

Revealing SEI Morphology: A Novel Modelling Approach

Lithium-ion batteries are the technology of choice for a broad range of applications due to their performance and long-term stability. The solid electrolyte interphase (SEI) is the key to merge these properties because it enables the combination of low-voltage anodes such as graphite with high performance liquid electrolytes. Direct contact between these phases results in continuous reduction of electrolyte solvent and salt. However, these reduction reactions produce solid SEI particles which quickly form a thin film during the first charge of a pristine graphite electrode. This thin film separates electrode and electrolyte, reducing the rate of electrolyte reduction considerably. However, this reaction is never absolutely suppressed and long-term SEI growth remains the biggest contributor to capacity fade in lithium-ion batteries.

Our model describes the long-term evolution of a porous SEI [1]. It extends the approach of previous models [2,3] which describe SEI thickness evolution using a single rate-limiting transport mechanism. In this way, they avoid specifying reaction kinetics because the reaction rate equals the incoming throughput of SEI precursors. We instead consider all potentially rate-limiting transport mechanisms, namely electron conduction and solvent diffusion. These mechanisms transport SEI precursors through the film and its pores, as shown in figure 1. This allows us to trace the evolution of the SEI volume fraction in a spatially resolved way, see figure 2.

The first model considers a single representative SEI formation reaction and predicts 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 plausible mechanisms suggested in literature (such as diffusion of neutral lithium interstitials through the SEI [4]) leads to qualitatively similar results. Adding a second SEI formation reaction leads to the formation of a dual-layer SEI. The properties of the additional layer depend on the type of the second reaction, i.e., solvent reduction or reduction of SEI compounds. Furthermore, we predict an equilibrium relation between the thickness of the inner layer and the total SEI thickness. Different SEI profiles generated in our model are studied with impedance simulations of graphite anodes. All predictions above are observable with suitable experimental techniques, such as neutron reflectometry, and can be used for model validation.

SEI porosity is an output of our model, when SEI growth is limited by electron conduction. However, structural constraints potentially impose a larger porosity onto the system. Our model can smoothly transition to the other rate-limiting transport mechanism which is solvent diffusion by considering these constraints. This enables us to systematically compare SEI formed by qualitatively different mechanisms.

[1] Single, F., Horstmann, B., & Latz, A. (2016). *Phys. Chem. Chem. Phys.*, 18, 17810–17814. doi:10.1039/C6CP02816K

[2] Pinson, M. B., & Bazant, M. Z. (2012). *Journal of the Electrochemical Society*, 160(2), A243–A250. doi:10.1149/2.044302jes

[3] Christensen, J., & Newman, J. (2004). *Journal of The Electrochemical Society*, 151(11), A1977. doi:10.1149/1.1804812

[4] Shi, S., Lu, P., Liu, Z., Qi, Y., Hector, L. G., Li, H., & Harris, S. J. (2012). *Journal of the American Chemical Society*, 134(37), 15476–15487. doi:10.1021/ja305366r

