Modeling of degradation effects and its integration into electrochemical reduced order model for Li(MnNiCo)O$_2$/Graphite polymer battery for real time applications

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ABSTRACT

Previously, a highly efficient reduced order model (ROM) for Li(MnNiCo)O$_2$/Graphite polymer battery based on electrochemical principles has been developed for real time applications. The execution time is significantly reduced compared to that of the electrochemical thermal full order model while beginning of life of the battery with the approximately same accuracy can be predicted. However, prediction of the end of life associated with degradation effects of battery was not included. Our investigations on aging mechanisms of the Li(MnNiCo)O$_2$ (MNC) lithium ion batteries have revealed that side reaction is the main cause among others for capacity and power fade of the battery. The production of the side reaction forms thin unsolvable layers that adhere to the surface of the graphite particles and grow as cycled, which is called solid electrolyte interphase (SEI). Growth of the SEI leads to loss of the lithium ions, loss of the electrolytes and loss of the active volume fraction. These effects are described using the Butler-Volmer kinetics and aging parameters. Particularly, electrolyte solvent diffusion described by Fick's law is integrated into the degradation model, which results in quantifying the electrolyte solvent concentration in SEI. The exchange current density of the side reaction is formulated as a function of electrolyte solvent and lithium ion concentration, which justifies the reaction rate in the aspect of reactants. In addition, temperature dependency of the model parameters is also considered by adopting the energy equations. Finally, the degradation model is incorporated into the ROM.

Performances of the integrated ROM are compared with the experimental data collected from a high power pouch type lithium ion polymer battery with Li [MnNiCo]O$_2$/Graphite chemistry.

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1. Introduction

Lithium ion batteries have been widely adopted as energy storage for different power systems due to their high power and energy density. The safety and reliability of the battery operations are ensured by battery management system (BMS) that monitors overcharge and undercharge of batteries using state of charge and health estimated based on model. The model can be constructed using equivalent electric circuit or electrochemical thermal principles [1]. Computation of the responses of the battery using electrochemical models is performed numerically, which requires high computational time. As a result, the model is not appropriate for real time applications. Recently, we proposed a highly efficient

reduced order model (ROM) based on the electrochemical and thermal principles for real time applications [2]. The ROM employed different model reduction techniques that include Padé approximation, residue grouping, proper orthogonal decomposition and linearization, so the computational time has been substantially reduced compared to that of the electrochemical thermal full order model, while the accuracy is still maintained. However, the developed ROM can only predict the responses at beginning of life of batteries. Lacking of aging effects in the model limits its practical uses for BMS, particularly in estimation of capacity and power fade. Degradation of performance of batteries is primarily induced by operating conditions and results in production of byproducts, morphology changes of electrodes and ion diffusivity of electrolyte.

The major causes and effects for degradation are summarized in Table 1.

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Nomenclature

A	sandwich area of the cell (cm^2)
a_s	specific surface area of electrode (cm^{-1})
c	ion concentration ($mol\,L^{-1}$)
D	diffusion coefficient($cm^2\,s^{-1}$)
F	Faraday constant ($96,487\,C\,mol^{-1}$)
I	current of the cell (A)
i_0	exchange current density of intercalation (Acm^{-2})
j^{Li}	reaction rate of intercalation (Acm^{-3})
k_{iso}	isolation coefficient due to SEI
L	thickness of the micro cell (cm)
MNC	$Li(MnNiCo)O_2$
OCV	open circuit voltage (V)
Q	capacity of the cell (Ah)
q	amount of ion loss caused by the side reaction (Ah)
R	resistance ($\Omega\,cm^2$) or universal gas constant ($8.3143\,J\,mol^{-1}\,K^{-1}$)
R_s	radius of spherical electrode particle (cm)
r	coordinate along the radius of electrode particle (cm)
SOC	state of charge
SEI	solid electrolyte interphase
T	cell temperature (K)
t	time (s)
U	potential (V)
V	voltage (V) or volume of the composite electrode (cm^3)
$\overline{V}$	molar volume ($cm^3\,mol^{-1}$)
x	stoichiometric number of the anode
y	stoichiometric number of the cathode

Greek symbols

α	transfer coefficient for an electrode reaction
δ	thickness (cm)
ε	volume fraction of a porous medium
ϕ	Finite element method (FEM) solution of potentials
η	surface overpotential of electrode reaction (V)
κ	ionic conductivity of electrolyte ($S\,cm^{-1}$)
σ	conductivity ($S\,cm^{-1}$)

Subscripts and superscripts

a	anodic
ave	average value
c	cathodic
D	diffusion
EC	ethylene carbonate
e	electrolyte phase
eff	effective
$equi$	equilibrium
Li	Lithium ion
$main$	main reaction
max	maximum
r	radial direction in electrode particle
s	solid phase
sep	separator
$side$	side reaction
$surf$	electrode particle surface
T	terminal
0%	0% SOC
100%	100% SOC
+	positive electrode (cathode)
-	negative electrode (anode)

Among the aging causes, the side reaction taking place at the anode graphite particle surfaces is the most predominant cause of the battery degradation. The main reaction is the process that lithium ions intercalate and de-intercalate on the surface of the electrode particles when cycling. In contrast, the side reaction refers to the electrolyte decomposition reaction that is sustained slowly but constantly throughout the battery life. It is particularly severe during charging process when the anode is polarized and its potential becomes low, which is then stimulated by elevated temperature and high SOC range [3].

The side reaction consumes lithium ions as well as solvents of electrolyte, and produces deposits that form thin unsolvable layers that adhere to the surface of the anode graphite particles. A schematic diagram reproduced from Ref. [4] below in Fig. 1 shows the main and side reaction that take place concurrently at the anode graphite particle surface and the formation of the solid electrolyte interphase (SEI).

Several possible reaction mechanisms and products dependent upon various electrolyte solvent mixtures are reported in the literature [5,6]. Since ethylene carbonate (EC) is the organic solvent used for the electrolyte of the investigated batteries, only two predominant side reactions as shown below are considered [5]:
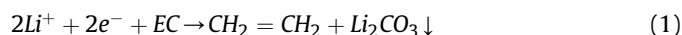
$$2Li^+ + 2e^- + EC \rightarrow CH_2 = CH_2 + Li_2CO_3 \downarrow \qquad (1)$$

Table 1
Summary of degradation mechanisms.

Components	Major causes	Effects and consequences	Enhanced by
Graphite particle anode	• Side reaction (electrolyte solvent decomposition)	• SEI formation • Loss of lithium ion • Loss of active material • Increase of impedance • Gas generation and particle cracking • Corrosion of current collector • Self-discharge	• High temperature • High SOC range
	• Low temperature operation • Overcharge	• Lithium plating • Loss of lithium ion (Loss of electrolyte in subsequent reaction with Li metal)	• Low temperature • High charge rate
Separator (electrolyte)	• Side reaction	• SEI formation • Loss of electrolyte	• High temperature • High SOC range
Metal oxide cathode	• Mechanical stress and strain	• Phase transition and structural changes • Cracking and fracture	• High temperature