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Modeling of degradation effects considering side reactions for a pouch type Li-ion polymer battery with carbon anode

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HIGHLIGHTS

- We have experimentally characterized degraded cells by studying their capacities, impedances, morphologies and compositions.
- Based on the experimental findings, four degradation parameters are identified and a degradation model is developed.
- The deposits electronically isolate certain anode particles, reducing the amount of active anode and causing capacity fade.
- The resistance of the deposit layer estimated by the degradation model has the same trend as its thickness measured by SEM.

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ABSTRACT

When a lithium ion polymer battery (LiPB) is being cycled, one major cause for degradations is the irreversible side reactions between ions and solvent of electrolyte taking place at the surface of anode particles. SEM analysis of cycled battery cells has revealed that the deposits from the side reactions are dispersed not only on particles, but also between the composite anode and the separator. Thus, the solid electrolyte interface (SEI) becomes thicker and extra deposit layers are formed between composite anode and separator. Also, XPS analysis showed that the deposits are composed of Li_2CO_3, which is ionic conductive and electronic nonconductive. Based on the mechanisms and findings, we identified four degradation parameters, including volume fraction of accessible active anode, SEI resistance, resistance of deposit layer and diffusion coefficient of electrolyte, to describe capacity and power fade caused by the side reactions. These degradation parameters have been incorporated into an electrochemical thermal model that has been previously developed. The terminal voltage and capacity of the integrated model are compared with experimental data obtained for up to 300 cycles. Finally, the resistance of the deposit layer calculated by the model is validated against the thickness of the deposit layer measured by SEM.

1. Introduction

The lithium ion battery has become the most preferred electrochemical energy storage device because of its high energy density, power density and columbic efficiency. When a cell is being cycled, there are various degradation processes that take place in different cell components as a function of operating conditions. These processes have not been well understood, so it is very hard to predict the life of the battery. One of the causes for degradation that has been identified is the side reactions caused by reduction of the electrolyte [1–8]. The side reactions take place in the region where the composite carbon anode is mixed with electrolyte and consumes lithium ions and the electrolyte solvents to produce deposits. The deposits cover anode particles, which reduces the active area and increase ionic resistance. As a result, capacity and power fade occur.

One of the causes for the side reactions at the anode is the low potential difference between electrode and electrolyte. When charging starts, the flow direction of ions is reversed from electrolyte to solid, so the potential between the electrode and electrolyte decreases [7]. When the potential across the anode and electrolyte is less than 0.5 V, a reduction process between the solvent of electrolyte and Li^+ is induced [8]:

$$S + 2Li^+ + 2e^- \rightarrow P$$

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Nomenclature

A	sandwich area of the cell (cm^2)
a_s	specific surface area of electrode (cm^{-1})
c_s	ion concentration in solid phase ($mol\ L^{-1}$)
c_e	ion concentration in electrolyte ($mol\ L^{-1}$)
C_p	heat capacity ($J\ kg^{-1}\ K^{-1}$)
D	diffusion coefficient ($cm^2\ s^{-1}$)
E_{chem}	electrochemical energy ($J\ cm^{-3}$)
F	Faraday constant (96,487 $C\ mol^{-1}$)
h_c	convective heat transfer coefficient ($W\ cm^{-2}\ K^{-1}$)
I	current of the cell (A)
i	current density ($A\ cm^{-2}$)
i_0	reference exchange current density ($A\ cm^{-2}$)
j	reaction rate ($A\ cm^{-3}$)
L	thickness of micro cell (cm)
l	coordinate along the thickness of micro cell
n	amount of Li ion (mol)
OCV	open circuit voltage (V)
P_{chem}	power contributing to the increase of chemical energy ($W\ cm^{-3}$)
Q_{max}	capacity of the cell (A h)
q_{rev}	reversible heat generation rate ($W\ cm^{-3}$)
q_{irr}	irreversible heat generation rate ($W\ cm^{-3}$)
q_{convec}	heat convection rate ($W\ cm^{-3}$)
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
T	cell temperature (K)
T_∞	ambient temperature (K)
t	time (s)
U_{equi}	equilibrium potential (V)
V	voltage (V) or volume of the composite electrode (cm^3)
x	stoichiometric number in anode
y	stoichiometric number in cathode
t_+^0	initial transference number

Greek symbols

α	transfer coefficient for an electrode reaction
δ	thickness (cm)
ε	volume fraction of a porous medium
ϕ_e	potential in electrolyte phase (V)
ϕ_s	potential in solid phase (V)
η	surface overpotential of electrode reaction (V)
κ	ionic conductivity of electrolyte ($S\ cm^{-1}$)
κ_D	concentration driven diffusion conductivity ($A\ cm^{-1}$)
σ	conductivity ($S\ cm^{-1}$)

Subscripts

cc	current collector
cell	micro cell
DL	deposit layer
EIS	measured by EIS
e	electrolyte phase
max	maximum
n	negative electrode (anode)
p	positive electrode (cathode)
r	radial direction in electrode particle
SEI	solid–electrolyte interface
SEM	measured by SEM
s	solid phase
T	terminal
0%	0% state of charge
100%	100% state of charge

Superscripts

eff	effective
Li	lithium ion
*	dimensionless

where S denotes lithium ions and the solvent of electrolyte and P denotes the product that is deposited at the anode side [5–7]. In contrast, the potential at the cathode is high enough, so no electrolyte reduction can take place during either charge or discharge.

The deposits produced from the side reactions are composed of organic materials, such as $(CH_2OCO_2Li)_2$, and inorganic materials, such as Li_2CO_3 [7,8,10] and form a very thin extra film that adheres to the surface of the anode particles as solid electrolyte interface (SEI) [8]. Although the SEI is intentionally formed during the initial charging cycles by manufacturers, the side reactions continue and produce deposits that accumulate during cycling over a long time scale [1,4,9,10]. The accumulation of the deposits changes the thickness of the SEI. Since the deposits are ion conductive, the ionic resistance of the SEI increases, which leads to power fade. In contrast, these deposits are all electronic isolators [7,8,10] that completely isolate certain number of particles from electrons needed for chemical reactions so that these particles are no more available for active chemical reaction, which causes loss of active material and leads to capacity fade [3,4,7,21].

There have been various experimental attempts to characterize effects of side reactions on the morphology and compositions of materials using SEM, XRD, TEM, etc. [7–9,11–17]. In addition, electrochemical impedance spectroscopy (EIS) has been used to extract the electrochemical parameters [11,18,19].

On the other hand, there have been many approaches to theoretically analyze the degradation mechanism using electrochemical models, where changes of internal parameters subject to the degradation processes are considered [1–6,20,24,29].

Several authors have developed physical equations for the side reactions and incorporated them into electrochemical models [1,2,4]. Doyle et al. firstly proposed equations based on the Butler–Volmer equation that describe the side reactions that take place on the anode side [2], but no simulation was carried out. Based on the Dolye's work, Ramadass et al. developed a model for side reactions that is incorporated into electrochemical model and simulated capacity fade caused by loss of ions [1]. Both works described the side reactions based on the reaction current rate, j^{Li}, that is a sum of the intercalation and side reaction current. The amount of deposits from the side reactions is determined by integrating the side reaction current density. Sikha proposed a similar model for the side reactions, where effect of deposits on the porosity is considered [4]. However, none of the models aforementioned have considered the effects of deposits on capacity fade or have been validated experimentally.

Other authors have proposed semi-empirical models that are derived from experimental data collected at different stages of degradation, where the parameters are dependent upon operating conditions, particularly as functions of cycle number [3,5,6,21]. Typical parameters used for modeling the capacity fade are the anode SOC [3,4,21] and cathode SOC [3,4] that are adjusted at the