

Autolab Application Note BAT04

Potentiostatic Intermittent Titration Technique (PITT)

Keywords

Batteries; Li-ion batteries; Potentiostatic; Titration; PITT; Diffusion coefficient.

Summary

Lithium-ion (Li-ion) batteries are one of the most investigated energy storage devices, due to their relatively high energy and high power performances. During charge and discharge of a Li-ion battery, lithium ions are transported from one electrode, through the electrolyte, to the other electrode. Here, the Li-ion diffusion into the bulk material occurs.

In this respect, knowing the chemical diffusion coefficient of electrode materials is of extreme importance. The potentiostatic intermittent titration technique (PITT) is, together with its galvanostatic counterpart (please refer to GITT application note BAT03), one of the most used techniques to retrieve insights on the diffusion coefficient of the electrodes' active materials [1-3].

The present application note illustrates how to build and exploit a PITT procedure and how the diffusion coefficient can be calculated from the resulting signal.

The PITT NOVA procedure

In a typical PITT measurement, a cell composed of metallic lithium (counter and reference electrode); electrolyte and positive (working) electrode is employed. In this way, the diffusion coefficient of the active material present in the positive electrode can be calculated.

The experiment starts by recording the OCP of the battery (V_{OCP}). Then, a step composed of 15 minutes pulse at V_{OCP} , followed by 15 minutes of relaxation with the cell switched off is applied. Afterwards, a positive potential increment of 0.02 V is applied on V_{OCP} , and the signal is recorded for 15 minutes, followed by 15 minutes of relaxation time. The same potential increment is consecutively applied, starting from the voltage resulting from the previous step and the signal is recorded for 15 minutes. The potential pulses are applied until the upper limit of 4.2 V is reached. Each potential pulse is followed by 15 minutes of relaxation time. Afterwards, negative potential increments of -0.02 V are consecutively applied to the voltage

resulting from the previous step, and the signal is recorded for 15 minutes. The potential pulses are repeated until the lower limit of 2.8 V is reached. Each potential pulse is followed by 15 minutes of relaxation time.

During the 0.02 V potential pulses, Li-ions are de-intercalated from the positive electrode and intercalated to the negative one. The reverse occurs during the negative discharging potential pulses, where the Li-ions are de-intercalated from the negative electrode and intercalated to the positive electrode. In both cases, the intercalation and de-intercalation processes result in current development, described in the Equation 1.1 [4]:

$$i = \frac{2FS(C_s - C_0)D}{L} \exp\left(-\frac{\pi^2 Dt}{4L^2}\right) \quad (1.1)$$

Where F is the Faraday's constant, S is the surface area of the electrode, $(C_s - C_0)$ is the concentration difference of Li ions at the surface at time t and at the beginning of the potential pulse ($t = 0$), D is the diffusion coefficient and L is the characteristic length of the electrode active material.

From Equation 1.1, it can be seen that the current signal brings information about the diffusion coefficient of the electrode material.

More in detail, the diffusion coefficient D of the active material present in one electrode is related to the current i developed from the constant voltage pulses via the following formula [4, 5]:

$$D = \frac{d \ln(i)}{dt} \frac{4L^2}{\pi^2} \quad (1.2)$$

Experimental setup

For the experiments, an Autolab PGSTAT302N has been used, together with a 2.2 Ah Li-ion battery from Enix Energies, with a nominal voltage of 3.75 V and a nominal energy of 8.25 Wh, has been investigated.

Experimental results

Figure 1 shows the plot of potential (blue line) and current (red line) vs. time.

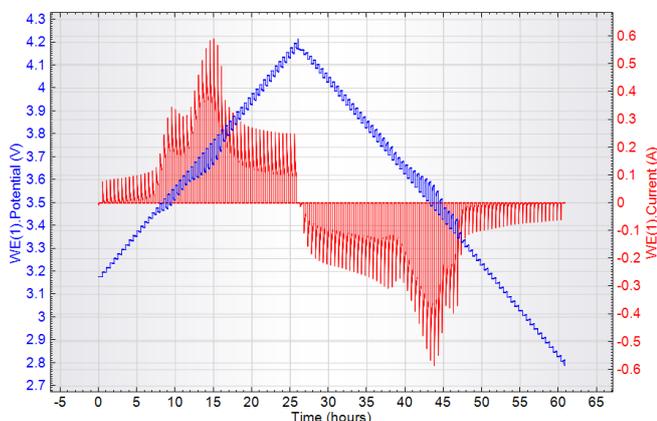


Figure 1 – Potential (blue line) and current (red line) vs. time resulting from the PITT experiment

Regarding the potential signal, it can be noticed the consecutive 0.02 V pulses, from OCV to 4.2 V, and the following relaxation step, in which the potential decreases. The opposite holds during discharge, where the potential slightly increases after each -0.02 V potential pulse.

Figure 1 shows also the relative current behavior during the PITT experiment. This behavior can be better depicted in Figure 2, where the potential around the 4.2 V upper limit is plotted against the time, together with the developed current.

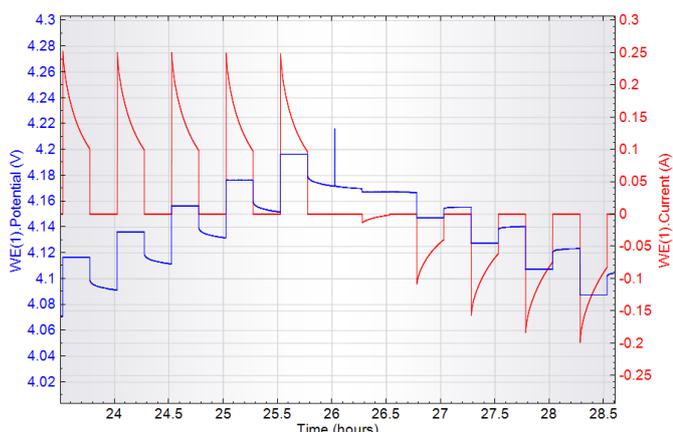


Figure 2 – Potential and current vs. time, around 4.2 V

During each relaxation period, the cell is switched off. then, at the beginning of each charging pulse, a peak in the current signal is observed. Afterwards, the current signal decreases in an exponential fashion (see Equation 1.1), before being set

to 0 A during the following relaxation time. During the discharge potential pulses, the current has a sudden negative peak, after then increasing in an exponential way.

In Figure 3, the logarithm of the current is plotted against time, together with the potential signal. From this plot, the diffusion coefficient D for each potential pulse can be calculated.

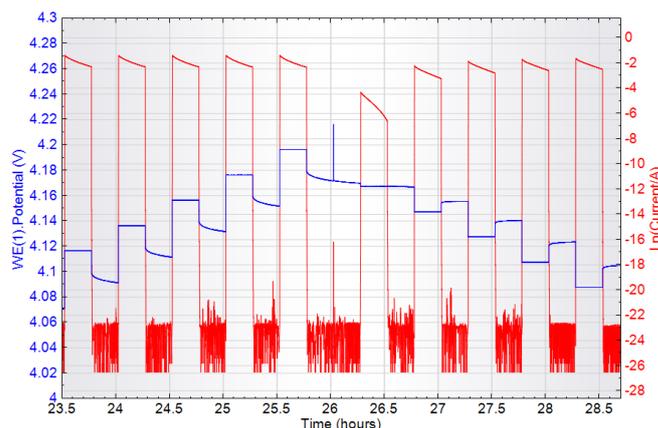


Figure 3 – Potential and logarithm of current vs. time, around 4.2 V

The diffusion coefficient is proportional to the slope of the $\ln(i)$ vs. t curve in Figure 3. Such information can be retrieved with the regression tool present in NOVA, as Figure 4 shows.

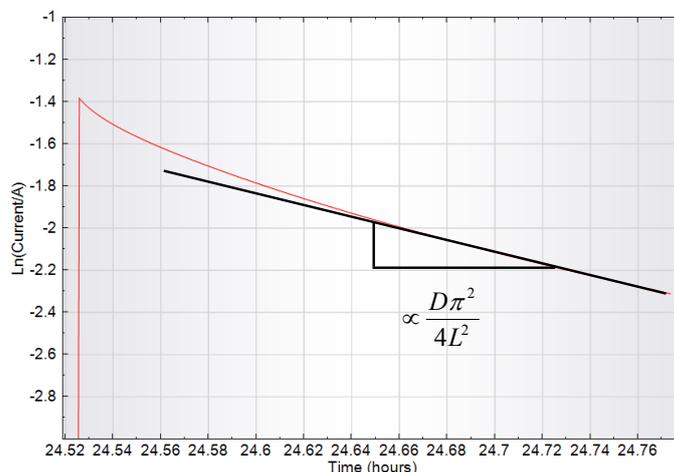


Figure 4 – Logarithm of the current vs. time of a PITT charging pulse. Where the signal becomes linear, the linear regression tool allows the diffusion coefficient calculation

Conclusions

This application note showed how to perform PITT measurements on a commercial Li-ion battery, with the help of AUTOLAB and NOVA. Here, potentiostatic charge pulses are applied, each followed by relaxation time, until the upper

potential limit is reached. Then, discharge pulses are applied, followed by relaxation time, until the lower potential limit is reached. From the logarithm of the current vs. time plot, important information to calculate the diffusion coefficient can be obtained.

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Date

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