min}^*$, $\psi_{\max}^*$, L^* , a_2^* , ν_{p1} , ν_{p2} , D_2^* , z_2^* , σ_p^* , σ_c^* , L_p^* , and L_c^* were identical to those identified in Ref. [35] for CV simulations of electric double layer capacitors with binary and asymmetric electrolytes. For hybrid supercapacitors with redox reactions and intercalation in the pseudocapacitive electrode, four additional dimensionless numbers appear, namely, $D_{1,P}^*$, $c_{1,P,\max}^*$, k_0^* , and $\Delta\psi_{eq}^*$.

2.3.4. Constitutive Relationships

A total of 22 input parameters were needed to solve the dimensional governing Equations (4) to (22) of Ref. [22] including (i) the electrolyte properties ϵ_r , a_1 , a_2 , z_1 , z_2 , D_1 , D_2 , and $c_{1,\infty}$, (ii) the carbon and pseudocapacitive electrode properties σ_c , σ_p , $c_{1,P,0}$ and $D_{1,P}$, (iii) the redox reaction parameters α , k_0 , and $\Delta\psi_{eq}$, (iv) the cell dimensions L , L_p , and L_c , and (v) the operating conditions T , $\psi_{\max}$, $\psi_{\min}$, and v . In the present study, the values and ranges of the parameters were taken from the literature whenever available and are reported in Table 1. In particular, the electrode parameters L_p and $D_{1,P}$ were taken as variables within a range of reasonable values. Furthermore, to evaluate the rate behavior of the device, the scan rate v was also varied. The transfer coefficient of the redox reaction α is generally assumed to be 1/2 corresponding to equal energy barriers for forward and backward redox reactions [37]. The baseline case corresponded to Case B of Ref. [22] considering a Nb_2O_5 pseudocapacitive electrode and a carbon electrode separated by an electrolyte consisting of LiClO_4 salt in organic solvent propylene carbonate (PC) at 1 M. Note that we verified that the cell charging/discharging was not limited by ion diffusion in the electrolyte by increasing the diffusion coefficients D_1 and D_2 of Li^+ and ClO_4^- by a factor of 10 without seeing any change in the predicted potential, concentrations and currents.

2.3.5. Method of Solution and Data Processing

The dimensional governing Equations (4) to (22) of Ref. [22] were solved using the commercial finite element solver COMSOL 4.3b run in parallel on 8 cores with 64 GB of RAM. The numerical convergence was considered to be reached when the maximum relative difference in the predicted current densities j_C and j_F at the Stern/diffuse layer interface near the pseudocapacitive electrode ($x = -L+H$) was less than 1% when dividing both the mesh size and the time step by a factor two. This led to imposing a time step of $\Delta t \approx \tau_{CV} / 1000 = (\psi_{\max} - \psi_{\min}) / 1000v$. The mesh size was the smallest at the electrode/electrolyte interface due to the large potential and concentration gradients and was gradually increased further from the electrode. The mesh size was specified to be less than 0.025 nm at the Stern/diffuse layer interface while it was less than $L/50$ in the diffuse layer and less than $L_p/25$ and $L_c/25$ in the electrode domains. The total number of finite elements was about 500 for all cases simulated in the present study.

The instantaneous total current density $j_T(t)$ at the pseudocapacitive electrode/electrolyte interface was computed as the sum of the capacitive and faradaic current densities, i.e., $j_T(t) = j_C(t) + j_F(t)$. CV curves at a specific scan rate were obtained by plotting $j_T(t)$, $j_C(t)$,

Table 1
Electrode and electrolyte properties and dimensions used in the simulations reported in this study.

Parameters	Symbol	Value	Unit	Ref.
Temperature	T	298	K	
Relative permittivity	ϵ_r	64.4		[47]
Li ⁺ ion diameter	a_1	0.67	nm	[48]
ClO ₄ ⁻ ion diameter	a_2	1.0	nm	[48]
Li ⁺ valency	z_1	1		
ClO ₄ ⁻ valency	z_2	-1		
Li ⁺ diffusion coefficient	D_1	2.6×10^{-10}	m ² /s	[48]
ClO ₄ ⁻ diffusion coefficient	D_2	3.3×10^{-10}	m ² /s	[48]
Stern layer thickness	H	0.5	nm	[35]
Initial bulk ion concentration	$c_{1,\infty} = c_{2,\infty}$	1	mol/L	[33,49,50]
Initial intercalated Li ⁺ concentration	$c_{1,p,0}$	1 to 5	mol/L	[51]
Pseudocapacitive electrode conductivity	σ_p	10^{-5}	S/m	[52]
Carbon electrode conductivity	σ_c	5	S/m	[53]
Reaction rate	k_0	10^{-7} to 10^{-13}	m ^{2.5} mol ^{-0.5} s ⁻¹	[54–56]
Intercalated Li ⁺ diffusion coefficient	$D_{1,p}$	10^{-14} to 10^{-10}	m ² /s	[55]
Half electrolyte thickness	L	1	μm	
Pseudocapacitive electrode thickness	L_p	20 to 500	nm	[32,57]
Carbon electrode thickness	L_c	20 to 500	nm	
Equilibrium potential difference	$\Delta\psi_{eq}$	0	V	[58]
Transfer coefficient	α	1/2		
Scan rate	ν	10^{-3} to 10	V/s	[33,49,50]
Potential window	$\psi_{max} - \psi_{min}$	1.6	V	[33,49,50]

and $j_F(t)$ as a function of $\psi_s(t)$. Finally, the areal integral capacitance of the device $C_{s,int}$ (in F/cm²) was computed from the total current $j_T(t)$ and the imposed potential $\psi_s(t)$ according to [40]

$$C_{s,int} = \frac{1}{\psi_{max} - \psi_{min}} \oint \frac{j_T(\psi_s)}{2\nu} d\psi_s. \quad (28)$$

3. Results and Discussion

3.1. Faradaic Potential Window

Figure 2 shows (a) the capacitive $j_C(t)$, faradaic $j_F(t)$, and total $j_T(t)$ current densities as well as (b) the intercalated Li⁺ concentration $c_{1,p}(-L, t)$ at the pseudocapacitive electrode/electrolyte interface as functions of cell potential $\psi_s(t)$ between $\psi_{min} = -0.8$ V and $\psi_{max} = +0.8$ V at a scan rate ν of 1 V/s. The results were obtained for pseudocapacitive electrode thickness $L_p = 50$ nm and for Li⁺ diffusion coefficient $D_{1,p} = 10^{-14}$ m²/s. Figure 2a demonstrates that the cell exhibited two distinct regimes. In the lower part of the potential window, the faradaic regime prevailed as the faradaic current dominated, i.e., $j_T(t) \approx j_F(t)$. In the higher part of the potential window, the capacitive regime was observed as the capacitive current j_C contributed the most to the total current density j_T . In the discharging step, the transition between the faradaic and capacitive regimes was caused by the slow outward diffusion of Li⁺ in the pseudocapacitive electrode causing Li⁺ starvation at the electrode/electrolyte interface, as illustrated in Figure 2b. In the charging step, the transition from capacitive to faradaic regime, marked by a red square, corresponded to steep increase in the absolute value of the total current density observed on Figure 2a. Note that this transition also corresponded to the end of the dissolution of the ClO₄⁻ EDL. Then, the capacitive current vanished during the entire faradaic regime.

The faradaic potential window, represented by a double arrow in Figure 2, was defined as $\Delta\psi_f = \psi_f - \psi_{min}$ where ψ_f is the potential at which Li⁺ starvation occurs during discharging, as shown by the onset of the capacitive current (blue circle in Figure 2). Experimentally, it may be easier to determine the faradaic potential window by the sharp increase in current density $j_T(t)$ in the charging step. Either definition led to very similar faradaic potential window as illustrated by the proximity of the red square and blue circle in Figure 2b. More importantly, the magnitude of the total current was

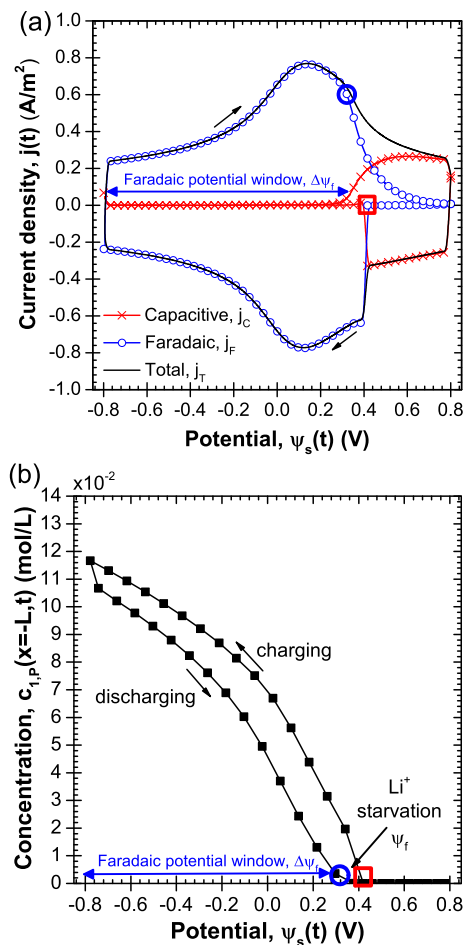


Fig. 2. (a) Capacitive $j_C(t)$, faradaic $j_F(t)$, and total $j_T(t)$ current densities at the pseudocapacitive electrode and (b) concentration of intercalated Li⁺ $c_{1,p}(-L, t)$ in the pseudocapacitive electrode at the electrode/electrolyte interface as functions of cell potential $\psi_s(t)$ at scan rate $\nu = 1$ V/s for pseudocapacitive electrode thickness $L_p = 50$ nm and Li⁺ diffusion coefficient in the electrode $D_{1,p} = 10^{-14}$ m²/s.

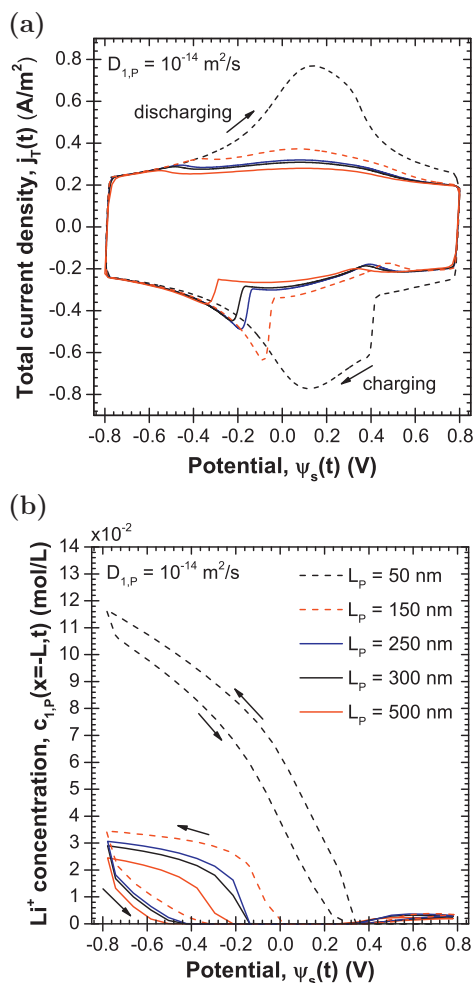


Fig. 3. (a) Total current density $j_T(t)$ and (b) concentration of intercalated Li⁺ $c_{1,p}(-L, t)$ in the pseudocapacitive electrode at the electrode/electrolyte interface as functions of imposed cell potential $\psi_s(t)$ at scan rate $\nu = 1$ V/s for pseudocapacitive electrode thickness L_p ranging from 50 to 500 nm with a relatively small diffusion coefficient of Li⁺ in the electrode $D_{1,p} = 10^{-14}$ m²/s.

significantly smaller in the capacitive regime than in the faradaic regime. This stresses the need for widening the faradaic potential window by delaying or eliminating Li⁺ starvation. In addition, eliminating Li⁺ starvation would eliminate the transition from the faradaic to the capacitive regime. This would eliminate the dip in b -value caused by the transition and improve high rate performance [22].

3.2. Effect of the Pseudocapacitive Electrode Thickness

Figure 3 shows (a) the total current density j_T and (b) the intercalated Li⁺ concentration $c_{1,p}(-L, t)$ at the pseudocapacitive electrode/electrolyte interface as functions of the cell potential $\psi_s(t)$ for pseudocapacitive electrode thickness ranging from $L_p = 50$ to 500 nm in the case of a relatively small Li⁺ diffusion coefficient $D_{1,p} = 10^{-14}$ m²/s. Here also, the scan rate was 1 V/s. Figure 3a indicates that thinner electrodes resulted in larger current densities and larger capacitances. In fact, the device with a pseudocapacitive electrode of thickness $L_p = 50$ nm had an areal integral capacitance $C_{s,int}$ of 40 μ F/cm². This was almost twice as large as that with electrode thickness $L_p = 500$ nm found to be $C_{s,int} = 25$ μ F/cm². Figure 3a also illustrates that the CV curves exhibited similar peaks for all thicknesses considered. The most prominent peak was observed during charging and indicated the onset of the faradaic charging as

indicated in Figure 3b by the sharp rise in $c_{1,p}(-L, t)$ as Li⁺ started intercalating in the electrode. This peak was found to shift toward larger potentials from $\psi_s = -0.3$ V to $\psi_s = +0.1$ V as the pseudocapacitive electrode thickness decreased. Similarly, the hump in the discharging current also shifted from lower to higher potentials as the electrode thickness decreased. In other words, the faradaic potential window $\Delta\psi_f$ widened as the electrode thickness L_p decreased.

Figure 3b indicates that thinner electrodes led to larger maximum concentration of intercalated Li⁺ at the electrode surface at the end of the charging step. This was due to (i) the wider fraction of the potential window dominated by faradaic reactions, (ii) the large faradaic current density, and (iii) the smaller electrode volume in which Li⁺ ions could intercalate. Thicker electrodes provided more volume for Li⁺ insertion but suffered from a narrower faradaic potential window and a smaller current magnitude. Figure 3b also features hysteresis in the concentration $c_{1,p}(-L, t)$ suggesting that charging and discharging were limited by slow Li⁺ intercalation caused by the relatively small value of $D_{1,p}$. Note that, in all cases, the Li⁺ concentration $c_{1,p}$ remained significantly smaller than its theoretical maximum of $c_{1,p,max} = 37$ mol/L, corresponding the the fully intercalated electrode.

Overall, this section has demonstrated that, in the case of hybrid pseudocapacitors limited by Li⁺ intercalation in the pseudocapacitive electrode, a thinner electrode led to larger faradaic potential window. In turn, this led to larger current densities and overall larger areal capacitance by delaying the Li⁺ starvation during the discharging step.

3.3. Effect of the Intercalated Li⁺ Diffusion Coefficient

Figure 4 shows (a) the total current density j_T as well as (b) the Li⁺ concentration $c_{1,p}(-L, t)$ at the pseudocapacitive electrode/electrolyte interface as functions of cell potential $\psi_s(t)$ at a scan rate ν of 1 V/s for a relatively thick electrode ($L_p = 500$ nm) and for intercalated Li⁺ diffusion coefficients $D_{1,p}$ ranging from 10^{-14} to 10^{-11} m²/s. Figure 4a indicates that the current peak observed during charging increased in magnitude and shifted from $\psi_s = -0.25$ V to $\psi_s = 0$ V as the diffusion coefficient $D_{1,p}$ increased. Similarly, the peak observed during discharging also shifted toward higher potential with increasing diffusion coefficient. This suggests that the faradaic potential window $\Delta\psi_f = \psi_f - \psi_{min}$ widened and Li⁺ starvation was delayed as the diffusion coefficient $D_{1,p}$ increased. In fact, the device's areal integral capacitance increased from 25 to 47 μ F/cm² as $D_{1,p}$ increased from 10^{-14} to 10^{-11} m²/s. Note that the maximum Li⁺ concentration $c_{1,p}(-L, t)$ reached at the end of the charging step at the electrode/electrolyte interface decreased with increasing diffusion coefficient $D_{1,p}$. Furthermore, the CV curves for relatively large diffusion coefficient $D_{1,p}$ of 10^{-12} and 10^{-11} m²/s were superimposed and the capacitive current was negligibly small across the entire potential window. Indeed, Figure 4b establishes that, for these values of $D_{1,p}$, no starvation of Li⁺ occurred at the electrode/electrolyte interface. Instead, the concentration of intercalated lithium was uniform in the electrode and increased up to an oscillatory steady-state with a very narrow hysteresis. Then, the faradaic process was not diffusion limited, the device operated only in the faradaic regime, and the faradaic potential window was maximal, i.e., $\Delta\psi_f = \psi_{max} - \psi_{min}$.

3.4. Effect of the Reaction Rate

Figure 5a shows the total current density j_T as a function of imposed cell potential $\psi_s(t)$ for different values of the reaction rate k_0 ranging from 10^{-7} to 10^{-13} m^{2.5}mol^{-0.5}s⁻¹. Figures 5b to 5d show the capacitive j_C , faradaic j_F , and total j_T current densities as functions of cell potential $\psi_s(t)$ for reaction rate k_0 of (b) 10^{-7} , (c) 10^{-10} , and (d) 10^{-13} m^{2.5}mol^{-0.5}s⁻¹. In all cases, the scan

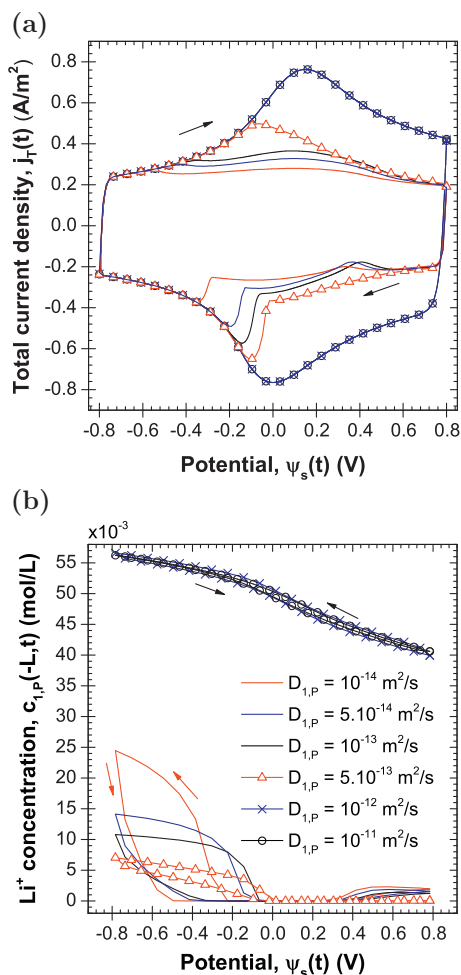


Fig. 4. (a) Total current density $j_T(t)$ and (c) concentration of intercalated Li⁺ $c_{1,p}(-L, t)$ in the pseudocapacitive electrode of thickness $L_p = 500$ nm at the electrode/electrolyte interface as functions of imposed cell potential $\psi_s(t)$ at scan rate $\nu = 1$ V/s for diffusion coefficient $D_{1,p}$ ranging from 10^{-14} to 10^{-11} m²/s.

rate was $\nu = 1$ V/s and the potential window extended from -0.8 V to -0.2 V. Figure 5a indicates that for reaction rates larger than 10^{-9} m^{2.5}mol^{-0.5}s⁻¹ the CV curves were nearly identical. Figure 5b suggests that the behavior displayed involved a transition between faradaic and capacitive regimes similar to that discussed previously (Figure 2). This regime transition coincided with the charging peak in the total current density and was found to occur at the same potential for all reaction rates larger than 10^{-9} m^{2.5}mol^{-0.5}s⁻¹. In other words, when the cell was not limited by the reaction rate, the latter had no effect on the CV curves and on the width of the faradaic potential window. Figure 5c shows that for a smaller reaction rate $k_0 = 10^{-10}$ m^{2.5}mol^{-0.5}s⁻¹, the capacitive current dominated for the entire potential window and thus no regime transition was observed. For even lower reaction rates, Figure 5d shows that the current was exclusively capacitive and the device behaved as an EDLC. Finally, note that Figure 5a indicates that a larger capacitance was achieved for $k_0 = 10^{-13}$ m^{2.5}mol^{-0.5}s⁻¹ than for $k_0 = 10^{-10}$ m^{2.5}mol^{-0.5}s⁻¹. In the latter case, the faradaic and capacitive currents had opposite signs which led to a smaller total current density.

Overall, this section established that both the pseudocapacitive electrode thickness L_p and the diffusion coefficient $D_{1,p}$ of intercalated Li⁺ have dramatic effects on the CV curves and on the faradaic potential window. The reaction rate constant k_0 was found to have a small effect on charge storage in the device for a reasonably

large value. The interplay between the pseudocapacitive electrode parameters L_p and $D_{1,p}$ and their respective effects on the faradaic potential window can be further studied and quantified by performing a scaling analysis. Such analysis considered a sufficiently large reaction rate k_0 so that it was not limiting.

4. Scaling

4.1. Validation of the Scaling

In order to demonstrate the validity of the scaling described in the Analysis section, four different cases were considered with various electrode and electrolyte properties and cell dimensions. Table 2 summarizes the different values of the input parameters of Cases 1 through 4. However, these four cases featured identical dimensionless numbers governing the problem namely $\nu^* = 1.13 \times 10^{-8}$, $\psi_{\max}^* = 31.2$, $\psi_{\min}^* = 7.79$, $L^* = 3641.5$, $a_2^* = 3.65$, $\nu_{p,1} = 1.21$, $\nu_{p,2} = 0.36$, $D_2^* = 1.27$, $z_2^* = -1$, $\sigma_p^* = 0.165$, $\sigma_c^* = 0.165$, $L_p^* = L_c^* = 36,415$, $D_{1,p}^* = 3.8 \times 10^{-5}$, $c_{1,p,\max}^* = 32.9$, $k_0^* = 3.34 \times 10^{-8}$, and $\Delta\psi_{eq}^* = 0$. Figures 6a and 6b respectively show the predicted capacitive and faradaic current densities j_C and j_F as functions of surface potential ψ_s for these four cases. They indicate that capacitive and faradaic current densities j_C and j_F varied significantly among these four cases due to the large difference in input parameters. However, Figures 6d and 6e plot the corresponding dimensionless current densities j_C^* and j_F^* versus ψ_s^* as defined in Equations (21) and (22), respectively. They demonstrate that the dimensionless CV curves overlapped for all four cases considered.

Similarly, Figure 6c shows the predicted Li⁺ concentration in the pseudocapacitive electrode at the electrode/electrolyte interface, $c_{1,p}(-L, t)$ as a function of potential ψ_s for the four cases considered. Again, the plots differed significantly both in terms of magnitude and shape. However, Figure 6f plots the dimensionless concentration of Li⁺ in the pseudocapacitive electrode at the electrode/electrolyte interface $c_{1,p}^*(-L, t)$ as a function of dimensionless potential ψ_s^* . It indicates that the dimensionless plots overlapped for the four cases considered. These results establish that the governing equations and boundary and initial conditions were properly scaled and that the dimensionless CV curves are uniquely determined by the 17 similarity parameters given by Equations (27).

4.2. Scaling of Faradaic Potential Window

The faradaic potential window $\Delta\psi_f$ was previously shown to be a good indicator of the performance of the hybrid pseudocapacitor simulated. Ideally, a device should operate exclusively in the faradaic regime to achieve large energy and power densities, as discussed previously [22]. However, most actual hybrid pseudocapacitors suffer from Li⁺ starvation in the course of a typical cycle [6]. The fraction R_f of the potential window dominated by faradaic reactions can be defined as

$$R_f = \frac{\Delta\psi_f}{\Delta\psi_s} = \frac{\psi_f - \psi_{\min}}{\psi_{\max} - \psi_{\min}} \quad (29)$$

According to scaling analysis, this dimensionless parameter should be a unique function of the 17 similarity parameters given by Equations (27). Here, we will limit our study to those parameters associated with the faradaic reaction and with the intercalation of Li⁺ to obtain design guidelines for the pseudocapacitive electrode. For the sake of simplicity, the width of the potential window and the ion valencies were kept constant and equal to $\psi_{\min} = -0.8$ V, $\psi_{\max} = 0.8$ V, and $z_1 = -z_2 = 1$. Similarly, the ion diffusion coefficients in the electrolyte were those reported in Table 1. They were large enough that the device operated in the ion diffusion-independent regime, at the scan rates considered. In other words, favorable yet realistic

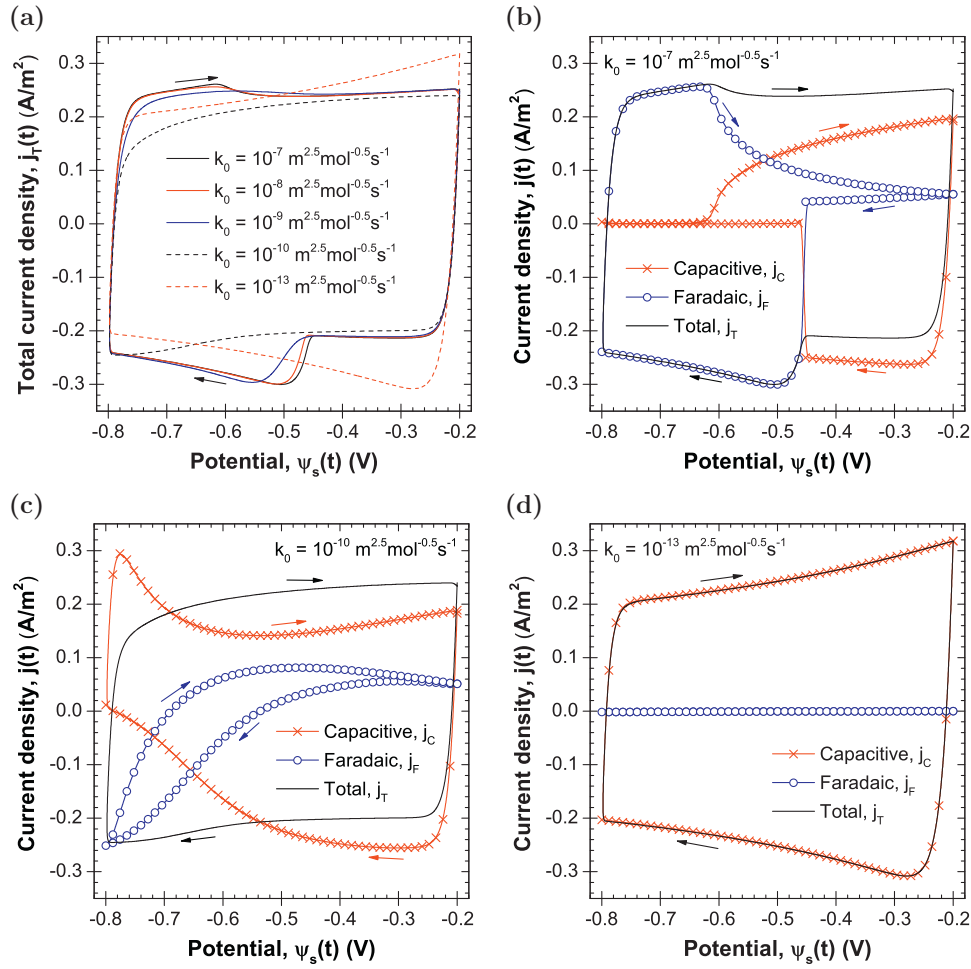


Fig. 5. (a) Total current density j_T as a function of cell potential $\psi_s(t)$ at the pseudocapacitive electrode for five different values of the reaction rate k_0 . Capacitive j_C , faradaic j_F , and total j_T current densities as functions of cell potential $\psi_s(t)$ at the pseudocapacitive electrode for reaction rate constant k_0 equals to (b) 10^{-7} , (c) 10^{-10} , and (d) $10^{-13} \text{ m}^2 \text{ mol}^{-0.5} \text{ s}^{-1}$.

values of the parameters associated with the choice of the electrolyte were considered. The maximum concentration of Li^+ in the electrode $c_{1,P,\max}$, the equilibrium potential $\Delta\psi_{eq}$, and the reaction rate k_0 were also kept constant. First, the maximum intercalated Li^+ concentration $c_{1,P,\max}$ was never reached in any of our simulations.

In addition, the equilibrium potential $\Delta\psi_{eq}$ was found to have a negligible effect on the behavior of the device [22]. Finally, the reaction rate constant k_0 was found to only affect the shape and magnitude of the faradaic current but not the faradaic potential window. Therefore, only the dimensionless parameters L_p^* , $D_{1,p}^*$, and ν^* were

Table 2

Parameters used in CV simulations reported in Figure 6 with $\Delta\psi_{eq} = 0 \text{ V}$ and $z_1 = -z_2 = 1$ for all cases considered. In these four cases, the dimensionless numbers identified in Equation (27) were identical and equal to $\nu^* = 1.13 \times 10^{-8}$, $\psi_{\max}^* = 31.2$, $\psi_{\min}^* = 7.79$, $L^* = 3641.5$, $a_2^* = 3.65$, $\nu_{p,1} = 1.21$, $\nu_{p,2} = 0.36$, $D_2^* = 1.27$, $z_2^* = -1$, $\sigma_p^* = 0.16$, $\sigma_c^* = 12$, $L_p^* = L_c^* = 36415$, $D_{1,p}^* = 3.8 \times 10^{-5}$, $k_0^* = 3.34 \times 10^{-8}$, and $\Delta\psi_{eq}^* = 0$.

Parameters	Case 1	Case 2	Case 3	Case 4
$\nu \text{ (V/s)}$	1	0.1	0.215	0.0091
$\psi_{\max} \text{ (V)}$	0.8	0.8	0.8	0.6
$\psi_{\min} \text{ (V)}$	0.2	0.2	0.2	0.15
$T \text{ (K)}$	298	298	298	223.5
$a_1 \text{ (nm)}$	0.67	0.67	1.44	1.92
$a_2 \text{ (nm)}$	1.0	1.0	2.16	2.88
$D_1 \text{ (m}^2/\text{s)}$	2.6×10^{-10}	2.6×10^{-11}	2.6×10^{-10}	2.6×10^{-11}
$D_2 \text{ (m}^2/\text{s)}$	3.3×10^{-10}	3.3×10^{-11}	3.3×10^{-10}	3.3×10^{-11}
$c_{1,\infty} \text{ (mol/L)}$	1.0	1.0	0.1	0.042
ϵ_r	78.5	78.5	36.4	36.4
$L \text{ (}\mu\text{m)}$	1.0	1.0	2.15	2.87
$\sigma_P \text{ (S/m)}$	0.069	0.0069	0.0069	3.88×10^{-4}
$\sigma_C \text{ (S/m)}$	5	5	5	5
$L_P = L_C \text{ (}\mu\text{m)}$	10	10	21.5	28.7
$D_{1,p} \text{ (m}^2/\text{s)}$	10^{-14}	10^{-15}	10^{-14}	10^{-15}
$c_{1,P,\max} \text{ (mol/L)}$	32.9	32.9	3.29	1.39
$k_0 \text{ (m}^2 \text{ mol}^{-0.5} \text{ s}^{-1})$	10^{-9}	10^{-10}	1.47×10^{-9}	1.69×10^{-10}

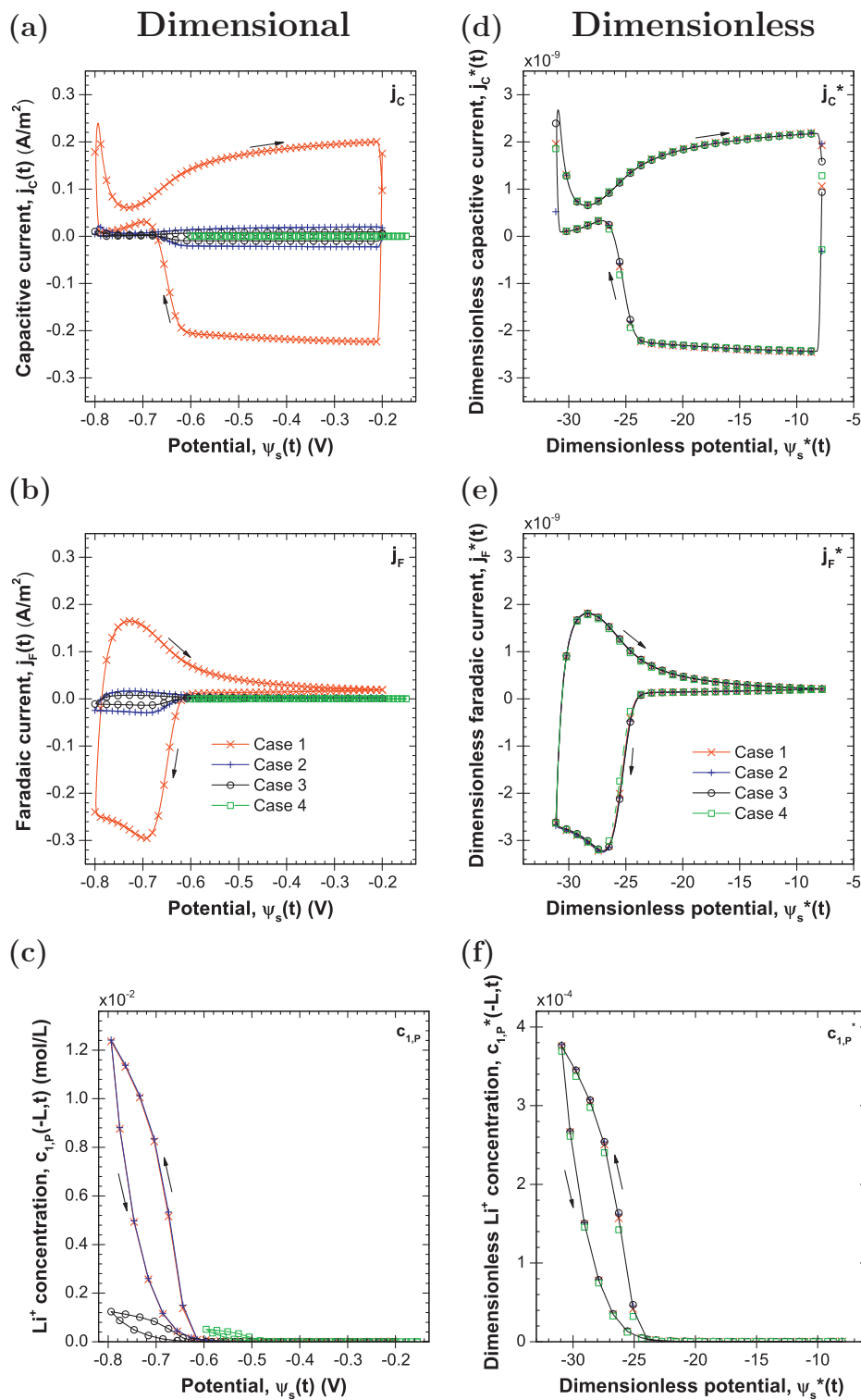


Fig. 6. Predicted dimensional currents (a) j_c , (b) j_f , and (c) concentration $c_{1,p}$ as functions of imposed potential ψ_s along with the corresponding dimensionless currents (d) j_c^* , (e) j_f^* , and (f) concentration $c_{1,p}^*$ as functions of dimensionless imposed potential ψ_s^* for cases 1 through 4 summarized in Table 2.

investigated. Their respective ranges were based on realistic values of the associated dimensional variables. The dimensionless electrode thickness L_p^* ranged from 36 to 2.9×10^3 , while the dimensionless scan rate ranged from 1.1×10^{-11} to 1.1×10^{-8} , and the dimensionless Li⁺ diffusion coefficient ranged from 3.8×10^{-5} to 1.9×10^{-1} . The latter corresponded to differences in diffusion coefficient $D_{1,p}$ between crystalline and amorphous or among eligible metal oxide materials. All the other dimensionless parameters were

kept constant with the following values: $a_2^* = 3.63$, $z_2^* = -1$, $\psi_{\max}^* = 31.2$, $\psi_{\min}^* = -31.2$, $L^* = 3.63 \times 10^3$, $\nu_{p1} = 3.62 \times 10^{-1}$, $\nu_{p2} = 1.20$, $D_2^* = 1.27$, $c_{1,p,\max}^* = 32.9$, $k_0^* = 3.35 \times 10^{-7}$, and $\Delta\psi_{eq}^* = 0$.

Figure 7a shows the faradaic fraction R_f as a function of dimensionless pseudocapacitive electrode thickness L_p^* for different values of dimensionless Li⁺ diffusion coefficient $D_{1,p}^*$ and dimensionless scan rate ν^* . For each set of ($D_{1,p}^*$, ν^*), the solid line represents a power law fitting R_f to L_p^* according to $R_f \propto (L_p^*)^{-1/2}$.

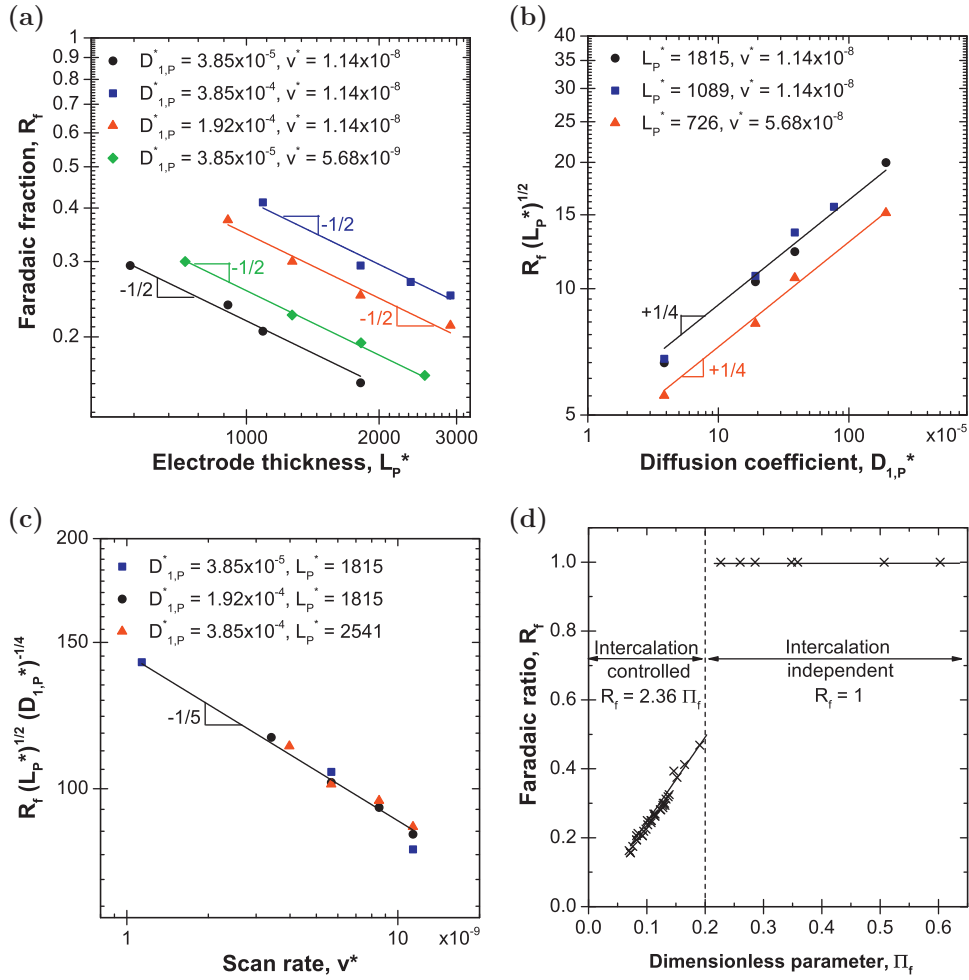


Fig. 7. (a) Faradaic fraction R_f as a function of dimensionless electrode thickness L_p^* for different values of the dimensionless diffusion coefficient of Li^+ inside the pseudocapacitive electrode $D_{1,p}^*$. (b) $R_f (L_p^*)^{1/2}$ as a function of the dimensionless Li^+ diffusion coefficient $D_{1,p}^*$. (c) $R_f (L_p^*)^{1/2} (D_{1,p}^*)^{-1/4}$ as a function of dimensionless scan rate v^* . (d) Faradaic fraction R_f as a function of dimensionless parameter Π_f defined in Equation (30).

This is consistent with previous results (Figure 3) indicating that the faradaic potential window narrowed as the electrode thickness increased.

Figure 7b shows the dimensionless number $R_f (L_p^*)^{1/2}$ as a function of dimensionless Li^+ diffusion coefficient $D_{1,p}^*$ in the pseudocapacitive electrode for different values of L_p^* and v^* . Cases with identical dimensionless scan rate v^* but different L_p^* aligned along the same line according to the power law $R_f (L_p^*)^{1/2} \propto (D_{1,p}^*)^{1/4}$. This confirms that the effect of the electrode thickness was captured by the power law obtained from Figure 7a. Note that the faradaic fraction R_f was unity for larger diffusion coefficients. In these cases, the current was exclusively faradaic and there was no Li^+ starvation, as reported in Section 3.3.

Figure 7c shows the dimensionless number $R_f (L_p^*)^{1/2} (D_{1,p}^*)^{-1/4}$ as a function of dimensionless scan rate v^* for different values $D_{1,p}^*$ and L_p^* . All the cases aligned along a single line according to the power law $R_f (L_p^*)^{1/2} (D_{1,p}^*)^{-1/4} \propto (v^*)^{-1/5}$. This confirms that the effects of the electrode thickness and diffusion coefficient were correctly captured by the previous scaling.

Finally, Figure 7d shows the faradaic fraction R_f as a function of the dimensionless parameter Π_f capturing the combined effects of L_p^* , $D_{1,p}^*$, and v^* and defined as

$$\Pi_f = \frac{(D_{1,p}^*)^{1/4}}{(L_p^*)^{1/2} (v^*)^{1/5}} = \left(\frac{\tau_d}{\tau_{d,p}} \right)^{1/4} \left(\frac{\tau_{th}}{\tau_d} \right)^{1/5}. \quad (30)$$

Π_f can be interpreted as the product of the ratios of (i) the characteristic time for Li^+ ion diffusion across the EDL, defined as $\tau_d = \lambda_D^2 / D_1$, and the characteristic time for Li^+ intercalation in the pseudocapacitive electrode defined as $\tau_{d,p} = L_p^2 / D_{1,p}$, and of (ii) the characteristic time for reaching the thermal potential $R_u T / z_1 F$ at scan rate v defined as $\tau_{th} = (R_u T / z_1 F) / v$ and τ_d . Figure 7d features an intercalation-controlled regime and an intercalation-independent regime with a sharp transition at $\Pi_f = 0.2$. In the intercalation-controlled regime, the faradaic fraction R_f was linearly proportional to Π_f according to $R_f = 2.36 \Pi_f$ for $\Pi_f < 0.2$. In the intercalation-independent regime, the entire potential window was dominated by the faradaic current and R_f was unity.

In practice, hybrid pseudocapacitors should operate in the intercalation-independent regime and the pseudocapacitive electrode should satisfy the design criterion $\Pi_f > 0.2$. This criterion can be achieved by reducing the scan rate or charging rate so that Li^+ intercalation has the time to respond to changes in surface potential. This is equivalent to reducing power to maximize energy density. Alternatively, the pseudocapacitive electrode thickness can be reduced to compensate for slow Li^+ intercalation and to delay Li^+ starvation. This would correspond to reducing energy density to achieve maximum power. The most desirable solution is to select a pseudocapacitive material with fast Li^+ intercalation to enable the use of large electrode thickness and thus achieve both large power and energy densities. This can be obtained with crystalline structures providing fast diffusion pathways in the electrode

material [43]. Actual electrodes are porous with sometimes a conductive scaffold supporting the redox active materials [5]. The above design criterion can be applied using effective properties to reflect the porosity and 3D morphology of actual electrodes. Similarly, the presence of a conductive scaffold would have to be taken into account with an effective electrical conductivity. The presence of phase transition in the electrode material may lead experimentally to additional peaks being observed in the CV curves. Materials exhibiting a phase transition upon Li^+ insertion are not however considered good pseudocapacitive materials [39]. In addition, nanostructuring of transition metal oxide tends to suppress the phase transition upon lithiation [44–46]. Therefore, they were excluded from the object of this study.

5. Conclusion

This paper presented the dimensional analysis of a continuum model simulating hybrid pseudocapacitors accounting simultaneously for (i) charge transport in the electrodes and electrolyte, (ii) formation of an EDL at the electrode/electrolyte interfaces, (iii) steric repulsion due to finite ion size, (iv) redox reactions at the pseudocapacitive electrode/electrolyte interface, and (v) intercalation of the reaction product in the pseudocapacitive electrode. A parametric study was conducted to identify the role of the pseudocapacitive electrode thickness, Li^+ diffusion coefficient, and reaction rate constant on the CV curves of the device for different scan rates. Two regimes were identified: a faradaic regime dominated by redox reactions and Li^+ intercalation and a capacitive regime dominated by EDL formation. The faradaic regime exhibited the largest current density. The transition from the faradaic to the capacitive regime observed in most cases was caused by the starvation of Li^+ at the electrode/electrolyte interface. The fraction of the potential window dominated by faradaic reactions was found to be a good indicator of the total capacitance of the hybrid pseudocapacitor. It increased with increasing diffusion coefficient of Li^+ in the pseudocapacitive electrode and with decreasing electrode thickness and scan rate. The scaling analysis led to a dimensionless parameter Π_f , defined in Equation (30), relating these parameters to the faradaic fraction. It also established that for $\Pi_f > 0.2$, the entire potential window was dominated by the faradaic current and the device operated in an intercalation-independent regime. This design criterion can be used to optimize the pseudocapacitive electrode in hybrid pseudocapacitors.

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References

- [1] US Department of Energy, Basic Research Needs for Electrical Energy Storage, <http://www.osti.gov/accomplishments/documents/fullText/ACC0330.pdf>, 2007.
- [2] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nature Materials* 7 (11) (2008) 845–854.
- [3] Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, Progress of electrochemical capacitor electrode materials: A review, *International Journal of Hydrogen Energy* 34 (11) (2009) 4889–4899.
- [4] Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li, H.-M. Cheng, Graphene/metal oxide composite electrode materials for energy storage, *Nano Energy* 1 (1) (2012) 107–131.
- [5] G. Wang, L. Zhang, J. Zhang, A review of electrode materials for electrochemical supercapacitors, *Chemical Society Reviews* 41 (2) (2012) 797–828.
- [6] V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.-L. Taberna, S.H. Tolbert, H.D. Abruna, P. Simon, B. Dunn, High-rate electrochemical energy storage through Li^+ intercalation pseudocapacitance, *Nature Materials* 12 (2013) 518–522.
- [7] Q. Qu, P. Zhang, B. Wang, Y. Chen, S. Tian, Y. Wu, R. Holze, Electrochemical performance of MnO_2 nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors, *Journal of Physical Chemistry C* 113 (31) (2009) 14020–14027.
- [8] J.W. Long, D. Bélanger, T. Brousse, W. Sugimoto, M.B. Sassin, O. Crosnier, Asymmetric electrochemical capacitors—stretching the limits of aqueous electrolytes, *Material Research Society Bulletin* 36 (7) (2011) 513–522.
- [9] Z. Fan, J. Yan, T. Wei, L. Zhi, G. Ning, T. Li, F. Wei, Asymmetric supercapacitors based on graphene/ MnO_2 and activated carbon nanofiber electrodes with high power and energy density, *Advanced Functional Materials* 21 (12) (2011) 2366–2375.
- [10] F. Wang, S. Xiao, Y. Hou, C. Hu, L. Liu, Y. Wu, Electrode materials for aqueous asymmetric supercapacitors, *RSC Advances* 3 (32) (2013) 13059–13084.
- [11] L. Demarconnay, E. Raymundo-Piñero, F. Béguin, Adjustment of electrodes potential window in an asymmetric carbon/ MnO_2 supercapacitor, *Journal of Power Sources* 196 (1) (2011) 580–586.
- [12] B. Pillay, Design of Electrochemical Capacitors for Energy Storage, Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley, CA (1996).
- [13] C. Lin, J.A. Ritter, B.N. Popov, R.E. White, A mathematical model of an electrochemical capacitor with double-layer and Faradaic processes, *Journal of The Electrochemical Society* 146 (9) (1999) 3168–3175.
- [14] H. Kim, B.N. Popov, A mathematical model of oxide, carbon composite electrode for supercapacitors, *Journal of the Electrochemical Society* 150 (9) (2003) 1153–1160.
- [15] K. Somasundaram, E. Birgersson, A.S. Mujumdar, Analysis of a model for an electrochemical capacitor, *Journal of The Electrochemical Society* 158 (11) (2011) 1220–1230.
- [16] H. Farsi, F. Gopal, A mathematical model of nanoparticulate mixed oxide pseudocapacitors; part II: the effects of intrinsic factors, *Journal of Solid State Electrochemistry* 15 (1) (2011) 115–123.
- [17] S. Devan, V.R. Subramanian, R.E. White, Transient analysis of a porous electrode, *Journal of The Electrochemical Society* 152 (5) (2005) 947–955.
- [18] J.A. Staser, J.W. Weidner, Mathematical modeling of hybrid asymmetric electrochemical capacitors, *Journal of The Electrochemical Society* 161 (8) (2014) E3267–E3275.
- [19] T. Kadyk, M. Eikerling, Charging mechanism and moving reaction fronts in a supercapacitor with pseudocapacitance, *Journal of The Electrochemical Society* 161 (3) (2014) A239–A246.
- [20] C. Lin, B.N. Popov, H.J. Ploehn, Modeling the effects of electrode composition and pore structure on the performance of electrochemical capacitors, *Journal of the Electrochemical Society* 149 (2) (2002) A167–A175.
- [21] G. Sikha, R.E. White, B.N. Popov, A mathematical model for a lithium-ion battery/electrochemical capacitor hybrid system, *Journal of the Electrochemical Society* 152 (8) (2005) A1682–A1693.
- [22] H.-L. Girard, H. Wang, A. d'Entremont, L. Pilon, Physical interpretation of cyclic voltammetry for hybrid pseudocapacitors, *Journal of Physical Chemistry C* 119 (21) (2015) 11349–11361.
- [23] B.E. Conway, V. Birss, J. Wojtowicz, The role and utilization of pseudocapacitance for energy storage by supercapacitors, *Journal of Power Sources* 66 (1) (1997) 1–14.
- [24] P. Guillemet, T. Brousse, O. Crosnier, Y. Dandeville, L. Athouel, Y. Scudeller, Modeling pseudo capacitance of manganese dioxide, *Electrochimica Acta* 67 (2012) 41–49.
- [25] J.F. Robinson, Y.P. Kaynamura, Charge transport in conducting polymers: Insights from impedance spectroscopy, *Chemical Society Reviews* 38 (12) (2009) 3339–3347.
- [26] Y. Liu, F. Zhou, V. Ozolins, Ab Initio study of the charge-storage mechanisms in RuO_2 -based electrochemical ultracapacitors, *Journal of Physical Chemistry C* 116 (1) (2012) 1450–1457.
- [27] V. Ozolins, F. Zhou, M. Asta, Ruthenium-based electrochemical supercapacitors: Insights from first-principles calculations, *Accounts of Chemical Research* 46 (5) (2013) 1084–1093.
- [28] J. Kang, S.-H. Wei, K. Zhu, Y.-H. Kim, First-principles theory of electrochemical capacitance of nanostructured materials: Dipole-assisted subsurface intercalation of lithium in pseudocapacitive TiO_2 anatase nanosheets, *Journal of Physical Chemistry C* 115 (11) (2011) 4909–4915.
- [29] D.A. Tompsett, S.C. Parker, P.G. Bruce, M.S. Islam, Nanostructuring of $\beta\text{-MnO}_2$: The important role of surface to bulk ion migration, *Chemistry of Materials* 25 (4) (2013) 536–541.
- [30] H. Ding, K.G. Ray, V. Ozolins, M. Asta, Structural and vibrational properties of $\alpha\text{-MoO}_3$ from van der Waals corrected density functional theory calculations, *Physical Review B* 85 (2012) 012104.
- [31] L. Shao, J.-W. Jeon, J.L. Lutkenhaus, Porous polyaniline nanofiber/vanadium pentoxide layer-by-layer electrodes for energy storage, *Journal of Materials Chemistry A* 1 (26) (2013) 7648–7656.
- [32] J. Wang, J. Polleux, J. Lim, B. Dunn, Pseudocapacitive contributions to electrochemical energy storage in TiO_2 (anatase) nanoparticles, *Journal of Physical Chemistry C* 111 (40) (2007) 14925–14931.
- [33] M.C. López, G.F. Ortiz, P. Lavela, R. Alcántara, J.L. Tirado, Improved energy storage solution based on hybrid oxide materials, *ACS Sustainable Chemistry & Engineering* 1 (1) (2013) 46–56.
- [34] H. Wang, J. Fang, L. Pilon, Scaling laws for carbon-based electric double layer capacitors, *Electrochimica Acta* 109 (2013) 316–321.

- [35] H. Wang, A. Thiele, L. Pilon, Simulations of cyclic voltammetry for electric double layers in asymmetric electrolytes: A generalized modified Poisson-Nernst-Planck model, *Journal of Physical Chemistry C* 117 (36) (2013) 18286–18297.
- [36] J.H. Masliyah, S. Bhattacharjee, *Electrokinetic and Colloid Transport Phenomena*, John Wiley & Sons, 2006.
- [37] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, NY, 2001.
- [38] S. Umino, J. Newman, Diffusion of sulfuric acid in concentrated solutions, *Journal of the Electrochemical Society* 140 (8) (1993) 2217–2221.
- [39] J. Come, V. Augustyn, J.W. Kim, P. Rozier, P.-L. Taberna, P. Gogotsi, J.W. Long, B. Dunn, P. Simon, Electrochemical kinetics of nanostructured Nb₂O₅ electrodes, *Journal of The Electrochemical Society* 161 (5) (2014) A718–A725.
- [40] H. Wang, L. Pilon, Physical interpretation of cyclic voltammetry for measuring electric double layer capacitances, *Electrochimica Acta* 64 (2012) 130–139.
- [41] J.H. Masliyah, S. Bhattacharjee, *Electrokinetic and Colloid Transport Phenomena*, John Wiley & Sons, Hoboken, NJ, 2006.
- [42] A.A. Kornyshev, Double-layer in ionic liquids: Paradigm change? *Journal of Physical Chemistry B* 111 (20) (2007) 5545–5557.
- [43] J.W. Kim, V. Augustyn, B. Dunn, The effect of crystallinity on the rapid pseudocapacitive response of Nb₂O₅, *Advanced Energy Materials* 2 (1) (2012) 141–148.
- [44] V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage, *Energy & Environmental Science* 7 (5) (2014) 1597–1614.
- [45] H.-S. Kim, J.B. Cook, S.H. Tolbert, B. Dunn, The development of pseudocapacitive properties in nanosized-MoO₃, *Journal of The Electrochemical Society* 162 (5) (2015) A5083–A5090.
- [46] G.A. Muller, J.B. Cook, H.-S. Kim, S.H. Tolbert, B. Dunn, High performance pseudocapacitor based on 2D layered metal chalcogenide nanocrystals, *Nano letters* 15 (3) (2015) 1911–1917.
- [47] G.J. Janz, R.P.T. Tomkins, *Nonaqueous Electrolytes Handbook*, Vol. I, Academic Press, New York, NY, 1972.
- [48] K. Nishikawa, Y. Fukunaka, T. Sakka, Y.H. Ogata, J.R. Selman, Measurement of LiClO₄ diffusion coefficient in propylene carbonate by Moiré pattern, *Journal of The Electrochemical Society* 153 (5) (2006) 830–834.
- [49] Y.-P. Lin, N.-L. Wu, Characterization of MnFe₂O₄/LiMn₂O₄ aqueous asymmetric supercapacitor, *Journal of Power Sources* 196 (2) (2011) 851–854.
- [50] E. Lim, H. Kim, C. Jo, J. Chun, K. Ku, S. Kim, H.I. Lee, I.-S. Nam, S. Yoon, K. Kang, et al., Advanced hybrid supercapacitor based on a mesoporous niobium pentoxide/carbon as high-performance anode, *ACS nano* 8 (9) (2014) 8968–8978.
- [51] M. Toupin, T. Brousse, D. Bélanger, Charge storage mechanism of MnO₂ electrode used in aqueous electrochemical capacitor, *Chemistry of Materials* 16 (16) (2004) 3184–3190.
- [52] D. Bélanger, T. Brousse, J.W. Long, Manganese oxides: battery materials make the leap to electrochemical capacitors, *Interface* 17 (1) (2008) 49–52.
- [53] L.L. Zhang, R. Zhou, X.S. Zhao, Graphene-based materials as supercapacitor electrodes, *Journal of Materials Chemistry* 20 (29) (2010) 5983–5992.
- [54] S.R. Subramanian, V. Boovaragavan, V. Ramadesigan, M. Arabandi, Mathematical model reformulation for lithium-ion battery simulations: Galvanostatic boundary conditions, *Journal of The Electrochemical Society* 156 (4) (2009) 260–271.
- [55] A.M. Colclasure, R.J. Kee, Thermodynamically consistent modeling of elementary electrochemistry in lithium-ion batteries, *Electrochimica Acta* 55 (28) (2010) 8960–8973.
- [56] G.M. Goldin, A.M. Colclasure, A.H. Wiedemann, R.J. Kee, Three-dimensional particle-resolved models of Li-ion batteries to assist the evaluation of empirical parameters in one-dimensional models, *Electrochimica Acta* 64 (2012) 118–129.
- [57] J. Zhu, S. Tang, H. Xie, Y. Dai, X. Meng, Hierarchically porous MnO₂ microspheres doped with homogeneously distributed Fe₃O₄ nanoparticles for supercapacitors, *ACS Applied Material Interfaces* 6 (20) (2014) 17637–17646.
- [58] R. He, S. Chen, F. Yang, B. Wu, Dynamic diffuse double-layer model for the electrochemistry of nanometer-sized electrodes, *Journal of Physical Chemistry B* 110 (7) (2006) 3262–3270.