Dynamics of Electrochemical Thin Films for Memory and Battery Applications

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Abstract

Thin films only nanometers thick often govern the behavior of electrochemical devices. Some of these films are engineered deliberately, as in electrochemical memory, where a thin active layer stores information and dictates device density; others form as unintended by-products of degradation, as with the solid electrolyte interphase (SEI) that grows on the negative electrode of lithium-ion batteries. In both cases the decisive physics plays out on a lengthscale where direct characterization is specialized, difficult to scale, and frequently frustrated by films too unstable for ex-situ measurement. This thesis takes a modeling-focused approach to this problem, developing interpretable continuum theories that connect physical mechanism descriptions to non-invasive electrochemical characterization of these devices. My thesis work addresses (1) the mechanisms driving ion-based ultrafast memory, and (2) a method for rapid, non-invasive assessment of SEI quality.

The first study focuses on uncovering new mechanisms behind fast memory switching in ion-based memory devices. Three-terminal protonic synapses based on a tungsten oxide (WO_3) channel have been shown to switch on nanosecond timescales, far faster than the bulk ion-diffusion timescale conventionally believed to limit them. We provide a theoretical explanation using multiphase polarization theory, showing that an electric-field-driven phase separation relocates the memory into a thin, high-conductivity interfacial phase, so that linear and symmetric conductance modulation is achieved over a much faster timescale.

The second study focuses on the diagnosis of the SEI in lithium-ion batteries. Because the interphase cannot be measured directly in a working cell, its properties must be inferred from current and voltage. We develop a physics-based electrochemical diagnostic that uses trajectory-based electrochemical impedance to both confirm a simplified description of the highly amorphous, unstructured layer and provide a platform for inverting the parameters that dictate its "quality". We anchor these diagnostics with direct observation, validating against operando atomic force microscopy of SEI growth on copper electrodes. These results show that a non-invasive electrical measurement can be turned into a quantitative probe of interphase formation and quality.

Collectively, the studies in this thesis provide insights into the mechanisms driving both ultrafast ionic memories and degradation modes in batteries. More broadly, these methods act as a pipeline to investigate other electrochemical thin films through non-invasive electrochemical diagnostics.

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