



# Activity correction on electrochemical reaction and diffusion in lithium intercalation electrodes for discharge/charge simulation by single particle model



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## ABSTRACT

The activity correction for the electrochemical reaction and diffusion of lithium in the intercalation electrodes where structurally phase transition occurs during discharge and charge processes was examined. The equilibrium potentials for the lithium intercalation electrodes were represented successfully by the Nernst equation with the activity correction, which was expressed by the activity coefficient models for non-ideal behavior in LiCoO<sub>2</sub> and mesocarbon-microbeads (MCMB) electrodes. Particularly for the LiCoO<sub>2</sub> electrode, the NRTL model with the heterogeneous treatment was found to be suitable to describe accurately the concentration dependence of equilibrium potentials and phase transition in the electrode. Thereby, we formulated the particle-scale model by using the activity correction with the heterogeneous treatment for the diffusion of lithium in the intercalated electrodes and the electrochemical reaction on the surface of electrode particles in order to reproduce the discharge/charge voltage profile. In the heterogeneous treatment, we considered that the effective diffusivity and electrochemical reaction rate in coexisting region of two different phases for LiCoO<sub>2</sub> electrode were able to be calculated by a linear function of lithium concentration. It was observed that the activity correction and heterogeneous treatment improved the prediction accuracy for the particle-scale diffusion model coupled with the electrochemical reaction model.

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## 1. Introduction

Lithium-ion batteries are widely used in various application field, owing to their high energy density and long cycling capability. The composite electrodes used in lithium-ion batteries consist of active particles for anode, cathode, binders, and conductive connectors. A transition metal oxide such as LiCoO<sub>2</sub> is commonly used as the active material in the cathode. The anode active material is often made out of lithiated graphite such as mesocarbon-microbeads (MCMB). The composite electrodes formed by LiCoO<sub>2</sub> with MCMB are known to be more energy efficient and keep longer than others in a lithium-ion battery at this time. To understand the discharge/charge voltage profiles for the composites of LiCoO<sub>2</sub> with MCMB, it is important to examine the lithium intercalation process in the composite electrodes intensively. Recently, the modeling of the intercalation of lithium in the electrodes has attracted increasing attention in the design and development of lithium-ion batteries. Santhanagopalan et al. [1] reviewed the approximate modeling for the prediction of the cycling performance of lithium

ion batteries, in which two simplified models referred to as the single particle model [2,3] and the porous electrode model with the polynomial approximation [4–6] were compared with the porous pseudo two dimension model [7]. It was demonstrated that the single particle model among them has a distinct advantage over other models with respect to the computation time. The model can also successfully simulate the cycling performance of lithium ion batteries up to 1 C rate. Also, Santhanagopalan et al. [8] reproduced the discharge/charge voltage profiles accurately by fitting the single particle model and porous electrode model to their experimental results with the kinetic rate constants, diffusion coefficients and initial lithium concentration of lithium intercalation electrodes as adjustable parameters. However, a special spline interpolation was used to obtain the equilibrium potential curves of the intercalation electrodes required in the application of the discharge/charge experimental data reduction.

In recent years, a few approaches accounting for the equilibrium potentials in terms of the activity correction were reported. For example, the equilibrium potential of the intercalated lithium and the diffusion of lithium in the intercalation electrode were expressed by the chemical potential's gradient with concentration-dependence as the driving force [9–11]. In our previous work [12], we presented the equilibrium potentials and phase transition

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## Nomenclatures

$A_m$	: binary parameter in the Redlich–Kister equation ( $\text{J mol}^{-1}$ )
$a_i$	: activity
$c_{1,j}^{\text{max}}$	: maximum concentration of lithium ( $\text{mol cm}^{-3}$ )
$c_e$	: concentration of the electrolyte ( $\text{mol cm}^{-3}$ )
$D_{1,j}$	: diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
$D_{\text{eff},j}$	: effective diffusivity ( $\text{cm}^2 \text{s}^{-1}$ )
$E_j$	: solid phase potential (V)
$E^{\text{eq}}$	: equilibrium potential (V)
$E^\circ$	: standard equilibrium potential (V)
$F$	: Faraday constant ( $96,485 \text{ C mol}^{-1}$ )
$F_{\text{objf}}$	: objective function
$G_{ij}$	: parameter in NRTL equation
$\Delta g_{ij}^E$	: energy parameter in NRTL equation ( $\text{J mol}^{-1}$ )
$g^E$	: excess molar Gibbs free energy ( $\text{J mol}^{-1}$ )
$g^M$	: molar Gibbs free energy of mixing ( $\text{J mol}^{-1}$ )
$I_{\text{app}}$	: applied current (A)
$k_j$	: rate constant for electrochemical reaction ( $\text{cm}^{2.5} \text{ mol}^{-0.5} \text{ s}^{-1}$ )
$m$	: number of parameters
$N$	: number of data points
$N_k$	: number of data points in the $k$ th curve
$n$	: number of charge or discharge curves in the regression
$R$	: ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )
$R_j$	: average radius of electrode particle (cm)
$r_j$	: radial coordinate (cm)
$\bar{r}$	: normalized dimensionless coordinate
$S_j$	: electro-active surface area ( $\text{cm}^2$ )
$T$	: temperature (K)
$t$	: time (s)
$V$	: voltage (V)
$w_j$	: weight of active material inside electrode (g)
$x_i$	: mole fraction
$x_0^{1,j}$	: initial lithium mole fraction in electrode

### Greek letters

$\alpha_{12}$	: non-randomness parameter in NRTL equation
$\gamma_i$	: activity coefficient
$\eta_j$	: over potential (V)
$\lambda$	: discretized parameter of diffusion equation ( $\text{cm}^2 \text{s}^{-1}$ )
$\rho_j$	: density of the active material ( $\text{g cm}^{-3}$ )
$\tau_{ij}$	: parameter of NRTL equation

### Subscript

1	: intercalated lithium
2	: lithium vacancy
$i$	: intercalated lithium or lithium vacancy
$j$	: anode or cathode
$n$	: anode
$p$	: cathode
$\text{ref}$	: reference electrode

### Superscript

$m$	: space discretization point
$n$	: time discretization point
$\alpha$	: $\alpha$ -phase
$\beta$	: $\beta$ -phase

phenomena of  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$  electrodes that were estimated by using Nernst equation with the activity correction. The non-random two-liquid (NRTL) model and Redlich–Kister equation were used to represent the excess Gibbs energy for the equilibrium potentials. As a result, the concentration dependence of  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$  equilibrium potentials was described successfully by taking into account the phase transition of  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$  electrodes. Karthikeyan et al. [10] considered the activity correction but no phase transition for  $\text{LiCoO}_2$  and MCMB electrodes to correlate the equilibrium potential curves by the Redlich–Kister equation. Furthermore, they simulated the galvanostatic discharge profile of lithium-ion battery using the single particle model with the concentration-dependence diffusion coefficient of lithium in the electrode. Eventually, the calculated equilibrium potentials apparently agreed well with the experimental results, but the simulation results were not compared with the experimental discharge/charge voltage profiles.

In this work, we examined the activity correction through the phase transition of the electrode to the equilibrium potentials as well as the electrochemical reaction and diffusion of lithium in the intercalation electrodes in order to calculate the voltage profiles accurately during the discharge/charge processes in the lithium ion battery composed of  $\text{LiCoO}_2$  cathode and MCMB anode. The activity correction expressed in terms of activity coefficients was included in the Nernst equation for the equilibrium potentials and in the single particle model for the diffusion of lithium intercalated in the anode and cathode as well as in the Butler–Volmer equation for the electrochemical reaction at the surface of electrode particle. Moreover, the validity of the activity corrections was investigated by the NRTL model and Redlich–Kister equation with homogeneous and heterogeneous treatments for intercalated  $\text{LiCoO}_2$  electrodes. In the heterogeneous treatment, we considered the phase transition of  $\text{LiCoO}_2$  electrode during the intercalation process. The effective diffusivity and electrochemical reaction rate in coexisting region of two different phases of  $\text{LiCoO}_2$  electrode were calculated in accordance with the thermodynamic criteria of phase transition described by the Gibbs energy of mixing in  $\text{LiCoO}_2$  electrode. The workability of these models and treatments were evaluated by comparing the experimental values of galvanostatic discharge/charge profiles with the simulated ones.

## 2. Thermodynamics of lithium intercalated electrode

### 2.1. Activity correction for the Nernst equation

The charge-transfer reaction of lithium-insertion at the surface of intercalated electrode can be described by [9,12,13]



where  $\text{Li}^{\text{I}}(\text{b})$  represents an active material occupied by lithium intercalated in the bulk phase of the electrode, hereafter denoted by subscript 1.  $\text{Li}^{\text{V}}(\text{b})$  indicates a vacant active material in the bulk electrode phase, indicated by subscript 2.  $\text{Li}^+(\text{e})$  is the lithium ion within the electrolyte phase. The measured equilibrium potential refers to the potential of the active material relative to that of a reference electrode placed in solution. The electric potential in the electrolyte phase is not easily determined, but the potential of the intercalation electrode can be measured relative to the pure lithium-metal electrode as a reference. Therefore, we obtain the equilibrium potential  $E^{\text{eq}}$  between the lithium intercalated in the bulk electrode and lithium metal in the reference electrode

$$E^{\text{eq}} = E^\circ + \frac{RT}{F} \ln \left( \frac{a_2}{a_1} \right) \quad (2)$$

where  $E^\circ$  is the standard equilibrium potential,  $a_1$  and  $a_2$  are the activity for the active material intercalated by lithium and

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