

Thermodynamic theory and simulation of transport and intercalation of solvated ions in Li ion batteries
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In ^{1,2} 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 ³. 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 a few nanometer. Electroneutrality is used explicitly in the derivation of the transport equations. This assumption accounts for the fact that quasi-neutral solvated ions or electrically shielded ions are transported in the electrolyte and active particles, respectively. The basic variables of the transport theory are the concentration of the solvated ions, the electrochemical potential of the Li ions and the temperature. To couple the transport of the ions in the electrolyte and the active particles, the formulation of proper interface conditions for the exchange current between electrolyte and active materials is necessary. Usually global Butler Volmer expressions are used to describe the exchange current. These expressions do not explicitly account for the multi-step mechanism underlying the intercalation of solvated ions. The full intercalation process consists of desolvation, transfer of charged ions between two different chemical environments (electrolyte and solid active particle) and finally local electronic polarization in the solid particles to shield the charges of the ions. The actual ionic nature of the charged Li ion is either completely preserved as in graphite ⁴⁻⁶ or is integrated in the host lattice to form a new phase with the host material. The reduction of the Li ions to metallic ions occurs if a metallic phase is formed, which is of course one of the major degradation mechanisms. Also from the theoretical point of view the description of these three steps is necessary, since the transport theory describes the motion of quasi-neutral solvated complexes of positive and negative ions in the electrolyte and electrically shielded Li ions in the active particles. For being able to describe the interface conditions for the transfer of only the positive ions it is necessary to account for the desolvation in the intercalation step.

Our derivation of the proper interface condition is based on a formulation of the law of mass action for non-ideal strong electrolytes due to Haase ^{7,8}. In this theory the reaction rate is derived with very general assumptions in terms of the activities of the educts and products of the reactions. This theory will be applied to the multi-step intercalation process with additional assumptions on the transition states for the different intercalation steps. It can be shown, that the transfer step of the desolvated charged ions from the electrolyte to the active material obeys a Butler Volmer expression if and only if a transition state is assumed, which is in dynamic equilibrium with the ions in electrolyte and active material ⁹. The functional dependence of the amplitude of the exchange current on

the ion concentration of the electrolyte and the active particles is also obtained from the theory.

We apply the new intercalation theory to half-cell and full cell configurations and compare the results for the overpotentials with the usual one step Butler Volmer reaction scheme. Especially the influence of the temperature dependence of the desolvation step on the intercalation will be investigated.

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