

## A Process Model for Electrochemical Impedance Spectroscopy of LiCoO<sub>2</sub> Batteries

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This paper provides the results of preliminary impedance measurements on commercial LiCoO<sub>2</sub> coin cells. The impedance response was shown to be very sensitive to state-of-charge (SOC), temperature, and abuse such as overcharging and over-discharging. A process model was developed to reveal the influence of these conditions on electrochemical parameters.

### Experimental Method

Electrochemical experiments were performed on commercial LiCoO<sub>2</sub> coin cells. Impedance spectroscopy was used to monitor changes associated with different SOC and with different surrounding temperature conditions, imposition of overcharge, and imposition of over-discharge.

### Battery Cells

Commercial secondary 2032 button (or coin) cells were purchased from AA Portable Power Corp. (Richmond, CA, <http://www.batteryspace.com>). The cathode was LiCoO<sub>2</sub>, the anode was graphite, the electrolyte was the composition of lithium hexafluorophosphate (LiPF<sub>6</sub>) salt in a mixture of organic solvents such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). The normal potential range of the cells is between 3.00 and 4.20 volts.

### Instrumentation

Electrochemical experiments were performed using a Gamry PCI4/750 Potentiostat connected to a desktop computer. Gamry's Virtual Front Panel (VFP600) and Electrochemical Impedance Spectroscopy (EIS300) software packages were employed. A Tenney Jr. environmental test chamber was used to control the temperature of a battery and its surroundings.

### Protocol

The impedance response and capacity were analyzed during different SOC profiles. The impedance response of batteries was analyzed in the normal potential range and under overcharge and over-discharge profiles. To obtain the battery capacity, the LiCoO<sub>2</sub> cells were initially charged to 4.20 V under galvanostatic control, with a current of 2 mA. Each cell was discharged to 3 V with a 1C rate and charged back to 4.20 V with the same bias, i.e., at a constant 30 mA current. The cells were potentiostatically held at constant cell potential until the current was less than 20 μA. After the constant-potential rest period, the impedance was measured using a 10 mV ac perturbation and a 10 kHz – 20 mHz frequency range. Following each impedance measurement, the cell potential was potentiostatically modified for the discharge profile in 0.20 V steps. In the same manner, the charge profile was executed immediately following the discharge schedule. Impedance measurements were implemented between -20 and 60 °C having 10 °C increments starting from 20 °C. In addition, the effect of overcharging and over-discharging were analyzed in which the impedance

was measured at 80 mV increments up to 5 V and down to 2.2 V.

### Results

The impedance data obtained under normal operation conditions, i.e. at 4.2 V, revealed a depressed capacitive loop at high and intermediate frequencies and a straight line at low frequencies with slope greater than 45°. A model was developed that was based on the reactions proposed to take place at the cathode and anode. The resulting model can be expressed as

$$Z = R_c + Z_c + Z_a \quad (1)$$

where

$$Z_c = \frac{R_{t,c} + Z_{d,c}}{1 + (j\omega)^{\alpha_c} (R_{t,c} + Z_{d,c}) Q_c} \quad (2)$$

and

$$Z_a = \frac{R_{t,a}}{1 + (j\omega)^{\alpha_a} R_{t,a} Q_a} \quad (3)$$

The impedance data could not be described by a Warburg impedance because the slope of the low-frequency impedance in a Nyquist plot is near 56°, which is much larger than the 45° associated with the Warburg impedance. Instead, an anomalous diffusion impedance was used which is associated with systems that show a diffusion hindered by sporadic adsorption of diffusing species to a fixed substrate. The associated impedance response, with a reflecting boundary condition, was solved by Bisquert and Compte.<sup>1</sup> As the measured frequency range does not reveal the sharp increase associated with the reflecting boundary condition, an asymptotic form of their expression was used, and the resulting diffusion impedance is given as,

$$Z_{d,c}(\omega) = \left( \frac{Z_{d,c}(0)}{\tau^{\gamma/2}} \right) (j\omega)^{\gamma/2-1} \quad (4)$$

where  $Z_{d,c}(0)/\tau^{\gamma/2}$  is a lumped parameter that includes the diffusion time constant  $\tau$  and the zero-frequency asymptote for the real part of the diffusion impedance.

A sample regression result is presented in Figure 1 for a cell held at 4.2 V. The quality of the fit is excellent.

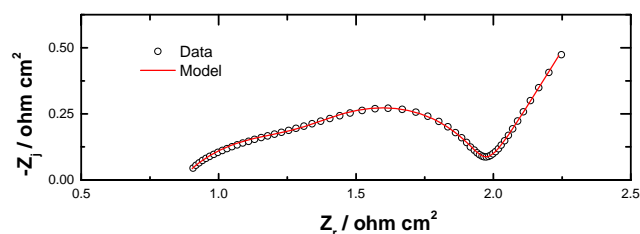


Figure 1: Impedance data for a battery held at 4.2 V. The line represents the fit of equation (1) to the data.

### Reference

1. J. Bisquert and A. Compte, *Journal of Electroanalytical Chemistry* **499** (2001) 112-120.