# Chem 524 - Experiment 3
Electrochemical Impedance Spectroscopy of a Lithium Ion Battery

Background: This experiment will introduce you to the use of electrochemical impedance spectroscopy (EIS) for the characterization of an electrochemical cell.

EIS experiment. In the EIS experiment, the cell is held at a constant potential (or at a fixed current) and a small AC voltage is applied. The frequency is varied over a broad range (typically 0.01 Hz to 100's of kHz or even MHz), and the in-phase and out-of-phase components of the current response are fitted to an equivalent circuit that models the electrochemical cell. These models are described in some detail in Ch. 11 of the text. Components of the equivalent circuit (resistances, capacitances, Warburg impedance) are used to model physical quantities 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.

Equivalent circuits for electrochemical cells. The working electrode of a simple three-electrode electrochemical cell has, at relatively high frequency where mass-transport effects are minimal, an equivalent circuit that looks like:
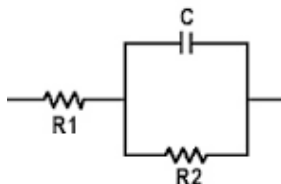
In this circuit (called a Randles circuit), R1 represents the series resistance of the electrolyte, C is the double-layer capacitance, and R2 is the charge-transfer resistance. At low frequency, we must consider also the effects of mass-transfer, which cannot be modeled as a simple resistor or capacitor. As explained in your textbook, the mass-transfer impedance is represented by a Warburg circuit element and the equivalent circuit of the cell becomes:
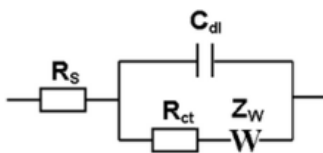

A lithium battery is more complex still, because it is a two-electrode cell, in which we must consider all the series impedances of both electrodes and the electrolyte. The battery contains high surface area anodes and cathodes, as well as a liquid electrolyte. A solid-electrolyte interphase (SEI) layer is formed on the surface of the Li metal or LiC_6 anode. A typical battery equivalent circuit might look like this:
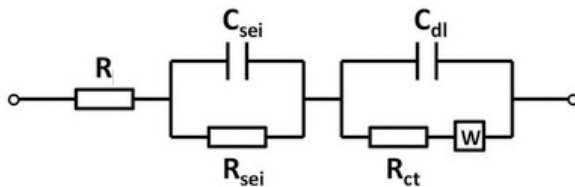
Because $C_{dl}R_{ct} \gg C_{sei}R_{sei}$, the SEI impedance is more important at high frequency and the circuit element at the far right (containing C_{dl}, R_{ct}, and W) is dominant at lower frequency. At very high frequency the series resistance R (together with some inductance from the metal casing and wiring of the battery) dominates the circuit, because both C_{sei} and C_{dl} effectively become short circuits.

Voltage response of a discharging battery. The effects of these series impedances are easily seen in a current-step experiment, where the discharging current is abruptly stepped from a low constant value to a higher value. The typical voltage response of a battery during a current step looks like the red trace in this figure:
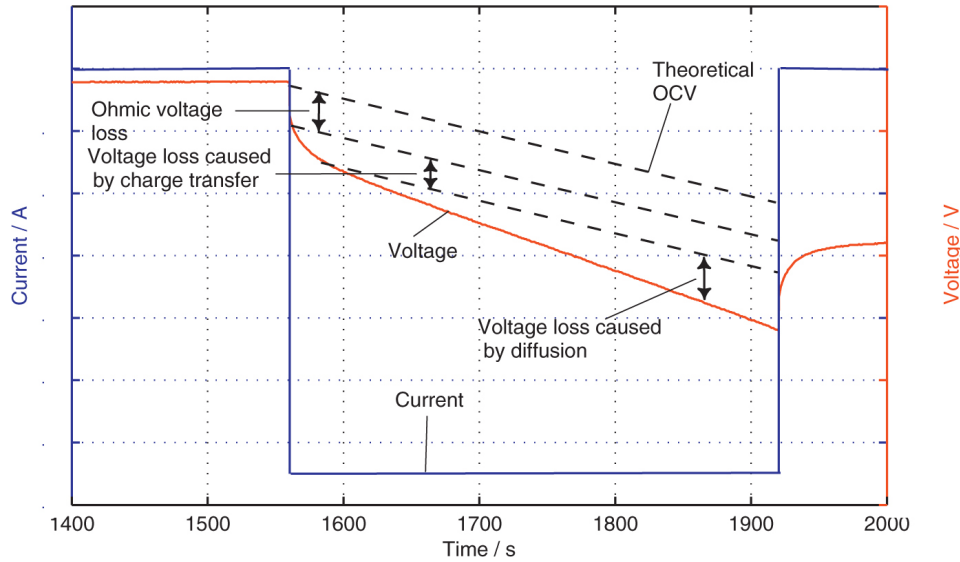
Referring to the battery equivalent circuit above, we can identify the series resistance components $R + R_{sei}$ with the instantaneous voltage drop at the moment of the current step. There is then an exponential current decay on a timescale of seconds (the $C_{dl}R_{ct}$ timescale), resulting in a second voltage drop that corresponds to R_{ct}. Finally there is a slower voltage drop that arises from the mass transfer impedance of the cell. This mass transfer effect is most evident on long timescales (i.e., at very low frequency).

Nyquist plots. We can get more detailed information about the series impedances in an electrochemical cell by plotting impedance in the complex plane, with the real and imaginary components (Z' and Z", respectively) on the horizontal and vertical axes. A typical Nyquist plot for the working electrode of a three-electrode cell is shown below. Each RC component of the cell (in this case there is only one) results in a semicircle of diameter R centered at $\omega = 1/RC$. The Warburg impedance results in a low frequency "tail." From this kind of plot we can obtain accurate values for R and R_{ct}, as well as the mass transfer parameter σ. Because the value of the capacitance can be frequency-dependent, C_{dl} (and C_{sei} in the more complex battery circuit) are sometimes replaced by constant phase elements (CPE) in the fitting of experimental data.
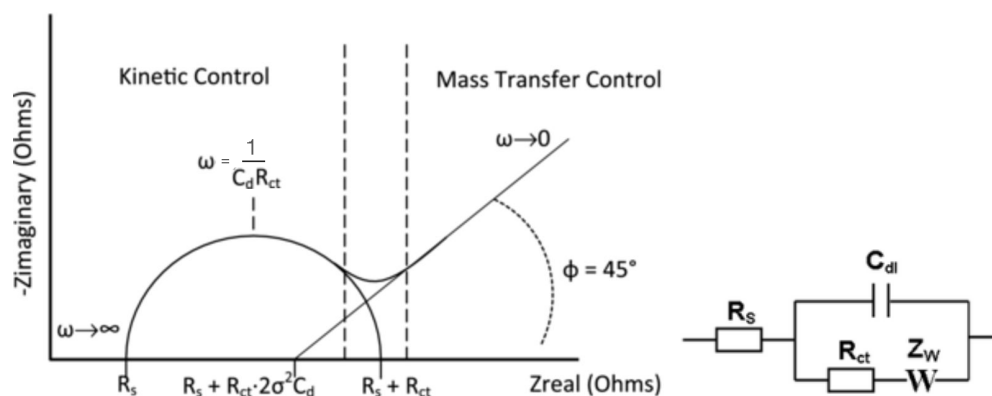
Procedure:

You will measure the impedance spectrum of a lithium coin cell battery, and then repeat the experiment with a simple RC dummy circuit in order to practice fitting the data. You will then do a current step experiment with your battery to get approximate values of the series and charge tranfer resistances. Finally you will fit your battery EIS data to obtain the impedances in the equivalent circuit.

1. *EIS spectrum of a Li coin cell battery.* Obtain an Energizer CR2025 lithium ion battery from your instructor (or from the grocery store) and wire it as shown in the picture below.
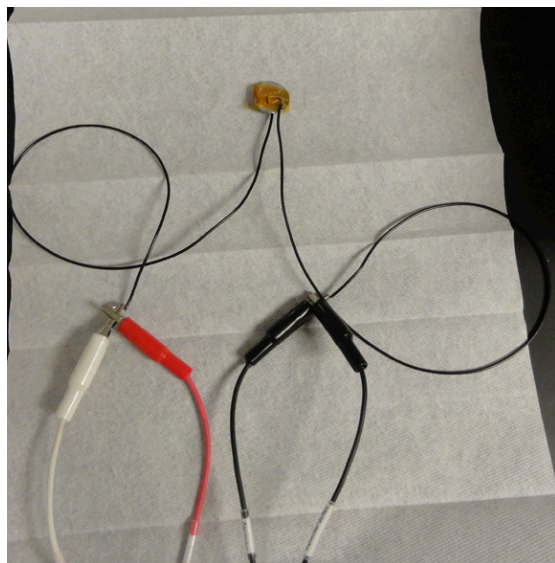

The positive face of the battery (marked with a + sign) should be connected to the two working electrode leads (black), which are shorted together.

The negative face of the battery should be connected to the reference (white) and counter electrode (red) leads, which are shorted together.

Use insulated wire to avoid short circuits between the electrode leads (alligator clips) and the battery. The exposed ends of the insulated wire can be secured to faces of the battery with transparent tape as shown.

Typical settings for the EIS module of the EZstat-pro are shown below. Before starting the experiment, the potentiostat will read the open circuit voltage of the battery as the cell potential, in this example 3.207 V. Set the bias potential a few mV lower than the open circuit voltage to allow a trickle discharge current during the EIS experiment. Set the AC amplitude to 10 mV, and set the frequency limits to collect data between 0.1 Hz and 10 kHz. When you press the "run" arrow the instrument will start to collect the impedance data. If everything goes right you should see two semicircles in your Nyquist plot, with the low frequency semicircle overlapping the Warburg tail.

Save the data for later analysis.
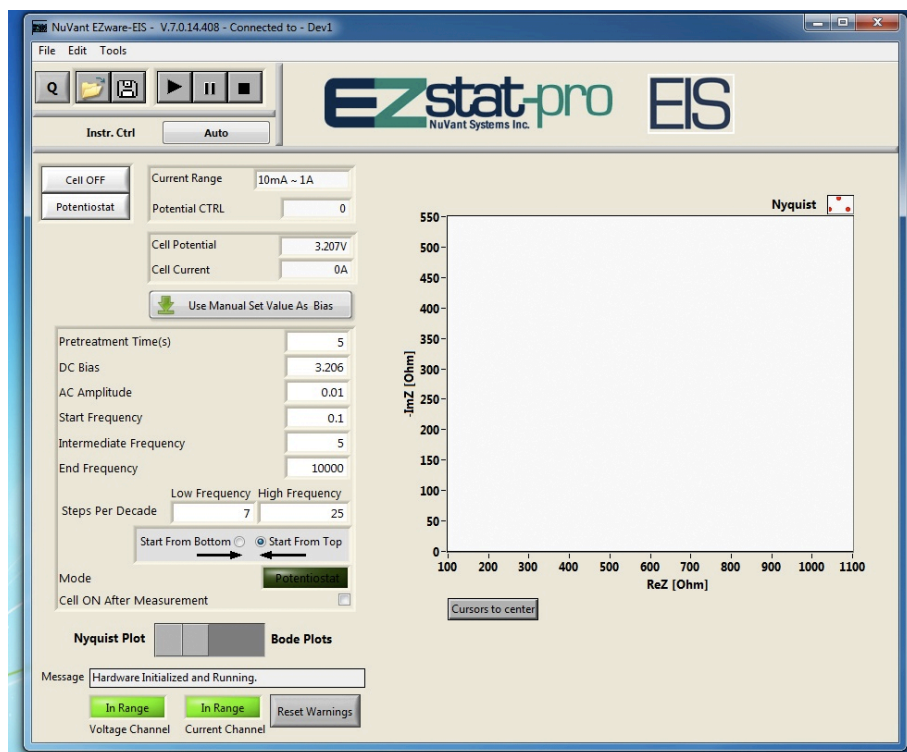
2. *EIS spectrum and analysis of a simple RC circuit.* Using the dummy cell shown below, obtain an EIS spectrum between 0.1 Hz and 10 kHz at a bias potential of zero volts. Verify that the Nyquist plot shows the correct impedances corresponding to the circuit you chose. For example, using the Randles circuit shown below you should obtain a single semicircle.
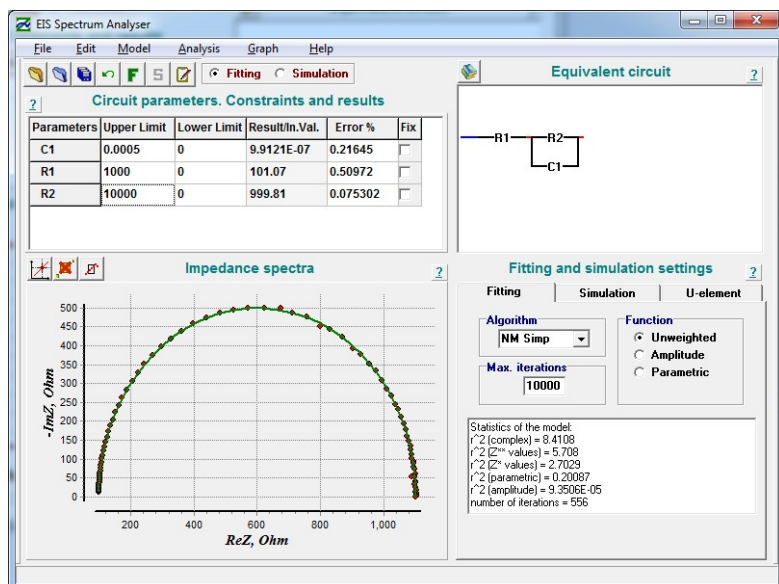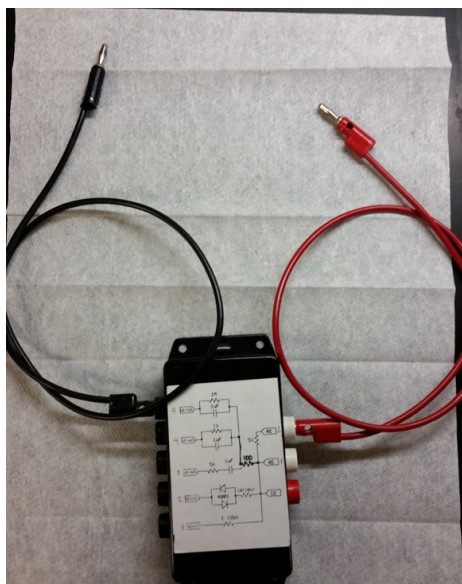
Use the EIS Spectrum Analyzer program on the EZstat-pro to fit the impedance spectrum of the dummy cell. The program will allow you to draw whatever equivalent circuit you like in the upper right box and then fit the impedance parameters starting with trial "upper limit" values. Because the program uses a nonlinear fitting routine, it can get lost if these trial parameters are too far off the mark. However, you should be able to get a good estimate of the parameters by looking at your semicircle. For example, in the one shown above, we can see that R1 is about 100 Ω and R2 is about 1000 Ω from the two x-intercepts of the semicircle. Also, from the frequency at the top of the semicircle we can estimate the RC time constant and thus obtain a trial value for C.

3. *Current step experiment with the Li ion battery.* Using the pre-programmed current step recipe on the EZstat-pro, discharge your battery at 0.5 mA for one minute, and then step to 1.0 mA and hold for three minutes. The data should look something like the figure below. From your data, obtain trial values of $R_{series} + R_{sei}$, C_{dl}, and R_{ct}.
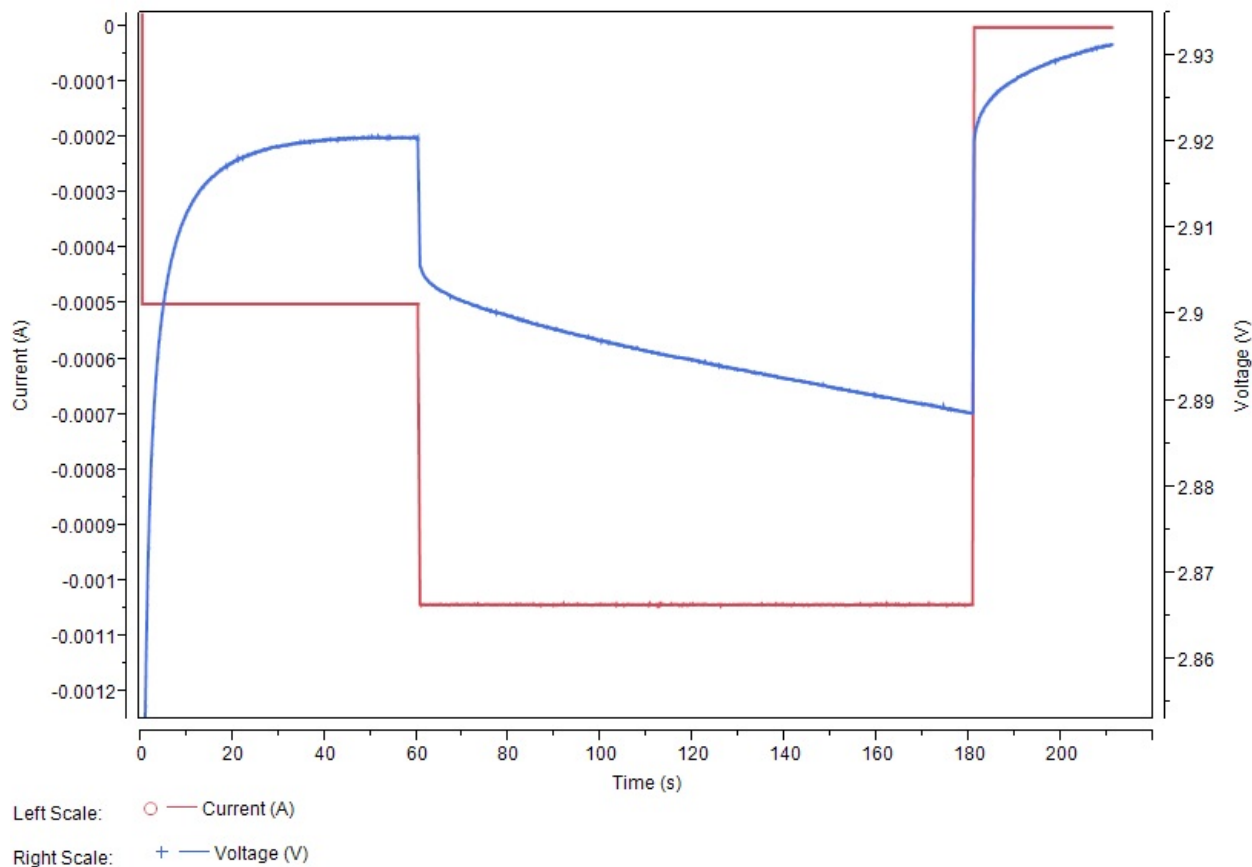
4. *Fitting the EIS spectrum of the Li battery.* Using the EIS Spectrum Analyzer program, draw an equivalent circuit for your Li battery. Now fit the Nyquist plot you obtained in the first step using the trial R and C values you obtained in the current step experiment.

Questions:

- Plot your EIS data for the Li battery as Z_{Im} vs. Z_{Re} and superimpose your fit to the data. Are you able to obtain a better fit with capacitive or CPE circuit elements?

- From the data and the fit, determine and report R_{series}, R_{sei}, R_{ct}, C_{sei}, C_{dl}, and the mass transfer parameter σ for your Li ion battery.

- According to the spec sheet for the Energizer CR2025 battery, it is recommended for use with electronic devices that have an impedance of about 15 kΩ. Considering the internal resistances in the cell, what fraction of its power would be a wasted internally as heat when it powers such a device? How would this change if it were powering a 10 Ω device, such as a flashlight bulb?

- The double layer capacitance of a typical planar electrode is about 10 μF/cm^2. Compare this number to the value of C_{dl} you determined from the Nyquist plot and/or current step experiment. What does it imply about the surface area of the electrodes in the coin cell?

References:

Bard & Faulkner, Electrochemical Methods, 2nd Edition, Ch. 10.

D. Andre et al., "Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy. I. Experimental investigation," *Journal of Power Sources* 196 (2011) 5334–5341.