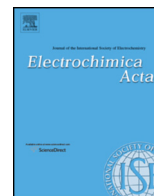




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Thermodynamic derivation of a Butler–Volmer model for intercalation in Li-ion batteries

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ABSTRACT

We present an exclusively thermodynamics based derivation of a Butler–Volmer expression for the intercalation exchange current in Li ion insertion batteries. In this first paper we restrict our investigations to the actual intercalation step without taking into account the desolvation of the Li ions in the electrolyte. The derivation is based on a generalized form of the law of mass action for non ideal systems (electrolyte and active particles). To obtain the Butler–Volmer expression in terms of overpotentials, it is necessary to approximate the activity coefficient of an assumed transition state as function of the activity coefficients of electrolyte and active particles. Specific considerations of surface states are not necessary, since intercalation is considered as a transition between two different chemical environments without surface reactions. Differences to other forms of the Butler–Volmer used in the literature [1,2] are discussed. It is especially shown, that our derivation leads to an amplitude of the exchange current which is free of singular terms which may lead to quantitative and qualitative problems in the simulation of overpotentials. This is demonstrated for the overpotential between electrolyte and active particles for a half cell configuration.

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1. Introduction

Every continuum theory of Li ion insertion cells is based on models of Li ion transport in electrolyte and active particles on one side and on chemical kinetics at the interfaces between active particles and electrolyte on the other side. Most of the commonly used models concentrate on homogenized theories, which do not resolve single particles, but treat the electrodes as effective porous media [1–6]. Therefore porous electrode theories are necessarily restricted to spatial scales much larger than the size of active particles, which range from the nanometer to the micrometer scale. Since electrodes often have a thickness of about 100 μm , the validity of this models is sometimes at least problematic. Only a few authors deal with microscopic models, which resolve the active particle scale [7–12]. But also these models are restricted to scales above about 3 nm due to their continuum nature. Once the microscopic models are consistently formulated the homogenized porous electrode theory can be derived by e.g. volume averaging techniques [13,14,11]. Both type of models have to deal with the conceptual problem that the spatial scale of chemical kinetics is the scale of the molecules. On the scale of the transport models,

reaction terms appear either as averaged source terms in the balance equations for mass, momentum, energy and entropy [15] or as boundary and interface conditions for the resulting partial differential equations. It is in both cases important to formulate them for exactly the same quantities, which are used in the transport equations. This goal is achieved best, if the missing expressions for chemical reactions are derived within the same theoretical frame and on the same spatial scale as the theory of transport. Pure thermodynamical theories of transport and chemical reactions in Li ion batteries are being developed in recent years [16–20,11,5,6], dealing foremost with the problem of phase transitions in Li ion batteries or porous electrode theory. In this paper, we concentrate on a derivation of the expression for the exchange current due to ion intercalation at the interface between electrolyte and one active particle. Only concepts from nonequilibrium thermodynamics are used. They are applied to the assumption that ion intercalation can be simply understood as a transition between two different chemical environments where the actual ionic nature of e.g. the Li^+ is preserved. There are strong experimental indications that this picture is valid for graphitic materials in most of the cases [21–23]. We assume this picture also to hold for the positive electrodes. It is therefore not necessary to formulate interface reactions, in which Li^+ is reduced to metallic Li. This reaction at the surface would rather be interpreted as the initiation of Li plating.

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Summary of notations.

F	Faraday number
R	universal gas constant
T	temperature
$a_{e,s}^+$	activity of Li ions in electrolyte and solid particle
c_e	salt concentration
$c_{e,s}^0$	initial salt concentration in electrolyte and active particle
$c_{s,max}$	maximum Li concentration
c_{Li}	concentration of Lithium in metallic state
$c_{s,ref}$	concentration in reference state for active particles
c^*	concentrations of transition state
$c^{0,*}$	initial concentrations of transition state
i_{es}	exchange current
i_0	amplitude of exchange current
j	electrical current
\hat{j}	dimensionless electrical current
K	equilibrium reaction rate
r	net reaction rate
U_0	open circuit potential
U_{ref}	open circuit potential at reference concentration
$c_{s,ref}$	
α_a	anodic transfer number
α_c	cathodic transfer number
ΔG	Gibbs free energy of reaction in the reference state
η	overpotential
$\gamma_{e,s}$	Activity coefficient
κ_r	reverse reaction rate
$\mu_{e,s}$	chemical potentials of electrolyte and active particle
$\varphi_{e,s}$	electrochemical potential
$\tilde{\varphi}$	electrochemical potential in reference state
φ^*	electrochemical potential of transition state
Φ	electrical potential

In Section 2 the underlying assumptions and the derivation of the intercalation model are presented. In Section 3 the new model is discussed and compared with the one proposed in [2]. Arguments on the thermodynamic consistency of the two different models are presented. In Section 4 the model is applied to a simple half cell configuration and the results for the overpotentials are compared with results of the Butler–Volmer expression used in [2].

2. Derivation of intercalation model

In [9,10] a fully thermodynamic consistent derivation of the transport equations for Li ion concentration and charges in the microscopic structure of a Li ion battery was presented and validated in [12]. The derivation is valid for transport in the electrolyte as well as in the active particles on a spatial scale in which electroneutrality holds i.e. for a spatial resolution larger than $\Delta_{min} \sim 50$ nm. Electroneutrality is used explicitly in the derivation of the transport equations. This assumption accounts for the fact that quasineutral solvated ions or electrically shielded ions are transported in the electrolyte and active particles, respectively. The basic variables are ion concentration,¹ electric potential and temperature. To couple the transport between electrolyte and active particles expressions for exchange current have to be formulated. In [10] the commonly used Butler–Volmer expression for the

intercalation current i_{se} in Li ion batteries with liquid electrolytes introduced in [2] was used

$$i_{se} = i_0 \left(\exp \left[\frac{\alpha_a F}{RT} \eta_s \right] - \exp \left[-\frac{\alpha_c F}{RT} \eta_s \right] \right) \quad (1)$$

α_A and α_C with $\alpha_A + \alpha_C = 1$ are weighting the anodic and the cathodic contribution of the current to the overall reaction induced by the measured overpotential η_s . The current is positive for deintercalation i.e. Li ions leaving the active particles and negative for intercalation. To point out more explicitly the origin of the overpotential it is written in the form

$$\eta_s := \Phi_s - \frac{\delta\varphi_e}{F} - U_0. \quad (2)$$

Here U_0 is the half cell open circuit potential of the respective electrode. As shown in [10] it is necessary to formulate the overpotential in this unsymmetrical form based on the electrical potential Φ_s in the active particle and the electrochemical potential $\delta\varphi_e = \varphi - \mu_{Li}$ relative to the electrochemical potential of pure Li in the electrolyte. Only in this form the experimentally defined open circuit potential (OCP) $U_0 = -(\mu_s - \mu_{Li})/F$ and electrical potential Φ_s appear explicitly in the theory. The exchange current density i_0 proposed by Newman [1,2] is given by

$$i_0 = k c_e^{\alpha_a} c_s^{\alpha_c} (c_{s,max} - c_s)^{\alpha_a} \quad (3)$$

k is a reaction rate and $c_{s,max}$ is the maximum concentration which can be stored in the active particle. The postulated concentration dependence of i_0 is cumbersome for situations in which the concentration of Li ions in the active particle is close to its maximum concentration or close to zero, as well as for a completely depleted electrolyte in the neighborhood of the active particle. In all these situations the intercalation rate approaches zero independent of the direction of the current, if the singular behavior of i_0 is not exactly balanced by corresponding singularities in the OCP. The problem is, that in most practical applications of the theory, U_0 is fitted independently from the choice of i_0 . For simulations this behavior poses a severe problem, since it would lead to the seemingly paradoxical situation that independent of the sign and the size of the applied external potential no current could flow if e.g. the battery is fully charged i.e. the concentration in the anode has reached its maximum value. It is also clear that the prediction of the overpotential will depend very sensitively on the correct choice of the prefactor i_0 . It is therefore important to obtain an expression for the exchange current in which the prefactor i_0 as well as the form of the exponentials in the Butler–Volmer expression are consistently derived instead of trying to model both independently.

On the scale of the transport model, intercalation happens at a sharp interface between electrolyte and active particles. On a molecular scale this “interface” is composed of the full double layer (diffuse, Helmholtz and Stern layer) in the electrolyte as well as of a spatial polarization charge layer in the solid particle. The intercalation of the Li ions can therefore be interpreted as a process consisting of at least three steps [23]. First, the Li ions have to get rid of their solvation shell. After that the charged ion is transferred from the electrolyte environment to the solid particle via some transition state. Finally the charge of the ion is shielded by reorganization of the electric charges and molecules in the solid lattice structure.

In the current paper we restrict ourself to the transition of the Li ion from the electrolyte into the solid active particle after desolvation in order to establish a purely thermodynamic consideration which later can be generalized to the full intercalation process. To describe the intercalation reaction we will make use of the law of mass action in a form valid for non ideal systems. Such a theory was formulated by Haase in a series of papers [24–27] using only very general assumptions without making use of transition state

¹ After some trivial change of variables from chemical potential to concentration.

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