Operando Electrochemical Impedance Spectroscopy and Its Application to Commercial Li-Ion Batteries

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Abstract:

Electrochemical impedance spectroscopy (EIS) is a powerful non-invasive tool for characterizing electrochemical systems. Applied to Li-ion batteries, EIS is shown to be an informative indicator for their state-of-health (SoH). However, EIS is limited by the constraints of linearity and stationarity, while Li-ion batteries inherently behave in a nonlinear and nonstationary way. Regarding linearity, the voltage over the electrodes is a nonlinear function of the current through the electrodes. Linearity is achieved by applying a small amplitude zero-mean current excitation around an operating point, such that the nonlinear function is quasi linear in this range. Regarding time-variation, the impedances of fully charged and fully discharged cells are different, the same for pristine and aged cells, or cells kept at room temperature and in freezing environments. For Li-ion batteries, this means that EIS experiments should be performed in steady-state when at a specific state-of-charge (SOC) and temperature. The impedance therefore depends on the operating point (temperature and SOC) and the constraints of linearity and stationarity are very restrictive.
Lately, we have developed operando EIS to reveal impedance data from measurements not satisfying linearity and stationarity. This technique allows to measure the impedance of electrochemical systems along a time-varying trajectory, for instance, while charging or discharging Li-ion batteries. For this purpose, a nonzero-mean odd random phase multisine current excitation is used, and the time-varying impedance along the trajectory is estimated from the spectrum of the voltage response.

Moreover, nonlinear distortions in the measurements are detected and quantified, the noise level is estimated, and uncertainty bounds are enclosed on the time-varying impedance. For Li-ion batteries most time-variation happens at low frequencies. However, obtaining time-varying impedance data at low frequencies is a challenging problem. This on the one hand due to drift signals, for instance the increasing voltage while charging a battery, hiding the low frequency content, and on the other hand due to low-frequency noise. Operando EIS implements a drift signal suppression such that obtaining impedance data at low frequencies becomes attainable.

In this talk we present operando EIS measurements while charging and discharging commercial Li-ion batteries, demonstrating that the battery's impedance while charging, discharging and resting are different from each other. Prospectives are given for utilizing operando EIS data for smart-charging and SOH prognosis applications.