

Local Inhomogeneities and their Impact on Lithium Plating in Lithium-Ion Batteries

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The deposition of metallic lithium on the surface of graphite electrodes, also known as lithium plating, is one of the major degradation mechanisms in lithium-ion batteries. The common approach for electrochemical simulation of lithium plating is the use of a volume averaged microstructure combined with a phenomenological approach describing the plated lithium [1,2]. The impact of metallic lithium is hybridized with the growth of a solid-electrolyte-interphase into an additional resistance term included in the overpotential of the lithium intercalation reaction. Even though volume average models allow for some investigation of spatial inhomogeneities on electrode level and a mismatch of electrodes [3], inhomogeneities on pore scale cannot be resolved. We will present a new electrochemical model, which includes plated lithium as an explicit surface phase. This allows for a smooth transition from dominantly intercalation to pure lithium deposition. This approach is able to describe the well-known stripping plateau occurring during discharge of a plated lithium-ion battery. Additionally, an impact of the plating onset on the cell voltage could be identified.

The model describes the growth of a lithium film on the surface of anode graphite particles. Three reactions are relevant: the intercalation reaction between electrolyte and graphite, the metallic lithium deposition and a charge-neutral insertion of the plated lithium in the supporting graphite. Without the presence of plated lithium, lithium ions can intercalate from the electrolyte into the graphite. During plating the lithium ions get deposited from the electrolyte on the surface of the anode and form a neutral lithium atom. Prolonged deposition results in an growing lithium phase on the surface. The presence of a large lithium phase can prevent the intercalation from the electrolyte into the graphite. The metallic lithium on the surface is not thermodynamically stable. It can either react with the electrolyte to form the solid-electrolyte-interphase or intercalate charge neutral into the supporting graphite. The developed model is implemented in the electrochemical simulation framework BEST [4], which is based on a thermodynamically consistent transport theory [5].

The electrodes of lithium-ion batteries often do not exhibit a degradation, which is homogeneously distributed [6]. The new plating model is therefore applied to an anode microstructure, where several electrochemical parameters are spatially varied. It will be shown, that an inhomogeneous solid-electrolyte-interphase (SEI) can favour or hinder local lithium deposition.

References:

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