Theory of Diffusion Impedance in Nanostructured Electrochemical Systems

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Electrochemical energy storage is under the spotlight with ever-increasing interest in portable electronics, electric vehicles, and renewable energy sources. Batteries, capacitors, fuel cells, and their hybrids are being studied and applied at different scales for a wide variety of applications. In pursuit of higher energy and power density, as well as longer lifetime, modern electrochemical energy systems commonly employ nanostructured materials: battery electrodes consist of nanoparticles; capacitor electrodes are full of nanopores; and in fuel cells and flow batteries, electrolytes flow through nanoporous electrodes. While the nanostructures determine important parameters affecting the diffusion impedance, such as transport length and surface area, their configuration has been largely overlooked in interpreting the spectra. In this thesis, we investigate the diffusion impedance of nanostructured electrochemical systems by developing theoretical models and validating them with experimental spectra. We begin by studying the diffusion impedance of nanoparticle batteries, and extend the approach to other electrochemical energy systems, including capacitors, fuel cells, and flow batteries.

In general, nanostructures in electrochemical energy systems have inherent randomness, such as particle size distribution in batteries, pore size distribution in capacitors, tortuosity distribution in membranes and porous electrodes, and inhomogeneous boundary layer thickness in flow batteries. Such configurational randomness commonly introduces the distribution of diffusion time; that is, the diffusion time constant is not set to a single value but rather expands over a range. Therefore, not only nominal properties of the nanostructures, but also their distributions play an important role in diffusion impedance. The finite Warburg and Gerischer models are generalized by incorporating the distribution of diffusion time. Inversion of the model renders accurate image-equivalent information of the nanostructures, suggesting a nondestructive, global diagnostic method, "*impedance imaging*", by simple impedance measurement. An inversion method based on Tikhonov regularization is presented and demonstrated by its applications to experimental spectra of a capacitor, a battery, and a flow battery. This approach can be generally applied to all electrochemical systems employing nanostructures

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