Differential (Incremental) Capacity Analysis

I – INTRODUCTION
In recent years, the lithium-ion batteries have received an increased interest in the battery development and investment. These batteries are widely used in portable electronic devices and show promise as alternative technology to the Nickel Metal Hybrid battery commonly used in hybrid electric vehicle applications. The Li-ion battery technology offers a high voltage, high energy density and long cycle life. However, like all rechargeable batteries, the use (charge and discharge) of these batteries leads to a degradation of its performance (battery capacity, structural stability, cycle life and safety).

In order to understand the degradation and the loss of capacity of Lithium-ion battery, numerous studies were performed over the last decade [1-8]. These studies have linked battery degradation with mechanical, chemical or structural modifications of the electrodes material during charge/discharge process. The degradation results in an increase of the internal resistance, a decrease of the capacity and an increase of the self-discharge of the battery. The battery degradation and its origin can be studied using a new battery analysis tool available in the battery process of EC-Lab®: “Incremental Capacity Analysis” (ICA) or “Differential Capacity Analysis” (DCA). This process, available since EC-Lab® 10.21 (May 2012), highlights the phase transitions of the electrodes after cycling. The cycling is usually done at low rate (i.e C/24).

The "differential capacity" curve is obtained by differentiating the capacity $Q$ vs. voltage $E$.

It is defined in the equation below

$$\frac{dQ}{dE} = \frac{|Q_t - Q_{t-1}|}{E_t - E_{t-1}}$$

(1)

Where, $Q_t$, $E_t$ are capacity and voltage values measured at a given time $t$.
$Q_{t-1}$, $E_{t-1}$ are capacity and voltage values measured at a previous time $t-1$.

II – EXPERIMENT
Commercial 2.5 Ah LiFePO₄ batteries were charged/discharged at a constant current of C/25 rate between 3.6 V and 2.0 V using a GCPL technique at room temperature. The charge/discharge process was performed on a MPG2 battery cycler unit with EC-Lab®10.21 software.

The charge-discharge procedure was performed as follows:
1. Full charge of the battery (up to 3.6 V) before experiment start.
2. Discharge at C/25 rate until 2.0 V is reached. The potential was recorded every $dE_1$ and the recording time parameter $dt_1$ was disabled (set $dt_1 = 0$).
3. Charge at C/25 rate until 3.6 V is reached. The potential was recorded every $dE_1$ and the recording time parameter $dt_1$ was disabled (set $dt_1 = 0$).
III – RESULTS

The charge and the discharge of the 2.5 A.h battery are illustrated in Fig. 2 below.

Figure 2: Voltage vs. time during the discharge and the charge of LiFePO$_4$ battery.

In the process data window, the d($Q$-$Q_0$)/d$E$, $Q$ charge and $Q$ discharge boxes were checked.

Figure 3 shows the process data window used to calculate the differential capacity d$Q$/d$E$.

Differential Capacity curve can be plotted vs. voltage or charge $Q$ or vs. other parameters. The main presentation of DC curves used in the literature is d$Q$/d$E$ vs. $E$ (Fig. 4a) or $E$ vs. d$Q$/d$E$ (Fig. 4b). These curves are plotted from the charge/discharge data of the LiFePO$_4$. The charge/discharge data were processed by the process data tool available in the batteries analysis section of EC-Lab®10.21.
The Differential Capacity (DC) as a function of potential gives information about the structural transformations during charge/discharge process. The advantage of the DC curve is that plateaus in the $E$ vs. $Q$ charge curve can appear as clearly identifiable peaks in the $dQ/dE$ vs. $E$ curve. These peaks are associated to phase transitions of the electrode material.

The curve of the Figure 4b shows four main peaks: two peaks during the discharge (left peaks) and two during the charge (right peaks). Each peak corresponds to a flat plateau in the voltage versus charge curve indicating the coexistence of two phases in each plateau.

The appearance of the cathodic and the anodic curves gives information about the reversibility of the electrode reaction. Plotting differential capacity $dQ/dE$ versus cycle number allows the observation of any change (amplitude, width, ..) in the peaks from one cycle to the next and can help detect degradation over long test cycles.

**IV – CONCLUSION**

The Differential (Incremental) Capacity Analysis (DCA or ICA) process recently introduced in EC-Lab® provides a fast and a powerful tool for a good understanding of the mechanisms and the kinetics of intercalation-electrode material degradation. This degradation could be associated to side reactions or to reactions occurring inside the electrode material. The DCA tool transforms the voltage plateaus on $E$ vs. $t/E$ vs. $Q$ curves into clearly identifiable peaks. These peaks, mainly associated to phase transitions of the electrode material are easily exploitable.

Data files can be found in:

C:\Users\xxx\Documents\EC-Lab\Data\Samples\Battery\GCPL100mAch3dE5mV_03IQ_DCA

**REFERENCES**


Revised in 07/2018