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Modeling and Physical Interpretation of Cyclic Voltammetry for Pseudocapacitors

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Modeling and Physical Interpretation of Cyclic Voltammetry for Pseudocapacitors

A thesis submitted in partial satisfaction
of the requirements for the degree
Master of Science in Aerospace Engineering

by

Henri-Louis Jean-Paul Girard

2015
The present study investigates the complex multi-scale coupled transport and electrochemical phenomena involved in charge storage in pseudocapacitors. It presents rigorously developed models for simulating pseudocapacitive electrodes in both hybrid pseudocapacitors and in three-electrode systems under cyclic voltammetry. The models account 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. They were used to study the behavior of electrochemical pseudocapacitors and provide physical interpretation of experimentally obtained measurements.

First, this study determined the respective contributions of faradaic reactions and EDL formation to charge storage in hybrid pseudocapacitors. It demonstrated the existence of two regimes for hybrid pseudocapacitors. First, a faradaic regime dominated by redox reaction and limited by the diffusion of Li in the pseudocapacitive electrode. Second, a capacitive regime dominated by the formation and dissolution of the EDL. A $b$-value of unity was shown to be associated with both regimes. The dip in $b$-value often observed experimentally was attributed to the transition between the two regimes.
Second, this study presented an extensive parametric study for the design of the pseudocapacitive electrode in a hybrid pseudocapacitor. Increasing the fraction of the potential window dominated by faradaic current was found to increase the performance of the device. Indeed, the faradaic reactions resulted in a significantly larger current magnitude than the EDL charge storage. The effect of the electrode thickness and Li diffusion coefficient on this fraction were investigated for different scan rates. To study the interplay between these parameters, a scaling analysis was performed to identify the relevant dimensionless similarity parameters governing Li transport and intercalation in the pseudocapacitive electrode. A dimensionless parameters $\Pi_f$ was derived accounting for the respective contributions of the thickness, diffusion coefficient and scan rate. Furthermore, above a critical value of $\Pi_f$, the device was found to operate under a diffusion-independent regime.

Finally, this study presented a model for simulating individual pseudocapacitive electrodes in three-electrode experiments. Notably, this model accounted for the variation of the redox reaction equilibrium potential with the oxidation state of the electrode. It was found to agree qualitatively with experimental measurements well and was used to provide physical interpretation to experimental measurements for Nb$_2$O$_5$ electrodes.

These models and results could help in the design of pseudocapacitive electrodes to achieve maximum energy and power density.
The thesis of Henri-Louis Jean-Paul Girard is approved.

Bruce S. Dunn

Yongjie Hu

Laurent G. Pilon, Committee Chair

University of California, Los Angeles

2015
This thesis is dedicated to my family and friends who supported me throughout my studies.
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Nomenclature

\( a \) effective ion diameter (nm)

\( c_i \) ion concentration of 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, \( e = 1.602 \times 10^{-19} \) 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 constant in Equation (3.20) (m\(^{2.5}\)mol\(^{-0.5}\)s\(^{-1}\))

\( L \) half of inter-electrode distance (nm)

\( L_C \) thickness of the carbon electrode (nm)

\( L_P \) thickness of the pseudocapacitive electrode (nm)

\( m \) stoichiometric number of intercalated lithium, \( \text{Li}_{m} M_p O_q \)

\( M \) 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\(^{-2}\)s\(^{-1}\))

\( R_u \) universal gas constant, \( R_u = 8.314 \) J mol\(^{-1}\)K\(^{-1}\)

\( T \) local temperature (K)

\( t \) time (s)

\( v \) scan rate of the cyclic voltammetry (V/s)

\( x \) location in one-dimensional space (\( \mu \)m)
\( z_i \)  \hspace{1em} ion valency

**Greek symbols**

\( \alpha \)  \hspace{1em} transfer coefficient in Equation (3.20)

\( \epsilon_0 \)  \hspace{1em} vacuum permittivity, \( \epsilon_0 = 8.854 \times 10^{-12} \) F m\(^{-1}\)

\( \epsilon_r \)  \hspace{1em} relative permittivity of electrolyte

\( \Delta \psi_{eq} \)  \hspace{1em} equilibrium potential difference (V)

\( \Delta \psi_f \)  \hspace{1em} faradaic potential window defined as \( \psi_f - \psi_{min} \) (V)

\( \Delta \psi_H \)  \hspace{1em} potential drop across the Stern layer (V)

\( \Delta \psi_s \)  \hspace{1em} potential window (V)

\( \lambda_D \)  \hspace{1em} Debye length (m)

\( \eta \)  \hspace{1em} surface overpotential, \( \eta = \Delta \psi_H - \Delta \psi_{eq} \) (V)

\( \rho \)  \hspace{1em} density of the fully intercalated pseudocapacitive electrode (kg/m\(^3\))

\( \sigma_C \)  \hspace{1em} electrical conductivity of the carbon electrode (S/m)

\( \sigma_P \)  \hspace{1em} electrical conductivity of the pseudocapacitive electrode (S/m)

\( \tau_{CV} \)  \hspace{1em} cycle period (s)

\( \tau_d \)  \hspace{1em} diffusion time scale across the EDL, \( \tau_d = \lambda_D^2/D_1 \) (s)

\( \tau_{th} \)  \hspace{1em} thermal potential, \( \tau_{th} = R_u T/z_F \) (s)

\( \psi \)  \hspace{1em} local electric potential (V)

\( \psi_f \)  \hspace{1em} potential associated with the Li starvation (V)

\( \psi_s \)  \hspace{1em} imposed cell potential (V)

**Superscripts and subscripts**

\( * \)  \hspace{1em} refers to dimensionless variable

\( \infty \)  \hspace{1em} refers to bulk electrolyte

\( i \)  \hspace{1em} refers to ion species \( i \)

\( C \)  \hspace{1em} refers to the carbon electrode

\( P \)  \hspace{1em} refers to the pseudocapacitive electrode
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Finally I would like to thank my lab member Dr. Hainan Wang, Anna d’Entremont, Bingang Mei, Zander Thiele, just to name a few. I am also grateful to my friends who made my stay at UCLA a great experience.
1.1 Electrochemical Capacitors

Electrochemical capacitors, also known as supercapacitors, have attracted significant attention in recent years due to their promise as electrical energy storage devices for high energy and power applications [4–6]. They are typically classified as either electric double layer capacitors (EDLCs) or pseudocapacitors depending on the energy storage mechanism. EDLCs store energy physically in the electric double layers (EDLs) forming near the electrode/electrolyte interfaces [4–6]. Thus, the charge storage is highly reversible and the cycle life of EDLCs represents more than 100,000 cycles [4]. EDLCs are attractive for high power applications, such as in the regenerative braking system of hybrid electric vehicles as well as storing energy and balancing the load from intermittent renewable energy sources, due to their fast charging/discharging rates and long life [4–7]. However, the energy density of EDLCs remains low compared with that of batteries. Pseudocapacitors store energy via the electric double layers as well as via reversible oxidation-reduction (redox) reactions with or without insertion or intercalation [1, 4, 6, 8, 9]. Pseudocapacitors tend to feature larger capaci-
stances and energy densities than EDLCs because the amount of charge they can store is not limited by the surface area of the electrode/electrolyte interface [1, 6, 8, 9]. Finally, hybrid pseudocapacitors are devices combining a pseudocapacitive electrode made of a porous transition metal oxide (e.g., RuO$_2$, MnO$_2$, Nb$_2$O$_5$, MoO$_3$) and an EDLC-type electrode typically made of porous carbon [5,10–14]. These different devices hold great promise for meeting energy storage needs in current and emerging applications [1,4–6,8–14].

1.2 Motivation of the Present Study

In situ measurement of ion concentrations in the electrolyte and of intercalated species concentration profiles in the electrode during operation is very difficult, if not impossible. In addition, it is challenging to discriminate between the contributions of the redox reactions and of the EDL formation to the total current measured experimentally. This information can be obtained through physical modeling and simulations to improve the understanding of experimental measurements and to guide the optimization of the electrode and of the electrolyte.

1.3 Objectives of the Present Study

The present study aims to develop a physicochemical transport model for simulating hybrid pseudocapacitors and pseudocapacitive electrodes in three-electrode systems under cyclic voltammetry by accurately accounting for interfacial and transport phenomena occurring in the electrolyte and for redox
reactions and intercalation of the reaction product in the pseudocapacitive electrode. This model was derived from first principles in that it relies on the fundamental equations governing electrodynamics. It was used (i) to elucidate the physical phenomena contributing to charge storage in pseudocapacitors, (ii) to provide physical interpretation of experimental measurements, and (iii) to provide design guidelines for pseudocapacitive electrodes to achieve maximum faradaic performance.
CHAPTER 2

Background

2.1 Electrical Double Layer Structure

Figure 2.1: Schematic of the electric double layer for a binary and asymmetric electrolyte near a planar electrode.

According to the Stern model, the electrolyte is divided into two domains: the Stern layer and the diffuse layer [15]. The Stern layer is a compact layer of charges adjacent to the electrode surface characterized by the absence of free charges. Within the diffuse layer, ions are free to move under the combined influence of diffusion, electromigration, and steric repulsion [15]. The thickness of the EDL can be approximated as the Debye length $\lambda_D$ and
varies with the diameters, valencies, and concentrations of ions as well as with temperature [15].

2.2 Cyclic voltammetry

In cyclic voltammetry (CV) measurements, the cell potential $\psi_s(t)$ is imposed to vary periodically along a triangular shape with time. This type of measurement is defined by the scan rate $v$ (in V/s) and the potential window defined by the minimum potential $\psi_{\text{min}}$ and the maximum potential $\psi_{\text{max}}$. These parameters also define the cycle period $\tau_{\text{CV}} = 2(\psi_{\text{max}} - \psi_{\text{min}})/v$. The resulting current density $j_T(t)$ (in A/m$^2$) is measured and typically plotted as a function of the imposed potential resulting in so-called “CV curves”. This type of measurements enables the computation of the areal integral capacitance $C_{s,\text{int}}$ (in F/m$^2$) according to [16]

$$C_{s,\text{int}} = \frac{1}{\psi_{\text{max}} - \psi_{\text{min}}} \int j_T(\psi_s) \frac{d\psi_s}{2v}.$$  \hspace{1cm} (2.1)

2.3 Modeling of Pseudocapacitors

Different approaches have been used to develop physical models of electrochemical capacitors and pseudocapacitors.

2.3.1 Equivalent RC Circuit Model

Equivalent RC circuit and transmission line models consist of modeling a physical device by a succession of ideal capacitors and resistors integrated in
a circuit [17]. They have been used to study the charging/discharging dynamics of pseudocapacitors [17–19]. However, these models have to be fitted with experimental data to retrieve the values of the different resistances and capacitances [19]. They can be used to control the device operation but they cannot be used to design the electrodes or electrolyte of novel pseudocapacitors. Moreover, the classical RC circuit models neglect ion diffusion and non-uniform ion concentration in the electrolyte [20]. As faradaic reactions depend strongly on the ion concentrations at the reaction plane, these models are therefore not suitable for modeling pseudocapacitors with simultaneous faradaic and capacitive currents.

2.3.2 Molecular Dynamics Simulations

First-principles molecular dynamics (MD) simulations have been performed to explore the fundamental electrochemical behaviors of pseudocapacitive materials including RuO$_2$ [21, 22], TiO$_2$ [23], MnO$_2$ [24], and MoO$_3$ [25]. However, the computational complexity and cost limit MD simulations to extremely small time and length scales on the order of 10 ns and 10 nm, respectively [21, 26]. These are significantly smaller than those encountered in actual characterization methods such as cyclic voltammetry or galvanostatic cycling which are on the order of several micrometers and seconds [1, 10]. For example, He et al. [27] simulated cyclic voltammetry for two cylindrical pores with sub-nanometer width at unrealistically large scan rates of 1 to 10 MV/s to study the local dynamics of charging and discharging. Because of
the small time and length scales, such study cannot simulate relatively slow and long range diffusion processes across an electrode. Therefore, MD simulations seem inadequate for reproducing experimental cycling with realistic timescales for electrodes or devices with realistic dimensions.

2.3.3 Continuum Models

Continuum models, numerically solving the Poisson equation for electric field and the mass conservation equations for ion concentrations, have also been developed to analyze pseudocapacitors [28–36]. Different approaches investigated the effects of porosity [37], redox active particle size [28–30, 33], solid phase diffusion limitation in the case of ion intercalation [33], and moving reaction fronts [31]. However, these models imposed the double layer areal capacitance (in F/m²) or volumetric capacitance (in F/m³) as constant properties independent of the electric potential instead of predicting them [28–37]. Unfortunately, the double layer capacitance is known to vary nonlinearly with electric potential under large electric potentials and electrolyte concentrations [38]. Furthermore, some models assumed the concentration of ions at the reaction front in the electrolyte was the bulk concentration [28,30,31,35,37] although the electric field and the presence of EDLs near the electrodes affects the concentrations of the ions involved in the faradaic reaction.
CHAPTER 3

Physical Interpretation of Cyclic Voltammetry for Hybrid Pseudocapacitors

3.1 Introduction

A semi-empirical approach for analyzing CV measurements has been developed and used extensively to characterize capacitive effects in the total current. Specifically, the measured total current density $j_T$ at a given surface potential $\psi_s$ was assumed to relate to the scan rate $v$ according to the semi-empirical relationship [39]

$$\frac{j_T(\psi_s)}{v^{1/2}} = k_1(\psi_s) v^{1/2} + k_2(\psi_s)$$  \hspace{1cm} (3.1)

where $k_1(\psi_s)$ and $k_2(\psi_s)$ are semi-empirical functions independent of $v$ but dependent only on the cell potential $\psi_s$ imposed between the current collectors. The functions $k_1(\psi_s)$ and $k_2(\psi_s)$ respectively correspond to the slope and intercept in the plot of $j_T/v^{1/2}$ versus $v^{1/2}$ for a given potential $\psi_s$ [39].

This approach was supported by the facts that (i) the capacitive current $j_C$, associated with EDL formation or dissolution, is known to vary linearly with the scan rate $v$ in the absence of redox reaction [15, 40] and (ii) the theoretical faradaic current $j_F$ due to surface redox reactions in a semi-infinite
electrolyte domain is proportional to $v^{1/2}$ when the presence of the EDL and the associated capacitive current are ignored \[15\]. This method has been used for full-cell hybrid pseudocapacitors with a chemically inert counter electrode \[41\] as well as for pseudocapacitors with Li or Na metal as the counter electrode to measure specifically the performance of the metal oxide electrode \[42–49\]. Furthermore, three electrodes experiments also used this approach to characterize pseudocapacitive electrodes \[1,39,50–56\].

The presence of redox peaks in many pseudocapacitor CV curves shows that different processes can be dominant at different potentials. This led to another approach for analyzing experimental CV measurements. Assuming that the current at any potential is generally dominated by either a capacitive or a faradaic process, Equation (3.1) can replaced by

$$j_T(\psi_s) = k(\psi_s) v^{b(\psi_s)}$$

(3.2)

where the exponent $b(\psi_s)$ is the so-called $b$-value expected to vary between $b = 1/2$ in the case of purely faradaic current and $b = 1$ for purely capacitive current \[39,50\]. The value of $b$ is typically evaluated by least-squares fitting of $j_T(\psi_s)$ versus $v$ for given values of $\psi_s$ \[39,50\]. A $b$-value of 1 corresponds to a greater rate capability and is therefore desirable for all potentials in the operating window. It has been attributed to “capacitive current” \[39,50\] or described more cautiously as “capacitive behavior” \[47,56,57\], as “pseudocapacitive behavior” \[45,46\], or as “non-diffusion controlled charge storage” \[53\]. In addition, a dip is often observed in the $b$-value plotted as a function of
ψ \text{s} [43,50,53]. This has been attributed to the presence of redox peaks from the faradaic reaction in the CV curves [43,50,53]. To the best of our knowledge, despite its extensive usage, this semi-empirical analysis and its physical interpretation have not been rigorously demonstrated, particularly for simultaneous electric double layer formation, redox reactions, and ion insertion in the pseudocapacitive electrode.

This chapter aims to develop a continuum model to accurately simulate coupled interfacial, transport, and electrochemical phenomena in hybrid pseudocapacitors subjected to cyclic voltammetry. The model simultaneously accounted for (i) charge transport in both electrodes and electrolyte, (ii) the dynamics of the electric double layer, (iii) steric repulsion due to finite ion sizes, (iv) redox reactions, and (v) ion intercalation in the pseudocapacitive electrode. The goal of this chapter is also to rigorously examine the respective contributions of capacitive and faradaic current densities to the total current density and provide physical interpretations of experimentally obtained CV curves. Finally, it aims to assess whether \( b = 1 \) in Equation (3.2) can be associated with faradaic reactions and why a dip is often observed in the \( b \)-value versus potential plot [43,50,53].
3.2 Analysis

3.2.1 Schematic and Assumptions

Figure 3.1 shows the schematic of the one-dimensional hybrid pseudocapacitor simulated as well as the associated computational domain and coordinate system. The cell consisted of a planar thin-film pseudocapacitive electrode made of transition metal oxide $M_pO_q$ of thickness $L_P$ and a planar carbon electrode of thickness $L_C$. They were separated by an electrolyte of thickness $2L$ made of LiClO$_4$ salt in propylene carbonate (PC) solvent. The electrolyte domain was divided in three regions corresponding to a Stern layer of thickness $H$ near each electrode surface and a diffuse layer beyond. This simplified geometry was chosen in order to assess the contribution of multiple and closely coupled physical phenomena in details without considering the multidimensional nature of actual electrodes. Note also that the electrode curvature was found to have negligible effect on the areal capacitance of an EDL on a sphere of radii larger than 40 nm [58]. The following reversible redox reaction was assumed to take place at the pseudocapacitive electrode

$$m\text{Li}^+ + M_pO_q + me^- \iff \text{Li}_mM_pO_q.$$  \hspace{1cm} (3.3)

To make the problem mathematically tractable, the following assumptions were made: (1) electrodiffusion of Li$^+$ and ClO$_4^-$ ions in the electrolyte and insertion (or intercalation) of Li atoms in the electrode were one-dimensional. (2) The Stern layer thickness $H$ was approximated as the radius of the largest solvated ion species, namely ClO$_4^-$, so that $H = a_2/2$ [15,59,60]. In prac-
Figure 3.1: Schematic of the simulated one-dimensional hybrid pseudocapacitor cell consisting of a redox-active pseudocapacitive electrode and a carbon electrode with LiClO$_4$ electrolyte in PC. The dashed line encloses the computational domain simulated.

In practice, the ions may lose part or all of their solvation shell as they approach the electrode. Therefore, the solvated ion diameter may depend on the location considered [61]. However, to the best of our knowledge, no quantitative model exists relating the partially solvated ion diameter to the local electric field and position with respect to the electrode. (3) The diffusion coefficients of all ion species in the electrolyte and that of Li in the redox-active electrode were independent of their respective concentrations. Their values corresponded to those of dilute solutions reported in the literature. Note that in reality the ion diffusion coefficient vary with ion concentration. Umino and Newman [62] reported that the diffusion coefficient of H$^+$ and SO$_4^{2-}$ for H$_2$SO$_4$ in
water varied non-linearly with salt concentration. However, it did not exceed 40% of its asymptotic value corresponding to dilute solutions for concentrations ranging from 0.3 to 7.5 M. In fact, it was verified numerically that accounting for concentration-dependent diffusion coefficient had a negligible impact on the predicted current at the scan rates considered in this study when ion diffusion in the electrolyte was not limiting [63]. (4) Isothermal conditions prevailed throughout the device. (5) Advection in the electrolyte was negligible. (6) The reversible redox reaction given by Equation (3.3) was heterogeneous and occurred at the electrode/electrolyte interface near the pseudocapacitive electrode at $x = -L + H$ [15]. This assumption is commonly used in modeling battery and supercapacitor [15], as free electrons are assumed to be confined in the electrode and free $\text{Li}^+$ ions are confined in the electrolyte. (7) The intercalation and deintercalation of Li atoms into and out of the pseudocapacitive electrode were treated as diffusion processes. (8) The redox-active material did not undergo any phase transition. This assumption is consistent with observations on $\text{Nb}_2\text{O}_5$ thin films during lithium insertion [64]. (9) The electrical conductivity $\sigma_P$ and the Li diffusion coefficient $D_{1,P}$ of the pseudocapacitive electrode were constant. In practice, they may change with Li insertion. However, to the best of our knowledge, no quantitative model or experimental measurements exist capturing these effects in a thin film of metal oxide. (10) The specific ion adsorption due to non-electrostatic forces was assumed to be negligible. Note that previous simulations of EDLCs based on this assumption agreed well with experimen-
tal data [65,66]. The potential drop across the highly conducting current collectors was negligible so that only the electrodes and electrolyte domains were simulated. The goal of this chapter is to reproduce trends in CV curves and to provide physical interpretation of behaviors observed experimentally. The assumptions considered have been widely used in the literature to make possible simulations of pseudocapacitors.

3.2.2 Governing Equations

The local electric potential $\psi(x,t)$ in the pseudocapacitive ($-L_P - L \leq x \leq -L$) and carbon ($L \leq x \leq L + L_C$) electrodes is governed by the one-dimensional Poisson equation expressed as [59,67]

$$\frac{\partial}{\partial x} \left( \sigma_P \frac{\partial \psi}{\partial x} \right) = 0 \quad \text{in the pseudocapacitive electrode} \quad (3.4)$$

$$\frac{\partial}{\partial x} \left( \sigma_C \frac{\partial \psi}{\partial x} \right) = 0 \quad \text{in the carbon electrode} \quad (3.5)$$

where $\sigma_P$ and $\sigma_C$ are the electrical conductivities of the pseudocapacitive and carbon electrode, respectively.

The local molar concentration of intercalated Li atoms in the pseudocapacitive electrode, denoted by $c_{1,P}(x,t)$, is governed by the mass diffusion equation given by [67,68]

$$\frac{\partial c_{1,P}}{\partial t} = \frac{\partial}{\partial x} \left( D_{1,P} \frac{\partial c_{1,P}}{\partial x} \right) \quad \text{in the pseudocapacitive electrode} \quad (3.6)$$

where $D_{1,P}$ is the diffusion coefficient of intercalated lithium atoms in the pseudocapacitive electrode.
Moreover, the potential and ion concentrations in the diffuse layer of the electrolyte solution \((-L + H \leq x \leq L - H\) are governed by the generalized modified Poisson-Nernst-Planck (GMPNP) model derived by Wang et al. [59]. The GMPNP model was developed for asymmetric electrolytes with multiple ions species of finite size. For binary and asymmetric electrolytes the GMPNP in the diffuse layer is expressed as [59]

\[
\begin{align*}
\frac{\partial}{\partial x} \left( \epsilon_0 \epsilon_r \frac{\partial \psi}{\partial x} \right) &= -F \sum_{i=1}^{2} z_i c_i \quad (3.7a) \\
\frac{\partial c_i}{\partial t} &= -\frac{\partial N_i}{\partial x} \quad \text{for } i = 1, 2 \quad (3.7b)
\end{align*}
\]

where \(c_i(x, t)\) is the local molar concentration of ion species \(i\) in the electrolyte solution at time \(t\). Here, \(i = 1\) refers to \(\text{Li}^+\) and \(i = 2\) refers to \(\text{ClO}_4^-\). Moreover, \(F = 96 485 \text{ C mol}^{-1}\) is the Faraday constant, \(\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}\) is the free space permittivity, and \(\epsilon_r\) is the relative permittivity of the electrolyte solution. The local mass flux of ion species \(i\), denoted by \(N_i(x, t)\) in \(\text{mol m}^{-2} \text{s}^{-1}\), is defined for a binary and asymmetric electrolyte as [59]

\[
N_i(x, t) = -D_i \frac{\partial c_i}{\partial x} - \frac{D_i F z_i c_i}{R_u T} \frac{\partial \psi}{\partial x} - \frac{D_i c_i}{1 - \sum_{j=1}^{2} c_j / c_{j, \text{max}}} \frac{\partial}{\partial x} \left( \sum_{j=1}^{2} c_j / c_{j, \text{max}} \right) (3.8)
\]

where \(D_i\) and \(a_i\) are the diffusion coefficient and the effective ion diameter of ion species \(i\) in the electrolyte solution, respectively. The temperature is denoted by \(T\) (in K) while \(N_A = 6.022 \times 10^{23} \text{ mol}^{-1}\) and \(R_u = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}\) are the Avogadro constant and the universal gas constant, respectively. The maximum concentration \(c_{j, \text{max}} = 1/(N_A a_j^3)\) corresponds to simple cubic ion packing at the electrode surface. The first and second terms
of Equation (3.8) represent the ion flux due to diffusion and electromigration, respectively, while the last term represents a correction accounting for finite ion size [59]. Finally, the presence of the Stern layers near each electrode was accounted for via boundary conditions [59,66] and no governing equations for \( \psi(x, t) \) and \( c_i(x, t) \) needed to be formulated or solved within the Stern layer.

3.2.3 Boundary and Initial Conditions

The one-dimensional governing Equations (3.4) to (3.8) are second-order partial differential equations in space and first-order in time. Each equation requires two boundary conditions and one initial condition in each region it is solved.

First, the initial electric potential was assumed to be uniform across the device and given by

\[
\psi(x, 0) = 0 \text{ V.} \tag{3.9}
\]

Initially, the Li\(^+\) and ClO\(_4\)\(^-\) ion concentrations in the electrolyte \((-L + H \leq x \leq L - H)\) were taken as uniform and equal to their bulk concentrations satisfying electroneutrality according to

\[
c_1(x, 0) = c_{1,\infty} \quad \text{and} \quad c_2(x, 0) = -z_1c_{1,\infty}/z_2. \tag{3.10}
\]

Similarly, the initial Li concentration in the pseudocapacitive electrode \((-L - L_P \leq x \leq -L)\) was uniform and equal to \( c_{1,P,0} \), i.e.,

\[
c_{1,P}(x, 0) = c_{1,P,0}. \tag{3.11}
\]
The potential at the current collector/pseudocapacitive electrode interface was imposed as $\psi(-L - L_P, t) = \psi_s(t)$. During cyclic voltammetry measurements, $\psi_s(t)$ varied linearly with time according to [59]

$$
\psi_s(t) = \begin{cases} 
\psi_{\text{max}} - v[t - (n_c - 1)\tau_{CV}] & \text{for} (n_c - 1)\tau_{CV} \leq t < (n_c - 1/2)\tau_{CV} \\
\psi_{\text{min}} + v[t - (n_c - 1/2)\tau_{CV}] & \text{for} (n_c - 1/2)\tau_{CV} \leq t < n_c \tau_{CV}
\end{cases}
$$

(3.12)

where $n_c$ is the cycle number and $\tau_{CV}$ is the cycle period while $\psi_{\text{max}}$ and $\psi_{\text{min}}$ are the maximum and minimum values of the cell potential $\psi_s(t)$, respectively.

In addition, the carbon electrode surface was electrically grounded so that

$$
\psi(L + L_C, t) = 0 \text{V.}
$$

(3.14)

Note that the choice of electrical ground is arbitrary and was made for convenience. It did not affect the predicted CV curves or the associated physical interpretations.

The electric potential varied linearly across the Stern layers so that the electric fields at the pseudocapacitive and carbon electrodes satisfied [59, 66]

$$
-\frac{\partial \psi}{\partial x}(-L + H, t) = \frac{1}{H} [\psi(-L, t) - \psi(-L + H, t)]
$$

(3.15a)

$$
\frac{\partial \psi}{\partial x}(L - H, t) = \frac{1}{H} [\psi(L, t) - \psi(L - H, t)].
$$

(3.15b)

These boundary conditions accounted for the presence of the Stern layers at both electrodes without explicitly simulating them in the computational domain [66].
The current density at the pseudocapacitive electrode/electrolyte interface, located at $x = -L$ was equal to the sum of the capacitive $j_C(x, t)$ and faradaic $j_F(t)$ current densities (in A/m$^2$) at the Stern/diffuse interfaces, located at $x = -L + H$, so that [59,69]

$$-\sigma_P \frac{\partial \psi}{\partial x}(-L, t) = j_C(-L + H, t) + j_F(t). \quad (3.16)$$

On the other hand, near the carbon electrode at $x = +L$, only the capacitive current contributed to the total current density so that

$$-\sigma_C \frac{\partial \psi}{\partial x}(L, t) = j_C(L - H, t). \quad (3.17)$$

In both cases, $j_C(x, t)$ is the displacement current density due to the electric double layer formation at the pseudocapacitive and carbon electrodes and defined as [70]

$$j_C(\pm(L - H), t) = -\epsilon_0 \epsilon_r \frac{\partial^2 \psi}{\partial x \partial t}(\pm(L - H), t). \quad (3.18)$$

In addition, the faradaic current density $j_F(t)$ is typically described by the generalized Frumkin-Butler-Volmer model evaluated at the pseudocapacitive electrode/electrolyte interface and expressed as [15]

$$j_F(t) = j_{F,0}(t) \left\{ \exp\left[ \frac{(1 - \alpha)z_1F\eta}{R_uT} \right] - \exp\left[ -\frac{\alpha z_1F\eta}{R_uT} \right] \right\} \quad (3.19)$$

where $\eta = \Delta \psi_H - \Delta \psi_{eq}$ is the overpotential and $\Delta \psi_H = \psi(-L, t) - \psi(-L + H, t)$ is the electrical potential drop across the Stern layer near the pseudocapacitive electrode [15]. For electrodes made of transition metal oxides, the equilibrium potential difference $\Delta \psi_{eq}$ is typically fitted experimentally.
as a function of the state-of-charge $c_{1,P}/c_{1,P,max}$ where $c_{1,P,max}$ is the maximum concentration of intercalated lithium atoms in the pseudocapacitive electrode [33,36,71]. It can be obtained by fitting experimental data for the open-circuit potential [67,69]. The so-called exchange current density $j_{F,0}(t)$ can be written as [67,69]

$$j_{F,0}(t) = Fz_1 k_0 [c_1(-L + H, t)]^{1-\alpha} [c_{1,P,max} - c_{1,P}(-L, t)]^{\alpha} [c_{1,P}(-L, t)]^\alpha \tag{3.20}$$

where $k_0$ is the reaction rate constant expressed in $\text{m}^{1+3\alpha} \text{mol}^{-\alpha} \text{s}^{-1}$. Here, the transfer coefficient $\alpha$ was assumed to be 0.5, corresponding to identical energy barriers for forward and backward redox reactions [15]. In this case, the faradaic current $j_F(t)$ has the same sign as the overpotential $\eta(t)$.

Moreover, the current collector was impermeable to the lithium atoms intercalated in the pseudocapacitive electrode so that the mass flux of Li vanished at the pseudocapacitive electrode/current collector interface, i.e.,

$$-D_{1,P} \frac{\partial c_{1,P}}{\partial x} (-L - L_P, t) = 0 \text{ mol} \text{ m}^{-2} \text{ s}^{-1}. \tag{3.21}$$

The mass flux of Li exiting through the pseudocapacitive electrode/electrolyte interface was related to the faradaic current density $j_F(t)$ based on stoichiometry as

$$-D_{1,P} \frac{\partial c_{1,P}}{\partial x} (-L, t) = \frac{j_F(t)}{z_1 F}. \tag{3.22}$$

The mass flux of $\text{Li}^+$ ions ($i = 1$) across the Stern/diffuse layer interface near the pseudocapacitive electrode was related to $j_F(t)$ in the same way while it
vanished near the carbon electrode such that

\begin{align}
N_1(-L + H, t) &= \frac{j_F(t)}{z_1 F} \\
N_1(L - H, t) &= 0 \text{ mol m}^{-2} \text{s}^{-1}.
\end{align}

(3.23a) (3.23b)

Both the carbon and pseudocapacitive electrodes were impermeable to ClO$_4^-$ ions ($i = 2$) so that

\begin{align}
N_2(-L + H, t) = N_2(L - H, t) &= 0 \text{ mol m}^{-2} \text{s}^{-1}.
\end{align}

(3.24)

Finally, the present model can be extended to pseudocapacitors with two redox-active electrodes by adding the corresponding faradaic current $j_F$ at the Stern/diffuse layer interface near the counter electrode ($x = L - H$) and solving the mass conservation equation for intercalated Li in both electrodes. However, current symmetric pseudocapacitors have been shown to have numerous limitations, including lower gravimetric energy and power densities [72] and smaller potential window due to irreversible redox reactions occurring at one of the electrodes [72]. Hybrid pseudocapacitors enable better control of the intercalation reaction in the pseudocapacitive electrode and feature better overall performance [73].

### 3.2.4 Constitutive Relationships

A total of 23 input parameters were needed to solve Equations (3.4) to (3.24) including (i) the electrolyte properties $\epsilon_r(0)$, $\beta$, $n$, $a_1$, $a_2$, $z_1$, $z_2$, $D_1$, $D_2$, and $c_{1,\infty}$, (ii) the pseudocapacitive electrode properties $\sigma_P$, $D_{1,P}$, $c_{1,P,0}$, $k_0$, and
The electrolyte considered in the present study was LiClO$_4$ in the organic solvent propylene carbonate (PC) at $T = 298$ K. The relative permittivity of the electrolyte $\varepsilon_r$ is known to decrease significantly at large electric fields due to the saturation of the polarization of the solvent molecules. The Booth Model has been developed to account for this effect and is expressed as [74,75]

$$
\varepsilon_r(E) = n^2 + (\varepsilon_r(0) - n^2) \frac{3}{\beta E} \left[ \coth(\beta E) - \frac{1}{\beta E} \right]
$$

(3.25)

where $E$ is the norm of the local electric field, $\varepsilon_r(0)$ is the relative permittivity at zero electric field, $n$ is the index of refraction of the electrolyte at zero electric field, and $\beta$ is an empirically defined fitting parameter. For propylene carbonate, these parameters are as follows $\varepsilon_r(0) = 64.4$, $n = 1.42$, and $\beta = 1.314 \times 10^{-8}$ m/V [65]. The effective solvated ion diameters of Li$^+$ ($z_1 = +1$) and ClO$_4^-$ ($z_2 = -1$) in PC were taken as $a_1 = 0.67$ nm and $a_2 = 1.0$ nm, respectively [76]. The Stern layer thickness $H$, corresponding to the distance of closest approach to the electrode plane, was equal to the largest solvated ion radius, i.e., $H = a_2/2 = 0.5$ nm [59]. The ion diffusion coefficients of Li$^+$ and ClO$_4^-$ in PC were taken as $D_1 = 2.6 \times 10^{-10}$ m$^2$/s and $D_2 = 3.3 \times 10^{-10}$ m$^2$/s, respectively [76]. The initial bulk ion concentrations were imposed as $c_{1,\infty} = c_{2,\infty} = 1$ mol/L, typical of electrochemical capacitors [43,45,77].

The pseudocapacitive electrode properties were inspired by those of Nb$_2$O$_5$.
whenever available, since Nb$_2$O$_5$ was shown to be a good material for intercalation pseudocapacitance [78]. The electrical conductivity of metal oxides may increase with the amount of intercalated lithium [79]. Here, however, a constant value $\sigma_P = 10^{-5}$ S/m was selected based on the range of lithium concentration observed [80]. The electrical conductivity of the carbon electrode was taken as $\sigma_C = 5$ S/m corresponding to that of activated carbon [81]. The reaction rate constant $k_0$ for transition metal oxides has been reported to range between $10^{-11}$ and $10^{-8}$ m$^{2.5}$mol$^{-0.5}$s$^{-1}$ [67,69,82]. Its value was taken as $k_0 = 10^{-8}$ m$^{2.5}$mol$^{-0.5}$s$^{-1}$, i.e., the most favorable redox reaction condition. In addition, the equilibrium potential difference $\Delta \psi_{eq}$ was assumed to be constant and equal to zero for the sake of simplicity [83]. Note that using a constant but non-zero value, for instance $\Delta \psi_{eq} = -0.1$ V, was found to shift the potential window by $\Delta \psi_{eq}$ and affected the current magnitude by less than 6% and the areal integral capacitance by less than 2%. The maximum intercalated lithium concentration in the redox active electrode was estimated as $c_{1,P,max} = m \rho/M$ where $\rho$ and $M$ are the density and molar mass of the fully intercalated metal oxide. For Li$_2$Nb$_2$O$_5$, $\rho$ and $M$ were reported as $\rho \approx 4.6$ g/cm$^3$ and $M = 279.7$ g/mol [33] yielding $c_{1,P,max} \approx 32.9$ mol/L. The diffusion coefficient $D_{1,P}$ of intercalated lithium atoms in transition metal oxides typically ranges from $10^{-16}$ to $10^{-10}$ m$^2$/s [82]. Here, it will be treated as a variable parameter to explore asymptotic behaviors of hybrid pseudocapacitors. Finally, the initial concentration of Li in the electrode $c_{1,P,0}$ was adjusted on a case by case basis. First, imposing $c_{1,P,0} = 0$ mol/L initially
would prevent any faradaic current $j_F(t)$ [Equation (3.20)] and ion insertion at any later time. Similarly, if $c_{1,P,0}$ is too low during the first deintercalation step, the Li concentration in the electrode may reach zero resulting in the absence of faradaic current at any subsequent time. However, it is important to note that the choice of a sufficiently large value of $c_{1,P,0}$ had no effect on the oscillatory steady state solution. Note also that some metal oxide electrode synthesis processes result in electrodes preloaded with Li atoms [84].

Moreover, the electrolyte thickness was taken as $2L = 2 \mu\text{m}$ while the electrode thicknesses $L_P$ and $L_C$ were identical and equal to either 20 nm or 500 nm. The potential window was selected to be large enough to show all relevant phenomena occurring during charging and discharging. Consequently, the pseudocapacitive electrode potential was cycled between -0.8 V and +0.8 V while the carbon electrode was grounded. Finally, the scan rate $v$ was arbitrarily varied from $10^{-2}$ to 10 V/s. The scan rate values were large compared with those used experimentally due to the fact that diffusion limitation occurs at a much higher scan rate for the simulated planar electrodes than for actual porous electrodes. The scan rate was chosen to explore these effects. In addition, simulations with relatively large scan rate took less time and reached an oscillatory steady state faster.

3.2.5 Method of Solution and Data Processing

The governing Equations (3.4) to (3.8) were solved along with the boundary and initial conditions given by Equations (3.9) to (3.24) using the commercial
finite element solver COMSOL 4.3b running in parallel on 8 cores with 64 GB of RAM. The numerical convergence criterion was defined such that 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 corresponded 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 Stern/diffuse layer interface due to the large potential gradient and gradually increased away 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 $L_P/25$ and $L_C/25$ in the electrode domains and less than $L/50$ in the diffuse layer. The total number of finite elements was about 500 for all cases simulated in the present chapter. The criterion for reaching oscillatory steady state was similar when running an additional 10 cycles. This corresponded to running 10 cycles for each case studied.

The instantaneous total current density $j_T(t)$ at the pseudocapacitive electrode/electrolyte interface was computed as the sum $j_T(t) = j_C(t) + j_F(t)$ where the capacitive $j_C(t)$ and faradaic $j_F(t)$ current densities were given by Equations (3.18) and (3.19), respectively. CV curves at a specific scan rate were obtained by plotting $j_T(t)$, $j_C(t)$, and $j_F(t)$ as functions of $\psi_s(t)$. 
3.3 Results and Discussion

3.3.1 General CV Curves’ Behavior

To study the effects of the pseudocapacitive electrode properties on the performance of a hybrid pseudocapacitor, two extreme cases were defined. First, Case A corresponded to a thin-film pseudocapacitive electrode with fast Li intercalation such that $L_P = 20$ nm and $D_{1,P} = 10^{-10}$ m$^2$/s. Case B corresponded to a thick pseudocapacitive electrode with slow Li intercalation so that $L_P = 500$ nm and $D_{1,P} = 10^{-14}$ m$^2$/s. These electrode thicknesses are representative of actual pseudocapacitive nanoparticles on a conductive substrate [50] and thick film coating or microspheres [85], respectively. Additionally, the values of the diffusion coefficient $D_{1,p}$ was selected such that in Case A, the diffusion length $L_D$ defined as $L_D = \sqrt{D_{1,p} \tau_{CV}} / 2 = 12.6 \mu$m was significantly larger than the electrode thickness whereas in Case B, the diffusion length $L_D = 126$ nm was on the order of the electrode thickness. Thus, these parameters were chosen as extreme values to explore both the lithium diffusion limited and the diffusion-independent regimes in the pseudocapacitive electrode. The diffusion coefficient of Li in a metal oxide electrode would typically increase with the concentration of intercalated Li. However, to the best of our knowledge, no model capturing this effect is available. Therefore, the values were selected arbitrarily within a reasonable range to explore asymptotic behaviors. Other input parameters were identical for both cases and given in Constitutive Relationships. In both Cases A and B, charging
corresponded to reduction of Li\(^+\) ions into Li atoms which intercalated into the redox-active electrode. Discharging corresponded to deintercalation and oxidation of Li atoms into Li\(^+\) ions that diffused in the electrolyte.

Figure 3.2a shows the predicted capacitive \(j_C\), faradaic \(j_F\), and total \(j_T\) current densities for Case A under oscillatory steady state as functions of the imposed potential \(\psi_s(t)\) for scan rate \(v = 1\) V/s. The CV curve \(j_T\) vs. \(\psi_s\) featured a peak in both charging, for decreasing \(\psi_s\), and discharging, for increasing \(\psi_s\), currents around \(\psi_s = 0\) V. Figure 3.2a also shows that the faradaic current dominated during the entire cycle and the capacitive current was negligible. This can be attributed to fast redox reactions and intercalation of Li atoms in the thin electrode. Indeed, the large reaction rate guaranteed that Li\(^+\) ions at the Stern/diffuse layer interface were consumed by the redox reaction during charging. In addition, the large diffusion coefficient of Li\(^+\) ions in the electrolyte ensured sufficient supply of Li\(^+\) during charging. Similarly, the large diffusion coefficient of Li in the pseudocapacitive electrode ensured sufficient supply of Li atoms to be oxidized at the electrode/electrolyte interface during discharging. Then, no significant capacitive current resulting from EDL formation was observed.

Figure 3.2b shows the intercalated lithium saturation in the redox-active electrode as a function of \(\psi_s(t)\) defined (i) at the electrode/current collector interface as \(c_{1,P}(-L - L_P, t)/c_{1,P,max}\) and (ii) at the electrode/electrolyte interface as \(c_{1,P}(-L, t)/c_{1,P,max}\). First, the two curves were superimposed indicating that the concentration of intercalated Li was uniform throughout the
Figure 3.2: Top: Capacitive $j_C$, faradaic $j_F$, and total $j_T$ current densities versus cell potential $\psi_s$ for a scan rate $v = 1 \text{ V/s}$ for (a) Case A and (c) Case B. Bottom: Intercalated lithium concentration normalized by the maximum concentration at the pseudocapacitive electrode surface ($x = -L$) and at the current collector ($x = -L - L_P$) for (b) Case A and (d) Case B at scan rate $v = 1 \text{ V/s}$. The red circle and blue square are guides corresponding to the same instant in the cycle in figures (c) and (d).
pseudocapacitive electrode. This was verified by plotting the concentration profile in the electrode. Second, neither curve shows any hysteresis during the entire cycle. This can be attributed to the fast intercalation and deintercalation and to the small electrode thickness which did not limit the redox reactions.

Figure 3.2c shows the current densities $j_C$, $j_F$, and $j_T$ predicted for Case B under oscillatory steady state as functions of potential $\psi_s(t)$ ranging between $-0.8 \text{ V}$ and $0.8 \text{ V}$ for a scan rate $v$ of $1 \text{ V/s}$. In contrast to Case A (Figure 3.2a), Figure 3.2c shows that, for slow Li diffusion in a thick electrode, the faradaic current $j_F$ dominated only in the lower end of the potential window while the capacitive current $j_C$ dominated in the higher end during both charging and discharging. In addition, the total current $j_T$ and the integral capacitance were smaller in Case B than in Case A for the same $v = 1 \text{ V/s}$. In Case B, the CV curve featured three peaks in the total current: at $\psi_s = 0 \text{ V}$ in both the charging and the discharging phase, and at $\psi_s = -0.15 \text{ V}$ in the charging phase. Figure 3.2d shows the intercalated lithium saturation in the redox active electrode as a function of $\psi_s(t)$ (i) at the electrode/current collector interface $c_{1,P}(-L - L_P, t)/c_{1,P,max}$ and (ii) at the electrode/electrolyte interface $c_{1,P}(-L, t)/c_{1,P,max}$. At the current collector/electrode interface, the saturation $c_{1,P}(-L - L_P, t)/c_{1,P,max}$ remained constant throughout the entire cycle. Indeed, the low diffusion coefficient $D_{1,P}$ and the thick electrode prevented the intercalated lithium from reaching the current collector before the current was reversed. Note, however, that
the value of \( c_{1,P}(-L - L_P, t) \) was different from its initial value \( c_{1,P,0} \). During charging, the saturation \( c_{1,P}(-L, t)/c_{1,P,max} \) at the electrode/electrolyte interface increased sharply at potential \( \psi_s \approx -0.15 \) V corresponding to the sudden increase in the faradaic current reaching a peak at \(-0.15\) V, as observed in Figure 3.2c (red circle). During discharging, the saturation at the pseudocapacitive electrode/electrolyte interface reached zero around \( \psi_s = -0.3 \) V corresponding to the steep drop observed in the faradaic current \( j_F \) in Figure 3.2c (blue square). Then, \( c_{1,P}(-L, t)/c_{1,P,max} \) was very small and the faradaic current was limited by the diffusion of Li out of the pseudocapacitive electrode. Note that this behavior illustrates the need to account simultaneously for redox reactions and EDL formation and to determine the concentration of each species in the electrodes and in the electrolyte during the entire cycle. Indeed, previous models [28,30,31,35,37] assumed constant and uniform ion concentrations in the electrodes and electrolyte when simulating faradaic reactions. The present results indicate that such assumptions may be valid for parts of the cycle but not for others. Then, diffusion limitations or reactant starvation cannot be accounted for while they play an important role in the energy storage mechanisms.

Overall, Case B featured two regimes: a faradaic regime and a capacitive regime. Note that the faradaic regime is desirable because it results in larger total current and capacitance. Indeed, the integral areal capacitance \( C_{s,int} \) was 47.9 \( \mu F/cm^2 \) in Case A at 1 V/s when the current was exclusively faradaic. This was almost double the capacitance of 24.8 \( \mu F/cm^2 \) achieved
by the device simulated in Case B, also at 1 V/s. To further elucidate these
regimes, it is worth considering the temporal variation of other important
variables.

Figure 3.3 shows the temporal evolution of (a) the faradaic $j_F$ and capaci-
tive $j_C$ current densities, (b) the overpotential $\eta(t)$, (c) the exchange current
density $j_{F,0}(t)$, and (d) the ion concentrations of Li$^+ c_1(-L + H, t)$ and of
ClO$_4^-$ $c_2(-L + H, t)$ at the Stern/diffuse layer interface as functions of dimen-
sionless time $t/\tau_{CV}$ for Case B at scan rate $v = 1$ V/s. Figure 3.3a clearly
shows the two prevailing regimes. A dominant capacitive current was ob-
served at the beginning of the charging step for $t/\tau_{CV} < 0.3$ and during part
of the discharging step for $t/\tau_{CV} > 0.65$. This corresponded to $0.8$ V $> \psi_s$
$> -0.3$ V encompassing charging and discharging. A dominant faradaic cur-
rent prevailed for $t/\tau_{CV}$ between 0.3 and 0.65 across the charging/discharging
transition corresponding to $-0.8$ V $< \psi_s < -0.3$ V.

Figure 3.3b shows that the overpotential $\eta(t)$ varied linearly with a large
slope during the capacitive regime and a smaller slope around $\eta = 0$ V dur-
ing the faradaic regime. Indeed, in the case of $\Delta\psi_{eq} = 0$ V, $\eta(t)$ is such
that $\eta(t)/H = \Delta\psi_{H}/H \approx \partial\psi/\partial x(-L + H, t)$. Then, combining this expres-
sion with the expression of $j_C(t)$ given by Equation (3.18) yields $\partial\eta/\partial t \approx
j_C(t) H/\varepsilon_0\varepsilon_r$. Thus, the time rate of change of $\eta(t)$ depends on the value of
the capacitive current $j_C(t)$. The latter is significant during the capacitive
regime and very small during the faradaic regime. This explains the large
differences in slopes of $\eta(t)$ in the two regimes shown in Figure 3.3b.
Figure 3.3: Temporal evolution of (a) the faradaic $j_F(t)$ and capacitive $j_C(t)$ current densities, (b) the overpotential $\eta(t)$, (c) the exchange current density $j_{F,0}(t)$, and (d) the ion concentrations $c_1(-L+H,t)$ of Li$^+$ and $c_2(-L+H,t)$ of ClO$_4^-$ at the Stern/diffuse layer interface near the pseudocapacitive electrode as functions of dimensionless time $t/\tau_{CV}$ for Case B at scan rate $v = 1$ V/s. Here, the vertical dashed lines indicate transitions at $t/\tau_{CV} = 0.3$ ($\psi_s = -0.15$ V) and $t/\tau_{CV} = 0.65$ ($\psi_s = -0.3$ V). The red circle and blue square correspond to the identical indicators in Figure 3.2.
Figure 3.3c shows the exchange current density $j_{F,0}(t)$ computed from the concentrations of Li$^+$ at the Stern/diffuse layer interface $c_1(-L+H,t)$ and of Li at the pseudocapacitive electrode/electrolyte interface $c_{1,P}(-L,t)$, according to Equation (3.20). During the capacitive regime, the exchange current density was negligibly small. This was due to the fact that $c_{1,P}(-L,t)$ was nearly zero during this regime (Figure 3.2d). It explains why faradaic current $j_F(t)$ was small despite the large overpotential $\eta(t)$ (Figure 3.3b). Similarly, during the faradaic regime, $j_{F,0}(t)$ was large resulting in large faradaic current $j_F(t)$ despite the small overpotential $\eta(t)$. Notably, during the discharging step $c_{1,P}(-L,t)$ reached zero at dimensionless time $t/\tau_{CV} = 0.65$ corresponding to $\psi_s = -0.3$ V (blue square). This corresponded to (i) a vanishing exchange current density $j_{F,0}$, (ii) the start of the sharp decrease in the faradaic current $j_F(t)$ around $\psi_s = -0.3$ V, (iii) the onset of the EDL formation (Figure 3.3d), and to (iv) the associated capacitive current (Figure 3.3a). This confirms that the lack of lithium atom at the electrode surface was the cause of the transition from the faradaic to the capacitive regime corresponding to a switch in the charge storage mechanism observed in the CV curve around $-0.3$ V during discharging shown in Figure 3.2c (blue square). Then, the faradaic current was limited by out-diffusion (or deintercalation) of intercalated Li in the electrode.

Similarly, Figure 3.3d also displays the two distinct regimes in the Li$^+$ and ClO$_4^-$ concentrations at the Stern/diffuse layer interface. During the faradaic regime, both ion concentrations remained constant and nearly equal to the
bulk concentration, i.e., \( c_1(-L + H, t) = c_2(-L + H, t) \approx c_{1,\infty} = c_{2,\infty} = 1 \text{ mol/L} \). This indicates that the redox reaction was fast enough to consume any excess Li\(^+\) at the interface while ion diffusion in the electrolyte was sufficiently fast to replenish the ions consumed by the reaction and available in large amounts in the relatively large electrolyte domain. Therefore, during this regime, the contribution of the capacitive current \( j_C \) to the total current \( j_T \) was negligible. By contrast, during the capacitive regime, the anion ClO\(_4^-\) formed an EDL near the pseudocapacitive electrode surface resulting in a significant capacitive current (Figure 3.3a). Indeed, in the capacitive regime, the overpotential \( \eta(t) \) was positive so that the electric field attracted the negatively charged anions electrostatically to the electrode surface. In fact, \( c_2(-L + H, t) \) quickly reached its maximum value \( c_{2,\text{max}} = 1/N_A a_2^3 \). The saturation of the electrode surface with ClO\(_4^-\) ions caused the capacitive current to reach a maximum around \( t/\tau_{CV} = 0.8 \) (Figure 3.3a) and was responsible for the hump observed in the CV curve at \( \psi_s = 0 \text{ V} \) in the discharging step (Figure 3.2b). Note that similar observations were made in CV curves of EDLCs [16].

Finally, Figure 3.3a shows that the faradaic current remained positive, corresponding to deintercalation of Li, during most of the charging step. The late reversal of the faradaic current was due to the fact that \( j_F(t) \) always has the same sign as \( \eta(t) \) [Equation (3.19)]. Therefore, \( \eta(t) \) had to become negative for the faradaic current to change sign. However, Figure 3.3b shows that, in the capacitive regime during the discharging step, the overpotential
increased due to the formation of the EDL by the anion \( \text{ClO}_4^- \) at the electrode surface. This EDL had to dissolve before the overpotential became negative and the faradaic current reversed sign. Figure 3.3d confirms that the onset of the faradaic regime coincided with the complete dissolution of the \( \text{ClO}_4^- \) EDL while the concentration of \( \text{Li}^+ \ c_1(-L + H, t) \) at the Stern/diffuse layer interface increased from zero to \( c_{1,\infty} \). As a consequence, the formation of a thick EDL of \( \text{ClO}_4^- \) ions in the capacitive regime during the discharging step causes the late onset of the faradaic current during the charging step. Therefore, preventing or delaying the capacitive regime during discharging would also increase the length of the faradaic regime during charging.

### 3.3.2 Analysis of the \( b \)-value

Figures 3.4a and 3.4b show the numerically predicted CV curves for scan rates \( v \) ranging from 0.1 to 10 V/s for Cases A and B, respectively. Figure 3.4a indicates that, in the case of a thin electrode with fast intercalation (Case A), the CV curves were similar in shape with the total current density \( j_T(\psi_s) \) increasing with scan rate. This suggests that the cell was not limited by diffusion of any species for the range of scan rates considered. Figure 3.4b shows similar CV curves for different scan rates in the case of a thick electrode with slow intercalation corresponding to Case B. The peaks and humps apparent during charging shifted to lower potential \( \psi_s \) as the scan rate \( v \) increased. Note that this was consistent with experimental observations of \( \text{Li}^+ \) insertion in nanocrystalline films of orthorhombic \( \text{Nb}_2\text{O}_5 \) [1] or in
Figure 3.4: CV curves for multiple scan rates for (a) Case A and (b) Case B. Total current density $j_T$ as a function of scan rate $v$ in log scale for a selection of imposed potentials $\psi_s(t)$ for (c) Case A and (d) Case B. Computed $b$-value as a function of imposed potential $\psi_s(t)$ for (e) Case A and (f) Case B using the charging current for all scan rates shown in (a) and (b) respectively. The regression coefficient $R^2$ obtained in the fitting of the $b$-value was larger than 0.95 for all values of $\psi_s$. 
TiO\textsubscript{2} anatase [39]. Here also, the total current \( j_T \) achieved in Case B was much smaller than that observed in Case A, for any given scan rate \( v \) and potential \( \psi_s \). In other words, the capacitance of the thin electrode with fast intercalation (Case A) was much larger than that of the thick electrode with slow intercalation (Case B).

Figures 3.4c and 3.4d show the total current density \( j_T(t) \) during charging as a function of scan rate \( v \) in log scale for different values of potential \( \psi_s(t) \) for Cases A and B, respectively. Figure 3.4c shows that, for Case A, the total current \( j_T \) increased linearly with scan rate \( v \) for \( \psi_s = -0.4 \text{ V} \) and \( +0.4 \text{ V} \). The same observation was made for all potentials across the potential window including the current at the charging peak, also known as cathodic peak. On the other hand, Figure 3.4d indicates that, for Case B, the evolution of the total current density \( j_T(t) \) with the scan rate \( v \) depended on the potential considered. The \( b \)-value was equal to (i) 1 for \( \psi_s = -0.5 \text{ V} \), when the current was exclusively faradaic, (ii) 0.96 for \( \psi_s = 0.5 \text{ V} \) when the total current was exclusively capacitive, and (iii) 0.91 for \( \psi_s = 0 \text{ V} \) when the total current was a combination of faradaic and capacitive contributions. In addition, the current at the charging peak evolved as \( j_{T,pa} \propto v^{0.64} \). This decrease in the \( b \)-value around the peak associated with the faradaic process was consistent with experimental observations for both two- and three-electrode experiments [1, 43, 47, 50–52, 54]. As discussed earlier, the charging peak, corresponding to the lowest \( b \)-value, was located at the transition between the faradaic and capacitive regimes, as shown in Figure 3.2c.
Figures 3.4e and 3.4f show the $b$-value as a function of the potential $\psi_s$ computed by the least-square method from the total current density $j_T$ vs. scan rate $v$ shown in Figures 3.4c and 3.4d for Cases A and B, respectively. Figure 3.4e indicates that for Case A, the $b$-value was independent of $\psi_s$ and close to unity across the potential window. Note that the faradaic current with fast intercalation dominated for all potentials (Figure 3.2a). Thus, these results indicate that a $b$-value of unity can be associated with fast reversible faradaic reaction in thin electrodes. Then, the faradaic current $j_F$ was proportional to the scan rate $v$, as also observed in EDLCs. Thus, this behavior can be referred to as “capacitive behavior”. However, the charge storage mechanism is truly faradaic and not capacitive. By contrast, for Case B, Figure 3.4f indicates that the $b$-value featured a drop from 1 to about 0.6, as often observed in experimental studies of pseudocapacitors [39,50,86]. In fact, it is interesting to note that Figure 3.4f is analogous to Figure 10c of Ref. 47 obtained experimentally with a two-electrode cell with a working electrode made of anatase TiO$_2$ and a counter electrode made of lithium metal with 1 mol/L LiPF$_6$ in a 1:1 ethylene carbonate and dimethyl carbonate mixture as electrolyte [47]. Similar results were also reported in Figure 5 of Ref. 50 obtained experimentally in a three-electrode experiment with a working electrode made of nanocrystalline anatase TiO$_2$ nanoparticles deposited on glassy carbon with 1 mol/L LiClO$_4$ salt in PC as electrolyte and lithium metal for both the counter and the reference electrodes [50].

The dip in the $b$-value has often been attributed to the intercalation process
on the basis that \( j_T \propto v^{1/2} \) for reversible redox reactions with semi-infinite diffusion of the reaction products and in the absence of electric double layers, as previously discussed [15]. However, the dip in the \( b \)-value predicted numerically did not occur during the faradaic regime but for \(-0.2 \text{ V} < \psi_s < 0 \text{ V}\) corresponding to the transition between the capacitive and faradaic regimes (Figure 3.2c). Previous models accounting separately for redox reactions and for electric double layer [28–37] would not be able to predict the dip in the \( b \)-value caused by the interplay between the two phenomena requiring the prediction of the concentrations of all species in the entire domain to account for reactant starvation. For larger potentials, \( \psi_s > 0 \text{ V} \), the \( b \)-value increased again to a value close to unity. In this region, the capacitive current dominated and the \( b \)-value was consistent with the expression of capacitive current evolution with the scan rate given by \( j_C = C_s v \) where \( C_s \) is the areal capacitance [15, 40].

### 3.4 Conclusion

This chapter presented a new physicochemical model, derived from first principles, for hybrid supercapacitors featuring a pseudocapacitive electrode and a carbon electrode subjected to cyclic voltammetry. The model simultaneously accounted for (i) charge transport in both electrodes and electrolyte, (ii) the dynamics of the electric double layer, (iii) steric repulsion due to finite ion sizes, (iv) redox reactions, and (v) intercalation. The results showed that for fast intercalation in a thin electrode, the current was always due to the
faradaic reaction and the $b$-value was unity across the potential window. For relatively thick electrodes and slow intercalation, the CV curves exhibited two distinct regimes. First, a faradaic regime prevailed for the more negative potentials and was dominated by the faradaic reaction and limited mainly by the diffusion of Li in the pseudocapacitive electrode during discharge. Second, a capacitive regime dominated at larger potentials with current due to the formation of an EDL at the electrode surface. A $b$-value of unity was associated with both regimes. The dip in $b$-value, often observed experimentally [43,50,53], was shown to occur during the transition between these two regimes.
CHAPTER 4

Optimization of Charge Storage in Hybrid Pseudocapacitors

4.1 Introduction

The optimization of pseudocapacitive electrodes in hybrid pseudocapacitors is made difficult by the 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 [63]. In fact, it has been established numerically that hybrid pseudocapacitors operate under two distinct regimes: a faradaic and a capacitive regime. The first is dominated by charge storage via faradaic reactions while the second is dominated by EDL formation. The current density is smaller in the capacitive regime,
as previously discussed. Numerical simulations can 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 [17–19], molecular dynamics simulations [21–25], and continuum modeling [28–37]. 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 in the pseudocapacitive electrode [63]. This model enables accurate prediction of trends in the evolution of cyclic voltammetry (CV) curves with varying scan rate $v$ [63].

Scaling analysis is a powerful tool used for the simplification of complex models by reducing the number of variables by non-dimensionalizing the governing equations and initial and boundary conditions. This process typically leads to the introduction of dimensionless numbers or similarity parameters characterizing competing physical phenomena and to the identification of different regimes of operation. Scaling analysis can also be used to uncover scaling laws or correlations governing the evolution of various parameters of interest. These correlations can then be used to design a device operating in the most favorable regime. For example, Wang et al. [59] identified the transition between diffusion-limited and diffusion-independent regimes in
cyclic voltammetry. They also used scaling analysis to identify a self-similar behavior for the EDL capacitance for EDLCs with binary and symmetric electrolytes under equilibrium conditions [87]. They then derived a correlation relating the electrode capacitance to the average pore size and electrolyte properties for experimental data for various porous carbon electrodes [87].

The objective of this chapter is to provide design guidelines for pseudo-capacitive electrodes in order to improve the overall capacitance of hybrid pseudocapacitors by ensuring that they operate in the faradaic regime. The study aims (i) to identify some of the relevant parameters affecting the extend of the faradaic regime, namely the electrode thickness $L_P$, the Li diffusion coefficient $D_{1,P}$, and the scan rate $v$, (ii) to quantitatively determine the respective effects of these parameters on the device’s performance, and (iii) to perform dimensional analysis of the continuum model developed recently [63] to capture their combined effect in a single dimensionless parameter that can be used to ensure the device operates in a diffusion-independent regime.

4.2 Analysis

4.2.1 Schematic and Assumptions

The device simulated in this chapter is the same one-dimensional hybrid pseudocapacitor as in Chapter 3. Figure 3.1 shows the schematic of the cell with the associated coordinate system. Furthermore, the assumptions described in Section 3.2.1 were also used in this chapter.
The model used in this chapter was described in Equations (3.4) to (3.24) of Chapter 3 and need not be repeated. It accounts 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 one-dimensional Poisson equations for the local electrical potential $\psi(x,t)$ in both electrodes and in the electrolyte coupled to the time-dependent one-dimensional 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 $\text{Li}^+$ of valency $z_1 = 1$ while $i = 2$ refers to anions $\text{ClO}_4^-$ 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 $\psi_{\text{min}}$ and $\psi_{\text{max}}$ while maintaining the carbon
electrode 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 [15].

4.2.3 Dimensional Analysis

4.2.3.1 Dimensionless Variables

Based on our previous studies [16,59], 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

$$
\begin{align*}
x^* &= \frac{x}{\lambda_D}, \\
t^* &= \frac{t}{\lambda_D^2/D_1}, \\
\psi^* &= \frac{\psi(x,t)}{R_uT/z_1F}, \\
c_i^* &= \frac{c_i(x,t)}{c_{1,\infty}}, \text{ and } c_{1,P}^* &= \frac{c_{1,P}(x,t)}{c_{1,P,\text{max}}}
\end{align*}
$$

(4.1)

where $\lambda_D = \sqrt{\epsilon_0\epsilon_r R_uT/F^2 \sum_{i=1}^{2} z_i^2 c_{i,\infty}}$ is the Debye length for binary and asymmetric electrolytes. It represents an estimate of the EDL thickness [88]. The time $t$ was scaled by the timescale for ion diffusion across the electric double layer $\tau_d = \lambda_D^2/D_1$ 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 $\tau_{th} = R_uT/z_1F$ representing the electric potential at which the electrical potential energy of one mole of Li$^+$ ions is equals to its thermal energy $R_uT$. 44
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.

### 4.2.3.2 Dimensionless Governing Equations

The Poisson equations governing the electric potential in the pseudocapactive and carbon electrodes assuming constant electrical conductivities, respectively denoted by $\sigma_P$ and $\sigma_C$, can be expressed in dimensionless form as

\[
\frac{\partial}{\partial x^*} \left( \sigma_P^* \frac{\partial \psi^*}{\partial x^*} \right) = 0 \quad \text{for} \quad -(L^* + L_P^*) \leq x^* < -L^* \quad (4.2)
\]

\[
\frac{\partial}{\partial x^*} \left( \sigma_C^* \frac{\partial \psi^*}{\partial x^*} \right) = 0 \quad \text{for} \quad L^* < x^* \leq L^* + L_C^* \quad (4.3)
\]

where the dimensionless electrode conductivities are given by $\sigma_{P/C}^* = [\sigma_{P/C}(\psi_{max} - \psi_{min})/L_P]/(Fz_1c_{1,\infty}D_1/L)$, where subscript $P$ refers to the pseudocapacitive electrode and subscript $C$ refers to the carbon electrode. They represent the ratios of the characteristic electric current density in the pseudocapacitive and carbon electrodes, respectively, 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 elec-
trode was non-dimensionalized as
\[
\frac{\partial c_{i,P}^*}{\partial t^*} = \frac{\partial}{\partial x^*} \left( D_{1,P}^* \frac{\partial c_{i,P}^*}{\partial x^*} \right) \quad \text{for} \quad -(L^* + L_P^*) \leq x^* \leq -L^* \quad \text{(4.4)}
\]
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 \( \text{Li}^+ \) ions in the electrolyte \( D_1 \).

Moreover, the GMPNP model in the diffuse layer of the binary asymmetric electrolyte, between \(-L^* + H^* \) and \( L^* - H^* \), has already been written in dimensionless form as [59]
\[
\begin{align*}
\frac{\partial^2 \psi^*}{\partial x^*^2} &= -c_1^* + z_2^* c_2^* \quad \text{(4.5a)} \\
\frac{\partial c_i^*}{\partial t^*} &= -\frac{\partial N_i^*}{\partial x^*} \quad \text{for } i = 1 \text{ or } 2. \quad \text{(4.5b)}
\end{align*}
\]
Here, \( H^* = H/\lambda_D = a_2^*/2 \) where \( a_2^* = a_2/\lambda_D \) is the effective diameter \( a_2 \) of the largest ion (\( \text{ClO}_4^- \) with \( i = 2 \)) scaled by the Debye length \( \lambda_D \). Additionally, \( z_i^* = z_i/z_1 \) is the ratio of the valency of the ion considered to that of the cation \( \text{Li}^+ \) (\( i = 1 \)). The dimensionless mass flux \( N_i^* \) of ion species \( i \) was given by [59]
\[
N_i^*(x^*, t^*) = -D_i^* \frac{\partial c_i^*}{\partial x^*} - D_i^* z_i^* c_i^* \frac{\partial \psi^*}{\partial x^*} - \frac{D_i^* c_i^*}{2} \frac{\partial}{\partial x^*} \left( \sum_{j=1}^{2} \nu_{pj} c_j^* \right) \quad \text{(4.6)}
\]
where \( D_i^* = D_i/D_1 \) is the ratio of the diffusion coefficient of the ion species \( i \) and that of the cation \( \text{Li}^+ \). 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 \( a_i \) [89].
4.2.3.3 Dimensionless Initial and Boundary Conditions

The initial dimensionless electric potential was uniformly zero across the device, i.e.,
\[ \psi^*(x^*, 0) = 0 \quad \text{for} \quad -L^* - L_P^* \leq x^* \leq L^* + L_C^* \] (4.7)

The initial dimensionless concentration of lithium was uniform in the pseudocapacitive electrode \((-L^* - L_P^* \leq x^* \leq -L^*)\) such that
\[ c_{1,P}^*(x^*, 0) = c_{1,P,0} = c_{1,P,0}/c_{1,P,\text{max}}, \] (4.8)

where \(c_{1,P,0}\) is the initial concentration of Li in the pseudocapacitive electrode.

The concentrations of \(\text{Li}^+\) and \(\text{ClO}_4^-\) in the electrolyte \((-L^* + a_2^*/2 \leq x^* \leq L^* - a_2^*/2)\) were also initially uniform and satisfied electroneutrality so that [59]
\[ c_1^*(x^*, 0) = 1, \quad \text{and} \quad c_2^*(x^*, 0) = -1/z_2^*. \] (4.9)

The dimensionless electric potentials imposed at the current collector/electrode interfaces were given by [59],
\[ \psi^*(L^* + L_C^*, t^*) = 0 \quad \text{and} \quad \psi^*(-L^* - L_P^*, t^*) = \psi^*_s(t^*) \] (4.10)

where \(\psi^*_s(t^*)\) is the dimensionless surface potential. For cyclic voltammetry, it is given by [59]
\[ \psi^*_s(t^*) = \begin{cases} \psi_{\text{max}}^* - v^*[t^* - (n_C - 1)\tau_{CV}^*], & \text{for} \quad (n_C - 1)\tau_{CV}^* \leq t^* \leq (n_C - 1/2)\tau_{CV}^* \\ \psi_{\text{min}}^* + v^*[t^* - (n_C - 1/2)\tau_{CV}^*], & \text{for} \quad (n_C - 1/2)\tau_{CV}^* \leq t^* \leq n_C\tau_{CV}^* \end{cases} \] (4.11a)
where \( n_C \) is the cycle number and \( \psi_{\text{max}}^* = \psi_{\text{max}}/(R_u T/z_1 F) \) and \( \psi_{\text{min}}^* = \psi_{\text{min}}/(R_u T/z_1 F) \) are the maximum and minimum dimensionless surface potentials, respectively. Here, the dimensionless scan rate \( v^* = (\lambda_D^2/D_1)/(R_u T/z_1 F) \) 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., \( v^* = \tau_d/\tau_{th} \). [59].

Finally, \( \tau_{CV}^* = \tau_{CV}/\tau_d = (\psi_{\text{max}}^* - \psi_{\text{min}}^*)/v^* \) represents the dimensionless cycle period.

Moreover, the boundary conditions accounting for the Stern layer at both electrodes can be written in dimensionless form as [59],

\[
\frac{\partial \psi^*}{\partial x^*}(L^* - a_2^*/2, t^*) = \frac{2}{a_2^*} [\psi^*(L^*, t^*) - \psi^*(L^* - a_2^*/2, t^*)] \quad (4.12a) \\
- \frac{\partial \psi^*}{\partial x^*}(-L^* + a_2^*/2, t^*) = \frac{2}{a_2^*} [\psi^*(-L^*, t^*) - \psi^*(-L^* + a_2^*/2, t^*)] \quad (4.12b)
\]

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

\[
- \frac{\sigma_p^*}{\psi_{\text{max}}^* - \psi_{\text{min}}^*} \frac{L_p^*}{L^*} \frac{\partial \psi^*}{\partial x^*}(-L^*, t^*) = j_{\text{C}}^*(-L^* + a_2^*/2, t^*) + j_{\text{F}}^*(t^*) \quad (4.13a)
\]

Similarly, across the carbon electrode/electrolyte interface [59]

\[
- \frac{\sigma_C^*}{\psi_{\text{max}}^* - \psi_{\text{min}}^*} \frac{L_C^*}{L^*} \frac{\partial \psi^*}{\partial x^*}(L^*, t^*) = j_{\text{C}}^*(L^* - a_2^*/2, t^*) \quad (4.13b)
\]

The current densities \( j_{\text{C}}(x, t) \) and \( j_{\text{F}}(t) \) given by Equations (3.18) and (3.19), respectively, can be scaled by a characteristic ionic current density
\( F_zD_1c_{1,\infty}/\lambda_D \) corresponding to diffusion of \( \text{Li}^+ \) (i=1) over the characteristic concentration gradient \( c_{1,\infty}/\lambda_D \) to yield the dimensionless current densities

\[
j_C^*(x^*, t^*) = \frac{j_C(t)}{F_zD_1c_{1,\infty}/\lambda_D} \quad \text{and} \quad j_F^*(t^*) = \frac{j_F(t)}{F_zD_1c_{1,\infty}/\lambda_D}. \quad (4.14)
\]

In dimensionless form, these current densities can be expressed as

\[
j_C^*(\pm(L^* - a_2^*/2), t^*) = -(1 - z_2^*) \frac{\partial^2 \psi^*}{\partial x^* \partial t^*}(\pm(L^* - a_2^*/2), t^*) \quad (4.15)
\]

and

\[
j_F^*(t^*) = j_{F,0}(t^*) \left\{ \exp [(1 - \alpha)\eta^*] - \exp [-\alpha\eta^*] \right\}. \quad (4.16)
\]

Here, \( \eta^* \) 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

\[
j_{F,0}^*(t^*) = k_0 c_{1,\infty} \alpha_{\lambda D/D_1} \left( -L^* + H^*, t^* \right)^{1-\alpha} (1 - c_{1,P}(-L^*, t^*))^{\alpha} \quad (4.17)
\]

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 time scale given by \( \tau_f = \lambda_D/k_0 c_{1,\infty} \).

In addition, the dimensionless mass fluxes of \( \text{Li}^+ \) (i = 1) and \( \text{ClO}_4^- \) (i = 2) at the Stern/diffuse layer interface near the pseudocapacitive electrode satisfied

\[
N_1^*(-L^* + a_2^*/2, t^*) = j_F^*(t^*) \quad \text{and} \quad N_2^*(-L^* + a_2^*/2, t^*) = 0. \quad (4.18)
\]

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

\[
N_1^*(L^* - a_2^*/2, t^*) = N_2^*(L^* - a_2^*/2, t^*) = 0. \quad (4.19)
\]
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

\[ v^* = \frac{\lambda_D^2/D_1}{(R_u T/z_1 F)/v}, \quad \psi_{max}^* = \frac{\psi_{max}}{R_u T/z_1 F}, \quad \psi_{min}^* = \frac{\psi_{min}}{R_u T/z_1 F}, \quad L^* = \frac{L}{\lambda_D}, \]

\[ a_2^* = \frac{a_2}{\lambda_D}, \quad \nu_{\mu 1} = 2a_1^3 N_A c_{1,\infty}, \quad \nu_{\mu 2} = 2a_2^3 N_A c_{1,\infty}, \quad D_2^* = \frac{D_2}{D_1}, \quad z_2^* = \frac{z_2}{z_1}, \]

\[ \sigma_P^* = \frac{\sigma_P (\psi_{max} - \psi_{min})/L_P}{F z_1 c_{1,\infty} D_1/L}, \quad \sigma_C^* = \frac{\sigma_C (\psi_{max} - \psi_{min})/L_C}{F z_1 c_{1,\infty} D_1/L}, \]

\[ L_P^* = \frac{L_P}{\lambda_D}, \quad L_C^* = \frac{L_C}{\lambda_D}, \quad D_{1,P}^* = \frac{D_{1,P}}{D_1}, \quad c_{1,P,max}^* = \frac{c_{1,P,max}}{c_{1,\infty}}, \]

\[ k_0^* = \frac{k_{0,1,\infty} \lambda_D}{D_1}, \quad \text{and} \quad \Delta \psi_{eq}^* = \frac{\Delta \psi_{eq}}{R_u T/z_1 F}, \quad (4.20) \]

Note that \( v^*, \psi_{max}^*, \psi_{min}^*, L^*, a_2^*, \nu_{\mu 1}, \nu_{\mu 2}, D_2^*, z_2^*, \sigma_P^*, \sigma_C^*, L_P^*, \) and \( L_C^* \) were identical to those identified in Ref. [59] 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 \( \Delta \psi_{eq}^*. \)

### 4.2.4 Constitutive Relationships

A total of 22 input parameters were needed to solve the dimensional governing Equations (3.4) to (3.24) of Chapter 3 including (i) the electrolyte properties \( \epsilon_r, \ a_1, \ a_2, \ z_1, \ z_2, \ D_1, \ D_2, \) and \( c_{1,\infty}, \) (ii) the carbon and pseudocapacitive electrode properties \( \sigma_C, \ \sigma_P, \ c_{1,P,0} \) and \( D_{1,P}, \) (iii) the redox reaction parameters \( \alpha, \ k_0 \) and \( \Delta \psi_{eq}, \) (iv) the cell dimensions \( L, \ L_P, \) and \( L_C, \) and (v) the operating
conditions $T$, $\psi_{\text{max}}$, $\psi_{\text{min}}$, 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 4.1. 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 was also varied. The transfer coefficient of the redox reaction $\alpha$ is generally assumed to be 1/2 corresponding to equal energy barriers for forward and backward redox reactions [15]. The baseline case corresponded to Case B of Ref. [63] considering a Nb$_2$O$_5$ 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.

### 4.3 Results and Discussion

#### 4.3.1 The Faradaic Potential Window

Figure 4.1 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 $\psi_{\text{min}} = -0.8$ V and $\psi_{\text{max}} = +0.8$ V at a scan rate $v$ of 1 V/s. The results were obtained for the pseudocapacitive electrode thickness $L_P = 50$ nm and Li diffusion coefficient of $D_{1,P} = 10^{-14}$ m$^2$/s. Figure
### Table 4.1: Electrode and electrolyte properties and dimensions used in the simulations reported in this study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Temperature</td>
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<td>K</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>$\epsilon_r$</td>
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<td>[90]</td>
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<tr>
<td>Li$^+$ ion diameter</td>
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<td>[76]</td>
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<tr>
<td>ClO$_4^-$ ion diameter</td>
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<td>nm</td>
<td>[76]</td>
</tr>
<tr>
<td>Li$^+$ valency</td>
<td>$z_1$</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO$_4^-$ valency</td>
<td>$z_2$</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$^+$ diffusion coefficient</td>
<td>$D_1$</td>
<td>$2.6 \times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>[76]</td>
</tr>
<tr>
<td>ClO$_4^-$ diffusion coefficient</td>
<td>$D_2$</td>
<td>$3.3 \times 10^{-10}$</td>
<td>m$^2$/s</td>
<td>[76]</td>
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<td>Stern layer thickness</td>
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<td>nm</td>
<td>[59]</td>
</tr>
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<td>Initial bulk ion concentration</td>
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<td>mol/L</td>
<td>[43,45,77]</td>
</tr>
<tr>
<td>Initial intercalated Li concentration</td>
<td>$c_{1,P,0}$</td>
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<td>mol/L</td>
<td>[84]</td>
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<tr>
<td>Pseudocapacitive electrode conductivity</td>
<td>$\sigma_P$</td>
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<td>S/m</td>
<td>[80]</td>
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<tr>
<td>Carbon electrode conductivity</td>
<td>$\sigma_C$</td>
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<td>S/m</td>
<td>[81]</td>
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<tr>
<td>Reaction rate</td>
<td>$k_0$</td>
<td>$10^{-7}$ to $10^{-13}$</td>
<td>m$^2$mol$^{-0.5}$s$^{-1}$</td>
<td>[67,69,82]</td>
</tr>
<tr>
<td>Intercalated Li diffusion coefficient</td>
<td>$D_{1,P}$</td>
<td>$10^{-14}$ to $10^{-10}$</td>
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<td>[82]</td>
</tr>
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<td>Half electrolyte thickness</td>
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<td>µm</td>
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</tr>
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<td>Pseudocapacitive electrode thickness</td>
<td>$L_P$</td>
<td>20 to 500</td>
<td>nm</td>
<td>[50,85]</td>
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<tr>
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<td>nm</td>
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<tr>
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<td>[83]</td>
</tr>
<tr>
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<td>$\alpha$</td>
<td>1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan rate</td>
<td>$v$</td>
<td>$10^{-3}$ to 10</td>
<td>V/s</td>
<td>[43,45,77]</td>
</tr>
<tr>
<td>Potential window</td>
<td>$\psi_{max} - \psi_{min}$</td>
<td>1.6</td>
<td>V</td>
<td>[43,45,77]</td>
</tr>
</tbody>
</table>

4.1a demonstrates that the cell exhibited two distinct regimes. In the lower part of the potential window, the faradaic regime prevailed and 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 when the capacitive current $j_C$ contributed the most to the total current density $j_T$. The transitions between
Figure 4.1: (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 $v = 1$ V/s for pseudocapacitive electrode thickness $L_P = 50$ nm and Li diffusion coefficient in the electrode $D_{1,P} = 10^{-14}$ m$^2$/s.

The two regimes was caused by the slow diffusion of Li in the pseudocapacitive electrode causing Li starvation at the pseudocapacitive electrode/electrolyte interface, as illustrated in Figure 4.1b [63]. Note that in the charging step, the transition, marked by a red square, corresponded to steep increase in the absolute value of the total current density observed on Figure 4.1a. Furthermore, during discharging, the capacitive current vanished during the entire faradaic regime. The faradaic potential window, represented by a double arrow in Figure 4.1, was defined as $\Delta \psi_f = \psi_f - \psi_{min}$ where $\psi_f$ is the potential at which Li starvation occurs as shown by the onset of the capacitive cur-
rent (blue circle in Figure 4.1). Although capacitive current arose when the faradaic current became diffusion limited, the magnitude of the total current was significantly smaller in the capacitive regime than in the faradaic regime. This stresses the importance of widening the faradaic potential window by delaying or eliminating Li starvation.

4.3.2 Effect of Electrode Thickness

Figure 4.2: (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 $v = 1$ V/s for several pseudocapacitive electrode thicknesses $L_P$ ranging from 50 to 500 nm with a relatively small diffusion coefficient of Li in the electrode $D_{1,P} = 10^{-14}$ m$^2$/s.

Figure 4.2 shows (a) the total current density $j_T$ and (b) the intercalated Li concentration $c_{1,P}(-L, t)$ at the pseudocapacitive electrode/electrolyte in-
interface as functions of the cell potential $\psi_s(t)$ for various pseudocapacitive electrode thicknesses ranging from $L_P = 50$ to 500 nm in the case of a relatively small Li diffusion coefficient $D_{1,P} = 10^{-14}$ m$^2$/s. Here also, the scan rate was 1 V/s. Figure 4.2a indicates that thinner electrodes resulted in larger current densities and larger capacitances. In fact, the electrode of thickness $L_P = 50$ nm had an areal integral capacitance $C_{s,int}$ of 40 µF/cm$^2$. This was almost twice as large as that of the electrode of thickness $L_P = 500$ nm found to be $C_{s,int} = 25$ µF/cm$^2$. Figure 4.2a also illustrates that the CV curves for all thicknesses considered exhibited similar peaks. The most prominent peak was observed during charging and indicated the onset of the faradaic charging as indicated in Figure 4.2b 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 4.2b 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 could intercalate. Thicker electrodes provided more volume for Li insertion but suffered from a narrower
faradaic potential window and a smaller current magnitude. Figure 4.2b 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 $D_{1,P}$ chosen. 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 oxidized electrode.

Overall, this section has demonstrated that, in the case of hybrid pseudocapacitors limited by diffusion of Li 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.

4.3.3 Effect of Intercalated Li Diffusion Coefficient

Figure 4.3 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 $v$ 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 $10^{-11}$ m$^2$/s. Figure 4.3a 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
Figure 4.3: (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 $v = 1$ V/s for several diffusion coefficients $D_{1,P}$ ranging from $10^{-14}$ to $10^{-11}$ m$^2$/s.

the diffusion coefficient $D_{1,P}$ increased. In fact, the areal integral capacitance decreased from 47 to 25 $\mu$F/cm$^2$ as $D_{1,P}$ decreased from $10^{-11}$ to $10^{-14}$ m$^2$/s. Note that the maximum concentration reached at the end of the charging step at the electrode/electrolyte interface decreased with increasing diffusion coefficient. Furthermore, the CV curves for the relatively large diffusion coefficients $D_{1,P}$ of $10^{-12}$ and $10^{-11}$ m$^2$/s were superimposed and the capacitive current was negligibly small throughout the entire potential window. Indeed, Figure 4.3b establishes that, for these values of $D_{1,P}$, no starvation of Li occurred at the electrode/electrolyte interface. 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., $\Delta\psi_f = \psi_{max} - \psi_{min}$. Instead, the concentration of intercalated lithium was more uniform in the electrode and increased up to an oscillatory steady-state with a very narrow hysteresis.

4.3.4 Effect of Reaction Rate

Figure 4.4a 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$^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$. Figures 4.4b to 4.4d show the capacitive $j_C$, faradaic $j_F$, and total $j_T$ current densities as functions of cell potential $\psi_s(t)$ for a reaction rate $k_0$ of (b) $10^{-7}$, (c) $10^{-10}$, and (d) $10^{-13}$ m$^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$. In all cases, the scan rate was $v = 1$ V/s and the potential window extended from $-0.8$ V to $-0.2$ V. Figure 4.4a indicates that for reaction rates larger than $10^{-9}$ m$^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$ the CV curves were nearly identical. Figure 4.4b demonstrates that this behavior involved a transition between faradaic and capacitive regimes similar to that discussed previously (Figure 4.1). 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$^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$. 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 4.4c shows that for a smaller reaction rate $k_0 = 10^{-10}$ m$^{2.5}\text{mol}^{-0.5}\text{s}^{-1}$, the capacitive current dominated for the entire potential window and thus no regime transition was observed. For even lower reaction rates, Figure 4.4d shows that the current was exclusively capacitive.
Figure 4.4: (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) $10^{-13}$ m$^{2.5}$mol$^{-0.5}$s$^{-1}$. 
and the device behaved as an EDLC.

Finally, note that Figure 4.4a indicates that a larger capacitance was achieved for \( k_0 = 10^{-13} \text{ m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1} \) than for \( k_0 = 10^{-10} \text{ m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1} \). In the latter case, the faradaic reactions led to a smaller total current density when the device was limited by the reaction rate constant \( k_0 \).

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.

4.4 Scaling

4.4.1 Validation

In order to demonstrate the validity of the scaling described in the Analysis section, four different cases were considered with various properties and dimensions. Table 4.2 summarizes the different values of the input parameters of Cases 1 through 4. However, these four cases had identical dimensionless numbers governing the problem namely \( v^* = 1.13 	imes 10^{-8} \), \( \psi_{max}^* = 31.2 \),
Table 4.2: Parameters used in CV simulations reported in Figure 4.5 with $\Delta \psi_{eq} = 0$ V and $z_1 = -z_2 = 1$ for all cases considered. In these four cases, the dimensionless numbers were identical and equal to $v^* = 1.13 \times 10^{-8}$, $\psi_{max}^* = 31.2$, $\psi_{min}^* = 7.79$, $L^* = 3641.5$, $a_2^* = 3.65$, $\nu_{p,1} = 1.21$, $\nu_{p,2} = 0.36$, $D_2^* = 1.27$, $z_2^* = -1$, $\sigma_P^* = 0.16$, $\sigma_C^* = 12$, $L_P^* = L_C^* = 36415$, $D_1^* = 3.8 \times 10^{-5}$, $k_0^* = 3.34 \times 10^{-8}$, and $\Delta \psi_{eq}^* = 0$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ (V/s)</td>
<td>1</td>
<td>0.1</td>
<td>0.015</td>
<td>0.0091</td>
</tr>
<tr>
<td>$\psi_{max}$ (V)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>$\psi_{min}$ (V)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.15</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>298</td>
<td>298</td>
<td>298</td>
<td>223.5</td>
</tr>
<tr>
<td>$a_1$ (nm)</td>
<td>0.67</td>
<td>0.67</td>
<td>1.44</td>
<td>1.92</td>
</tr>
<tr>
<td>$a_2$ (nm)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.16</td>
<td>2.88</td>
</tr>
<tr>
<td>$D_1$ (m$^2$/s)</td>
<td>$2.6 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-11}$</td>
<td>$2.6 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>$D_2$ (m$^2$/s)</td>
<td>$3.3 \times 10^{-10}$</td>
<td>$3.3 \times 10^{-11}$</td>
<td>$3.3 \times 10^{-10}$</td>
<td>$3.3 \times 10^{-11}$</td>
</tr>
<tr>
<td>$c_{1,\infty}$ (mol/L)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1</td>
<td>0.042</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>78.5</td>
<td>78.5</td>
<td>36.4</td>
<td>36.4</td>
</tr>
<tr>
<td>$L$ (µm)</td>
<td>1.0</td>
<td>1.0</td>
<td>2.15</td>
<td>2.87</td>
</tr>
<tr>
<td>$\sigma_P$ (S/m)</td>
<td>0.069</td>
<td>0.0069</td>
<td>0.0069</td>
<td>$3.88 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\sigma_C$ (S/m)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$L_P = L_C$ (µm)</td>
<td>10</td>
<td>10</td>
<td>21.5</td>
<td>28.7</td>
</tr>
<tr>
<td>$D_{1,P}$ (m$^2$/s)</td>
<td>$10^{-14}$</td>
<td>$10^{-15}$</td>
<td>$10^{-14}$</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>$c_{1,P,\max}$ (mol/L)</td>
<td>32.9</td>
<td>32.9</td>
<td>3.29</td>
<td>1.39</td>
</tr>
<tr>
<td>$k_0$ (m$^{2.5}$mol$^{-0.5}$s$^{-1}$)</td>
<td>$10^{-9}$</td>
<td>$10^{-10}$</td>
<td>$1.47 \times 10^{-9}$</td>
<td>$1.69 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

$\psi_{min}^* = 7.79$, $L^* = 3641.5$, $a_2^* = 3.65$, $\nu_{p,1} = 1.21$, $\nu_{p,2} = 0.36$, $D_2^* = 1.27$, $z_2^* = -1$, $\sigma_P^* = 0.165$, $\sigma_C^* = 0.165$, $L_P^* = L_C^* = 36415$, $D_{1,P}^* = 3.8 \times 10^{-5}$, $c_{1,P,\max}^* = 32.9$, $k_0^* = 3.34 \times 10^{-8}$, and $\Delta \psi_{eq}^* = 0$. Figures 4.5a and 4.5b respectively show the predicted capacitive and faradaic current densities $j_C$ and $j_F$ as functions of surface potential $\psi_s$ for these four cases. They indicate that capacitive and faradaic current densities $j_C$ and $j_F$ varied significantly among
Figure 4.5: Predicted dimensional currents (a) $j_C$, (b) $j_F$, and concentration (c)$c_{1,P}$ as functions of imposed potential $\psi_s$ along with the corresponding dimensionless currents (d) $j_C^*$, (e) $j_F^*$, and concentration (f)$c_{1,P}^*$ as functions of dimensionless imposed potential $\psi_s^*$ for cases 1 through 4 summarized in Table 4.2.
these four cases due to the large difference in input parameters. However, Figures 4.5c and 4.5d plot the corresponding dimensionless current densities $j_C^*$ and $j_F^*$ versus $\psi_s^*$ as defined in Equations (4.15) and (4.16), respectively. They demonstrate that the dimensionless CV curves overlapped for all four cases considered.

Similarly, Figure 4.5c shows the predicted Li concentration in the pseudocapacitive electrode at the electrode/electrolyte interface, $c_{1,P}(-L,t)$ as a function of potential $\psi_s$ for the four cases. Again, they differed significantly both in magnitude and shape. However, Figure 4.5f 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 $\psi_s^*$. It indicates that the dimensionless concentrations 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 (4.20).

### 4.4.2 Scaling of the 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 [63]. However, most actual hybrid pseudocapacitors reach Li starvation in the course of a typical
cycle [1].

The fraction $R_f$ of the potential window dominated by faradaic reactions can be defined as

$$R_f = \frac{\Delta \psi_f}{\Delta \psi_s} = \frac{\psi_f - \psi_{\text{min}}}{\psi_{\text{max}} - \psi_{\text{min}}} \quad (4.21)$$

Table 4.3: Range of the dimensionless parameters studied

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{i,P}$</td>
<td>$3.8 \times 10^{-5}$ to $1.9 \times 10^{-1}$</td>
</tr>
<tr>
<td>$L_P^*$</td>
<td>$3.6 \times 10^{-1}$ to $2.9 \times 10^{+3}$</td>
</tr>
<tr>
<td>$v^*$</td>
<td>$1.1 \times 10^{-11}$ to $1.1 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

According to scaling analysis, this dimensionless parameter should be a unique function of the 17 similarity parameters given by Equations (4.20). 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 $\psi_{\text{min}} = -0.8 \text{ V}$, $\psi_{\text{max}} = 0.8 \text{ V}$, and $z_1 = -z_2 = 1$. Indeed, these parameters are determined by the properties of the electrolyte in actual devices. Finally, the maximum concentration of Li in the electrode $c_{1,P,\text{max}}^*$, the equilibrium potential $\Delta \psi_{\text{eq}}$, and the reaction rate $k_0$ were also kept constant. First, the maximum intercalated Li concentration $c_{1,P,\text{max}}^*$ was never reached in our simulations. In addition, the equilibrium potential $\Delta \psi_{\text{eq}}^*$ was found to have a negligible effect on the behavior of the device [63]. 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. Thus, only the dimensionless parameters \( \bar{L}_p \), \( \bar{D}_{1,P} \), and \( \bar{v} \) were investigated. Their respective ranges are summarized in Table 4.3 based on realistic values of the associated dimensional variables. The range of dimensionless electrode thickness \( \bar{L}_p \) spans a little over two orders of magnitude while the range of the scan rate \( \bar{v} \) and the dimensionless diffusion coefficient \( \bar{D}_{1,P} \) span a much larger range. The latter corresponds 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: \( a_2^* = 3.63, z_2^* = -1, \psi_{\text{max}}^* = 31.2, \psi_{\text{min}}^* = -31.2, \bar{L}_p = 3.63 \times 10^3, \nu_{P1} = 3.62 \times 10^{-1}, \nu_{P2} = 1.20, D_2^* = 1.27, c_{1,P,\text{max}}^* = 32.9, k_0^* = 3.35 \times 10^{-7}, \) and \( \Delta \psi_{eq}^* = 0. \)

Figure 4.6a shows the faradaic fraction \( R_f \) as a function of dimensionless pseudocapacitive electrode thickness \( \bar{L}_p \) for different values of dimensionless Li diffusion coefficient \( \bar{D}_{1,P} \) and dimensionless scan rate \( \bar{v} \). For each value of \( (\bar{D}_{1,P}, \bar{v}) \), the solid line represents a power law relating \( R_f \) to \( \bar{L}_p \) according to \( R_f \propto (\bar{L}_p)^{-1/2} \). This is consistent with previous results (Figure 4.2) indicating that the faradaic potential window narrowed as the electrode thickness increased.

Figure 4.6b shows the dimensionless number \( R_f (\bar{L}_p)^{1/2} \) as a function of dimensionless Li diffusion coefficient \( \bar{D}_{1,P} \) in the pseudocapacitive electrode for different values of \( \bar{L}_p \) and \( \bar{v} \). Cases with identical dimensionless scan rate \( \bar{v} \) but different \( \bar{L}_p \) aligned along the same line according to the power law
Figure 4.6: (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) Scaling of $R_f (L_p^*)^{1/2}$ as a function of the dimensionless Li diffusion coefficient $D_{1,p}^*$. (c) Scaling $R_f (L_p^*)^{1/2} (D_{1,p}^*)^{-1/4}$ as a function of dimensionless scan rate $v^*$. (d) Faradaic fraction $R_f$ as a function of dimensionless parameter $\Pi_f$ defined in Equation (4.22).
\( R_f (L_P^*)^{1/2} \propto (D_{1,P}^*)^{1/4} \). This confirms that the effect of the electrode thickness was captured by the relationship obtained from Figure 4.6a. 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 4.3.3.

Figure 4.6c 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 4.6d shows the faradaic fraction \( R_f \) as a function of the dimensionless parameter \( \Pi_f \) capturing the combined effects of \( L_P^* \), \( D_{1,P}^* \) and \( v^* \) and defined as

\[
\Pi_f = \left( \frac{D_{1,P}^*}{(L_P^*)^{1/2}(v^*)^{1/5}} \right)^{1/4} \left( \frac{\tau_{th}}{\tau_d} \right)^{1/5}.
\]

\( \Pi_f \) can be interpreted as the product of the ratios of (i) the characteristic time for Li\(^+\) ion diffusion across the EDL \( \tau_d = \lambda_2^2 / D_1 \) and the characteristic time for Li intercalation in the pseudocapacitive electrode \( \tau_{d,P} = L_P^2 / D_{1,P} \) and of (ii) the characteristic time for reaching the thermal potential \( R_u T / z_1 F \) at scan rate \( v \tau_{th} = (R_u T / z_1 F) / v \) and \( \tau_d \).

Figure 4.6d features a diffusion-controlled regime and a diffusion-independent regime with a sharp transition at \( \Pi_f = 0.2 \). In the diffusion-controlled regime, the faradaic fraction \( R_f \) was linearly proportional to \( \Pi_f \) and fol-
lowed $R_f = 2.36 \Pi_f$ with $\Pi_f < 0.2$. In the diffusion-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 diffusion-independent regime when electrode thickness $L_P$ and diffusion coefficient $D_{1,P}$ should satisfy the design criterion $\Pi_f > 0.2$. This criterion can be achieved by reducing the scan rate so that Li intercalation has the time to respond to changes in surface potential. Alternatively, the pseudocapacitive electrode thickness can be reduced to compensate for slow Li diffusion and delay Li starvation. A pseudocapacitive material with fast Li diffusion can also be used to compensate for a large electrode thickness. This can be achieved with crystalline structures providing fast diffusion pathways in the electrode material [3].

4.5 Conclusion

This chapter presented the dimensional analysis of a continuum model simulating hybrid pseudocapacitors accounting 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. The fraction of the potential window
dominated by faradaic reactions was a good indicator of the total capacitance of the hybrid pseudocapacitor. It was found to increase 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 $\Pi_f$, defined in Equation (4.22), 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 a diffusion-independent regime. This design criterion can be used to optimize the pseudocapacitive electrode in hybrid pseudocapacitors.
CHAPTER 5

Simulating Pseudocapacitive Electrodes in
Three-Electrode Experiments

5.1 Introduction

Most metal oxide materials can only be used as the positive or negative electrode of pseudocapacitors due to the equilibrium potential associated with the oxidation-reduction (redox) reaction. In addition, using two pseudocapacitive electrodes in the same device is made difficult by the fact that they have to be compatible, i.e., the potential window of one electrode should not cause irreversible redox reactions at the other electrode. For this reason, the electrodes are designed and characterized individually. To do so, three-electrode measurements are performed. The setup consists of (1) the working electrode under investigation, (2) a reference electrode setting the reference potential, and (3) a counter-electrode designed to measure the current without limiting it. This method ensures that no current flows through the reference electrode and its potential remains constant. It also enables precise control of the potential between the electrolyte and the pseudocapacitive electrode. This system enables one to characterize the working electrode independently from the rest of the system. For this reason, three-electrode
measurements are used in most experimental studies of pseudocapacitive elec-

trodes [1, 39, 50–56].

The design of a pseudocapacitive electrode aims to provide a large volume
for chemical charge storage readily accessible to ions in the electrolyte and to
electrons in the electrode. However, the relatively poor solid-state diffusion
and electrical conductivity of most transition metal oxides limit the practical
thickness of the electrode and its energy and power densities.

In order to mitigate the slow intercalation and/or the potential drop across
the electrode several approaches can be envisioned. First, the thickness can
be adjusted to reduce the total electrical resistance of the electrode and the
intercalation distance. The scan rate can also be reduced to slow the potential
variation and provide more time for the charge holders to diffuse [1]. Finally,
some metal oxides can also be synthesized with different crystalline structures
to achieve larger electrical conductivity and faster intercalation [3]. It is,
however, difficult to predict the onset of resistive behavior or intercalation
limitations that adversely affect the current densities. For this reason, the
determination of the actual performance of the pseudocapacitive electrode
requires extensive experimental testing.

The objective of this chapter is to provide physical interpretation of exper-
imentally measured cyclic voltammetry curves obtained from three-electrode
measurements and to characterize the interplay between faradaic and EDL
charge storage mechanisms. To do so, a numerical model for simulating such
experiments was developed. Furthermore, it can be used to optimize the
design of pseudocapacitive electrode parameters such as the thickness.

5.2 Analysis

5.2.1 Schematic and Assumptions

Figure 5.1: Schematic of the simulated one-dimensional pseudocapacitive electrode consisting
of a redox-active pseudocapacitive electrode in a three-electrode setup with LiClO$_4$ in PC
as electrolyte. The dashed line encloses the computational domain simulated.

Figure 5.1 shows a schematic of the simulated domain and of the associated coordinate system. The domain consisted of a pseudocapacitive electrode of thickness $L_P$ made of metal oxide $M_pO_q$ and a binary and symmetric
electrolyte of thickness $L$ containing lithium salt in a solvent at high concentration. The electrolyte was further divided in two regions (i) a Stern layer of thickness $H$ defining the distance of closest approach of the ions to the electrode and (ii) a diffuse layer where the ions were free to move under the combined influence of electrodiffusion and steric repulsion [15]. The origin $x = 0$ was located in the bulk of the electrolyte far from the electrode, i.e., $L >> \lambda_D$ where $\lambda_D$ is the Debye length defined, for a binary symmetric electrolyte, as $\lambda_D = (\epsilon_0 \epsilon_r R_u T/2F^2 z_i^2 c_{1,\infty})^{1/2}$, characterizing the thickness of the double layer.

The model used in this study was based on the GMPNP with faradaic reactions derived in Chapter 3 and governed by Equations (3.4) to (3.24) for (i) the potential $\psi(x,t)$ in the electrode and electrolyte, (ii) the ion concentrations $c_i(x,t)$ in the electrolyte, and (iii) the intercalated Li concentration $c_{1,P}(x,t)$ in the electrode. The same assumptions were made to make the problem mathematically tractable. The boundary conditions referring to the carbon electrode described in Equations (3.17) and (3.23b) were ignored. Instead, the potential was imposed as $\psi(0,t) = 0$ V in the bulk of the electrolyte. This set the reference potential for the system in a way similar to the reference electrode in a three-electrode system. Additionally, the ion concentrations $c_1(x,t)$ and $c_2(x,t)$ were imposed to be constant at $x = 0$ and equal to their bulk concentrations, i.e., $c_1(0,t) = c_2(0,t) = c_{1,\infty}$. This ensured that the reference electrode did not pass any current by preventing the formation of an EDL. No condition was imposed on the current flowing
at the electrode/current collector interface to account for the overcapacitive counter-electrode used experimentally.

Note that, the permittivity $\epsilon_r$ of the electrolyte was considered constant and independent of the electric field.

### 5.2.2 Constitutive Relationships

A total of 15 input parameters were needed to solve the governing, initial and boundary conditions equations including (i) the electrolyte properties, comprising the permittivity $\epsilon_r$, the ion diameter $a_1$, the ion valency $z_1$, the ion diffusion coefficient $D_1$, and the bulk concentration $c_{1,\infty}$, (ii) the pseudocapacitive electrode properties namely the electrical conductivity $\sigma_P$, the Li diffusion coefficient $D_{1,P}$, the initial Li concentration $c_{1,P,0}$, the reaction rate constant $k_0$, and the equilibrium potential for the redox reaction $\Delta \psi_{eq}$, (iii) the cell dimensions, specifically the electrolyte thickness $L$, and the electrode thickness $L_P$, and (iv) the operating conditions namely the temperature $T$, the potential window defined by $\psi_{max}$ and $\psi_{min}$, and the scan rate $v$. The values of these parameters were taken from the literature whenever possible with the electrode properties corresponding to Nb$_2$O$_5$ and the electrolyte properties taken for Li$^+$ in propylene carbonate (PC). These values are reported in Table 5.1.

Furthermore, the equilibrium potential difference $\Delta \psi_{eq}$, also known as the open circuit potential, varies with the oxidation state of the electrode [18].
Table 5.1: Electrode and electrolyte properties and dimensions used in the simulations reported in this study

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>T</td>
<td>298</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity</td>
<td>ϵr</td>
<td>64.4</td>
<td>[90]</td>
<td></td>
</tr>
<tr>
<td>Ion diameter</td>
<td>a₁ = a₂</td>
<td>0.67</td>
<td>nm</td>
<td>[76]</td>
</tr>
<tr>
<td>Ion valency</td>
<td>z₁ = −z₂</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion diffusion coefficient</td>
<td>D₁ = D₂</td>
<td>2.6 × 10⁻¹⁰</td>
<td>m²/s</td>
<td>[76]</td>
</tr>
<tr>
<td>Stern layer thickness</td>
<td>H</td>
<td>0.5</td>
<td>nm</td>
<td>[59]</td>
</tr>
<tr>
<td>Initial bulk ion concentration</td>
<td>c₁,∞ = c₂,∞</td>
<td>1</td>
<td>mol/L</td>
<td>[43,45,77]</td>
</tr>
<tr>
<td>Initial intercalated Li concentration</td>
<td>c₁,P,0</td>
<td>1 to 5</td>
<td>mol/L</td>
<td>[84]</td>
</tr>
<tr>
<td>Electrode conductivity</td>
<td>σₚ</td>
<td>10⁻⁴ to 10⁻³</td>
<td>S/m</td>
<td>[80]</td>
</tr>
<tr>
<td>Reaction rate</td>
<td>k₀</td>
<td>10⁻⁸</td>
<td>m².s⁻¹.mol⁻⁰.⁵</td>
<td>[67,69,82]</td>
</tr>
<tr>
<td>Intercalated Li diffusion coefficient</td>
<td>D₁,P</td>
<td>10⁻¹⁴ to 10⁻¹¹</td>
<td>m²/s</td>
<td>[82]</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>Lₚ</td>
<td>1</td>
<td>μm</td>
<td></td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>L₁</td>
<td>20 to 150</td>
<td>nm</td>
<td>[50,85]</td>
</tr>
<tr>
<td>Transfer coefficient</td>
<td>α</td>
<td>1/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan rate</td>
<td>v</td>
<td>0.5 to 10</td>
<td>V/s</td>
<td>[43,45,77]</td>
</tr>
<tr>
<td>Potential window</td>
<td>ψₚₘₐₓ − ψₘᵟᵣₙ</td>
<td>0.9</td>
<td>V</td>
<td>[43,45,77]</td>
</tr>
</tbody>
</table>

This variation is commonly assumed to be linear [18]. The parameters were measured for MnO₂ with potassium K intercalation as a function of the state of charge c₁,P/c₁,P,max [18]. In the absence of experimental data for Δψeq for Nb₂O₅, these parameters were used to account for the evolution of the equilibrium potential difference with the state-of-charge [18]

\[
Δψ_{eq}(t) = 10.5 \left( 4 - \frac{c₁,P(t)}{c₁,P,max} \right) - 39.9.
\] (5.1)

In order to preserve the continuity of all variables from the imposed initial conditions, the initial equilibrium potential was required to be zero, i.e., Δψeq(t = 0) = 0 V. This condition was satisfied by setting the initial Li
concentration in the electrode such that $c_{1,P}(0) = c_{1,P,0} = 6.578$ mol/L.

The baseline case used in the subsequent sections consisted of a pseudocapacitive electrode of thickness $L_P = 50$ nm with an electrical conductivity $\sigma_P = 10^{-4}$ S/m and a Li diffusion coefficient $D_{1,P} = 10^{-12}$ m$^2$/s based on realistic values of these parameters. The numerically predicted CV curves were compared with experimental measurements for various electrodes consisting of Nb$_2$O$_5$ with LiClO$_4$ in PC as electrolyte.

5.3 Results and Discussion

5.3.1 CV Curves Interpretation

Figure 5.2 shows CV curves obtained from (a) three-electrode experimental CV measurements for different scan rates and for (b) numerical predictions corresponding to the baseline case. Experimentally, the pseudocapacitive electrode consisted of T-Nb$_2$O$_5$ (orthorhombic) nanocrystal mixed 1:1 with carbon black on a stainless steel current collector with 1 mol/L LiClO$_4$ in PC as electrolyte [1]. Figure 5.2 indicates that the overall shape of the experimentally measured and numerically predicted CV curves was similar. They featured a large current density in the lower portion of the potential window and a smaller one at higher potentials. The evolution of the CV curves with increasing scan rate also followed a similar trend with the charging and discharging peak increasing in magnitude and shifting to lower and higher potentials, respectively. Finally, the shape of the CV curves during the po-
Figure 5.2: (a) Experimental measurements of the total current as a function of imposed potential for a pseudocapacitive electrode consisting of T-Nb$_2$O$_5$ (orthorhombic) nanocrystal mixed 1:1 with carbon black on a stainless steel current collector with 1 mol/L LiClO$_4$ in PC as electrolyte reported in Figure 1a of Ref. [1]. (b) Numerically predicted total current density $j_T$ as a function of imposed potential $\psi_s(t)$ for different scan rates $\nu$ ranging from 0.5 to 10 V/s.

Potential reversal between charging and discharging became more round as the scan rate increased. This can be attributed to the onset of resistive behavior. Indeed, the potential at the electrode/electrolyte interface became significantly lower and varied more slowly than the imposed potential $\psi_s(t)$. This delayed the EDL formation in the capacitive regime and reduced the electrode surface overpotential driving the redox reaction in the faradaic regime. Note also that the simulated scan rates were larger than those used in experimental measurements. This was due to the fact that diffusion limitations...
appear at a much higher scan rate for the simulated planar electrode than for the actual porous electrode.

Figure 5.3: (a) Numerically predicted capacitive $j_C$, faradaic $j_F$, and total $j_T$ current densities as functions of imposed potential $\psi_s(t)$ for the baseline pseudocapacitive electrode at scan rate $v = 5$ V/s. (b) Concentrations of the cation Li$^+$ $c_1(-L + H, t)$ and of the anion ClO$_4^-$ $c_2(-L + H, t)$ at the Stern/diffuse layer interface near the pseudocapacitive electrode ($x = -L + H$) as functions of imposed potential $\psi_s(t)$.

To further elucidate these observations, Figure 5.3 shows the numerically predicted (a) capacitive $j_C$, faradaic $j_F$ and total $j_T$ current densities as well as (b) the concentrations of the cation Li$^+$ $c_1(-L + H, t)$ and the anion ClO$_4^-$ $c_2(-L + H, t)$ at the Stern/diffuse layer interface as functions of the imposed potential $\psi_s(t)$ for the baseline case at scan rate $v = 5$ V/s. The CV curve displays two regimes: (i) in the lower portion of the potential window, the total current density was dominated by the faradaic current and (ii) in the
upper end of the potential window, the capacitive current dominated and the overall current magnitude was smaller. Figure 5.3b indicates that the anions ClO$_4^-$ formed the EDL during the capacitive regime. Their concentration $c_2(-L + H, t)$ at the Stern/diffuse layer interface near the pseudocapacitive electrode reached the maximum packing concentration of 5.52 mol/L quickly after the onset of the capacitive regime. Symmetrically, the cations Li$^+$ were repelled and their concentration $c_1(-L + H, t)$ at the electrode surface was negligible during the capacitive regime. This suggests that the steep drop in the faradaic current observed in the CV curve was due to the starvation of Li$^+$ ions at the electrode/electrolyte interface necessary for the faradaic reaction.

![Figure 5.4: Predicted b-value as a function of imposed potential $\psi_s(t)$ for constitutive relationships corresponding to the baseline case.](image)

Figure 5.4 shows the b-value, obtained from fitting the evolution of the cur-
rent with the scan rate according to the power law $j_T(\psi_s) = a(\psi_s)\psi_s^b(\psi_s)$ as a function of imposed potential $\psi_s(t)$. A dip in $b$-value was observed for potentials around 0.3 V. Such a dip was also observed in 3-electrode experimental measurements and attributed to the oxidation of the metal oxide [53]. However, the numerical simulations established that this potential corresponded to the transition potential between the faradaic and the capacitive regimes observed in Figure 5.3a. This transition corresponded to the steep drop in the total current density observed in both experimental data and numerical simulations shown in Figure 5.2.

5.3.2 Comparison with Equivalent EDL Electrode

Figure 5.5a compares experimental CV curves for an electrode made of carbon nanotubes and for a pseudocapacitive electrode consisting of T-Nb$_2$O$_5$ (orthorhombic) with 1 mol/L LiClO$_4$ in PC as electrolyte and Li metal for the counter and reference electrodes [2]. Similarly, Figure 5.5b shows the numerically predicted CV curves for the baseline pseudocapacitive electrode previously defined as well as for an equivalent electrode in which charge storage was exclusively through EDL formation. Here also, numerical and experimental results show similar behavior for both types of electrodes. The EDL electrode displayed a rectangular CV curve, characteristic of capacitive behavior. On the other hand, the pseudocapacitive electrode featured a large current in the lower portion of the potential window. Interestingly, in the upper end of the potential window, the current density of the pseudocapacitive
Figure 5.5: (a) Experimental measurements of the specific current as a function of imposed potential for a pseudocapacitive electrode consisting of 5 nm Nb$_2$O$_5$ nanocrystal mixed with PVDF (10%) and carbon black (10%) with 1 mol/L LiClO$_4$ in PC as electrolyte and Li metal for the counter and reference electrodes as well as an equivalent electrode consisting of Carbon nanotubes (EDLC). The experimental data was retrieved from Figure 3a of Ref. [2]. (b) Numerically predicted total current density $j_T$ as a function of imposed potential $ψ_s(t)$ for the pseudocapacitive electrode considered in the baseline case as well as for an equivalent EDL electrode.

Electrode matched that of the carbon electrode. This confirms that in this potential region, EDL formation was the main mechanism for charge storage at the pseudocapacitive electrode. Such comparison provide an experimental way to estimate the contribution of EDL formation to charge storage for a given electrolyte.
Figure 5.6: (a) Experimental measurements of the specific current as a function of imposed potential for a pseudocapacitive electrode consisting of T-Nb$_2$O$_5$ (orthorhombic) nanoparticles on a stainless steel current collector with 1 mol/L LiClO$_4$ in PC as electrolyte and Li metal for the counter and reference electrodes as well as a pseudocapacitive electrode consisting of amorphous Nb$_2$O$_5$ in the same conditions. The experimental data was retrieved from Figure 4a of Ref. [3]. (b) Numerically predicted total current density $j_T$ as a function of imposed potential $\psi_s(t)$ for a pseudocapacitive electrode with high conductivity ($\sigma_p = 10^{-3} \text{ S/m}$) and fast Li diffusion ($D_{1,p} = 10^{-12} \text{ m}^2/\text{s}$) as well as for a pseudocapacitive electrode with low conductivity ($\sigma_p = 10^{-4} \text{ S/m}$) and slow diffusion ($D_{1,p} = 10^{-14} \text{ m}^2/\text{s}$).

5.3.3 Crystalline vs. Amorphous pseudocapacitive material

Niobium oxide can be prepared in different phases depending on the synthesis method. The most common forms are amorphous, pseudo-hexagonal (TT-Nb$_2$O$_5$), and orthorhombic (T-Nb$_2$O$_5$). These phases exhibit different electrical conductivity and Li diffusion coefficient. In particular, crystalline phases display larger electrical conductivity than the amorphous phase due
to the increased domain size that enable the charge carriers to follow crystalline pathways [3]. They also feature larger solid-state diffusion coefficient due to the creation of diffusion pathways in the crystalline structure with low energy barrier for easier intercalation [91].

Figure 5.6a shows experimental CV curves for pseudocapacitive electrodes consisting of (i) T-Nb$_2$O$_5$ (orthorombic) nanoparticles or (ii) amorphous Nb$_2$O$_5$ nanoparticles on a stainless steel current collector with 1 mol/L LiClO$_4$ in PC as electrolyte and Li metal for the counter and reference electrodes [3]. Similarly, Figure 5.6b shows numerically predicted CV curves for $\nu = 5$ V/s for a pseudocapacitive electrode with (i) high conductivity ($\sigma_P = 10^{-3}$ S/m) and fast Li diffusion ($D_{1,P} = 10^{-12}$ m$^2$/s) simulating a crystalline phase of Nb$_2$O$_5$ and (ii) an electrode with lower conductivity ($\sigma_P = 10^{-4}$ S/m) and slower diffusion ($D_{1,P} = 10^{-14}$ m$^2$/s) corresponding to amorphous Nb$_2$O$_5$. Here also, numerical and experimental CV curves display very similar shapes and trends for both amorphous and crystalline electrode materials. They indicate that the capacitance was significantly larger for the crystalline phase of Nb$_2$O$_5$ because of better transport properties. Note that the diffusion coefficient $D_{1,P}$ had a stronger effect on the CV curves than the electrical conductivity $\sigma_P$. However, the current density in the capacitive regime appeared to be independent of the phases. This can be attributed to surface charge storage in the EDL in absence of faradaic reactions and Li intercalation.
5.3.4 Effect of Electrode Thickness

Figure 5.7: (a) Numerically predicted total current density $j_T$ as a function of imposed potential $\psi_s(t)$ for different pseudocapacitive electrode thicknesses ranging from 5 to 150 nm. (b) Integral capacitance $C_{s,int}$ as a function of electrode thickness. All other parameters are identical to the baseline case.

Figure 5.7a shows the numerically predicted total current density $j_T$ as a function of imposed potential $\psi_s(t)$ for different pseudocapacitive electrode thicknesses ranging from 5 to 150 nm at scan rate $v = 1 \text{ V/s}$. It indicates that, as the electrode thickness increased, the peak current magnitude initially increased. However, the shape of the CV curve became more rounded. This was due to the onset of a resistive behavior caused by the potential drop across the thicker electrode, as previously discussed.

Figure 5.7b shows the integral capacitance $C_{s,int}$ as a function of the thickness of the pseudocapacitive electrode $L_P$. For the parameters considered in
this chapter, the optimal electrode thickness was around $L_P = 65$ nm. These results illustrate the trade-off faced when designing a pseudocapacitive electrode between offering a large volume for redox intercalation while maintaining acceptable potential drop across the electrode to drive the faradaic reactions.

5.4 Conclusion

This chapter presented a model for simulating cyclic voltammetry of pseudocapacitive electrodes in a three-electrode setup. The model was able to capture accurately the behaviors observed experimentally and to provide unequivocal physical interpretation of actual CV curves reported for Nb$_2$O$_5$ pseudocapacitive electrodes. In particular, the rate behavior and the effect of crystallinity on the charge storage mechanism were clarified. Two regimes were identified: a faradaic regime dominated by redox reactions and a capacitive regime dominated by EDL formation. The transition between the regimes was shown to be caused by Li$^+$ starvation in the electrolyte due to the electrostatic repulsion associated with the ClO$_4^-$ EDL formation. This transition coincided with a dip in the $b$-value. Finally, the trade-off between large energy storage volume and small potential drop across the electrode was illustrated leading to an optimal electrode thickness that maximized the areal integral capacitance.
CHAPTER 6

Conclusion and Future Work

6.1 Main Contributions

6.1.1 Development of Continuum Model

The present study adapted the generalized modified Poisson-Nernst-Planck (GMPNP) model to account for redox reactions and insertion of the reaction product in a pseudocapacitive electrode to simulate hybrid pseudocapacitors subject to cyclic voltammetry. The model simultaneously accounted for (i) charge transport in both the electrodes and the electrolyte, (ii) the formation and dissolution of the electric double layer, (iii) steric repulsion due to finite ion sizes in the electrolyte, (iv) redox reactions at the pseudocapacitive electrode/electrolyte interface, and (v) intercalation of the reaction product in the electrode.

New boundary conditions were derived to simulate an individual pseudocapacitive electrode in three-electrode experiments under cyclic voltammetry accounting for the presence of a reference and a counter electrode. The variation of the equilibrium potential difference $\Delta \psi_{eq}$ with the oxidation state of the electrode was also accounted for, enabling the first simulation of an
individual pseudocapacitive electrode.

6.1.2 Physical Interpretation of Hybrid Pseudocapacitor Behavior

The multi-scale and multi-physics continuum model developed has enabled physical interpretation of experimentally observed features of CV curves. In particular, this study established that hybrid pseudocapacitors with a relatively thick electrode and slow diffusion coefficient can exhibit two distinct regimes. First, a faradaic regime dominated by redox reactions and limited by the diffusion of Li in the pseudocapacitive electrode. Second, a capacitive regime dominated by the formation and dissolution of an EDL at the electrode surface. A $b$-value of unity was associated with both regimes. The dip in $b$-value, often observed experimentally was found to occur at the transition between the two regimes.

Furthermore, the distinctive shape of the CV curve for pseudocapacitive electrodes under cyclic voltammetry was explained to be due to the starvation of Li$^+$ ions at the electrode/electrolyte interface due to the electrostatic repulsion caused by the formation of an EDL of the anions ClO$_4^-$.

6.1.3 Design Rules

The model reported here was used to conducted an extensive parametric study for the design of pseudocapacitive electrodes in a hybrid pseudocapacitor. This study found that the portion of the potential window dominated by
the faradaic regime, named the faradaic potential window, was a key factor of the performance of a hybrid pseudocapacitor. The effect of the electrode thickness and Li diffusion coefficient were investigated for different scan rates. It allowed to quantitatively demonstrate the effect of each of these parameters. Their effects were then combined in a scaling analysis leading to the definition of a dimensionless parameter $Π_f$ linearly related to the fraction of the potential window dominated by faradaic current. Furthermore, above a critical value of this parameter, $Π_f > 0.2$, the device was found to operate in a diffusion-independent regime and the performance was maximized.

6.2 Future Work

6.2.1 Property Measurement

The model derived in this study to simulate pseudocapacitive electrodes was shown to accurately predict the behaviors observed in experimental measurement. However, in order to conduct direct quantitative comparison with experimental observations, the properties of the electrode must be obtained. In particular, the conductivity of metal oxides in thin films increases dramatically with insertion of lithium or potassium. Similarly, the diffusion coefficient of Li in a crystalline metal oxide structure depends on its oxidation state. Finally, the equilibrium potential difference varies with the state of charge of the electrode. The effect of these properties on the performance of a pseudocapacitor was shown in this study and their determination would help further the understanding of the behavior of pseudocapacitive electrodes.
and enable a quantitative design process.

6.2.2 Effect of the 3D Geometry

Although effective properties can be used to account for the porosity of actual electrodes, certain effects cannot be modeled simply. In particular, the effect of curvature in the case of nanoparticles or nano-pores can only be accounted for by performing 3D simulations of pseudocapacitors. Similarly, simulating the effect of multi-scale micro-meso pores in EDLC or pseudocapacitive electrodes could help understand the physics of the phenomenon observed experimentally and lead to better design. Such simulations could help reveal the effects specific to 3D morphology. They would also enable direct comparison with experimental measurements for ordered porous electrodes.
REFERENCES


