Motivation:

The solid electrolyte interphase (SEI) is the key to merge performance and long-term stability. Direct contact between graphite electrodes and carbonate electrolytes results in continuous reduction of electrolyte solvent and salt. However, these reduction reactions produce a thin film separating electrode/electrolyte, and reducing the rate of electrolyte reduction considerably. However, this reaction is never absolutely suppressed and SEI constitutes the biggest safety concern in lithium-ion batteries.

Objective:

Our model describes the long-term growth of a porous SEI [1,2] and predicts SEI morphology. We extend previous models which describe SEI thickness evolution using a single rate-limiting transport mechanism. Instead, all potentially rate-limiting transport mechanisms are considered as shown in the attached figure. By comparing our theory with capacity fade measurements [3], we determine the rate-limiting charge-transport mechanism.

Methodology:

First, we consider a single representative SEI formation reaction and predict continuous growth of a porous SEI. Electron conduction drives film growth and thickness evolves with the square-root of time. We show that replacing electron conduction with alternative mechanisms suggested in literature (such as diffusion of neutral lithium interstitials through the SEI [4]) leads to qualitatively similar results. A second SEI formation reaction leads to the formation of a dual-layer SEI. Different SEI profiles generated in our model are studied with impedance simulations of graphite anodes. Our predictions are validated with SOC dependent capacity fade experiments.

Results and Discussions:

Our model predicts SEI porosity and dual-layer structure. It can smoothly transition between rate-limiting transport mechanisms and enables us to systematically compare SEI formed by qualitatively different charge transport mechanisms. From SOC dependent capacity fade measurements, we conclude that diffusion of neutral lithium is responsible for the transport of charges from the electrode to the electrolyte and the continuous SEI growth.

Literature:

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[4] Shi, S., Lu, P., Liu, Z., Qi, Y., Hector, L. G., Li, H., & Harris, S. J. (2012). JACS, 134(37), 15476–15487.