Least Squares Galvanostatic Intermittent Titration Technique (LS-GITT) for Accurate Solid Phase Diffusivity Measurement

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Solid phase diffusivity D_s is a key parameter in Lithium-Ion cell models because solid phase diffusion typically dominates the voltage transients. The Galvanostatic Intermittent Titration Technique (GITT) is easy to implement and universally accepted as the standard for diffusivity measurement, but the accuracy of GITT diffusivity measurement is unknown. This paper develops a Least Squares GITT (LS-GITT) that uses all of the voltage data from a GITT test to optimally tune the diffusivity in a reduced order solid phase diffusion model. The accuracies of the GITT and LS-GITT diffusivity measurements are evaluated using the RMS error between the model predicted and experimentally measured voltages. Based on experimental results from a NCM half cell, LS-GITT is more accurate than GITT, often by an order of magnitude. The GITT test overestimates D_s because the underlying model neglects the effects of bulk capacity on the voltage transients. LS-GITT gives results accurate to 1 mV RMS from 15%–100% SOC where GITT provides the same level of accuracy over less than half that SOC range. Neither technique provides accurate D_s measurements below 10% SOC.

Lithium-Ion batteries are excellent energy storage devices for many applications, such as renewable energy, consumer electronics, Hybrid Electric Vehicles (HEVs), and Electric Vehicles (EVs), due to their high energy and power density. In dynamic operations, solid phase diffusion in the electrodes dictates the cell response and performance. For most Lithium-Ion chemistries and cell designs, solid phase diffusivity (D_s) dominates the electrochemical dynamics because Li^+ intercalation is the slowest process during charge/discharge of the cell. To accurately model the response of a Lithium-Ion cell, D_s must be accurately measured. Solid phase diffusivity is one of the first parameters to be measured in a new cell design because it directly influences the cell's power performance. Diffusivity also varies with temperature, State of Charge (SOC), and electrolyte concentration.[1] Thus, the development of fast, reliable, and accurate D_s measurement has been a focus of researchers for decades. Many D_s measurement methods, using both time-domain and frequency-domain data, have been used by previous investigators, such as Potentiostatic Intermittent Titration Technique (PITT),[2–4] Galvanostatic Intermittent Titration Technique (GITT),[1,5,6] Electrochemical Impedance Spectroscopy (EIS),[8,9] and Cyclic Voltammetry (CV).[10,11] GITT is based on a solid theoretical foundation and convenient to implement, so it is widely used and the results are well accepted. GITT uses time-domain voltage data resulting from a prescribed, low C-rate, long rest time, current discharge pulse train. Solid phase diffusivities are calculated from the voltage response transients and a plot of D_s versus SOC is generated. The GITT D_s measurement formula is based on a simplified analytical solution to the fundamental electrochemical equations, so it is a model-based approach.[5] GITT assumes diffusion occurs in a thin layer on the surface of the solid phase material. This assumption requires a short time duration τ of the discharge pulses ($\tau \ll L_s^2/D_s$), where L_s is the characteristic dimension of the solid phase material. The low C-rate coupled with the short pulse time and long rest period mean that a GITT test can take many hours to produce an accurate D_s versus SOC curve. The final problem with the traditional GITT test is that the accuracy of D_s measurement is unknown. Orders of magnitude differences in D_s measurement for the same chemistry can be found in the literatures.[7,12] Are the measured D_s variations with SOC, for example, real or simply artifacts of the GITT test? Certainly, one can perform an uncertainty analysis using the GITT equations but the accuracy of the underlying model that provides the basis for the GITT D_s formula has never been quantified. This uncertainty is not desirable for such a critical parameter to cell performance.[6]

Figure 1 shows an example GITT test for a (1.2 mAh) coin cell with a Nickel Cobalt Manganese (NCM)[1] positive electrode and a metal Lithium negative electrode. Prior to the test, the cell is fully charged ($SOC = 100\%$) and rested for 1 hr. The GITT current input consists of 40 discharge pulses at 0.1C ($I_0 = 0.00012$ A). Each pulse lasts 15 minutes followed by 30 minutes of rest. After each pulse, the SOC has decreased by 2.5%, so the battery is completely discharged ($SOC = 0\%$) at the end of the test. The steady state voltages at the end of each rest period produce 40 points on the Open Circuit Potential (OCP) versus SOC curve. The negative electrode material of the coin cell produces negligible overpotential so the GITT transient response depends on the diffusivity of Li^+ in the NCM cathode.

Figure 1c shows the magnified voltage data of one discharge pulse at 92.5% SOC. The cell voltage quickly decreases from V_0 to V_1 due to the total resistance R_T (ohmic and charge transfer resistances), slowly decreases to V_2 due to the transport of Li^+ in the solid phase, and, when the current is removed, the voltage increases as the Li^+ concentration evenly distributes throughout the solid phase to produce the steady-state, post-discharge voltage V_3. The voltage drops ($\Delta V_s = V_0 - V_3$ and $\Delta V_t = V_1 - V_2$) are calculated from the four voltage measurements $V_0, \ldots, V_3$.

The GITT diffusivity formula,

$$D_s = \frac{4}{\pi\tau}\left(\frac{n_M V_M}{S}\right)^2 \left(\frac{\Delta V_s}{\Delta V_t}\right)^2, \qquad [1]$$

where n_M and V_M are the molar mass (mol) and volume (cm^3/mol) of the active material, respectively, S is the cell interfacial area, and τ is the time duration of the pulse. For the NCM cathode, we assume that the solid phase consists of spherical particles with radius R_s, so Eq. 1 becomes

$$D_s = \frac{4}{\pi\tau}\left(\frac{R_s}{3}\right)^2 \left(\frac{\Delta V_s}{\Delta V_t}\right)^2. \qquad [2]$$

The GITT formula suffers from several drawbacks that limit the accuracy of D_s measurement. First, the GITT formula uses only four, often hand-picked, data points from what could be hundreds if not thousands of data points in the voltage response, depending on the sample rate, pulse length, and rest period. V_1, in particular, is very sensitive to the sample rate and high frequency, unmodeled dynamics. Second, phase change materials such as lithium iron phosphate, lithium titanium oxide, and even graphite (present in almost all Lithium-Ion cells) have $\Delta V_s \approx 0$ due to flat OCP curves. Eq. 2 predicts $D_s \approx 0$ for these materials which is clearly not the case. One can quantify the error associated with GITT formula by calculating the error between the periodically sampled experimental voltage data and the simulated

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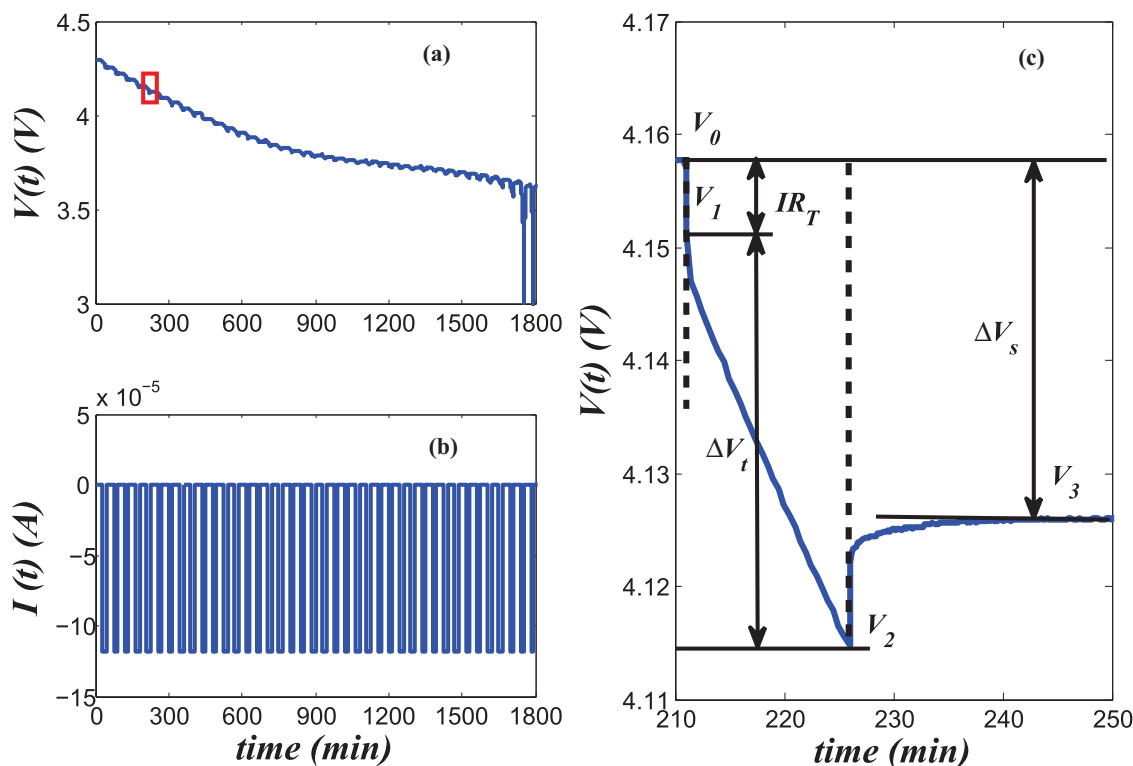
Figure 1. GITT data for a NCM coin cell: (a) Voltage, (b) Current, (c) Zoomed-in voltage corresponding to box in (a) (dashed lines delineate start and end of discharge pulse).

model response. The error $e_{GITT} = V_{GITT} - V$ and the RMS value

$$RMS_{GITT} = \sqrt{\sum e_{GITT}^2} \qquad [3]$$

gives an overall metric for the accuracy of the model and the model-based GITT formula.

To Calculate $V_{GITT}(t)$, we use the differential equation model for skin diffusion that produces the GITT formula:[5]

$$\frac{dV}{d\sqrt{t}} = \frac{2 V_M I_0}{S F z \sqrt{D_s \pi}} \frac{dV}{d\gamma}, \qquad [4]$$

where S is the total specific area, F is Faraday's constant, z is the charge number of the transport species, V_M is the molar volume of the sample, and I_0 is the input current. In Eq. 4, $t = 0$ at the beginning of the discharge pulse. I_0 and τ are assumed to be small and the rest period is assumed to be large, so the slope of the OCP curve $\frac{dV}{d\gamma}$ is approximately constant and equal to $\frac{\Delta V_s}{\Delta\gamma}$, where

$$\Delta\gamma = \frac{I_0 \tau M_B}{z m_B F} \qquad [5]$$

and M_B and m_B are the atomic and total weight of the active material, respectively.

Substitution of Eqs. 1 and 5 into Eq. 4 produces

$$\frac{dV}{d\sqrt{t}} = \frac{\Delta V_t}{\sqrt{\tau}}.$$

Hence, voltage response $V_{GITT}(t)$ in $t \in [0, \tau]$ is

$$V_{GITT}(t) = V_1 + \frac{V_2 - V_1}{\sqrt{\tau}}\sqrt{t}. \qquad [6]$$

Thus, RMS_{GITT} can be calculated from the experimental voltage data and the four manually selected voltages $V_0, \ldots, V_3$ using Eq. 6.

The limitations of GITT diffusivity measurement motivate new methods that can optimally measure D_s using all of current and voltage data. A new GITT method is developed in 7 for phase change materials. This technique is not applicable to single phase materials, however, which are the focus of the LSM in this paper.[13] presents a theoretical transient analysis of the Lithium ion intercalation process for accurate D_s measurement based on simulation data, but the corresponding experiments require specialized testing. The Least Squares Method (LSM) is a simple parameter estimation method for linear, time-invariant models. LSM measures the numerator and denominator polynomial coefficients of the impedance transfer function that optimally fit the current and voltage data,[14,15] and it can work with the standard GITT procedure and readily available time domain voltage and current measurements. In,[16] this method is successfully used to track the evolution of State-Of-Health (SOH)-related parameters, including diffusion time constant, capacity, and ohmic resistance, through a Lithium-Ion battery's cycle life. In this paper, we develop a Least Squares GITT (LS-GITT) that uses all of the voltage data from a GITT test to optimally tune the diffusivity in a reduced order solid phase diffusion model. The accuracy of GITT and LS-GITT are calculated and compared for the NCM coin cell data in Fig. 1.

Model Development

Figure 2 shows the half cell model with a NCM positive electrode and a metal Lithium negative electrode. The model assumes that: (i) the NCM material is a single solid phase spherical particle with radius R_s; (ii) Li^+ transport in the electrolyte is neglected; (iii) the discharge rate is low; (iv) the SOC change is small for each pulse; and (v) isothermal conditions apply. Assumptions (i) and (ii) are also used in the widely accepted Single Particle Model (SPM).[18] Assumptions (iii)–(v) are reasonable for the low C-rate GITT current input.

In,[19] a reduced-order Li-Ion cell model is developed using the Padé Approximation,[20] with the impedance transfer function coefficients explicitly correlated to physical and electrochemical parameters of the cell. For half cells, the same approach produces the second-order
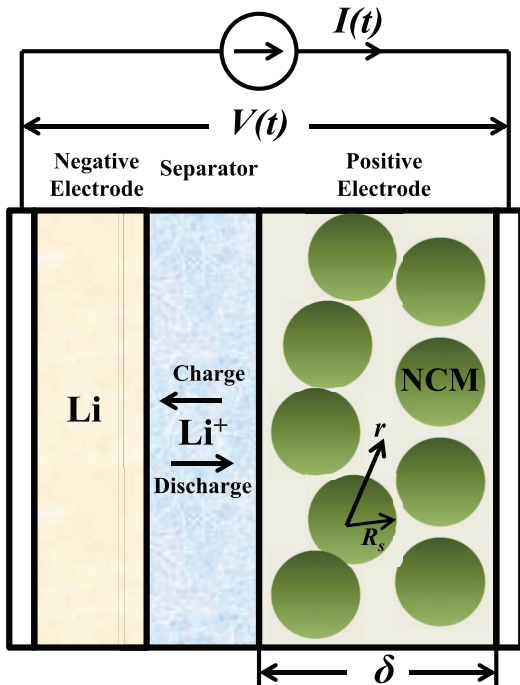
Figure 2. Schematic diagram of the half cell model.

impedance transfer function:

$$\frac{V(s)}{I(s)} = \frac{R_T s^2 + (35 R_T \alpha_2 + 10\alpha_1)s + 105\alpha_1\alpha_2}{s^2 + 35\alpha_2 s}, \qquad [7]$$

where $\alpha_1 = \frac{C_+}{3AF\delta\varepsilon_s}$, $\alpha_2 = \frac{D_s}{R_s^2}$, and total resistance $R_T = R_f + R_{ct}$, with charge transfer resistance $R_{ct} = \frac{RT}{i_0 a_s \delta F A(\alpha_a + \alpha_c)}$. The parameters are described in Table I.

In this work, the Least Squares Method (LSM) finds the α_2 that best-fits the voltage data. Using the GITT assumption that R_s is known, D_s can be calculated from α_2.

Under GITT conditions, the reduced order model in Eq. 7 is a reasonable and accurate representation of a full order battery model. The assumptions (i)–(v) are reasonable for the low C-rate and small SOC change associated with the GITT test. The Padé Approximation is the most efficient for spherical diffusion model order reduction.[17]

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For the second-order battery model in Eq. 7, the impedance transfer function of the cell is in the following form:

$$\frac{V(s)}{I(s)} = \frac{b_2 s^2 + b_1 s + b_0}{s^2 + a_1 s}, \qquad [8]$$

Table I. Model Parameters.

Parameter	Description
A	Cell cross-section area, cm^2
δ	Positive electrode thickness, cm
R	Universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
F	Faraday's constant, C/mol
T	Temperature, K
R_f	contact resistance, Ω
C_+	Setpoint OCP slope, $V \cdot mol^{-1} cm^3$
ε_s	Solid phase volume fraction
a_s	Specific solid phase area, cm^2/cm^3
i_0	Exchange current density, A/cm^2
α_a	Anodic transfer coefficient
α_c	Cathodic transfer coefficient

where the coefficients a_i and b_i are related to the parameters of the cell, including D_s. If a_1 is known, for example, $D_s = a_1 R_s^2 / 35$.

The LSM is a system identification technique for linear and time-invariant models that estimates the coefficients in Eq. 8 that optimally fit the time-domain current and voltage data.[14] By applying the LSM to the GITT current and voltage data, we develop a new D_s estimation method, the LS-GITT.

Figure 3 shows a diagram of the LS-GITT algorithm. Two digital low-pass filters process the N_{eval} current **I** and voltage **V** data points from a single current pulse to produce filtered current $\hat{\mathbf{I}}$, $\hat{\dot{\mathbf{I}}}$, and $\hat{\ddot{\mathbf{I}}}$, and voltage $\hat{\mathbf{V}}$ and $\hat{\dot{\mathbf{V}}}$ derivatives. The filter bandwidth is λ (rad/s).

Let $\mathbf{W}^T(s) = [\hat{I}(s), \hat{\dot{I}}(s), \hat{\ddot{I}}(s), \hat{V}(s)]$ and $\boldsymbol{\Theta}^T = [b_0, b_1, b_2, -a_1]$ so

$$\boldsymbol{\Theta}^T \mathbf{W}(s) = \frac{b_0 + b_1 s + b_2 s^2}{s^3 + 3\lambda s^2 + 3\lambda^2 s + \lambda^3} I(s)$$
$$+ \frac{a_1 s}{s^3 + 3\lambda s^2 + 3\lambda^2 s + \lambda^3} V(s). \qquad [9]$$

Substitution of Eq. 8 into Eq. 9 produces

$$\boldsymbol{\Theta}^T \mathbf{W}(s) = \frac{s^2}{s^3 + 3\lambda s^2 + 3\lambda^2 s + \lambda^3} V(s) = \hat{\ddot{V}}(s),$$

or, in the time domain,

$$\hat{\ddot{V}}(t) = \boldsymbol{\Theta}^T \mathbf{w}(t).$$

The digital filter outputs are stacked into

$$\mathbf{J} = [\mathbf{w}(0), \ \mathbf{w}(\Delta t), \dots, \ \mathbf{w}((N_{eval} - 1)\Delta t)] \in \mathbb{R}^{4 \times N_{eval}}$$

and $\hat{\ddot{\mathbf{V}}} = [\hat{\ddot{V}}(0), \ \hat{\ddot{V}}(\Delta t), \dots, \ \hat{\ddot{V}}((N_{eval} - 1)\Delta t)] \in \mathbb{R}^{N_{eval}}$.

We can minimize the parameter estimation error function $e = (\hat{\ddot{\mathbf{V}}} - \hat{\boldsymbol{\Theta}}^T \mathbf{J})^2$ by choosing the pseudoinverse

$$\hat{\boldsymbol{\Theta}} = [\mathbf{J}\mathbf{J}^T]^{-1} \mathbf{J} \hat{\ddot{\mathbf{V}}}. \qquad [10]$$

Finally, the LS-GITT diffusivity

$$\hat{D}_s = -\frac{\hat{\theta}(4) R_s^2}{35}. \qquad [11]$$

Diffusivity Measurement Results Using GITT and LS-GITT

Figure 4 compares the diffusivity measurements (a) and accuracies (b) of LS-GITT and GITT using the current and voltage data in Fig. 1 and $R_s = 5.3 \ \mu m$. Figure 4a shows that the D_s measurements range from $10^{-10} - 10^{-11} \ cm^2/s$ at $SOC > 10\%$, matching published results in the literature.[1] LS-GITT loses stability at extremely low SOC ($<5\%$) and the D_s estimate jumps dramatically and becomes negative. GITT is more stable and always produces positive D_s measurements.

Figure 4b evaluates the D_s measurement accuracy of GITT and LS-GITT using the RMS_{GITT} in Eq. 3 and

$$RMS_{LS} = \sqrt{\frac{1}{N_{eval}} \sum_{i=1}^{N_{eval}} (\hat{V}(t_0 + (i-1)\Delta t) - V(t_0 + (i-1)\Delta t))^2},$$

where $\hat{V}(t)$ is the voltage predicted by simulation of Eq. 8 with LS-GITT parameters estimates, t_0 is the start time of the discharge pulse, and N_{eval} is chosen so calculated for the discharge period $[t_0, t_0 + \tau]$. The LS-GITT algorithm, however, uses the entire data set, including discharge and the rest period, to calculate $\hat{D}_s$. At $SOC > 10\%$ (first 36 discharge pulses), $RMS_{LS} < RMS_{GITT}$ so the LS-GITT method is more accurate than GITT. Both methods have very high $RMS_V > 10 \ mV$ at low SOC because they fail to match the experimental voltage data. Even though GITT produces D_s measurements at $SOC < 5\%$, they are inaccurate and of questionable utility. GITT D_s measurements are not as accurate as LS-GITT for most SOC. In fact, from 60%–100% SOC LS-GITT is almost an order of magnitude more accurate than GITT. If we set a RMS accuracy cutoff of 1 mV
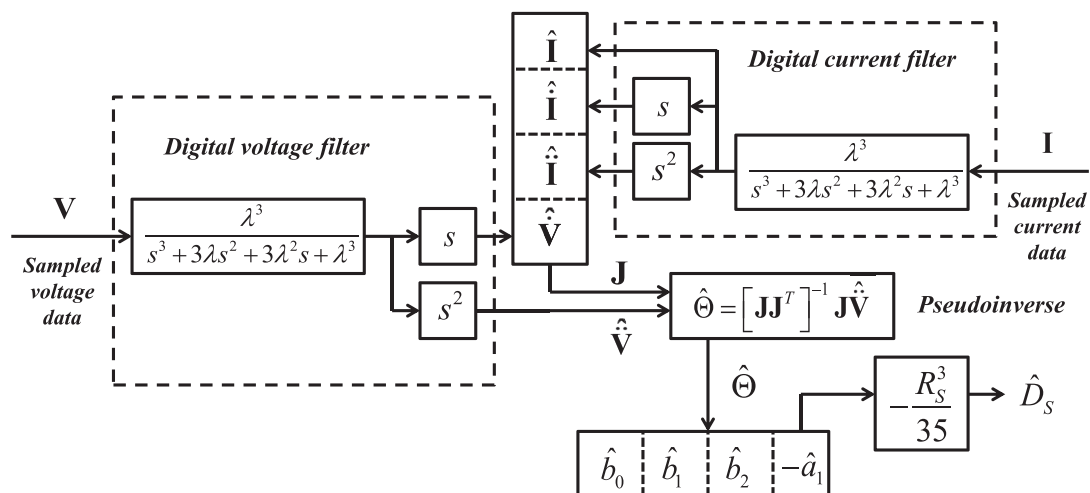
Figure 3. Block Diagram of the LS-GITT algorithm.

(roughly the RMS noise of the voltage sensor), then the LS-GITT has a working range of (15%–100%), more than double the GITT working range of (20%–60%).

The measured diffusivity from the GITT is larger than the more accurate LS-GITT because the GITT model neglects the bulk capacity of the active material particles by including only skin diffusion. The pulse length assumption, if strictly adhered to, can mitigate this effect but time constraints often dictate longer pulse lengths and the accuracy of GITT D_s measurement suffers. For the NCM cell tested, $R_s^2/D_s \approx 5000s$ and $\tau = 900s$, so $\tau < R_s^2/D_s$ but not necessarily $\tau \ll L_s^2/D_s$. As the pulse lengthens, the SOC and voltage integrate proportional to t, not proportional to $\sqrt{t}$ as required by the GITT model. The ΔV_s is larger than ΔU_s without SOC change assumed in the GITT model. The GITT method overestimates diffusivity because the voltage change is larger with the bulk capacity response included. This increases ΔV_s and the D_s measurement in Eq. 2. Thus, the GITT diffusivity measurement in Eq. 2 is larger than the actual

D_s. The accuracy of the underlying GITT diffusivity model increases with decreasing τ. Unfortunately, GITT experiments with smaller τ take longer to complete. Also, shorter pulses result in smaller ΔV_s so the signal to noise ratio decreases due to the small SOC change. Thus, the accuracy gains associated with closer adherence to the model assumptions may be swamped out by inaccuracies due to noise. The use of only four data points also is problematic because precise timing (high data sampling rate) and low noise are required. The four data points are manually selected, introducing a degree of non-repeatability to the results. A technique that uses all the data and is based on a more accurate model has the potential to average out the effects of timing and noise to produce a more representative diffusivity measurement.

Figure 5 shows representative pulse responses at 100% (a), 50% (b), and 2.5% (c) SOC. At 100% SOC, the voltage prediction of the LS-GITT model matches the experimental voltage data well ($RMS_{LS} = 0.19$ mV) but the GITT voltage estimate deviates considerably
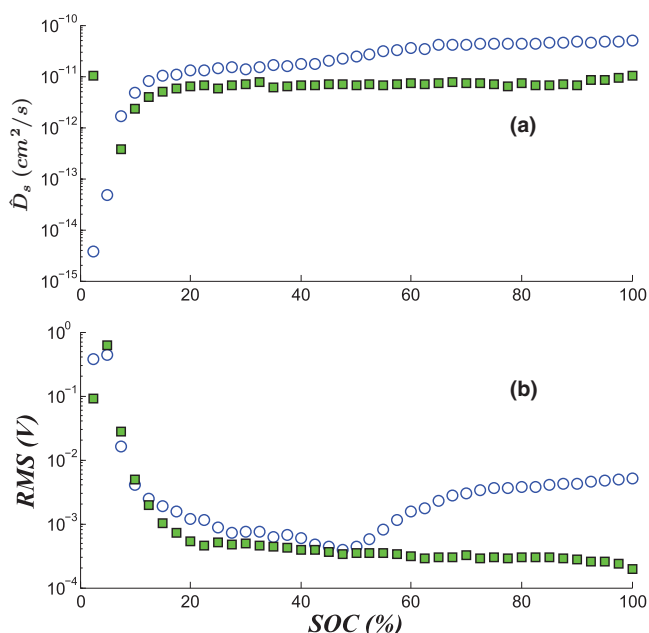

Figure 4. Measured diffusivities $\hat{D}_s$ (a) and RMS estimation errors (b) versus SOC for GITT (o) and LS-GITT (■).
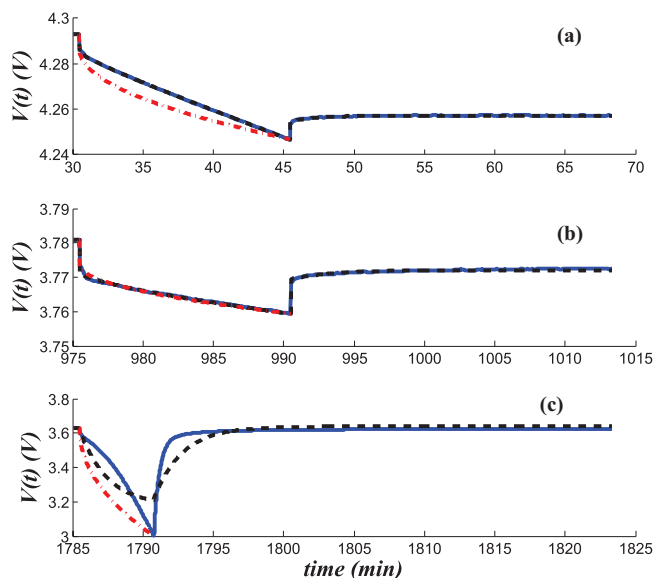

Figure 5. Voltage response versus time (experimental (solid), GITT model simulation (dash-dotted), and LS-GITT model simulation (dashed)): (a) 100% SOC, (b) 50% SOC, (c) 2.5% SOC.

from the experimental data ($RMS_{GITT} = 5.09$ mV). The GITT simulation passes through the points V_1 and V_2 exactly because they are inputs to the GITT formula. The transient response between V_1 and V_2, however, is not accurately captured by the model because the response includes responses proportional to $\sqrt{t}$ (GITT model) and t (bulk capacity). The LS-GITT response, on the other hand, accurately matches the ohmic drop and rise at the start and end of the discharge pulse, respectively, the transients during and after the pulse, and the steady state response. Clearly, the LS-GITT model more accurately fits the experimental data. The corresponding diffusivity is therefore a more accurate measurement. The GITT diffusivity measurement at 100% SOC is dubious at best. At 50% SOC, both methods produce accurate measurements of diffusivity as measured by the RMS error. Visual inspection of Fig. 5b also shows excellent agreement between the models and the experiment. It is interesting to note, however, that the models predict different diffusivities (LS-GITT $D_s = 6.9 \times 10^{-12}$ cm^2/s and GITT $D_s = 2.2 \times 10^{-11}$ cm^2/s). The LS-GITT has a smaller $RMS_{LS} = 0.33$ mV as compared to $RMS_{GITT} = 0.43$ mV but the GITT model more accurately captures the $\sqrt{t}$ diffusion. One can safely conclude that the actual D_s lies somewhere between 6.9×10^{-12} and 2.2×10^{-11} cm^2/s.

Figure 5c shows that neither model matches the experimental response at 2.5% SOC. It is impossible for either model to have the concave transient exhibitted in the experiment. Despite the low C-rate and small pulses, $\frac{dV}{d\gamma} \neq \frac{\Delta V}{\Delta \gamma}$, violating a GITT assumption and $\frac{dV}{d\gamma} \neq$ constant, violating an LS-GITT assumption. The large errors associated with these measurements mean that neither can be considered accurate. At low SOC, inaccurate D_s measurement is due to the strong OCP nonlinearity that is not included in the GITT and LS-GITT diffusion models. One simple solution to minimize this effect is to reduce the pulse size at low SOC so OCP nonlinearities are minimized. Smaller pulses, however, will result in smaller voltage swings and lower signal to noise ratios, potentially offsetting the error reduction. Alternatively, one could develop a nonlinear model-based approach to reduce estimation error.

Conclusions

Based on experimental results from a NCM half cell, LS-GITT is more accurate than GITT, sometimes by an order of magnitude. The GITT test overestimates D_s because the underlying model neglects the effects of bulk capacity on the voltage transients. LS-GITT gives results accurate to 1 mV RMS from 15%–100% SOC where GITT provides that level of accuracy over less than half that range. Neither technique provides accurate D_s measurements below 10% SOC.

Acknowledgment

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