

Probing Sensitivity of Discharge Characteristics to Model Selection using Uncertainty Quantification in an Aprotic Li-Oxygen Battery

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Currently, there are several models in the literature, such as kinetic models, microstructural models, and mass transport models that describe a Li-air battery's discharge behavior. Many of these models are calibrated and tested at low current densities and cannot be easily transferred to high current densities. Even at low current densities, there is no quantitative method for a researcher to choose a reaction kinetic model such as classical Butler-Volmer and its derivatives, and modified Marcus-Hush-Chidsey, a resistance model for lithium peroxide such as electron transport via tunneling or linear resistivity, a surface coverage model (lithium peroxide growth) such as partial coverage or full coverage, and mass transport model (discussed in Ref. [1]). Also, it is time-consuming to test different models at high current density ($\geq 1\text{C}$) due to a lack of well-tested models and well-calibrated model parameters. For this presentation, we will develop an analytical model, which acts as a surrogate model for a sophisticated finite element model to predict discharge time and discharge voltage. Next, we use an uncertainty quantifying technique called reduced-order stochastic optimization [2, 3] to determine the uncertainty in model parameters for rate kinetics, lithium peroxide resistivity, and parasitic resistance. Finally, a finite element simulation is performed to determine the error introduced by the surrogate model and its influence on the uncertainty in the model parameters.

Our preliminary polarization analysis shows that the resistance models, coupled with Butler-Volmer kinetics, cannot describe the voltage polarization observed in the experiments at high current densities. In order to quantify and rank kinetic models, first, an analytical model is developed to account for discharge product distribution, concentration polarization, and voltage polarization as a function of time, based on the previous work on aqueous electrolytes, presented in Ref. [4]. The analytical model considers reaction kinetics, oxygen mass transport, voltage polarization from lithium peroxide deposition as a conformal coating, and the change in porosity, lithium peroxide thickness, and the active surface is assumed to be uniform throughout the cathode.

In order to rank the kinetic and resistance models, the uncertainty in the model parameters is assumed using a probability distribution function, and the resulting statistics are gathered using the Stochastic Reduced Order Model (SROM) approach. SROM is a computationally lite approach that uses significantly less number of samples compared to Monte Carlo to represent the input distribution. Since the number of samples required for Monte Carlo increases with model complexity and the computational time and resources required for full finite element simulations increases significantly and the SROM approach can reduce the computational requirement atleast ten times without introducing significant algorithm errors.

Although the analytical model incorporates the important aspects to simulate a battery, it neglects the complexity of spatial distribution and temporal variation of the discharge product and the complex relationship between microstructure and mass transport of oxygen and lithium ions. This complexity introduces a model error in the final parameter estimation and needs to be accounted for to rank various models. The finite element model (FEM) is used to quantify the error in the surrogate model because of its low fidelity. The FEM model is implemented in COMSOL and considers porous electrode theory for the cathode, concentrated theory for the electrolyte, a resistance model for the discharge products, a kinetic model, Fickian diffusion for the oxygen transport, and an oxygen dissolution model [5].

References:

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