BFH Bern University of Applied Sciences

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BFH-CSEM Energy Storage Research Centre

Infrastructure

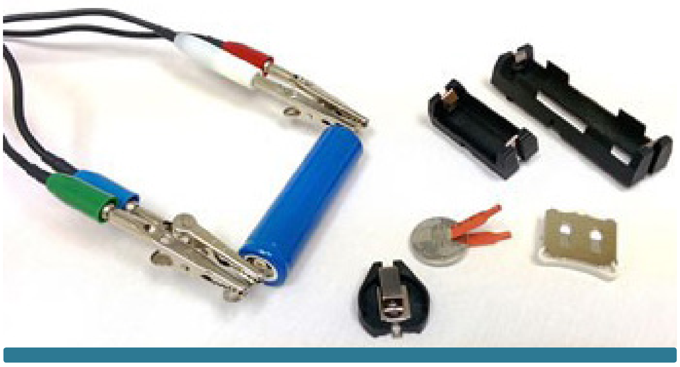
Electrochemical Impedance Spectroscopy for modeling of lithium-ion batteries

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an experimen-tal method used to characterize electrochemical systems. EIS is used to measure the impedance (AC resistance) of an electro-chemical device, e.g. a battery, a super capacitor or a fuel cell, over a range of frequencies by either applying a constant voltage (potentiostatic) or current (galvanostatic) to measure the current and voltage response of the sample, respectively.

$Z\omega = E\omega / I\omega$
$E\omega$ = Frequency-dependent potential
$I\omega$ = Frequency-dependent current

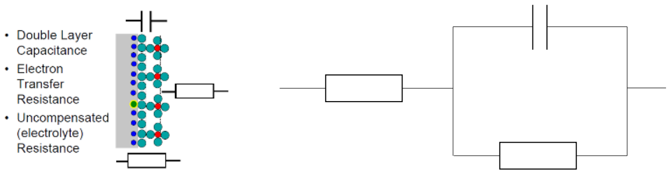
In the case of Li-ion batteries, the galvanostatic method is preferred. Here, the in-phase and out-phase components of the voltage response are fitted to an equivalent circuit that models the electrochemical cell. Such equivalent circuit components
(resistances, capacitances, etc.) are used to model physical quan-tities such as the series resistance, the double-layer capacitance, the charge transfer resistance, and the mass transfer resistance. The analysis takes advantage of the fact that these different circuit elements dominate the impedance in different frequency regimes.



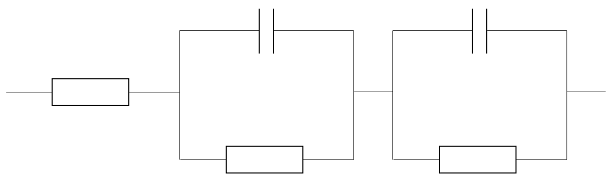
Pictures 1 and 2: Website Gamry

Equivalent circuits for electrochemical devices

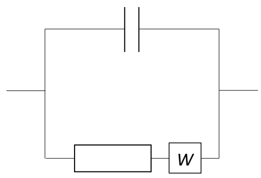
In its simplest form, the working electrode of a three-electrode electrochemical cell can be represented as a resistor connected in series to an RC circuit.



Such a circuit (Randles circuit) is valid for high-frequency ranges, where mass transport effects are minimal.
Because of the complexity of Li-ion batteries and because we have a two-electrode system, we must consider all the series im-pedances of both electrodes and the electrolyte. A typical battery equivalent circuit might look like this:



The mass-transfer effects obtained at low frequencies can addi-tionally be represented by a so-called Warburg circuit element W.

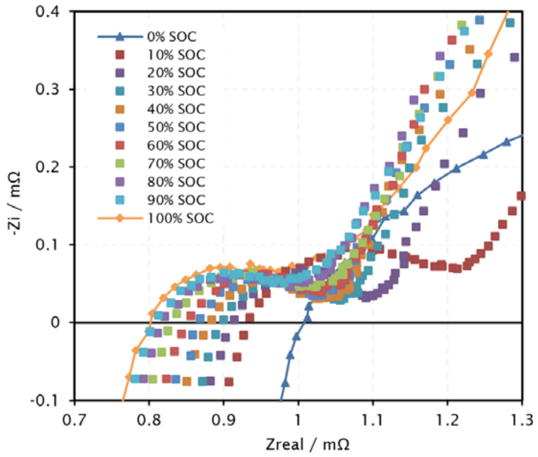


In general, electrolyte, insulating layer (SEI) and charge trans-fer resistance are dominant at high frequency and diffusion or mass-transfer resistance becomes significant at low frequencies.

Some of the benefits of EIS are:
- Validation of data sheet impedance values
- Extension of data sheet impedance values by measuring at different frequencies
- Highly accurate measurement of the impedance of a cell at different states of charge
- The impedance spectrum provides information about the electrochemical properties, interactions and changes of the cell components
- The energy storage and dissipating components of a cell can be represented with mathematical equations
- Impedance spectra are useful for Electrical Equivalent Circuit (EES) modeling and thus developing model-based SOC and SOH algorithms for advanced Battery Management Systems (BMS)

EIS at BFH Energy Storage Research Centre (ESReC)

The battery testing and BMS development group at ESReC takes advantage of the benefits provided by EIS, e.g. for analyzing the cell's behavior at different SOC and health status of the cell. EIS provides data necessary for the development of SOC estimation algorithms and SOH estimation and prediction models.
For example, the Nyquist diagram below shows the dependence of impedance on a NMC/LTO cell on the state of charge after being tested for more than 300 cycles.

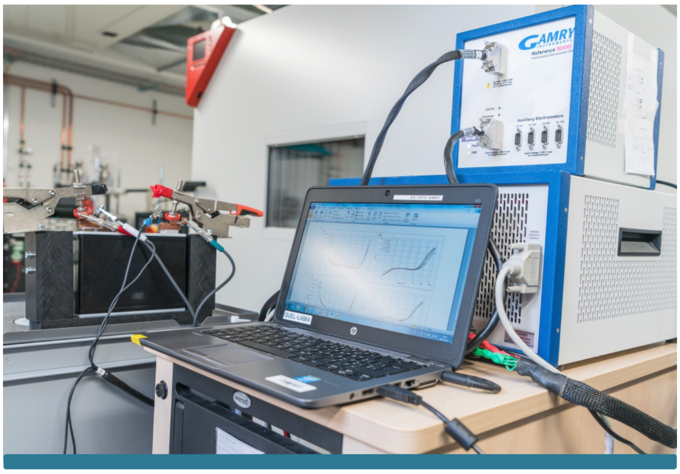


The measurements were obtained between 0.01 and 3000 Hz at 0.1 A using a "Gamry Reference 3000" EIS test equipment. The Nyquist plot clearly shows the dependence of the electrolyte or solution resistance (Zreal at zero Zi) and the semicircle range on the SOC of the cell. Lower impedance values are found at high-er SOC levels. The plot also differs from the one measured with the new cell, i.e. at zero cycles.

Such relationships and differences in the impedance response spectra were subsequently used to derive EEC for implementation in in-house developed SOC and SOH estimation algorithms.

EIS tester

Some features of our EIS tester are:
- Potentiostatic and galvanostatic EIS measurement
- Available frequency spectrum from10 µHz to 1MHz
- A 30 A booster for high currents is available
- Provides a set of analysis tools including statistical analysis, im-pedance spectra (Nyquist and Bode plots), histogram analysis, fitting tools and a graphical model editor for fitting spectra to equivalent circuit models



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