



# A lithium-ion battery model including electrical double layer effects



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## HIGHLIGHTS

- An analytical solution for concentration and potential within a separator pore without assuming electroneutrality.
- Examination of the potential drop contributed by the electrical double layer.
- Comparison of resistance predictions with experimental data.

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## ABSTRACT

This paper examines the effect of the electrical double layer on the performance of a lithium ion battery electrochemical cell. We begin by introducing the Poisson Nernst–Planck equations of electrochemistry to describe ion transport within a representative liquid solvent and derive an expression for the current–voltage relationship in the electroneutral liquid within the separator pores. Different assumptions about the electrical double layer lead to variation of the lithium ion concentration profiles in the liquid electrolyte, which alter the cell voltage during discharge. The contribution of the electrical double layer to the cell overpotential is combined with the bulk liquid potential difference and a simplified treatment of the electrode solid phase to obtain an expression for the time-varying cell terminal voltage. We conclude by presenting experimental data for a cell using a graphite anode and lithium iron phosphate cathode to validate the new model, which includes electrical double layer effects, and construct modifications to the model to compensate for resistive effects that are associated with the cathode solid phase.

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## 1. Introduction

Modeling is extremely important to advancing the science of electrochemical energy storage. Direct and dynamic measurements of concentration and electric potential profiles within a Lithium-ion (Li-ion) cell are currently not possible due to the micro-scale physical dimensions of the battery electrodes and separator. As a result, researchers have relied on modeling as a means of understanding the complex processes governing electrochemical cells. There have been a number of fundamental studies of Li-ion battery operation based on porous electrode theory [1] since the original work modeling a lithium-polymer insertion cell [2]. Porous electrode theory is an extremely powerful methodology which accounts for the presence of distinct phases within the battery using

superposition. Detailed knowledge of the surface morphology of electrodes and separator, which is difficult to obtain and computationally prohibitive to model, is not required. The solid microstructure of both electrodes and separator is accounted for only with a pore volume fraction and Bruggeman coefficient for tortuosity. Therefore, concentration and potential profiles are computed in a volume-averaged sense, and models based on porous electrode theory present a macroscopic interpretation of battery electrochemistry. The theory is flexible enough to allow for the inclusion of features that are unique to a given chemistry, such as phase change during intercalation, path dependence, or resistive-reactant nature of electrode active materials. All of these phenomena have been postulated to occur in the graphite/lithium iron phosphate couple that is studied in this paper [3–6].

Since porous electrode models compute averaged quantities over a region that is small with respect to the overall electrode dimensions but large compared to the pore structure [1], Li-ion battery modeling literature typically applies the assumption of electroneutrality within commonly used non-aqueous liquid electrolytes. This assumption is justified based on the assertion that charge separation over a macroscopically significant distance (the

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<sup>1</sup> Units within the Nomenclature section denote the units used for dimensional quantities indicated by the (\*) superscript. If the (\*) superscript is absent then the variables are dimensionless.

**Nomenclature**<sup>1</sup>

$\alpha$	Butler–Volmer transfer coefficient
$\gamma$	active material volume fraction
$\varepsilon$	ratio of Debye length to separator thickness, $\lambda/L_{\text{sep}}$
$\varepsilon_e$	electrical permittivity ( $\text{F m}^{-1}$ )
$\zeta$	zeta potential, or equivalently the potential difference across the diffuse layer (V)
$\lambda$	Debye length (m)
$\phi$	electric potential (V)
$A$	current collector area ( $\text{m}^2$ )
$C$	current magnitude in terms of cell capacity ( $1C = 2.3 A$ )
$c$	concentration ( $\text{mol m}^{-3}$ )
$c_0$	electroneutral concentration ( $\text{mol m}^{-3}$ )
$D$	diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$F$	Faraday constant ( $\text{C mol}^{-1}$ )
$I$	external current demand (A)
$J$	current density ( $\text{A m}^{-2}$ )
$J_D$	diffusion limited current density ( $\text{A m}^{-2}$ )
$J_s$	solid boundary flux scale ( $\text{A m}^{-2}$ )
$k_o$	chemical reaction rate constant for oxidation reaction ( $\text{A m mol}^{-1} \text{s}^{-1}$ )
$k_r$	chemical reaction rate constant for reduction reaction ( $\text{A m}^4 \text{mol}^{-2} \text{s}^{-1}$ )
$L$	thickness of separator, anode, or cathode (m)
$n$	index for infinite series solution
$Q$	capacity removed (Ah)
$R$	universal gas constant ( $\text{J mol}^{-1} \text{K}$ )
$R_c$	contact resistance ( $\Omega \text{m}^2$ )
$R_{rr}$	resistive reactant resistance ( $\Omega \text{m}^2$ )
SOC	state of charge
$T$	temperature (K)
$\tau$	separation of variables function of time
$t$	time (s)
$U$	open-circuit voltage relative to Li/Li <sup>+</sup> (V)
$V$	terminal voltage (V)

$V_L$	liquid phase voltage (V)
$V_{rr}$	resistive reactant overpotential (V)
$X$	separation of variables function of space
$x$	spatial variable in direction across unit cell thickness (m)
$y$	inner solution spatial variable, $x/\varepsilon$
$z$	ion valence

**Subscripts**

$\infty$	denotes a property at the interface between electroneutral liquid and EDL
$A$	refers to a cation (Li <sup>+</sup> ) property
$B$	refers to an anion (PF <sub>6</sub> <sup>-</sup> ) property
$a$	$c_{A,\text{an}}/c_{A,\text{an},\text{max}}$
an	denotes a property of the anode
$b$	$c_{A,\text{ca}}/c_{A,\text{ca},\text{max}}$
ca	denotes a property of the cathode
EDL	property of the electrical double layer in its entirety, including Stern and diffuse layers
$i$	refers to a cation property if $i = A$ or an anion property if $i = B$
$j$	refers to an anode property if $j = \text{an}$ or a cathode property if $j = \text{ca}$
max	denotes the saturation concentration value
$s$	Stern layer property
sep	refers to a separator property

**Superscripts**

+	denotes an ion with valence equal to 1
-	denotes an ion with valence equal to -1
*	dimensional quantity
~	refers to the non-equilibrium portion of EDL electric potential
^	refers to electric potential defined relative to the adjacent bulk potential

volume averaging distance) would require a prohibitively large electric field [7]. However at the boundary between the liquid and solid phases, an interfacial region known as the electrical double layer (EDL) exists where the assumption of electroneutrality no longer holds [8]. A method of accounting for capacitive effects of the EDL in cell terminal voltage has previously been presented [9]. The scope of Ref. [9] did not encompass some important features of the EDL such as the coupling between ion concentration and potential described in several classical works [10–13]. Given the general lack of literature pertaining to the EDL as it applies to Li-ion batteries, we feel it is appropriate to examine this feature in greater detail.

A more accurate understanding of the EDL is important for its impact on interfacial charge transfer. Porous electrode models postulate that charge transfer kinetics are governed by the potential difference between the solid phase and the electroneutral portion of the liquid outside the EDL [7]. This assumption is made implicitly in the application of Butler–Volmer kinetics, which is treated as a semi-empirical relationship (though possessing fundamental origins) between the local intercalation current and the potential difference between solid and liquid relative to the open-circuit voltage versus a hypothetical lithium reference electrode. However, the Stern layer is the location of the reaction plane and the potential difference across it represents the actual activation energy barrier for the intercalation reaction [10]. Thus it is of

fundamental interest to consider only the Stern layer potential difference when examining the current–voltage relationship of electrode kinetics. The two cases of EDL physics are that the entire potential difference occurs within either the Stern layer or the diffuse layer. A complete methodology for dividing the potential difference of the EDL between the diffuse layer and the Stern layer is discussed in Ref. [10] in relation to a micro-battery, and for galvanic cells in Ref. [14]. Results are presented for a range of kinetic rate constants selected to examine various limits of battery operation with no particular system studied. For an intercalation battery, the effective rate constant changes over the course of discharge due to the changes in active material lithium content. This phenomena is governed by the composition ranges of the electrodes chosen by the manufacturer and the cell state of charge (SOC), and provides a physical mechanism for alteration of the effective rate constants over the course of discharge.

The objective in this paper is to develop an analytical model that can predict battery voltage during discharge. The presented model structure accounts for the potential difference in the electroneutral liquid within the separator pores, as well as a microscopic interpretation of the EDL, which leads to a novel view of electrode kinetics. We first present the model development, where we make use of the Poisson–Nernst–Planck equations to model liquid phase transport and solve a representative solid diffusion problem in each electrode. Two alternate descriptions of the EDL potential are used

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