

Differential Coulometry Spectroscopy (DCS)

I – INTRODUCTION

As introduced in the application note #40 [1] the Differential Capacity Analysis (DCA) is a powerful tool to understand and investigate degradation mechanisms in lithium-ion batteries. The DCA tool processes battery cycling data obtained with a constant potential recording parameter (dE). For data obtained with a constant time recording parameter (dt), a new analysis tool, **Differential Coulometry Spectroscopy tool (DCS)** was developed. This tool extends and completes the process tools range available in EC-Lab®/BT-Lab® software.

The DCS tool is a convenient statistical method to investigate electrochemical behavior and performance of rechargeable batteries based on intercalation materials. The method consists of converting a raw battery cycling data (voltage profile) into a histogram. The histogram is the distribution of the number of measurement data over cell voltage. The number of measurement point n_i is counted for each voltage step E_i . Since the recording condition is a constant time difference and the applied current is constant, the number of points correspond to a charge/discharge difference. This number corresponds to the height of the histogram bar positioned at the abscissa E_i . The DCS plot corresponds to the envelope of the histogram vs. potential.

In contrast to DCA protocol, the DCS approach does not include differentiation or any other mathematical transformation of the raw data and so leads to an accurate and a precise evaluation without information loss due to mathematical transformations.

In order to separate the kinetics from the domination of the transport limitations and to support the analysis, a very low rate of testing

is required (ie a very low current or C-rate) [2-3].

The objective of this note is to introduce the DCS tool and compare the DCS and the DCA results.

II – EXPERIMENT

DCS analysis tool is aimed at processing raw battery cycling data. The data were obtained from galvanostatic discharge/charge tests performed with a very low rate using GCPL technique (Fig. 1).

The tested batteries were commercial graphite/LiFePO₄ cells (26650 cylindrical batteries model manufactured by A123 System) with a nominal capacity of 2500 mA h and a nominal voltage of 3.3 V. The tests were carried out under a fixed temperature of 30.0 ± 0.1 °C in a Memmert temperature chamber using a VMP3 potentiostat/galvanostat. The batteries were galvanostatically cycled at 100 mA (around C/24 rate) between the potential limits 3.6 V and 2.0 V. The batteries were completely charged prior to each test. During the discharge and charge processes, the voltage was recorded every $dt_1 = 2$ min time. The recording voltage parameter dE₁ was disabled (set dE₁ = 0).

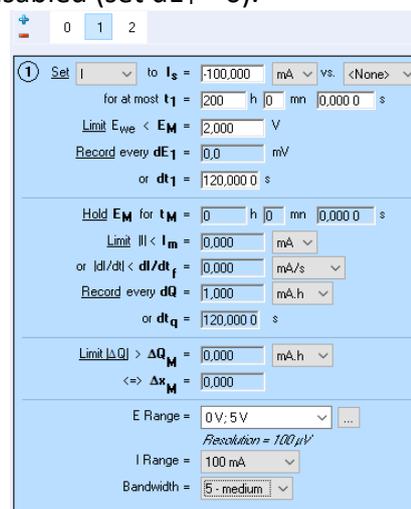


Figure 1: GCPL setting window

III – RESULTS

Figure 2 shows the voltage profile of the battery during one discharge/charge cycle with a sampling time of 2 min.

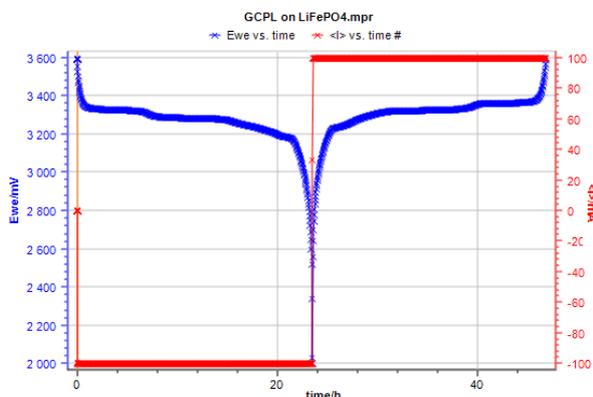


Figure 2: GCPL setting window.

The voltage vs. time profile shows numerous plateaus at upper voltages (potential range 3.1 V–3.4 V). These plateaus are associated to different phase transformations occurring on the cathode (graphite). A zoom on discharge plot at upper voltages is shown in Fig. 3 below.

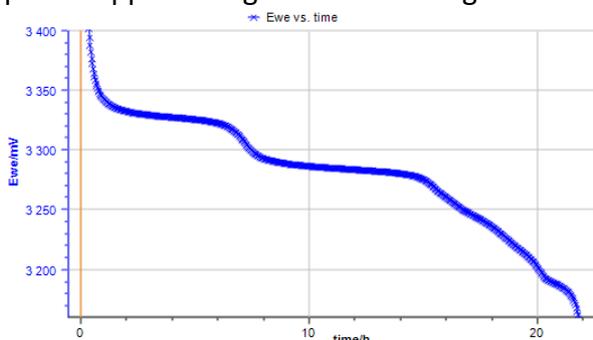


Figure 3: Zoom on discharge profile.

Figure 3 shows two main voltage plateaus: the first one, at around 3.33 V, corresponds to the coexistence of $\text{LiC}_6/\text{LiC}_{12}$ phases. The middle plateau corresponds to the coexistence of LiC_{18} and LiC_{12} . LiFePO_4 and FePO_4 coexist from 30 min into the experiment to 21 h into the experiment.

The discharge/charge data were processed by DCS tool available in the batteries analysis section. Figure 4 shows a screenshot of the DCS window used to plot the DCS graph.

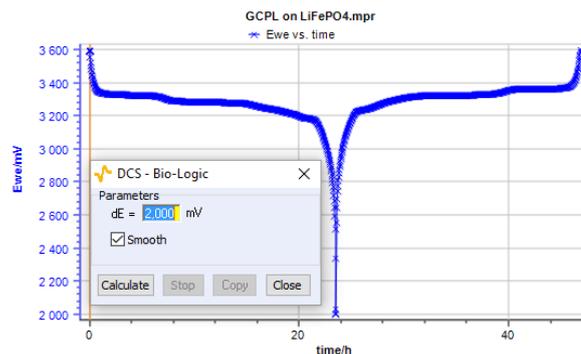


Figure 4: DCS tool.

During battery cycling, the amount of charge stored or released by the battery is measured. The DCS process consists in plotting the number of measured point per voltage step. The obtained graph from the discharge/charge data is illustrated in Fig. 5.

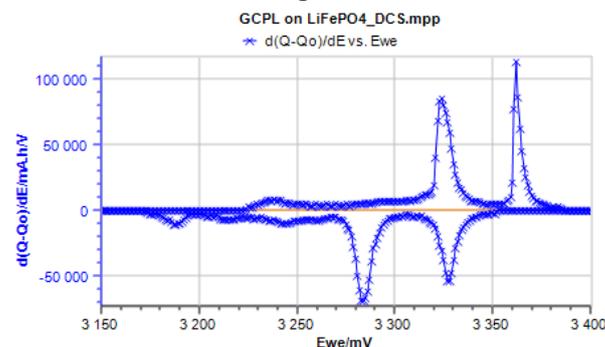


Figure 5: DCS plot.

DCS plot shows three main peaks (Fig. 5 and 6). These peaks represent phase transitions in the lithiated state of the electrode materials [4-7].

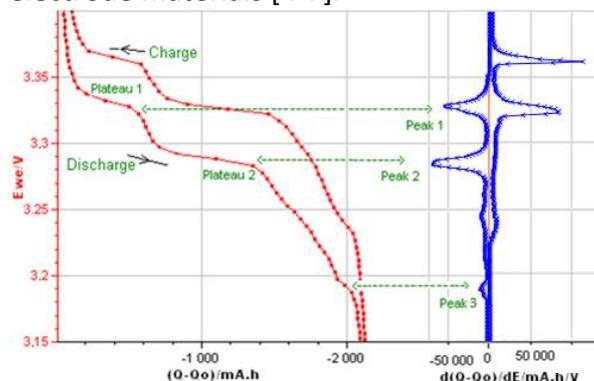


Figure 6: Phase transition peaks in DCS plot.

DCS plot displays the same transition peaks that are shown on the DCA plot [1-2]. Figure 7 shows an overlay of the DCS plot and the DCA plot.

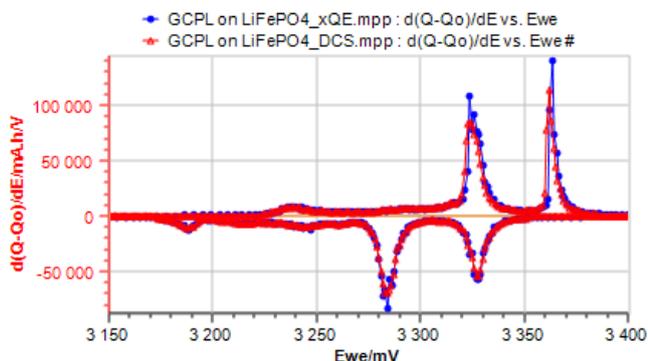


Figure 7: Overlay of DCS and DCA plots.

The DCS (and the DCA) plot helps the EC-Lab users to investigate degradation mechanisms through the study of the evolution of the shape, the height and the position of histogram peaks during battery cycling. So any change in the peak position or/and intensity in the DCS (or in DCA) plot is indicative of electrode degradation [4, 8]. Indeed, it is reported in the literature [4] that a decrease of the magnitude of the main peak at 3.33 V in the differential capacity plot is indicative of active material loss in the graphite electrode. A change of position peak in the differential capacity plot is indicative of an increase of battery impedance.

IV- CONCLUSION

DCS tool is a complementary analysis tool to DCA dedicated to process data obtained with **time recording ($dt \neq 0$ and $dE = 0$)** in EC-Lab. DCS provides information on structural transformations in the electrodes material and on degradation mechanisms occurring in the battery components (electrodes/electrolyte). DCS is compatible with experimental data obtained by numerous techniques (GCPL, PCGA, Modulo Bat, CP,..). DCS is tool is recommended for data obtained with a constant time recording parameter (dt) (Tab .1)

Table I: Recording parameters for DCS and DCA tools.

Recording parameter	dt	dE
DCS	X	
DCA		X

REFERENCES

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