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

I- Background

As expected, many Li-ion battery materials expand during lithiation, and shrink during de-lithiation. $LiCoO_2$ is a prominent exception from this rule.

$LiCoO_2$ consists of layers of lithium that lie between slabs of octahedra formed by cobalt and oxygen atoms. Lithium ions can be reversibly inserted into and extracted from 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_xCoO_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 the excessive SEI growth commencing already at 4.3 V are considered to cause the capacity fade observed at elevated potentials [1, 2] (Fig. 1 & 2).

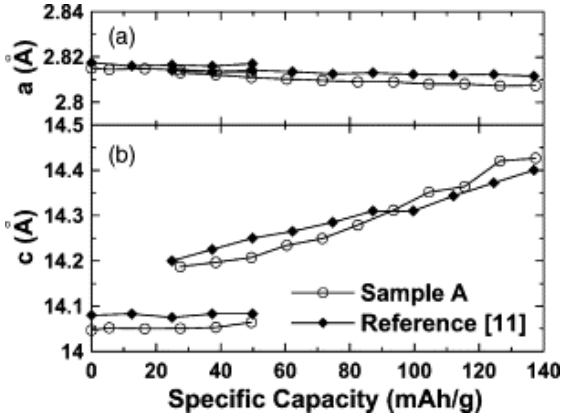

Fig. 1: (a) The lattice constants, a and c, measured from the XRD patterns collected during the first charge. The measurements were made on ZrO_2-coated $LiCoO_2$ (sample A) from [1]. (b) Data for un-coated $LiCoO_2$ from [2].

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

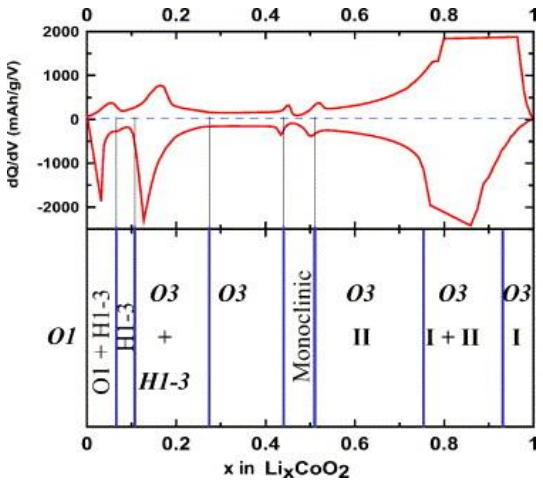

Fig. 2: (top) Differential capacity *vs.* Li concentration in Li_xCoO_2; (bottom) phase diagram of Li_xCoO_2 developed from dq/dV *vs.* diagram and *in situ* XRD measurements from [1].

In this application note, we report the charge-induced dilation of a $LiCoO_2$ electrode measured by the mean of the ECD-nano-DL from EL-CELL during a cycling controlled by a Bio-Logic potentiostat/galvanostat. Firstly, the set-up is described, followed by the resulting measurements.

The document is written in collaboration with EL-CELL.

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 with an active layer of 80 µm thick on Aluminum foil.
- Lithium metal for both the counter and the reference electrode
- $LiClO_4$ (1 mol/L) in Ethylene Carbonate/Dimethyl Carbonate (EC/DMC) with *ratio* of 1/1 as the electrolyte.

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

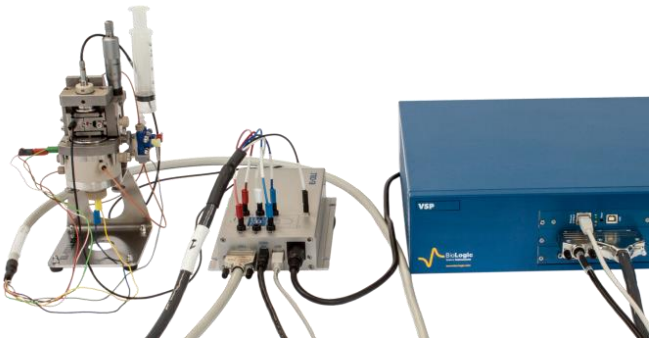

Fig. 3: Picture of the setup. Dilatometer (left), Data logger (center) & VSP (right).

The five leads of the cell cable are plugged into data logger box of the dilatometer as shown in Fig. 4.

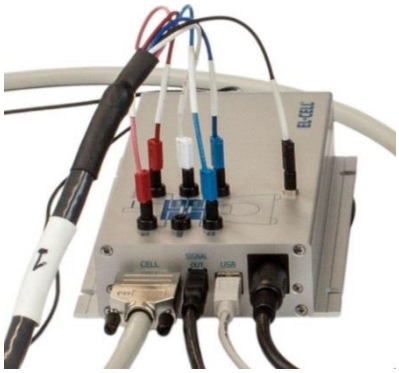

Fig. 4: Cell cable connected to the data logger box.

The dilatometer and electrochemical data are recorded 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.

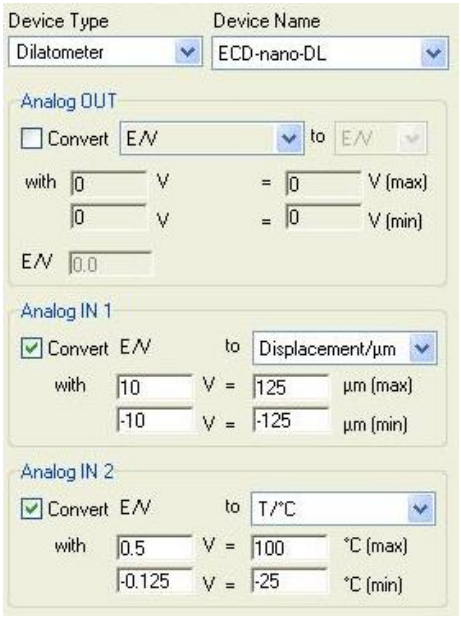

Fig. 5: ECD-nano-DL Dilatometer configuration in the "External Devices" window.

Note:
ECD-nano-DL operated in the 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 the $LiCoO_2$-based battery is performed at 200 µA in the extended potential range of 2.0 to 4.6 V. No floating period is set. The settings of the GCPL technique are shown in Fig. 6.

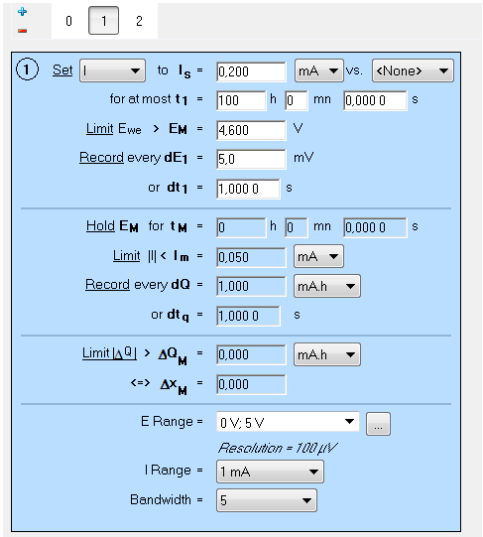

Fig. 6: GCPL settings. Only the charge is shown in the screenshot.

Fig. 7 shows the $LiCoO_2$ electrode dilation over seven subsequent cycles. The dilation curve nicely shows the anomalous expansion during de-lithiation, in good agreement with the *in situ* XRD results [1]. Further, 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.

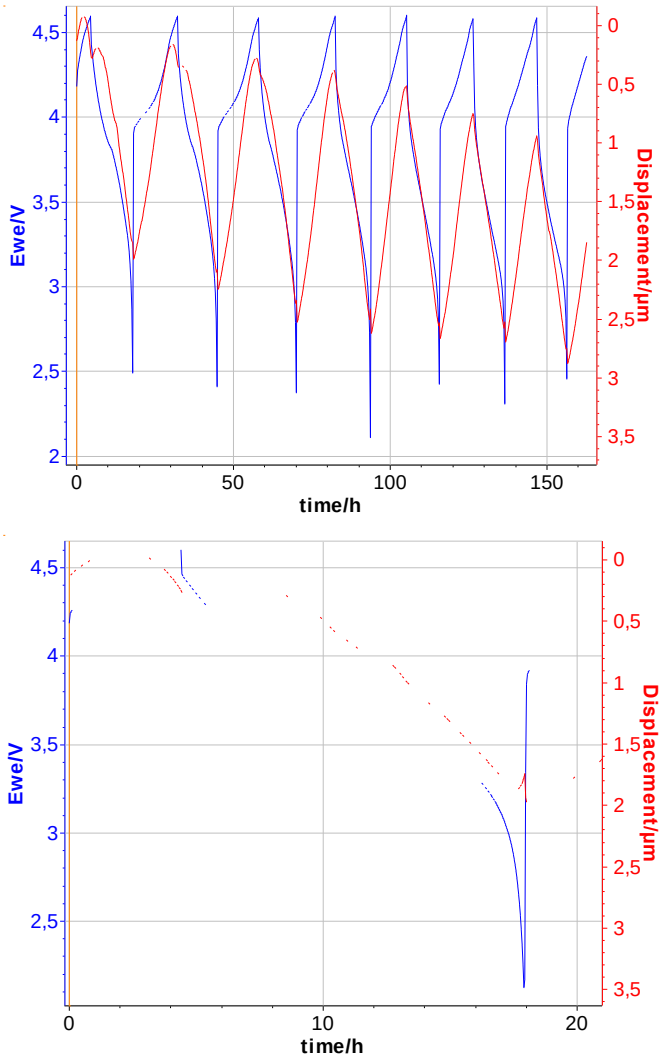

Fig. 7: Electrode potential and dilation changes during constant current cycling of a $LiCoO_2$ electrode. Bottom: focus on the phase transitions at the two vertex points and at the midpoint of the first discharge.

IV-Conclusion

This note shows how to connect the dilatometer and potentiostat/galvanostat together and perform an *in situ* dilation measurement during a battery cycling. The configuration of the EC-Lab® software is described as well.

It is noteworthy that similar measurements can be carried out on supercapacitor.

These coupled measurements are complementary to other characterizations such as X-ray measurement.

REFERENCES

[1] Z. Chen, J.R. Dahn, Electrochimica Acta, 49 (7) (2004) 1079.

[2] J.N. Reimers, J.R. Dahn, J. Electrochem. Soc. 139 (8) (1992) 2091.