

A Mathematical Model for the Lithium-ion Negative Electrode Solid Electrolyte Interphase

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Introduction

The passivating solid electrolyte interphase (SEI) layer forms at the surface of the negative electrode active material in lithium-ion cells. The SEI stabilizes the cell by preventing reduction of the solvent and the electrolyte. Some of the cell's capacity is lost during the formation of the film, and the resistance of the film increases as the film thickens. We would like to understand how these effects can be minimized in order to improve the efficiency of lithium-ion batteries.

Mathematical model

A continuum-scale mathematical model, similar to the iron-oxide film model of Battaglia and Newman,¹ has been developed to simulate the growth of the SEI and transport of lithium and electrons through the film. The model described here differs from the SEI formation model of Ramadass *et. al.*² in that migration is included as a driving force for lithium transport, a defect mechanism is used to describe transport in the film, film growth occurs at the film-solution interface rather than the electrode-film interface, and a multi-step film-formation mechanism is assumed.

Figure 1 gives a schematic of the one-dimensional model, in which transport of lithium occurs via interstitial (I_{Li}^+) and vacancy (V_{Li}^-) mechanisms, and film growth occurs at the film-solution interface via reduction of the solvent (ethylene carbonate) to form lithium carbonate, as proposed by Aurbach *et. al.*³ The model will be used to estimate the film growth rate, film resistance, and irreversible capacity loss due to film formation.

We have illustrated that film growth at the negative electrode is faster for charged batteries than for uncharged batteries (Fig. 2), and that higher electron mobility in the film leads to faster growth (Fig. 3). If electron mobility is low, the rate of film growth is limited by transport of electrons through the film, and the rate decreases as the thickness increases.

We have also shown that the irreversible capacity loss due to the formation of a 75-nm Li_2CO_3 film on charged graphite is only 0.2%. The film resistance increases with its thickness, but not as rapidly, since the conductivity of the film increases during the first few hours of growth. This conductivity rise is due to injection of lithium interstitials into the film. Because we would like to minimize the film resistance, we should use solvents or solution additives that form films with a high capacity for lithium-ion defects. We would also like to form films with low electronic mobility to prevent incessant reduction of the solvent.

Acknowledgement

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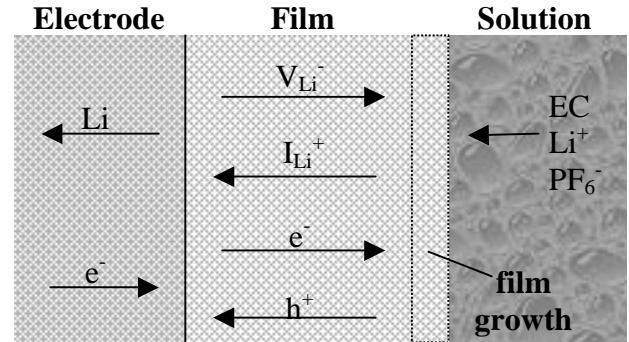


Figure 1. Model of the growing SEI film. V_{Li}^- indicates lithium vacancies, I_{Li}^+ indicates lithium interstitials, and h^+ indicates holes. Arrows indicate the direction of species motion on charge.

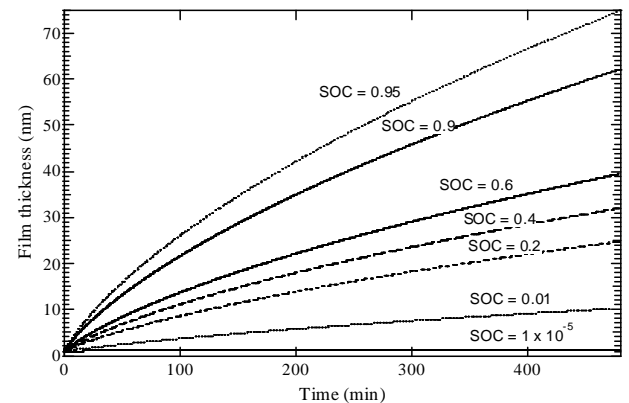


Figure 2. Film growth at open circuit ($t_{e^-}^0 = 10^{-4}$). SOC = initial "state of charge." $t_{e^-}^0$ = electronic transference number.

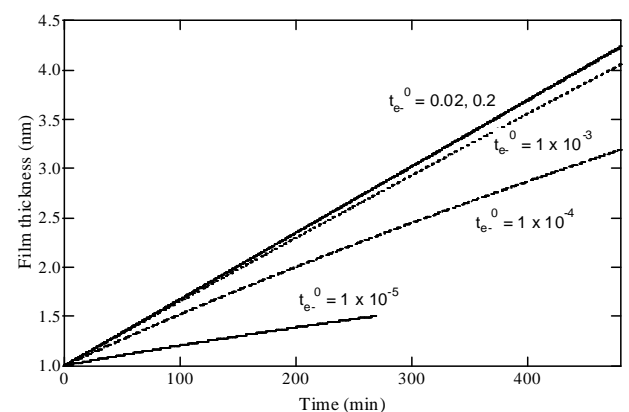


Figure 3. Film growth at open circuit (initial state of charge = 0.2).