In situ measurement of shrinking/dilation of energy storage device during cycling

I – INTRODUCTION
As expected, many Li-ion battery materials expand during lithiation, and shrink during delithiation. LiCoO$_2$ is a prominent exception from this rule.
LiCoO$_2$ consists of layers of monovalent lithium cations (Li$^+$) that lie between extended anionic sheets of cobalt and oxygen atoms, arranged as edge-sharing octahedra. Lithium ions can be reversibly inserted into this structure in the potential range 3.0 to 4.3 V corresponding to $x$ varying between 1 and about 0.5 in the formula Li$_x$CoO$_2$, and the capacity varying between 0 and 140 mAh/g. In this reversible potential range, the interlayer distance along the c-axis continuously decreases during lithium insertion as has been shown by in situ XRD [1, 2]. At above 4.5 V, the lithium ions undergo an order-disorder transition that is coupled to a change in the crystal lattice to a metastable (O1) state. This transition and as well the excessive SEI growth beginning already at 4.3 V are considered to induce a capacity fading at elevated potentials [1, 2] (Fig. 1 & 2).

II – SET-UP DESCRIPTION
Measurements are performed on a three-electrode cell. The electrodes and electrolyte are:
- LiCoO$_2$ electrode with a diameter of 9 mm and 80 µm thick on Aluminum foil.
- Lithium metal for both counter and reference electrode.
- LiClO$_4$ salt (1mol/L) in Ethylene Carbonate and Dimethyl Carbonate (EC/DMC) with ratio of 1/1 as electrolyte.

The outputs of dilatometer data logger are connected to the analog inputs of the VSP instrument (Fig. 3).

The shrinking & dilation measurement during battery cycling is helpful for battery development. This method can also be applied to super capacitor testing.

Figure 2: (top) Differential capacity vs. Li concentration in Li$_x$CoO$_2$; (bottom) phase diagram of Li$_x$CoO$_2$ developed from dq/dV vs. diagram and in situ XRD measurements from [1].

In this application note, we report the charge-induced dilation of a LiCoO$_2$ electrode measured with ECD-nano-DL from EL-CELL and controlled by a Bio-Logic potentiostat/galvanostat. The set-up is described first, followed by the resulting measurements.

Figure 1: (a) The lattice constants, $a$ and $c$, measured from the XRD patterns collected during the first charge. The measurements were made on ZrO$_2$-coated LiCoO$_2$ (sample A) from [1]. (b) Data for uncoated LiCoO$_2$ from [2].
The five leads of the cell cable are plugged into dilatometer data logger box as shown in Fig. 4.

The dilatometer and electrochemical data are recorded directly by EC-Lab® (no need to synchronize two software interfaces). The “External Devices” window has been configured as follows (Fig. 5):

- Select “Dilatometer” in the “Device Type” combo box.
- Select “ECD-nano-DL” in the “Device Name” drop box.

The settings of the device are already set by default.

Note:
ECD-nano-DL operated in 250 µm (i.e. +/- 125 µm) displacement range. Displacement range of 100 µm is also available with the ECD-nano-DL.

III – MEASUREMENTS
The cycling of a LiCoO₂ cathode based battery is performed at 200 µA in a potential window of 2.0 to 4.6 V. No floating period is set. The settings of the GCPL technique are shown in Fig. 6.
Figure 7 shows the LiCoO$_2$ electrode dilation over seven successive cycles. As expected with the in situ XRD results [1], the dilation curve nicely shows an anomalous expansion during delithiation. Furthermore, the reported phase transitions close to the vertex points of the electrochemical cycle can clearly be seen. The phase transition at the upper vertex point at around 4.5 V fades out during cycling.

The configuration of the EC-Lab$^*$ software is described as well. It is noteworthy that similar measurements can be carried out on supercapacitors. These coupled measurements are complementary to other characterizations such as X-ray measurement.

REFERENCES

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