Electrochemical Impedance Spectroscopy of a LiFePO4/Li Half-Cell

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Abstract

Introduction: Li-ion battery models designed with COMSOL Multiphysics are usually intended for simulating the battery behavior during a period of time going from few minutes to many hours. However, most of Li-ion battery models designed today are based on equivalent circuit models. These models are composed of electrical components (resistances, inductances, capacitances, etc.) whose values are identified when the battery is at equilibrium by an experimental method called "Electrochemical Impedance Spectroscopy" (EIS). Therefore, we tried to simulate a model of a LiFePO4/Li half-cell, for which we had EIS experimental data, in order to see if our model was also able to simulate the battery behavior for frequencies going from 10 mHz to 200 kHz. Use of COMSOL Multiphysics: The battery model designed in this work has been derived from the most famous papers published in this field of activity [1-5]. The critical task in this modeling approach is not the equations, since they are well known and understood, but the identification of many physical parameters in order to fit the experimental data. COMSOL Multiphysics is thus used with the LiveLink™ for MATLAB® to simulate our time-dependent model as if it was a simple MATLAB® function. This allows us to automatically optimize the parameters and process the results in order to get a simulated EIS matching the experimental one. Results: The results we got so far are presented in Figure 1 by comparing the simulated EIS (red) and the experimental EIS (blue). The spectra begin with high frequencies on the left and moves to the right along with the decreasing frequencies. Our fit is of course not perfect, but getting to it showed us what was actually missing in our model. It is worth mentioning that no one really tried such a comparison so far, according to the available literature. This could be a first step to create a link between battery multiphysics models and equivalent circuit models, with the intention of understanding the physical meaning of electrical components usually selected just to fit experimental data. Conclusion: EIS measurement data can be used to identify specific battery parameters, such as kinetic and transport parameters, in order to improve existing battery models. We demonstrate that it was suitable for a Li-ion coin cell. The possibility offered by COMSOL Multiphysics to take into account two different models in one (particles at the micro-scale and battery components at the macro-scale) gives a clear insight of what is going on inside the batteries when they are subjected to EIS. Moreover, one can see the impact of the EIS signal amplitude and number of periods on the quality of the impedance we get in return.

Reference

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Figures used in the abstract

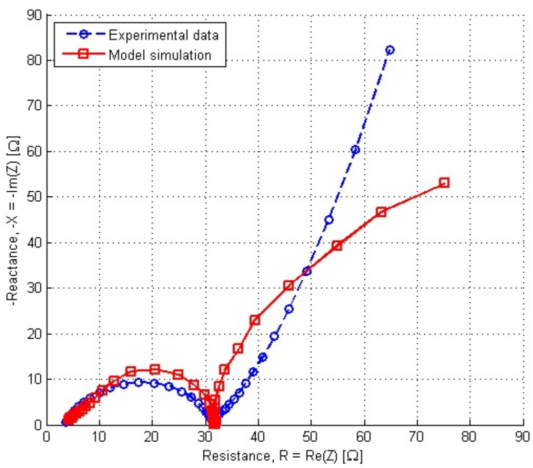

Figure 1: Comparison between the simulated EIS (red) and the experimental EIS (blue).