

恒流歇滴定技 (GITT)

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, lithium ions are forced to move from the positive to the negative electrode, through the electrolyte. During discharge, lithium ions move in the opposite direction, from the negative to the positive electrode. At the electrodes surface, Li-ion diffusion into the bulk occurs.

In this respect, the performances of a Li-ion battery depend, among all, on the diffusion

coefficient of the active materials present in the electrodes. Therefore, knowing the chemical diffusion coefficient of electrode materials is of extreme importance. Furthermore, the thermodynamic properties of the electrodes materials can give a better understanding of their electrochemical behavior.

The galvanostatic intermittent titration technique (GITT) is a procedure useful to retrieve both thermodynamics and kinetic parameters, such as the diffusion coefficient. [1,2]

THE GITT PROCEDURE

The GITT procedure consists of a series of current pulses, each followed by a relaxation time, in which no current passes through the cell. The current is positive during charge and negative during discharge.

During a positive current pulse, the cell potential quickly increases to a value proportional to the iR drop, where R is the sum of the uncompensated resistance R_u and the charge transfer resistance R_{ct} . Afterwards, the potential slowly increases, due to the galvanostatic charge pulse, in order to maintain a constant concentration gradient. When the current pulse is interrupted, i.e., during the relaxation time, the composition in the electrode tends to become homogeneous by Li-ions diffusion. Consequently, the potential first suddenly decreases to a value proportional to the iR drop, and then it slowly decreases until the electrode is again in equilibrium (i.e., when $dE/dt = 0$) and the open circuit potential (OCP) is reached. Then,

the galvanostatic pulse is applied again, followed by current interruption. This sequence of charge pulse followed by a relaxation time is repeated until the battery is fully charged.

During a negative current pulse, the opposite holds. The cell potential quickly decreases to a value proportional to the iR drop. Then, the potential slowly decreases, due to the galvanostatic discharge pulse. During the relaxation time, the potential suddenly increases by a value proportional to the iR drop, and then it slowly increases, until the electrode is again in equilibrium (i.e., when $dE/dt = 0$) and the OCP of the cell is reached. Then, the following galvanostatic pulse is applied, followed by current interruption. This sequence of discharge pulse followed by a relaxation time is repeated until the battery is fully discharged.

The chemical diffusion coefficient can be calculated at each step, with the following formula:[1-3]

$$D = \frac{4}{\pi} \left(\frac{iV_m}{z_A F S} \right)^2 \left[\frac{(dE/d\delta)}{(dE/d\sqrt{t})} \right]^2 \quad (1)$$

Where i (A) is the current; V_m (cm^3/mol) is the molar volume of the electrode; z_A is the charge number; F (96485 C/mol) is the Faraday's constant and S (cm^2) is the electrode area. Besides, $dE/d\delta$ is the slope of the coulometric titration curve, found by plotting the steady state voltages E (V) measured after each titration step δ and $dE/d\sqrt{t}$ is the slope of the linearized

plot of the potential E (V) during the current pulse of duration t (s). In **Figure 1**, an example of potential versus the square root of time plot is shown. Using the linear regression tool provided in NOVA, information about ΔEt can be obtained from the slopes of the galvanostatic pulses versus the square root of time[4].

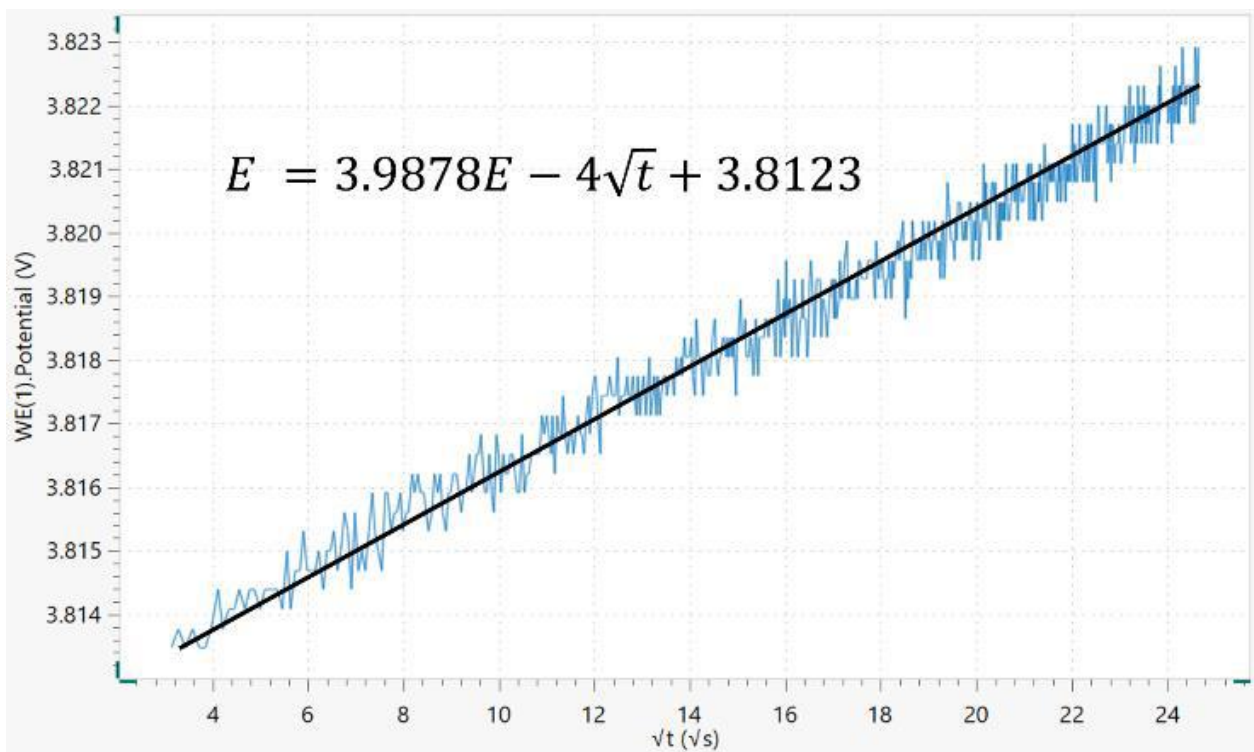


Figure 1. Potential vs. \sqrt{t} plot. In addition, the linear regression line and its equation are shown.

If sufficient small currents are applied for short time intervals, then $dE/d\sqrt{t}$ can be considered linear, as well as the coulometric titration curve

over the composition range involved in that step. With these conditions, **Equation (1)** can be simplified to:

$$D = \frac{4}{\pi\tau} \left(\frac{n_m V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (2)$$

Here, τ (s) is the duration of the current pulse; n_m (mol) is the number of moles; V_m (cm^3/mol) is the molar volume of the electrode; S (cm^2) is the electrode area; ΔE_s (V) is the steady-state

voltage change, due to the current pulse and ΔE_t (V) is the voltage change during the constant current pulse, eliminating the iR drop.

EXPERIMENTAL SETUP

For the experiments, an Autolab PGSTAT302N was employed, together with a commercial 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.

THE NOVA PROCEDURE

The NOVA GITT procedure consists of galvanostatic charge pulses, each 10 minutes long, followed by 10 minutes of relaxation time, with no current passing through the cell; from OCP to 4.2 V. Then, GITT discharge steps are applied. Each step is composed of a 10 minutes discharge pulse followed by 10 minutes of rest, with no current passing through the cell. In

order to have sufficiently slow potential changes, a current rate of C/10 has been chosen, either for charge or for discharge. This means that, with a C/10 current rate, the battery could be completely charged (or discharged) in ten hours. For the battery under investigation, a C/10 rate resulted in 220 mA of current for the charge, and -220 mA for the discharge.

RESULTS

Figure 2 shows the complete GITT potential profile. The procedure starts at OCP 3.62 V. Then, GITT charge pulses are applied; each followed by a relaxation period. Here, it can be noticed the potential drops between the pulses and the relaxation times, and that the overall

potential increases until 4.2 V. After charging, the potential decreases, due to the galvanostatic discharge pulses, each followed by the relaxation time, until potential of 2.8 V is reached.

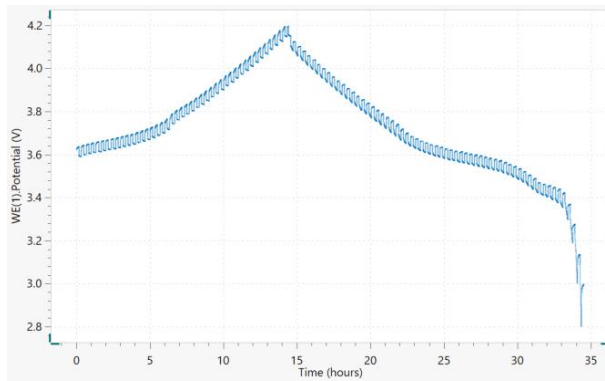


Figure 2. Galvanostatic intermittent titration curve vs. time The duration of the charge and discharge pulses have been calculated based on a $C/10$ current rate.

In order to shed more light on the GITT steps, in **Figure 3** the first two charge pulses are shown. Here, it is assumed that the currents are so small that $dE/d\delta$ and $dE/d\sqrt{t}$ holds and **Equation (2)** can be exploited. Note the increasing potential and ΔE_t value can be calculated. Afterwards, the 10 minute relaxation step is applied. Here, it should be noted the sudden potential decrease,

due to the iR drop. Then, the potential slowly decreases. After the relaxation time, a sudden increase in the potential occurs. This is again due to the iR drop of the cell. Another 10 minutes galvanostatic potential step is then applied. Here, it can be better noticed the linear region. After the iR drop, the relaxation step is finally applied, and the ΔE_s value can be calculated.

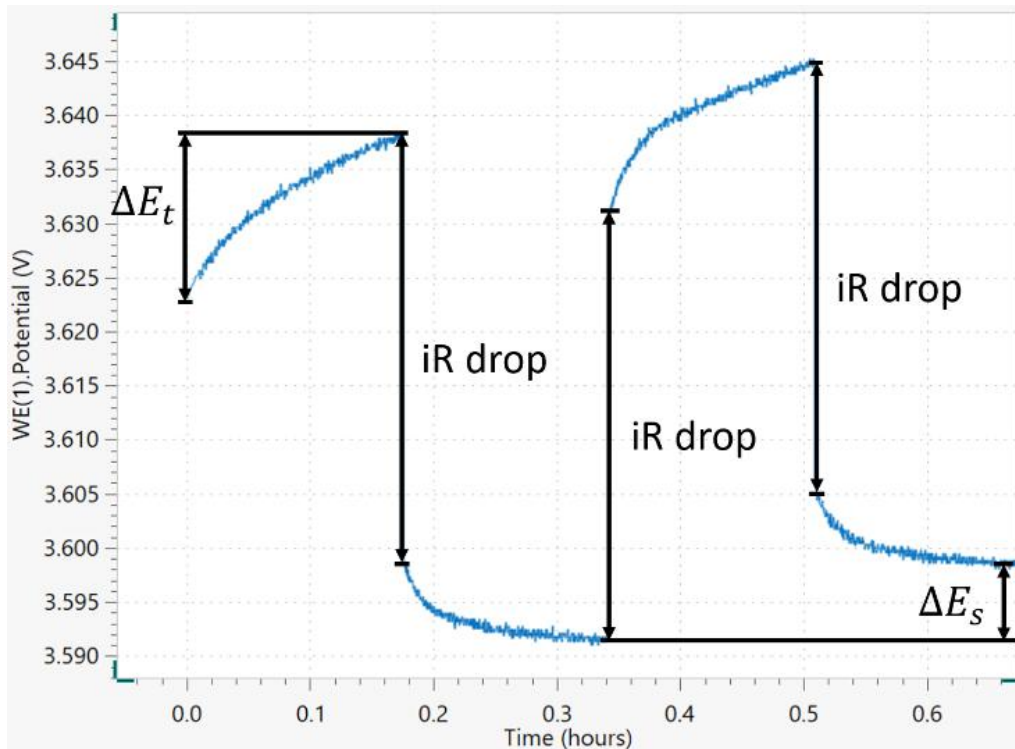


Figure 3. First two charge steps, each composed by 10 minutes of C/10 galvanostatic charge, followed by 10 minutes of relaxation time. The iR drop is shown, together with the ΔE_t and ΔE_s .

REMARKS

Since a commercial Li-ion battery has been used, it was not possible to distinguish the contribution to the overall chemical diffusion given by the positive and the negative electrodes. Besides, some quantities like the molar volume V_m and the surface area S were missing, in order to complete the calculations on **Equations (1) and (2)**.

The GITT procedure is usually performed in a half cell, i.e., made of the electrode with the active material under investigation, which will become

the positive electrode, and a negative electrode made of metallic lithium, plus the electrolyte. If possible, a three-electrode setup is preferable, with a small metallic lithium crumb as pseudo-reference electrode. In this way, knowing the composition of the material under investigation and the working electrode's surface area, it is possible to calculate the chemical diffusion coefficient per potential step dE and/or per coulometric titration step $d\delta$. In literature, plots of $\log(D/cm^2s^{-1})$ vs. V or vs. δ are common.

CONCLUSIONS

This application note showed how AUTOLAB and NOVA could be used to perform GITT tests on a Li-ion battery. Here, galvanostatic charge pulses are applied, each followed by relaxation time, until the upper potential limit is reached. Then, discharge pulses are applied, followed by

equilibration time, until the lower potential limit is reached. From the potential vs. time plot, important information to calculate the diffusion coefficient and thermodynamics parameters quantities can be obtained.

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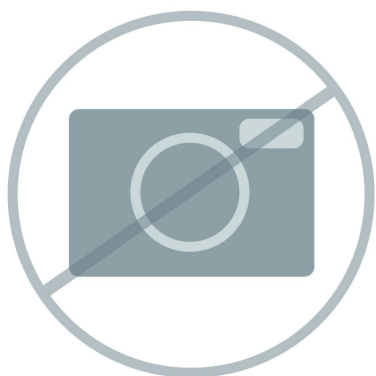


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