

Experimental and Theoretical Investigation of Solid-Electrolyte-Interphase Formation Mechanisms on Glassy Carbon

Maureen Tang,^{a,b,c} Sida Lu,^d John Newman^{a,b}

^a Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

^b Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720-1462

^c Department of Chemical Engineering, Stanford University, Stanford, CA, 94305-5025

^d Department of Chemistry, University of California, Berkeley, CA 94720-1462

Formation and growth of the solid-electrolyte interphase (SEI) increases the processing costs and reduces the lifetime of lithium-ion batteries. Despite decades of study, the mechanism by which an SEI succeeds or fails to passivate the graphite electrode is still not understood. In this work, we determine the formation mechanism of the SEI on glassy carbon using electrochemical experiments and theoretical calculations. Forming the SEI on glassy carbon instead of graphite both reduces experimental complexity and permits steady-state rotating disk electrode (RDE) measurements in addition to the stationary-electrode techniques of impedance and cyclic voltammetry. Our results indicate that formation of the SEI is limited by precipitation of soluble intermediates, a mechanism that is less frequently considered in battery aging studies.^{1,2}

Glassy carbon was held at potentials ranging between 0.1 and 0.9 V vs. Li/Li⁺ for 5 seconds to 3 hours. Fig. 1 shows formation charge versus the square root of time. All of the curves appear to be straight lines on these coordinates, with two regions showing different slopes at long time and short time. At all potentials, the transition from short-time to long-time is approximately $2\text{ s}^{0.5}$ or 4 seconds. The linearity with $\sqrt{t}$ indicates clearly that the SEI follows parabolic growth, consistent with reported capacity-fade measurements³. As formation potential decreases, the rate of SEI growth increases, consistent with a higher driving force for reduction.

Theoretical $Q - t$ growth curves were developed for several different formation mechanisms of a two-layer SEI. Comparison with the experiments in Fig. 1 shows that transport of a charged species is limiting. Thus, electron tunneling or high-field migration through the compact layer of the SEI does not appear to be the limiting process for SEI growth. Formation also does not appear to follow a partially-blocked-electrode mechanism.

After forming the SEI potentiostatically, 1 mL of electrolyte containing approximately 10 mM of ferrocene and ferrocenium hexafluorophosphate was added to the cell, and the lithium counter electrode was replaced by a platinum mesh. The through-film ferrocene reduction current was then measured using steady-state Koutecky-Levich analysis and impedance spectroscopy using previously developed methods^{1,2}.

Nyquist plots of the through-film ferrocene reaction are shown in Fig. 2. Fig. 2 shows spectra measured after SEI formation at 0.9 V for 30 minutes, 0.6 V for 10 minutes, 0.45 V for five minutes, and 0.3 V for 2 minutes. The amount of charge passed in these formation experiments

ranged from 4.89 to 4.38 mC/cm². Two arcs are visible in the spectrum. The arc at high frequency corresponds to the charge-transfer resistance of the through-film ferrocene reaction and increases for more passivated electrodes, while the low-frequency arcwidth corresponds to bulk ferrocene and ferrocenium transport. This arcwidth is independent of the surface phenomena. The high-frequency intercept, which corresponds to the ohmic resistance of both the bulk electrolyte and the SEI, does not change between experiments. The results of Fig. 2 demonstrate that films formed at lower potential are more passivating, but do not affect the ohmic resistance of the system.

Future work will discuss how these and other experiments support the hypothesis of precipitation-limited SEI growth and suggest strategies for SEI mitigation and control.

References:

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2. M. H. Tang, S. Lu, & J. Newman (2012). *J. Electrochem. Soc.*, 159 (11), A1775–A1785.
3. M. Safari, M. Morcrette, A. Teyssot, & C. Delacourt (2009). *J. Electrochem. Soc.* 156(3), A145–A153.

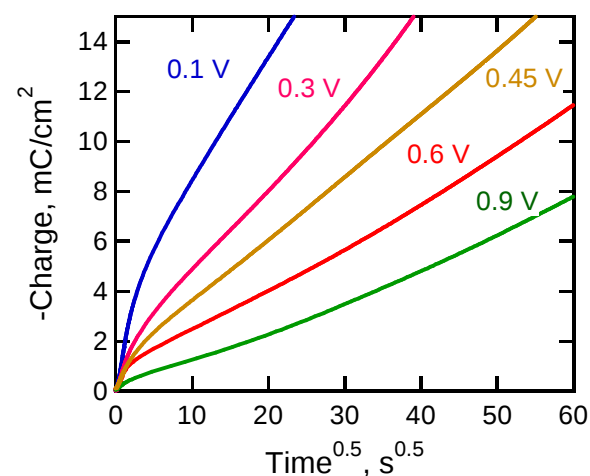


Fig. 1: Formation charge during potentiostatic SEI formation vs. the square root of time, at different formation potentials. Parabolic potential-dependent growth demonstrates that formation is limited by the transport of a charged species.

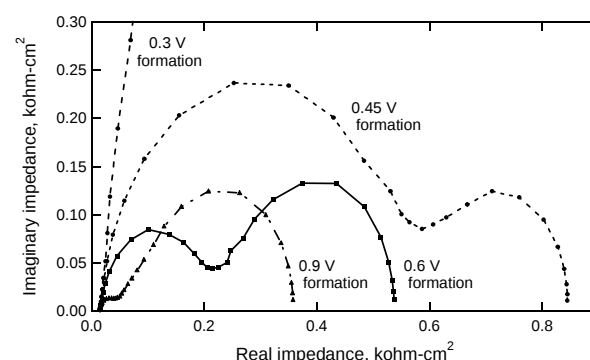


Fig. 2: Impedance spectra of through-film ferrocene redox kinetics for the SEI formed at different potentials. The amount of formation charge is similar between experiments, but the degree of passivation increases with decreasing formation potential. For 0.3 V formation, the high-frequency arc width is too big to fit on the same plot as the other curves.