Voltammetric Methods Augmented with Physical Models and Statistical Inference

by

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Increasing adoption of low-cost renewable energy technologies can enable global sustainability goals. However, the intermittency of variable resources inhibits broad deployment, necessitating a suite of energy management systems including rechargeable batteries (e.g., redox flow batteries (RFBs), lithium-ion batteries). RFBs are particularly attractive because their system architecture enables largely decoupled energy capacity and power output—along with long service life and simplified maintenance—but their present-day costs remain prohibitively high. A promising pathway to economically competitive RFBs is the use of redox-active organic compounds (RAOs), which can be functionalized to improve battery performance (e.g., cell voltage, energy density). However, state-of-the-art RAOs often decompose during operation, shortening battery lifetime. Understanding and mitigating this degradation is thus crucial; corresponding efforts typically rely on *ex situ* and *post mortem* analyses to elucidate the decay pathway(s) which, while often successful, may be time-consuming and expensive. These processes may potentially be streamlined by using *in situ* or *operando* electrochemical methods such as voltammetry, a powerful technique able to accurately estimate the composition of an electrolyte solution in an automated fashion. However, proposed voltammetric routines usually do not leverage physical models, meaning they may perform poorly when confronting conditions not included in training data.

In this thesis, I seek to advance voltammetric methods to characterize degrading RAOs by developing physics-informed protocols that leverage statistical inference. I utilize different voltammetric waveforms—cyclic voltammetry and cyclic square wave voltammetry—and a range of electrode radii (*ca*. 5 μm – 1 mm) to modulate reaction and transport behavior, extracting unique descriptor sets for different molecules and evaluating features of interest (e.g., species identity and concentration) within multicomponent solutions. Specifically, I first construct an algorithm that utilizes reaction-transport models and Bayesian inference to correctly identify RAOs using cyclic voltammetry and cyclic square wave voltammetry in several independently prepared multicomponent solutions in near-real-time (< 5 min). I subsequently estimate the degree to which an electrolyte solution is charged, as well as the total RAO concentration, with high accuracy (< 4 % average error), in real-time (< 1 min), and in an automated fashion. Finally, I present a protocol that jointly evaluates microelectrode (electrode radius *ca*. 5–50 μm) and macroelectrode (radius *ca*. 1 mm) voltammograms to improve the performance of the initial compound identification protocol. Through these developments, I lay a foundation for refined *in situ* or *operando* voltammetric methods to aid in understanding, and consequently mitigating, RAO decay; this, in turn, may accelerate the development of new electrochemical technologies for a sustainable energy economy.

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