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]

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

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].

$$E = 3.9878E - 4\sqrt{t} + 3.8123$$
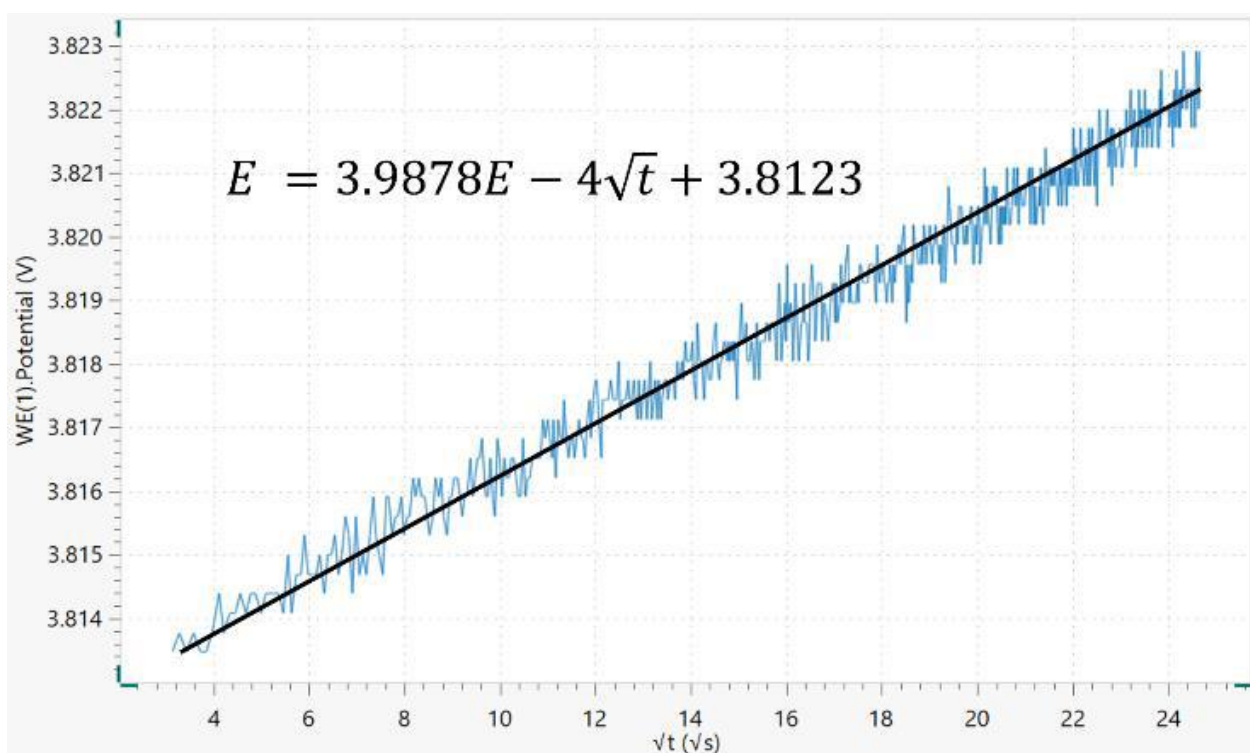
Figure 1. Potential vs. $\sqrt{t}$ plot. In addition, the linear regression line and its equation are shown.

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:

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

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.

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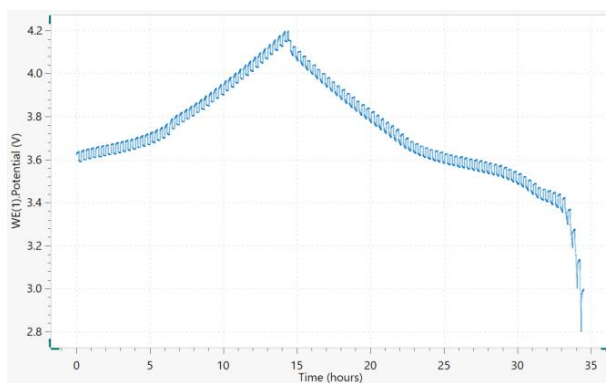
Figure 2. Galvanostatic intermittent titration curve vs. time The duration of the charge and discharge pulses have been calculated based on a C/10 current rate.

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.

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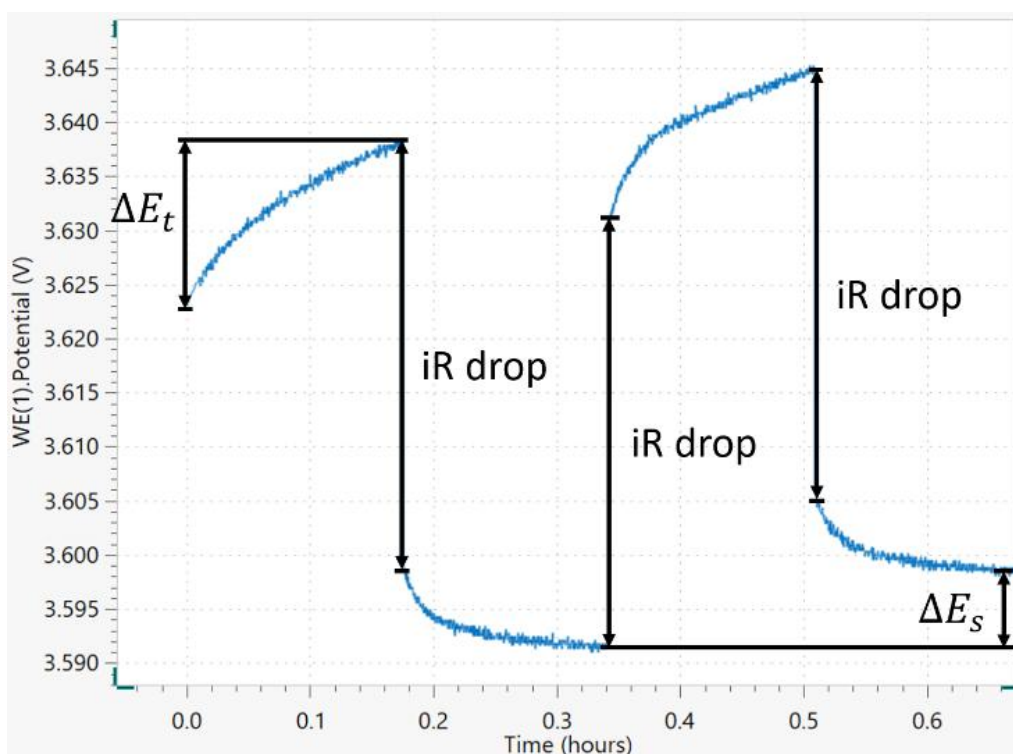
Figure 3. First two charge steps, each composed by 10 minutes of C/10 galvanostatic charge, followed by 10 minutes of relaxation time. The iR drop is shown, together with the and .

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.

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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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Autolab PGSTAT302N

高端高流恒位/恒流,具有 30 V 从, 1 MHz,可与我的 FRA32M 模用,化学阻抗而。
PGSTAT302N 是流行的 PGSTAT30 的后款型。最大流 2 A,借助 BOOSTER20A 流范可展至 20 A,当流范 10 nA 流分辨率 30 fA。

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Autolab DuoCoin Cell Holder

Autolab DuoCoin Cell Holder 具有 4 点文金触,可的池研究提供最高精度的量果 。一个通用附件可所有尺寸的准化学池以及小和更大的非准化学池,可以一次理二个化学池。

Autolab DuoCoin Cell Holder 金触和金印刷路板可防止繁忙室中附件的腐和坏。

Autolab DuoCoin Cell Holder 具有可和接件(与Autolab 恒位/恒流色相),可化装置。Autolab 的重体在 Autolab DuoCoin Cell Holder 底部的硅表面爪上(其可使的装置具有定性)。
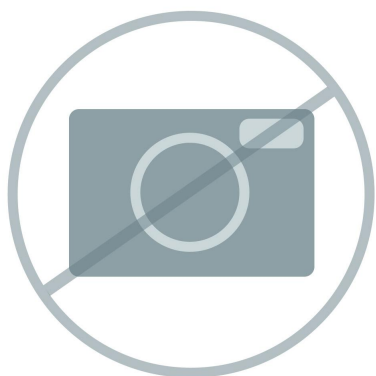
NOVA 是通 USB 接口控制所有 Autolab 器的件包。由化学家化学而,集成了超二十余年的用体和最新的.NET 件技,NOVA 使的 Autolab 恒位/恒流有更性能和活性。

NOVA 提供了以下的独特功能:

- 功能大且活的程序器
- 重要数据一目了然
- 大的数据分析和工具
- 集成化控制外器,如万通 LQH 液体理

Autolab PGSTAT204

PGSTAT204 合了小巧格和模化。器包括基本恒位/恒流,其从 20 V,最大流 400 mA 或 10 A,与BOOSTER10A 合使用。此恒位可随用附加模行展,例如 FRA32M 化学阻抗(EIS)模。

PGSTAT204 是一款惠的器,可置于室的任何位置。具有模和数字入/出,可控制 Autolab 附件和外部。PGSTAT204 包括内置模分器。与高性能的 NOVA件用,可用于大多数准化学技。

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