Analysis of the Galvanostatic Intermittent Titration Technique (GITT) as applied to a lithium-ion porous electrode

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ABSTRACT

Galvanostatic Intermittent Titration Technique (GITT) experiments were conducted to determine the lithium diffusion coefficient of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, used as the active material in a lithium-ion battery porous composite positive electrode. An electrochemical model, based on concentrated solution porous electrode theory, was developed to analyze the GITT experimental results and compare to the original GITT analytical theory. The GITT experimental studies on the oxide active material were conducted between 3.5 and 4.5 V vs. lithium, with the maximum lithium diffusion coefficient value being $10^{-10}\,cm^2\,s^{-1}$ at 3.85 V. The lithium diffusion coefficient values obtained from this study agree favorably with the values obtained from an earlier electrochemical impedance spectroscopy study.

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1. Introduction

High power density is a fundamental requirement for lithium-ion batteries under development for hybrid electric vehicles. The power density can be significantly affected by the diffusion rate of lithium in the active materials. One commonly utilized electrochemical technique to determine the lithium diffusion coefficient in electrode active materials is GITT, which was introduced by Weppner and Huggins [1]. For example, Ramana et al. used GITT to determine the lithium diffusion coefficient in pulsed laser deposited $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ films [2]. Also, Shaju et al. used GITT to determine the lithium diffusion coefficient for $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ active material particles in a composite positive electrode [3].

The GITT theory was originally developed for dense planar electrodes where the electrochemical reaction only occurs on the face of the electrode in contact with the electrolyte. Employing the GITT theory directly on today's lithium-ion porous composite electrodes is problematic, since the underlying assumptions are not generally applicable. Recognizing this, Yang et al. determined the lithium diffusion coefficient for graphite in a composite negative electrode assuming a uniform current distribution throughout the electrode and estimating the electrochemical active area from the microstructure of the graphite particles [4].

According to the GITT analytical theory [1], the lithium diffusion coefficient of the active material can be calculated by the following equation:

$$D_s = \frac{4}{\pi}\left(\frac{V_M}{SFz_i}\right)^2 \left[I_0\left(\frac{dE}{d\delta}\right)\bigg/\left(\frac{dE}{d\sqrt{t}}\right)\right]^2 \quad (t << L^2/D_s) \tag{1}$$

Table 1 contains a description of the nomenclature used in the equation. In addition to the assumption of a (i) dense planar electrode, in Eq. (1) it is further assumed that: (ii) the electrode current is constant and uniform, (iii) diffusion is one-dimensional, (iv) volume and structure changes in the material are not considered, (v) the diffusion coefficient can be considered constant during current passage, (vi) Fick's law of diffusion applies, and (vii) all other potential effects in the cell, not related to lithium diffusion in the active material, can be neglected. One or both differentials in Eq. (1) are often approximated by the finite changes in the quantities during the experiment, which is valid providing the current passage time is short enough. It is also important to note here that the time limitation for the validity of Eq. (1) refers to the depth to which the concentration gradient penetrates the active material. The approximation is for short times when the concentration gradient is close to the surface.

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Table 1
Symbol nomenclature for GITT analytical model.

Symbol	Units	Symbol description
D_s	$cm^2\,s^{-1}$	Chemical diffusion coefficient
E	V	Galvanic cell potential
F	$C\,mol^{-1}$	Faraday's constant
I_0	A	Applied constant electric current
L	cm	Diffusion length
S	cm^2	Electrode electrochemical active area (T-cell electrode geometric area: $0.97\,cm^2$)
t	s	Time
V_M	$cm^3\,mol^{-1}$	Molar volume of active material
z_i	–	Valence of species
δ	–	Deviation from the initial stoichiometry

In the present study, an in-depth theoretical and experimental analysis of GITT, as applied to lithium-ion porous composite electrodes, was conducted using a well-known layered nickel oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ or NCA) active material incorporated into an extensively studied positive electrode [5–10]. The importance of using a reference electrode in the cell during the GITT experimental polarization and relaxation measurements was examined. On the theoretical side, an electrochemical model was developed for lithium-ion GITT cells that accounts for the porous composite positive electrode structure, the non-uniform electrode current distribution, and the particle microstructure of the active material. The experimental results were analyzed using the original GITT analytical theory, as well as the electrochemical model.

2. Experimental

A three-electrode T-type cell was utilized in the present study, using a modified one-half inch Teflon Swagelok union-tee tube fitting with stainless-steel rods for the electrode connections. The positive electrode under study has a composite structure made of NCA active material, carbon black and graphite conductive additives for distributing current, and a PVDF binder all on an aluminum current collector (see Table 2). The counter and reference electrodes were both lithium metal. The electrolyte was $1.2\,M$ $LiPF_6$ dissolved in a mixture of EC and EMC and a Celgard microporous membrane was used as the separator.

The GITT measurements consisted of a series of current-pulses applied to the T-type cell at fixed voltages, each followed by a 5-h relaxation period. After cell formation, the GITT studies were conducted at predetermined initial open circuit cell potentials, specifically 3.67, 3.77, 3.84, 4.05, 4.27, and $4.47\,V$ vs. lithium. Cells were charged to each potential at a current density of $0.2\,mA\,cm^{-2}$ (approximately C/5) and allowed to relax for 5 h. Cell studies included four current-pulse times (i.e. 5, 10, 30, and 60 s) and three current densities (i.e. 0.2, 0.5, and $1.0\,mA\,cm^{-2}$). The experiments were performed at room temperature using multiple cells.

A typical voltage trace during a GITT experiment conducted on a cell initially at $3.77\,V$ is given in Fig. 1. Two voltage curves are shown in the figure, one for the composite positive electrode potential

Table 2
Cell components and chemistry.

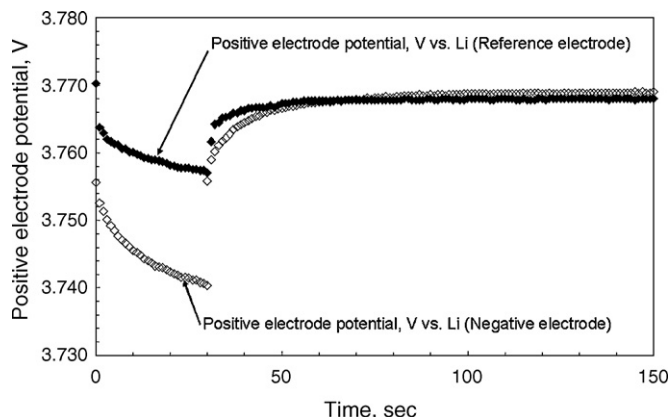| Positive electrode	Electrolyte
84 wt.% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	$1.2\,M$ $LiPF_6$ in EC:EMC (3:7 by wt.)
8 wt.% PVdF binder	Separator
4 wt.% SFG-6 graphite	25-μm-thick Celgard 2325 (PP/PE/PP)
4 wt.% carbon black	
8 mg cm^{-2} active-material loading density	
35-μm-thick coating	
30-μm-thick Al current collector	

Fig. 1. Typical voltage trace of the positive composite electrode potential vs. lithium (counter electrode) and the positive electrode potential vs. lithium (reference electrode) initially at $3.77\,V$. A 30-s constant current density discharge pulse of $0.5\,mA\,cm^{-2}$ is applied to the cell, followed by a long relaxation period.

vs. the lithium counter electrode and the other for the positive vs. lithium reference electrode. In Fig. 1, a 30-s constant current density discharge pulse of $0.5\,mA\,cm^{-2}$ is applied to the cell, followed by a long relaxation period. The full cell voltage is obviously very different from the positive electrode vs. reference voltage. There is a predictable significantly greater change in the cell voltage when the current is applied and stopped. More importantly for the discussion here, is the larger change in the cell voltage during the full 30 s that current is applied and the corresponding change while the cell voltage is relaxing. This is important because the shape of the cell voltage curve is significantly different from that of the positive vs. reference curve. While a minor portion of this difference can be attributed to diffusional effects in the electrolyte, the majority of the difference is associated with the lithium counter electrode. Instabilities in the lithium electrode's solid electrolyte interface (SEI) can interfere with the diffusional measurements on the positive electrode when the full cell voltage is used with a lithium counter electrode. In fact, in the present study, consistent reproducible modeling results were only possible with the use of a reference electrode in the cell.

3. Model description and development

An electrochemical model was developed for a porous composite intercalation electrode cell with a metallic planar lithium counter electrode, capable of following the galvanostatic studies in GITT experiments. The general methodology for the electrochemical model follows the work of Prof. Newman at Berkeley [11] and is similar to several other electrochemical models presented over the last 20 years [12–16]. The model development for the separator and porous composite electrode in the present study is also similar to our earlier work [17–19] except that a more simplified approach is utilized to account for interfacial effects [20]. Our earlier work developed both AC and DC versions of the electrochemical model utilizing the same set of constituent equations and parameters, which also focused on the same positive composite electrode studied in this paper.

In the DC electrochemical model, concentrated solution theory is used to describe the salt transport through the electrolyte and volume-averaged transport equations account for the porous separator and composite electrode structure. The electrolyte transport equations in this study, given by Eqs. (2) through (4) in Table 3 (see Table 4 for the nomenclature) are based on the volume-averaged velocity of the electrolyte. Also in Table 3 are the remaining current

Table 3
Transport and electrochemical reaction equations used in DC electrochemical model.

Equations		Description
$\varepsilon \dfrac{\partial c}{\partial t} = \dfrac{\varepsilon}{\tau} \dfrac{\partial}{\partial x}\left(D\dfrac{\partial c}{\partial x}\right) + \dfrac{1}{z_+\nu_+ F}\dfrac{\partial\left[(1-c\bar{V}_e)(1-t_+^0)i_2\right]}{\partial x}$	(2)	Concentrated solution volume-averaged binary electrolyte salt diffusion
$i_2 = -\dfrac{\kappa\varepsilon}{\tau}\dfrac{\partial \Phi_2}{\partial x} - \nu RT\dfrac{\kappa\varepsilon}{F\tau}\left(\dfrac{s_+}{n\nu_+}+\dfrac{t_+^0}{z_+\nu_+}\right)\left(1+\dfrac{\partial \ln f_\pm}{\partial \ln c}\right)\dfrac{1}{c}\dfrac{\partial c}{\partial x}$	(3)	Ohm's law for concentrated solution binary electrolyte
$\dfrac{\partial i_2}{\partial x} = Fz_+ a j_n$	(4)	Volume-averaged electrolyte current balance
$i_1 = -\sigma_{\text{eff}}\dfrac{\partial \Phi_1}{\partial x}$	(5)	Ohm's law for electronically conducting matrix
$I = i_1 + i_2$	(6)	Total cell current density
$i_n = i_0\left(\dfrac{c}{c_{\text{ref}}}\right)^{\alpha_A}\left(\dfrac{c_T-c_S}{c_T-c_{S,\text{ref}}}\right)^{\alpha_A}\left(\dfrac{c_S}{c_{S,\text{ref}}}\right)^{\alpha_C}*\left[\exp\left\{\dfrac{\alpha_A F}{RT}(\Phi_1-\Phi_2-U)\right\}-\exp\left\{-\dfrac{\alpha_C F}{RT}(\Phi_1-\Phi_2-U)\right\}\right]$	(7)	Butler–Volmer electrochemical reaction kinetic expression
$\dfrac{\partial c_S}{\partial t} = \dfrac{\partial}{\partial y}\left(D_S\dfrac{\partial c_S}{\partial y}\right)$	(8)	Lithium diffusion in active material (y-direction)

expressions (Eqs. (5) and (6)) needed for the cells overall current balance. The remaining transport expression in Table 3 (Eq. (8)) accounts for the lithium diffusion in the active material particle, where it is implicitly assumed that the lithium diffusion in the active material can be represented by a single characteristic length and diffusion coefficient.

The electrolyte–active material interface or SEI in lithium-ion electrodes is ill-defined and very complicated. The process of moving lithium ions across the SEI includes some combination of diffusion, migration, and reaction. While it is critically important to account for the potential effects associated with the SEI it is beyond the scope of this study to include a detailed description of the SEI in the model. In the present study, a Butler–Volmer electrochemical

Table 4
Symbol nomenclature for DC electrochemical model.

Symbol	Units	Symbol description
a	$1\,\text{cm}^{-1}$	Specific interfacial area
c	$\text{mol}\,\text{cm}^{-3}$	Electrolyte salt concentration
c_S	$\text{mol}\,\text{cm}^{-3}$	Lithium concentration in active material
c_T	$\text{mol}\,\text{cm}^{-3}$	Maximum lithium concentration in active material
D	$\text{cm}^2\,\text{s}^{-1}$	Salt diffusion coefficient in electrolyte
D_S	$\text{cm}^2\,\text{s}^{-1}$	Oxide lithium diffusion coefficient
$f_\pm$	–	Electrolyte salt activity coefficient
F	$\text{C}\,\text{mol}^{-1}$	Faraday's constant
i_1	$\text{A}\,\text{cm}^{-2}$	Superficial electronic current density
i_2	$\text{A}\,\text{cm}^{-2}$	Superficial ionic current density
i_0	$\text{A}\,\text{cm}^{-2}$	Kinetic exchange current density
i_n	$\text{A}\,\text{cm}^{-2}$	Electrochemical transfer current
I	$\text{A}\,\text{cm}^{-2}$	Superficial total cell current density
j_n	$\text{mol}\,(\text{cm}^2\,\text{s})^{-1}$	Pore-wall flux density
n	–	Electrons transferred in electrochemical reaction
R	$\text{J}\,(\text{K}\,\text{mol})^{-1}$	Universal gas constant
s_i	–	Stoichiometric coefficient
t	s	Time
t_+^0	–	Cation transference number
T	K	Temperature
U	V	Oxide open circuit potential
$\bar{V}_e$	$\text{cm}^3\,\text{mol}^{-1}$	Electrolyte partial molar volume
x	cm	Cell coordinate
y	cm	Oxide particle coordinate
z_+	–	Cation charge number
α_A, α_C	–	Transfer coefficients
δ_b	nm	Diffusion length
ε	–	Volume fraction of electrolyte
σ_{eff}	–	Effective electrode electronic conductivity
τ	–	Electrolyte tortuosity
ν	–	Electrons transferred in electrochemical reaction
ν_+	–	Cations per salt molecule
κ	$1\,(\Omega\,\text{cm})^{-1}$	Electrolyte conductivity
Φ_1	V	Potential of electronically conducting matrix
Φ_2	V	Electrolyte potential

reaction expression given by Eq. (7) in Table 3 is used to account for the interfacial impedance of the composite electrode. A similar reaction expression is used for the lithium counter electrode. The time constants for all the interfacial effects in the composite electrode under study are less than a second at room temperature and in this model they are assumed to be at steady-state.

The system of coupled time-dependent non-linear partial differential equations (Eqs. (2)–(8)) was solved using a partial differential equation solver (FlexPDE). In the model, the cell geometry is one-dimensional (x-direction) and the diffusion of lithium in the electrode active material particles adds a pseudo second dimension (y-direction). The solver was used in two dimensions to account for all the phenomena. The general approach to the parameter estimation and determination is described elsewhere [17,18]. In this study, the parameters determined by fitting the DC electrochemical model to the GITT experimental results were minimized. Specifically, the parameters determined by fitting of the present GITT data were the lithium diffusion coefficient (D_S) of the NCA oxide active material and the kinetic exchange current density for the electrochemical reaction. The exchange current density was determined from the step in electrode potential when current was applied to the cell and the slow change during the remainder of the current passage was used to determine the lithium diffusion coefficient in the active material. The electrode potential change during the relaxation time was used to further examine the overall fit of the model. The electrolyte transport and thermodynamic parameters were estimated using the advanced electrolyte model of Gering [21], which agreed well with experimental measurements [22]. The composite positive electrode's open circuit voltage curve was determined from slow cell cycling. The electrode's electrochemical active area, as well as the characteristic diffusion length of the active material, was based on the oxide active material's BET surface area.

4. Results and discussion

As discussed above for the GITT experimental studies, the value and variation of the full cell voltage (i.e. positive vs. lithium counter) were markedly different from the positive vs. lithium reference voltage. In addition, the quality and consistency of the fitting results were much better using the reference electrode measurements. Therefore the fitting results presented here are based on the composite positive electrode vs. lithium reference voltage measurements. A typical example of the fit obtained between the GITT experimental results and the DC electrochemical model, based on porous electrode theory, is shown in Fig. 2. As discussed in previous articles [17–19], improving the fit through the use of multiple active material particle size fractions should also be possible.
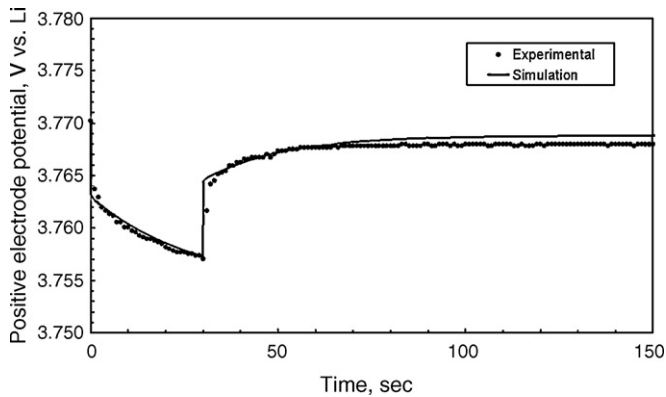
Fig. 2. DC elctrochemical model simulation of positive composite electrode potential vs. lithium reference electrode during a GITT experiment. A 30-s constant current density discharge pulse of 0.5 mA cm^{-2} is applied to the cell, initially at 3.77 V, followed by a long relaxation period.

In the following discussion three models are referenced in the text and figures. The DC electrochemical model, described in detail above, is referred to as the DC model in the figures. Also, the AC electrochemical model, mentioned in this article and described in detail in the reference material [18], is referred to as the AC model in Fig. 3(a). Finally, the GITT analytical theory, given by Eq. (1), is the third model and it is referred to as the GITT model in the figures.

The lithium diffusion coefficient (D_S) of the NCA oxide active material as a function of electrode potential obtained from the GITT

Fig. 3. (a) Comparison of lithium diffusion coefficients for the oxide active material obtained by applying the DC electrochemical model to the GITT results and applying the AC electrochemical model to EIS studies. (b) Comparison of lithium diffusion coefficients for the oxide active material obtained by applying the DC electrochemical model and the GITT analytical theory to the GITT results. The times indicate the current flowing times during the GITT experiment.

Fig. 4. Lithium diffusion coefficient in oxide active material at 3.77 V obtained by applying the GITT analytical theory (Eq. (1), dotted line) to the DC electrochemical model simulation results, using a constant current density of 0.5 mA cm^{-2} for 30 s. The solid line represents the lithium diffusion coefficient used in the DC model simulation.

experimental results using the DC electrochemical model is given in Fig. 3(a). Also presented in Fig. 3(a) are the lithium diffusion coefficient values obtained on the same composite electrode using electrochemical impedance spectroscopy (EIS) studies and an AC impedance electrochemical model [18]. Both the electrochemical models are based on the same constituent transport equations. The excellent agreement of the lithium diffusion coefficients obtained from modeling the GITT and EIS results is a strong indicator of the model's accuracy and self consistency.

Fig. 3(b) compares the lithium diffusion coefficient of the NCA oxide active material using both the DC electrochemical model and the GITT analytical theory (Eq. (1)). In order to best apply Eq. (1) to the GITT experimental results on the porous composite electrode the area term should be the electrochemical active area of the electrode, not its geometric area. This implicitly assumes that the current distribution throughout the electrode is uniform, which is an approximation. It is clear from Fig. 3(b) that the diffusion coefficient values obtained from the GITT analytical theory are consistently lower than those obtained from the DC electrochemical model. However, the GITT theory values are generally within an order-of-magnitude. Considering its ease of implementation and the degree to which the electrochemical active area of the electrode is known, order-of-magnitude accuracy may be adequate for some studies. It is important to note here that in general the shorter the current flowing time during the GITT experiment the better agreement of the diffusion coefficient. This fact can be contrasted to the diffusion coefficient obtained by the DC electrochemical model, which in general does not depend on the time of current flow.

The DC electrochemical model was utilized to examine the reasons for the variations in the diffusion coefficients. As a first step, all experimental artifacts in the above GITT studies were eliminated by treating the DC electrochemical model simulation as results from an ideal porous composite electrode. The GITT analytical theory (i.e. Eq. (1)) was then directly applied to the DC electrochemical model simulation results, as shown in Fig. 4. As in the experimental study, the active material lithium diffusion coefficient obtained from the GITT analytical theory was consistently low for all times of current passage, with the best agreement coming at the shortest times. Further analysis of the GITT analytical theory, using the electrochemical model to examine the cell concentration, potential, and current distributions identified two significant sources of the difference in diffusion coefficients.

First, as indicated above, the implicit assumption for the GITT analytical theory of a uniform current distribution in the compos-
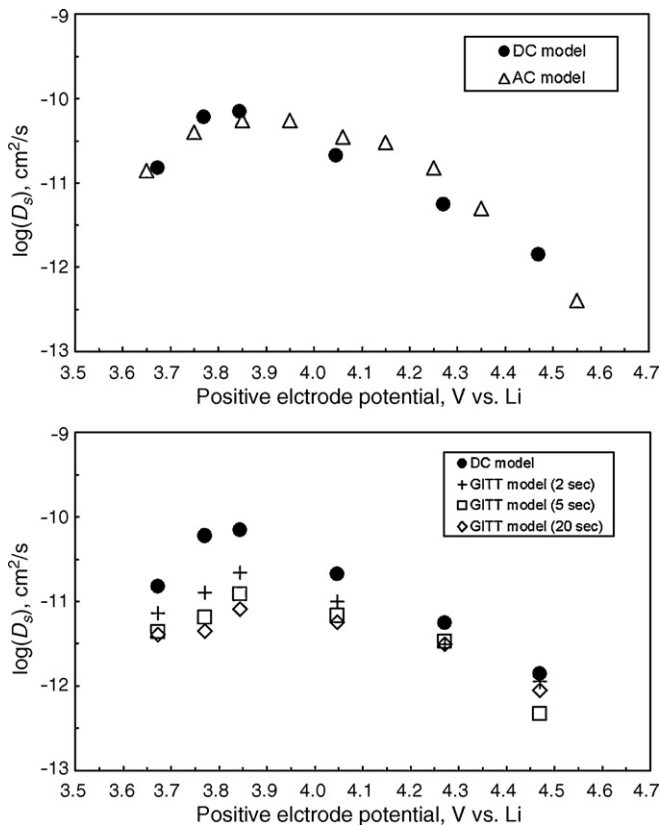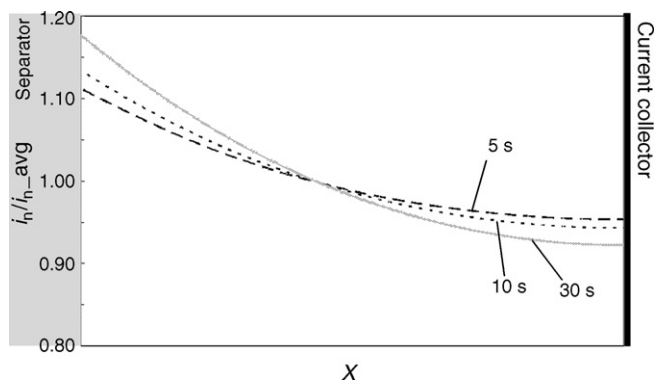
Fig. 5. Simulation of current distribution throughout the composite positive electrode during a GITT experiment. The time indicates length of current flow at 0.5 mA cm^{-2} with an initial positive electrode potential of 3.77 V.

Fig. 6. Simulation of lithium concentration distribution in NCA particles throughout the composite positive electrode during a GITT experiment. The time indicates length current flow at 0.5 mA cm^{-2} with an initial positive electrode potential of 3.77 V. (a) 5 s current flow, (b) 10 s, and (c) 30 s.

ite electrode is at best an approximation. The simulation of the current distribution in the composite positive electrode during a GITT experiment is given in Fig. 5. As typical in porous electrodes with the electronic conductivity significantly greater than the ionic conductivity, the highest current is on the separator side of the electrode. As can be seen in Fig. 5 the high interfacial resistance (i.e. based on the electrode's electrochemically active area) in these lithium-ion electrodes tends to make the current distribution relatively uniform, with less than a 20% variation. The sloping open circuit voltage curve of the NCA material also tends to make the current distribution more uniform. Changes in the current distribution with current passage are relatively small and are generally associated with the transport of lithium ions in the electrolyte and active material. In general, the changes in the current distribution with current passage are too small to fully explain why the analytical GITT theory results in a diffusion coefficient that is dependent on current passage time.

The second approximation in the GITT analytical theory that may be less obvious involves the definition of the diffusion length (L) in Eq. (1). The diffusion length in Eq. (1), as applied to a dense planar electrode, is typically the electrode thickness. For the present composite positive electrode, it is most appropriate to use the characteristic diffusion length of the NCA particles, which in the present case is estimated at 0.5 μm. This diffusion length combined with a diffusion coefficient of 6.0×10^{-11} cm^2 s^{-1} (i.e. the value at 3.77 V vs. lithium) results in a time limitation of much less than 40 s for Eq. (1) to be valid. As mentioned above, the time limitation is an estimate when the significant lithium concentration variation in the active material is close to the surface that allows the approximation used in Eq. (1) to be valid.

The DC electrochemical model is able to simulate the lithium concentration in the NCA particles throughout the composite electrode and is given in Fig. 6 for three times (i.e. 5, 10, and 30 s) after current is started. The lines in Fig. 6 represent evenly distributed iso-concentration lines for lithium in the NCA particles with the top of diagram being the surface of the particle and the bottom of the diagram representing the center. From Fig. 6 it is easy to see that lithium concentration variations extend well into the particles throughout the electrode even at 5 s. For typical lithium-ion composite electrodes, GITT experiments shorter than a few seconds are difficult to carryout because of the time constant for the interfacial effects. Of course, the smaller the diffusion coefficient or longer the characteristic diffusion length the more time available for current passage during the GITT experiment.

At least theoretically, it should be possible to perform a GITT experiment where the current passage time is short enough that the second assumption, discussed above, concerning the GITT ana-
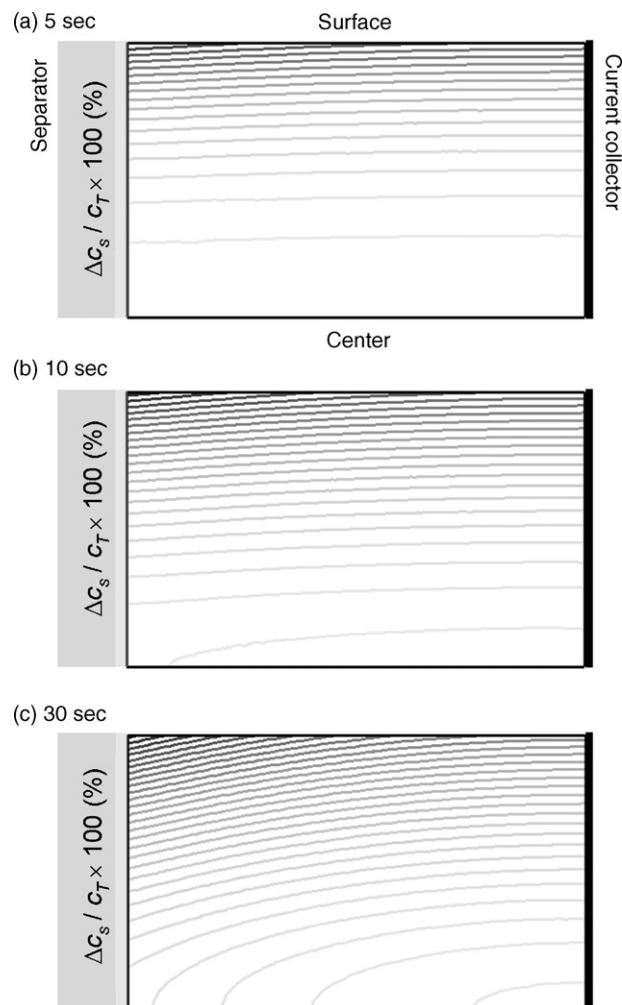
lytical theory is valid. Conversely, the current distribution in a lithium-ion porous composite electrode will generally never be totally uniform. However, the DC electrochemical model can be used to examine the errors associated with that assumption. To obtain a uniform current distribution throughout the composite electrode, the DC electrochemical model could be modified. However, it is much easier to either artificially increase the interfacial impedance (i.e. by reducing the Butler–Volmer kinetic exchange current density) or alternatively increase the slope of the open circuit voltage (OCV) curve (i.e. dU/dc_S). The latter was chosen here simply because increasing the slope of the OCV curve will also accentuate the electrode potential effects resulting from lithium diffusion in the active material.

In a manner described above for Fig. 4, the GITT analytical theory was applied directly to the DC electrochemical model simulation results with a uniform current distribution created by increasing the slope of the OCV curve and keeping all other parameters the same. The results, given in Fig. 7, show a much better correlation between the diffusion coefficient determined by GITT analytical theory and the value used in the DC electrochemical model. In fact for current passage times shorter than about 10 s the GITT analytical theory value is essentially equivalent to the full electrochemical model for the special case of a uniform current distribution. This
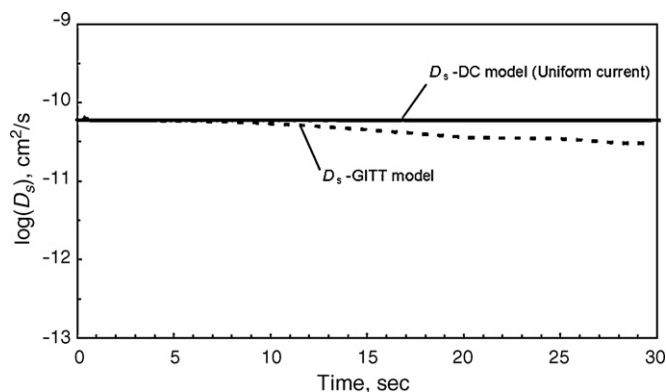
Fig. 7. Lithium diffusion coefficient in oxide active material at 3.77 V obtained by applying the GITT analytical theory (Eq. (1), dotted line) to the uniform current distribution DC electrochemical model simulation results, using a constant current density of 0.5 mA cm^{-2} for 30 s. The solid line represents the lithium diffusion coefficient used in the DC model simulation.

indicates that even a small non-uniformity in the composite electrode current distribution can have a significant adverse effect on the diffusion coefficient calculated by the GITT analytical theory in Eq. (1).

The current distribution in a composite electrode will depend on many factors as discussed above. It is entirely possible that another electrode would have a more uniform current distribution than the NCA electrode examined in this study. However, it is not likely that any lithium-ion composite electrode, especially industrially important electrodes, would have a totally uniform current distribution. It should also be noted here that all the theoretical models in this study assume that the active material remains single phase. The applicability of these models to active materials that are known to go through significant phase changes during cycling (e.g. LiMn$_2$O$_4$, Li$_4$Ti$_5$O$_{12}$, LiFePO$_4$ etc.) would have to be examined.

5. Conclusions

It is important to use a reference electrode in a GITT experimental cell to eliminate counter electrode diffusional effects or possible instabilities, as observed in the lithium metal electrodes in the present study. The DC electrochemical model developed for studying GITT experiments on lithium-ion porous composite electrodes was used to determine the lithium diffusion coefficient in the oxide active material. The lithium diffusion coefficient obtained from the DC electrochemical model agreed favorably with the values obtained from earlier EIS studies, using an AC version of the electrochemical model.

The GITT analytical theory, originally developed for dense planar electrodes, was applied to a lithium-ion porous composite electrode by defining the electrode area as the electrochemically active area. Diffusion coefficient results obtained with the GITT analytical theory were consistently lower than the DC electrochemical model values, but generally agreed within an order-of-magnitude. The DC electrochemical model was utilized to identify the reasons for the

variations in the diffusion coefficient. Applying the GITT analytical theory to the electrochemically active area implicitly assumes that the porous composite electrode has a uniform current distribution, which is an approximation. The agreement of the GITT analytical theory to the DC electrochemical model improved dramatically when the OCV curve was modified to artificially create an electrode with a uniform current distribution. Care must also be taken when establishing the length of time current is passed during the GITT experiment. The diffusion length used to establish the time constant for the current passage should be the characteristic length of the oxide particles in the electrode.

Acknowledgements

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