



A mass transfer based variable porosity model with particle radius change for a Lithium-ion battery



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ABSTRACT

Micro pore-clogging in the electrodes due to SEI growth and other side reactions can cause adverse effects on the performance of a Lithium-ion battery. The fundamental problem of volume fraction variation and particle radius change during the charge-discharge process in a lithium-ion battery is modelled in this paper with the help of mass transfer based formulation and demonstrated on a battery with LiCoO₂ chemistry. The model can handle the volume fraction change due to intercalation reaction, solvent reduction side reaction and the electrolyte density change due to side reaction contamination in the battery. The entire calculation presented in this paper models particle radius and volume fraction together and therefore gives greater accuracy in calculating the volume-specific-area of the reacting particles which is an important parameter controlling the Butler-Volmer kinetics. The mass deposit on the electrode (or loss of lithium) gives an indication of the amount of pre-lithiation required to maintain cell performance while the amount of mass deposited on the SEI helps to decide the safe operating condition for which the clogging of pores and capacity fade will be minimal. Moreover the model presented in this paper has wide applicability in analysing the stress development inside the battery due to irreversible porous filling.

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1. Introduction

A Pseudo Two Dimensional (P2D) model offers flexibility in solving the interlinked chemical governing equations of a Lithium-ion battery based on concentrated solution theory [1,2]. The volume fraction change during charging and discharging, and the Solid Electrolyte Interphase (SEI) grows over the particles forming a porous film, which is responsible for the lithium loss and voltage drop [3]. The pores expand and contract during normal charging and discharging imposing stress on the interior layers of the battery; [4] suggests that the stress could be of significant level and even could damage the particle near the separator. A higher stress development can be also observed in batteries with Silicon anode material [5,6]. The capacity fade of the battery can get accelerated by constriction of pores in the electrode, due to side reactions. SEI build up increases the internal resistance of the battery leading to excessive heat generation while charging and discharging. The

fact that excessive heat generation accelerates the SEI growth has been already proven by researchers and therefore this effect can lead to accelerated power fade and capacity fade. Parametric studies with different heat transfer coefficient and the resulting SEI growth can be found in Ashwin *et al.* [7] for a single cell battery and for a battery pack in Ashwin *et al.* [8]. Thus the intercalation and other side reactions need to be captured accurately to model the volume fraction change. Moreover, many of the empirical relations used in earlier models can be eliminated by including a time varying volume fraction. The motivation for this paper is to develop a more fundamental model which predicts the mass transfer across the anode-separator-cathode boundaries by measuring the Li⁺ concentration in the electrolyte within the framework of a P2D model.

Han *et al.* [9] modelled the intercalation process with phase field variables which is accurate and allows simpler tracking of phase boundaries than Fick's equation. There were other studies such as Singh *et al.* [10] who developed a continuum based theory for the intercalation process in a single crystal rechargeable battery. Another model was presented by Teixidor *et al.* [11] for the analysis of fractal-like electrodes for lithium-ion batteries and this study proved an optimal electrode configuration of the fractals for electrochemical energy storage. Thus, most of the intercalation studies are either on a crystalline battery or on flow batteries. There have

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Nomenclature

a	Active surface area per unit volume (cm^{-1})
A	Electrode plate area (cm^2)
c	Volume-averaged concentration (mol cm^{-3})
D	Diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
F	Faraday constant, 96487 C mol^{-1}
i_0	Exchange current density for intercalation reaction (A cm^{-2})
i_{os}	Exchange current density for solvent reduction reaction (A cm^{-2})
I_{app}	Applied current (A)
J_1	Reaction current for intercalation reaction (A cm^{-3})
J_s	Reaction current for solvent reduction reaction (A cm^{-3})
K	Number of spherical particles
L	Cell width (cm)
M, \hat{M}	Initial mass, Mass at a time step during battery operation (kg)
Q	Cycle number
r	Radial coordinate (cm)
R	Universal gas constant, $8.3143 \text{ (J mol}^{-1} \text{K}^{-1})$
ΔX	Length of the control volume (cm)
t	Time (s)
t_+^0	Transference number
V	Cell voltage (V)
\bar{V}	Volume (cm^3)
\hat{V}	Molar mass (g/mol)

Greek Symbols

ρ	Density (kg cm^{-3})
α_a, α_c	Charge-transfer coefficient
δ	Thickness (cm)
ϵ	Volume fraction of domain
Λ	Particle radius (cm)
η	Over potential (V)
κ	Conductivity of electrolyte (S cm^{-1})
κ_D	Diffusivity (A cm^{-1})
σ	Solid phase conductivity (S cm^{-1})
ϕ	Volume averaged potential (V)
χ	Volumetric mass of porous media (kg cm^{-3})

Superscript and subscript

avg	average
cv	Control volume
eff	Effective
e, s, f	Electrolyte, solid and binder
SEI	Solid Electrolyte Interphase
n, p, sep	Negative, positive and separator
t	time step

List of Acronyms

P2D	Pseudo Two Dimension
SEI	Solid Electrolyte Interphase
SoC	State of Charge

been many studies on SEI growth due to side reactions, but very few studies quantified mass deposition due to intercalation process for example Pinson and Bazant [12].

The existing models have helped to understand the intercalation process and the growth of chemical deposition in a battery more clearly. However, there are very few modelling contributions on the side reactions and mass deposition due to SEI growth. One of the novel contributions to model capacity fade in a battery is by

Ramadass [13] *et al.* who developed a capacity fade model under the assumption of a continuous solvent reduction side reaction. This model helped researchers to quantify the resistance increase due to SEI growth and the resulting change in voltage-current characteristics. The SEI growth has been studied by several other researchers, for example Radvanyi *et al.* [14] who used an impedance spectroscopy method to investigate the instability of the SEI on the surface of the silicon particles. A general model for the discharge deposit formation is studied by Wang [15] for a lithium-air battery, who found that the discharge products precipitate at reaction sites increasing the particle radius. The present work is inspired by this study to develop a variable volume fraction, variable particle radius model for a lithium-ion battery within the framework of a P2D model.

The internal stress imposed by the two chemical reactions of intercalation and the SEI deposition, is studied by few researchers. The modelling study by Renganathan *et al.* [4] shows that stress generation caused by phase transformation could be significant. The influence of external stress was investigated by few other researchers for example, Gao *et al.* [16] studied the yield stress of a Li_xSn battery material as the change of charge states. A detailed study on the effect of external stress on batteries can be found in Kim [17] who identified and quantified key sources of mechanical stresses including manufacturing-induced loads, thermal loads, kinetic loads and structural loads and the findings were verified using molecular dynamics simulations. The stress level is significantly large in Silicon anode batteries and a detailed study is presented by Beattie *et al.* [5,6]. A two-phase transition model has been developed by Li *et al.* [18] during galvanostatic charging and discharging for a lithium iron phosphate (LFP) battery. The lithiation and delithiation in LFP particles is approximated using a shrinking core with a moving interface between the two phases. However, to capture these effects accurately, the volume fraction change also should be modeled from fundamental chemical reactions.

There were attempts to simplify the chemical reactions in a battery using correlations or by using theoretical parameters. A correlation based electrochemical model for a graphite electrode was presented in Novak *et al.* [19]. The results show that by adjusting the volume fraction, the electrochemical performance of graphite electrodes could be improved. The present work is aiming to remove the correlation based approach used by models like Novak *et al.* and thereby modelling the chemical reactions from fundamental kinetics.

Later, Gu *et al.* [20] and Sikha *et al.* [21] modelled the change in volume fraction due to irreversible parasitic side reactions. In all of the referenced models, the volume change was linked to the partial molar volume of the reacting species, which is difficult to measure. Moreover, this model needs information about SEI growth to calculate irreversible porous filling therefore the research community is looking forward to overcoming this limitation. Moreover, there can be variations in molar concentration due to side reaction contamination [22]. Another notable attempt was made by Yoo *et al.* [23] who used a moving boundary to capture the volume change in a Lithium-air battery and Garrick *et al.* [24] who correlated volume fraction change to stress development. Ashwin *et al.* [7,8] developed a variable volume fraction model linked to capacity fading and distributed thermal model. This model was successful in predicting different amounts of micro-pore plugging but the volume fraction variation was again based on partial molar volume.

The above mentioned studies proved that the property variation in an electrolyte has severe implications on the performance of a battery. Unfortunately, to the best of authors knowledge, there were no theoretical investigations to quantify the density change or property change in an electrolyte of a lithium-ion battery caused by various side reactions. There are several experimental

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