An integrated reduced order model considering degradation effects for LiFePO$_4$/graphite cells

Xinchen Zhao [a], Yalan Bi [a], Song-Yul Choe [a, *], Soo-Yeol Kim [b]

[a] Department of Mechanical Engineering, Auburn University, AL, 36849, USA
[b] KEPCO R&D Center, 105 Munji-ro, Yuseong-gu, Daejeon, 305-760, South Korea

ABSTRACT

A reduced order model (ROM) considering degradation effects is proposed and validated against experiments for both fresh and cycled lithium iron phosphate (LFP)/graphite cells. The ion behaviors in the LFP particles such as two-phase transition and path dependence are modeled using a shrinking core with a moving interface between a lithium-rich and a lithium-deficient phase. The model errors are further minimized by employing the Extended Kalman Filter (EKF) to achieve a more accurate state-of-charge (SoC) estimation. The average error of SoC and voltage estimation is kept within 4% and 2%, respectively. Side reaction is regarded as the predominant cause of degradation, which can be accelerated by elevated temperatures, high SoC levels and large SoC cycling limits. The effects of operating conditions on degradation are described by a modified Butler-Volmer equation that is incorporated into the developed ROM. The integrated model facilitates to represent the degradation effects of side reaction, including loss of ions, loss of active material, growth of solid electrolyte interphase and deposit layer, and electrolyte decomposition. The model is capable of estimating capacity and power with an accuracy of 2% and 3% up to 1000 cycles, respectively.

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1. Introduction

Lithium iron phosphate (LFP), firstly introduced by Padhi [1] et al., is a potential cathode material undergone remarkable developments in the commercial market of lithium ion batteries (LiBs), due to the characteristics of good electrochemical and thermal stability [2]. Compared with the electrodes embedded by Ni, Mn, Co, LFP based electrodes have the characteristics of two-phase transition and path dependence in both charge and discharge cycles. Srinivasan and Newman [3], Wang et al. [4] and Kavasajjula et al. [5] successively proposed a full order model (FOM) based on the concept of a shrinking core to simulate the discharge behaviors of both half and full cells with consideration of phase transformation rate, two-phase interface mobility and diffusion coefficients in both lithium-rich (Li$_{1-\beta}$FePO$_4$) and lithium-deficient phase (Li$_{\alpha}$FePO$_4$). The electrochemical behaviors of charge profiles were validated by incorporating Laudau transformation to generate a moving boundary [6]. In spite of high accuracy, complexity of the parameters and high computational efforts limit the real-time

application of FOM. Plenty of reduction methods have been applied to reduce the execution time with accuracy maintained, such as single particle model (SPM) [7], enhanced SPM [8,9], state-variable model [10], reformulated model [11], proper orthogonal decomposition (POD) [12] model and volume averaging model [13]. However, the lack of predictive capability of end-of-life (EoL) performance impedes its use in the battery management system (BMS).

The degradation of LiBs corresponding to calendar life [14,15] and cycle life [16–19] is as the results of exposing to the ambient environment and cycling usage, respectively. The capacity and power fade are not caused by a single reason, but from large varieties. The inter-dependency of various degradation causes makes the comprehension of degradation mechanism more difficult. Schematic diagram of potential degradation mechanism taking place at composite electrodes, separator and current collectors is depicted in Fig. 1.

Degradation phenomena occurring at positive and negative electrode are significantly different. Researchers have identified the side reaction taking place at the interface between electrode and electrolyte at anode as the predominant cause of degradation for LiBs [20–30]. The main reaction is the intercalation/de-

Nomenclature

A	sandwich area of the cell (m^2)
a_s	specific surface area of electrode (m^{-1})
c	ion concentration ($mol\,L^{-1}$)
D	diffusion coefficient($m^2\,s^{-1}$)
F	Faraday constant ($96,487\,C\,mol^{-1}$)
I	current of the cell (A)
i_0	exchange current density of intercalation (Am^{-2})
j^{Li}	reaction rate of intercalation (Am^{-3})
k_s	isolation coefficient due to SEI
L	thickness of the micro cell (cm)
Q	capacity of the cell (Ah)
Q	amount of ion loss caused by side reaction (Ah)
R	resistance ($\Omega\,m^2$) or universal gas constant ($8.314\,J\,mol^{-1}\,K^{-1}$)
R_s	radius of spherical electrode particle (m)
R	coordinate along the radius of electrode particle (m)
T	cell temperature (K)
t	time (s)
U	potential (V)
V	voltage (V) or volume of the composite electrode (m^3)
$\tilde{V}$	molar volume ($m^3\,mol^{-1}$)
x	stoichiometric number of the anode
y	stoichiometric number of the cathode

Greek symbols

α	transfer coefficient for an electrode reaction
δ	thickness (m)
ε	volume fraction of a porous medium
Φ	potential (V)
η	over-potential of electrode reaction (V)
κ	ionic conductivity ($S\,m^{-1}$)
σ	conductivity ($S\,m^{-1}$)

Subscripts and Superscripts

a	anodic
act	actual
$aged$	aged cell
ave	average value
c	cathodic
e	electrolyte phase
eff	effective
equ	equilibrium
error	error
exp	experiment
$fresh$	fresh cell
Li	lithium ion
$main$	main reaction
max	maximum
r	radial direction in electrode particle
s	solid phase
$side$	side reaction
sim	simulation
$surf$	electrode particle surface
0%	0% SoC
100%	100% SoC
$+$	positive electrode (cathode)
$-$	negative electrode (anode)
Θ	standard

intercalation of lithium ions to/from the electrode solid matrix during cycling. The side reaction takes place between the lithium ions and the electrolyte solvents, which leads to the formation of the unsolvable byproducts that are the main components of the solid electrolyte interphase (SEI) layer. The side reaction is described in Eqs. (1) and (2).
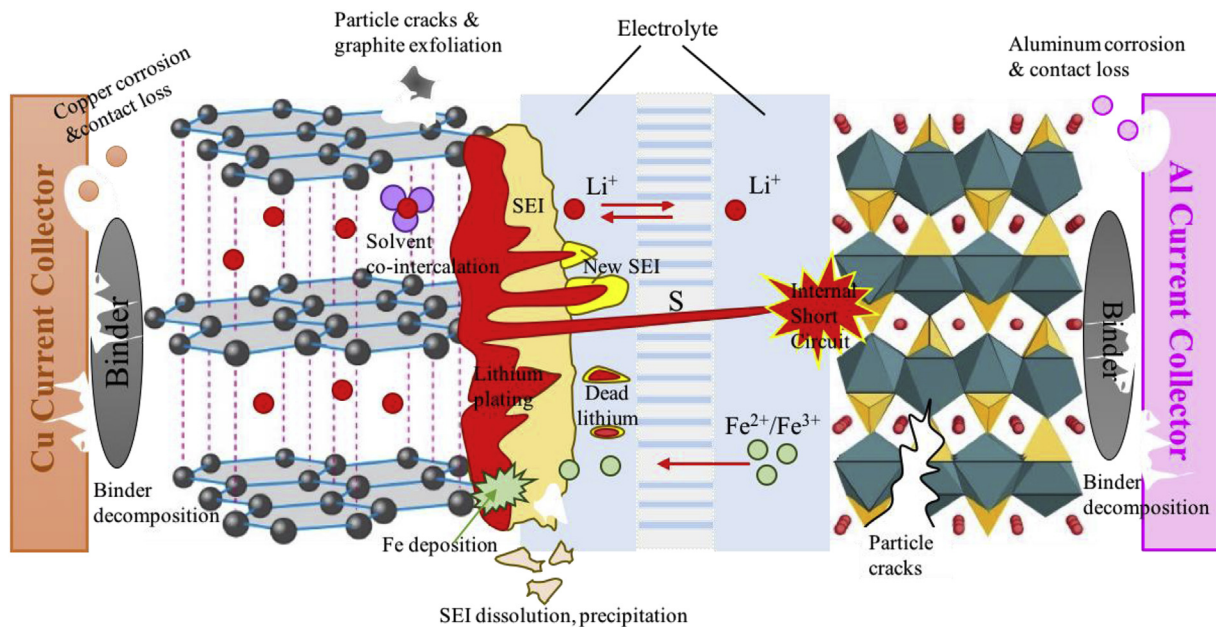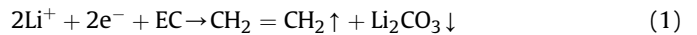
$$2Li^+ + 2e^- + EC \rightarrow CH_2 = CH_2 \uparrow + Li_2CO_3 \downarrow \qquad (1)$$

Fig. 1. Schematic diagram of degradation mechanism in LFP/graphite cells.