Application Note: Batteries

Potentiostatic Intermittent Titration Technique (PITT)

Keywords

Batteries; Diffusion coefficient, Li-ion batteries; Metrohm Autolab, PITT, Potentiostatic, Titration

Summary

Lithium-ion (Li-ion) batteries are one of the most investigated energy storage devices, due to their relatively high energy and 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, the diffusion coefficient of the active materials present in the electrodes is directly responsible for the battery performance. Therefore, knowing the chemical diffusion coefficient of electrode materials is of critical importance. The potentiostatic intermittent titration technique (PITT) is, together with its galvanostatic counterpart GITT, one of the most used techniques to retrieve insights on the diffusion coefficient of the electrode's active materials.[1–3]

This application note illustrates how to build and use a PITT procedure and how the diffusion coefficient can be calculated from the results.

The PITT procedure

The experiment starts by recording the open circuit potential (OCP) of the battery. Then 15 minutes of pulse at OCP is applied, followed by 15 minutes of relaxation with the cell switched off. Next a positive potential increment of 20 mV is applied on OCP, and the signal is recorded for 15 minutes, followed by 15 minutes of relaxation time. The same potential increment is consecutively applied, starting with the voltage of the previous step and the signal is recorded for 15 minutes. The potential pulses are applied until the upper potential limit is reached. Each potential pulse is followed by 15 minutes of relaxation time. Afterwards, negative potential increments of -20 mV are consecutively applied to the voltage from the previous step, and the signal is recorded for 15 minutes. The potential pulses are repeated until the lower potential limit is reached. Each potential pulse is followed by 15 minutes of relaxation time.

During the positive potential pulses, Li-ions de-intercalate from the positive electrode and intercalated to the negative electrode. The reverse occurs during the negative potential pulses, where the Li-ions de-intercalate from the negative electrode and intercalate to the positive electrode. In both cases, the intercalation and de-intercalation processes result in current development, described in the Equation 1.[4]

$$i = \frac{2FS(C_s - C_0)D}{L} \exp\left(-\frac{\pi^2 Dt}{4L^2}\right) \qquad 1$$

Where F is the Faraday's constant ($96485\ C/mol$), S is the surface area of the electrode (cm^2), $(C_s - C_0)$ (mol/cm^3) is the concentration difference of Li-ions at the surface at time t and at the beginning of the potential pulse ($t = 0$), D (cm^2/s) is the diffusion coefficient and L (cm) is the characteristic length of the electrode active material.

The diffusion coefficient D of the active material present in one electrode is related to the current i developed from the constant voltage pulses through Equation 2.[4, 5]

$$D = \frac{d\ ln(i/A)}{dt}\frac{4L^2}{\pi^2} \qquad 2$$

Experimental setup

An Autolab PGSTAT302N was employed. The battery under test, 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, was investigated.

Results and discussion

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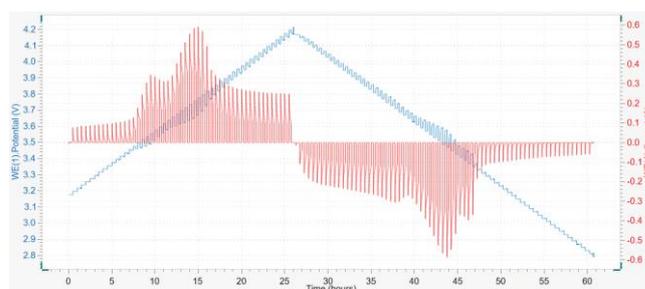

Figure 1 – Potential (blue line) and current (red line) vs. time resulting from the PITT experiment

The plot shows that during the charge, the potential signal decreasing during the relaxation step after each 20 mV pulses. The opposite holds during discharge, where the potential slightly increases after each -20 mV potential pulse.

Figure 1 shows also the relative current behavior during the PITT experiment. This behavior is more visibly depicted in Figure 2, where the potential (blue line) around the 4.2 V upper limit is plotted against the time, together with the current profile (red line).
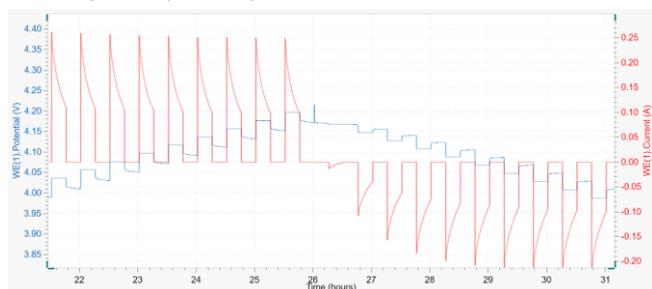

Figure 2 – Potential (blue line) and current (red line) vs. time, around 4.2 V

At the beginning of each charging pulse, a peak in the current signal is observed. Afterwards, while the potential is held, the current signal decreases in an exponential fashion (see Equation 1). Then, during the relaxation time, the cell is switched off and the potential is allowed to relax. During the discharge potential pulses, the current has a sudden negative peak, after then increases in an exponential way.

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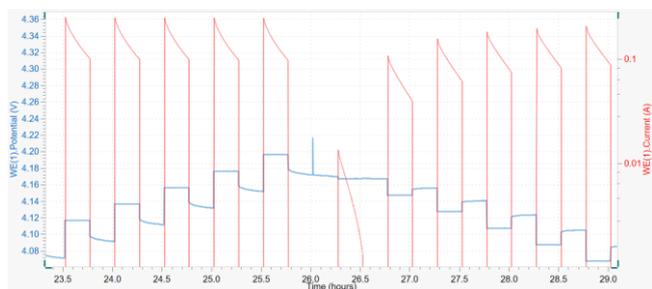

Figure 3 – Potential (blue line) and logarithm of current (red line) vs. time, around 4.2 V

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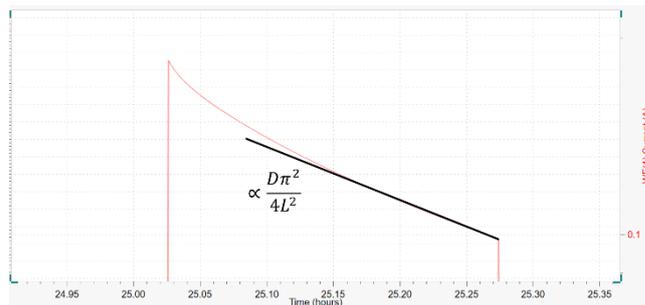

Figure 4 – Logarithm of the current vs. time of a PITT charging pulse. Where the signal becomes linear, the linear regression tool allows the diffusion coefficient calculation

Conclusions

This application note shows how to perform PITT measurements on a commercial Li-ion battery, with the help of an 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.

References

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Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/electrochemistry**.