

## *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.  $\text{LiCoO}_2$  is a prominent exception from this rule.

$\text{LiCoO}_2$  consists of layers of monovalent lithium cations ( $\text{Li}^+$ ) 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  $\text{Li}_x\text{CoO}_2$ , 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).

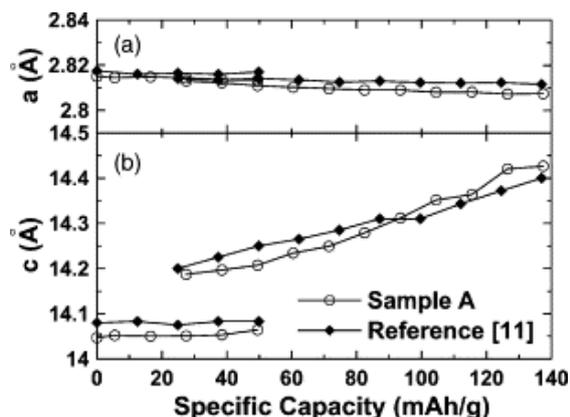


Figure 1: (a) The lattice constants,  $a$  and  $c$ , measured from the XRD patterns collected during the first charge. The measurements were made on  $\text{ZrO}_2$ -coated  $\text{LiCoO}_2$  (sample A) from [1]. (b) Data for uncoated  $\text{LiCoO}_2$  from [2].

The shrinking & dilation measurement during battery cycling is helpful for battery

development. This method can also be applied to super capacitor testing.

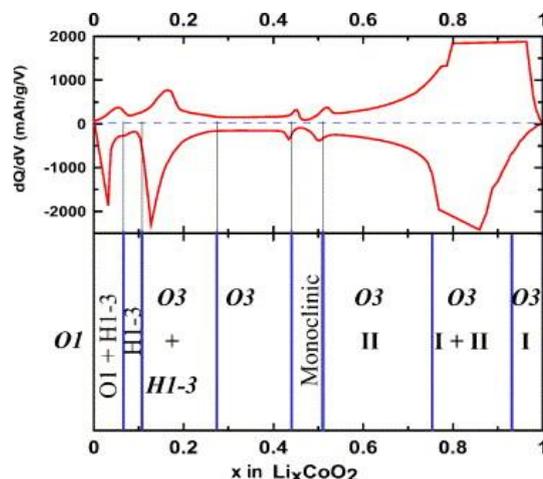


Figure 2: (top) Differential capacity vs. Li concentration in  $\text{Li}_x\text{CoO}_2$ ; (bottom) phase diagram of  $\text{Li}_x\text{CoO}_2$  developed from  $dq/dV$  vs. diagram and *in situ* XRD measurements from [1].

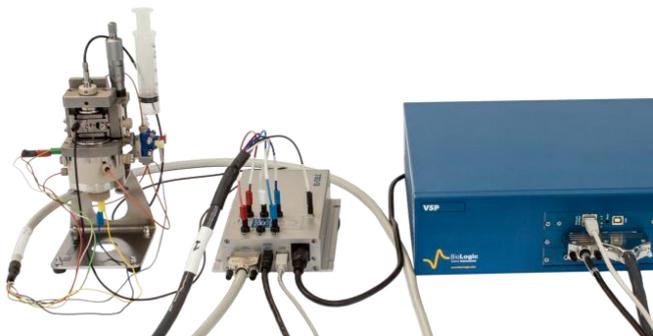
In this application note, we report the charge-induced dilation of a  $\text{LiCoO}_2$  electrode measured with ECD-nano-DL from EL-CELL and controlled by a Bio-Logic potentiostat/galvanostat. The set-up is described first, followed by the resulting measurements.

### II – SET-UP DESCRIPTION

Measurements are performed on a three-electrode cell. The electrodes and electrolyte are:

- $\text{LiCoO}_2$  electrode with a diameter of 9 mm and 80  $\mu\text{m}$  thick on Aluminum foil.
- Lithium metal for both counter and reference electrode.
- $\text{LiClO}_4$  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).



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

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

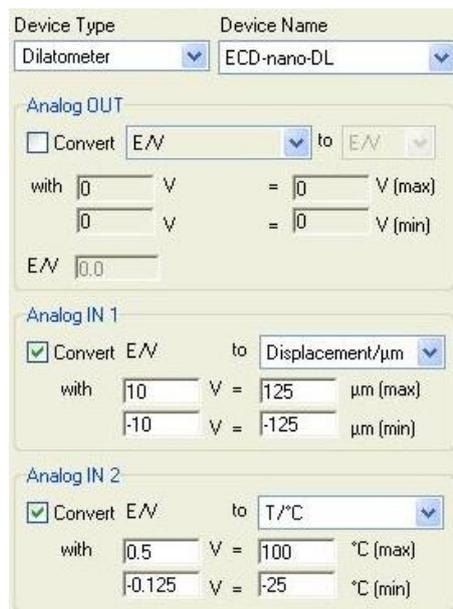


**Figure 4:** Cell cable connected to the data logger box.

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.



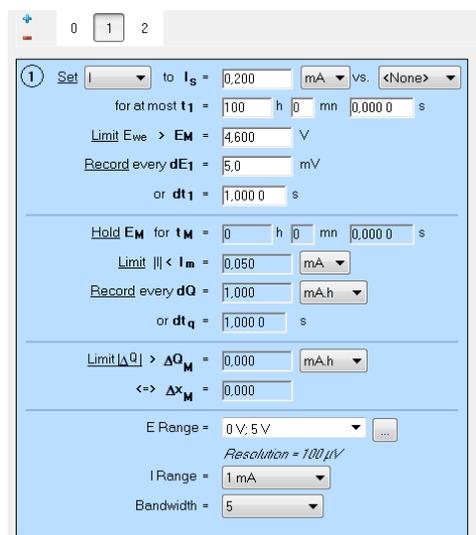
**Figure 5:** ECD-nano-DL Dilatometer configuration in the “External Devices” window.

**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.

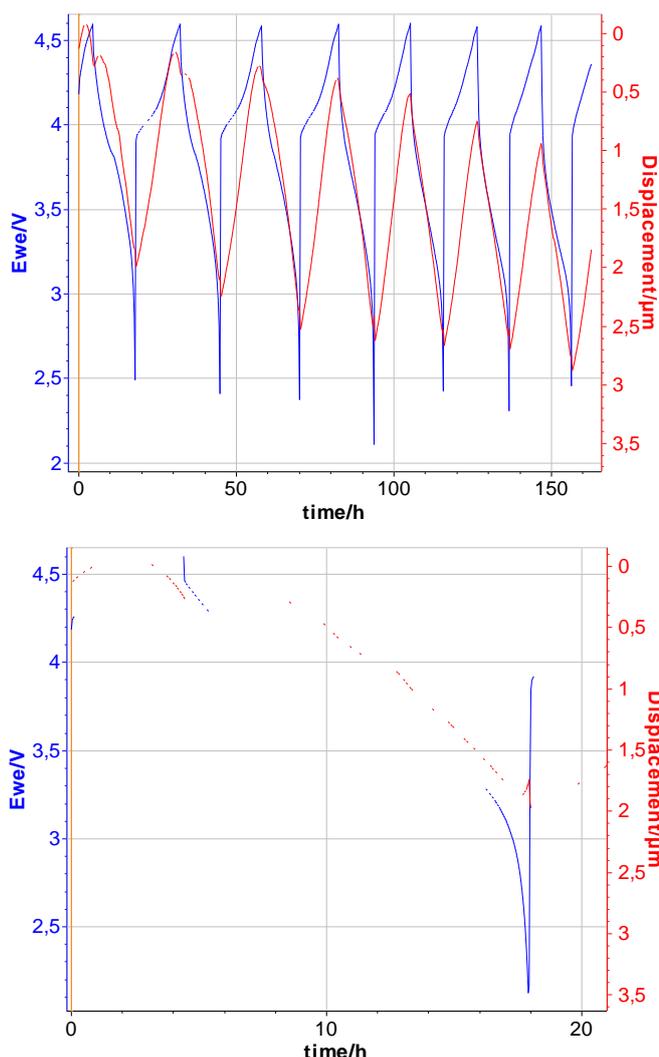
**III – MEASUREMENTS**

The cycling of a LiCoO<sub>2</sub> 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 6:** GCPL settings. Only the charge is shown in the screenshot.

Figure 7 shows the LiCoO<sub>2</sub> 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.



**Figure 7: Electrode potential and dilation evolution during constant current cycling of a LiCoO<sub>2</sub> electrode. Bottom: focus on the phase transitions at the two vertex points and at the first discharge midpoint.**

#### IV-CONCLUSION

This note presents how to connect the dilatometer and potentiostat/galvanostat together and perform an *in situ* dilation measurement during battery cycling. The

configuration of the EC-Lab<sup>®</sup> 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

- 1) Z. Chen, J. R. Dahn, *Electrochim. Acta*, 49(7) (2004) 1079.
- 2) J. N. Reimers, J. R. Dahn, *J. Electrochem. Soc.* 139(8) (1992) 2091.

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