Physicochemical modeling of nonlinear aging of lithium-ion cells

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The formation and growth of the solid-electrolyte interphase (SEI) is stated to be the dominant aging mechanism for most cycling conditions in lithium-ion cells that results in an almost linear aging behavior [1]. Another crucial aging mechanism is the deposition of metallic lithium on the anode surface, also called lithium plating, which occurs if the anode potential becomes negative vs Li/Li+ [2, 3]. With ongoing aging, it is assumed that lithium plating can become dominant which results in a nonlinear aging behavior accompanied by an accelerated capacity fade and a significant rise in impedance [1]. This implies that the transition from a linear to a nonlinear aging characteristic strongly depends on the dominating aging mechanism. Accurate modeling and simulation of these mechanisms can help to predict the aging behavior in order to adjust operating strategies to extend a cell’s lifetime.

Based on the pseudo-two-dimensional (p2D) Newman model [4], a physicochemical model is developed which allows to investigate the underlying mechanisms resulting in both linear and nonlinear aging characteristics of lithium-ion cells. Besides the main de-/intercalation reactions, two parasitic side reactions are implemented within the anode. The first side reaction describes SEI growth [5] and a second one describes lithium plating [1]. As lithium plating has been reported to be partially reversible [6], an additional side reaction was implemented to account for the so called lithium stripping.

A commercial 18650-type NMC/C lithium-ion cell was used to parameterize and validate the presented model. Different aging tests with varying cycling strategies and current loads were performed whereas the charging strategy was altered as follows: CC charging (I), CC-CV charging (II) and CC-CV charging with a subsequent relaxation of 24 hours (III). Dependent on the cycling strategy and applied current loads, the measurements clearly show the investigated transition from linear to nonlinear aging. Additionally, a certain voltage plateau can be observed during discharge, which is typical for lithium stripping after severe lithium plating [6]. With the aid of the presented model, the experimentally observed aging characteristics and dependencies can be depicted and explained. It can be shown, that SEI film growth decreases the anode’s porosity and accelerates lithium plating, causing the transition from linear to nonlinear aging. Furthermore, the ratio between plating and stripping is highly dependent on the cycling strategy as well as the applied current loads and prevailing temperature.

References: