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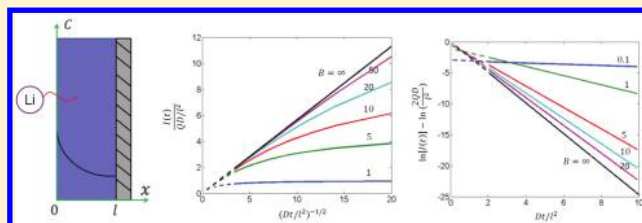
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 Supporting Information

ABSTRACT: The potentiostatic intermittent titration technique (PITT) is one of the widely used methods for determining the diffusion coefficient in electrochemical materials, such as lithium diffusion in lithium-ion battery electrodes. The conventional PITT analysis neglects interfacial resistance and assumes the system is diffusion-controlled. For real electrode systems, however, surface reaction as well as diffusion may be rate-limiting. In this Article, we analyze PITT measurements for material systems with finite surface reaction rates. For small amplitude potential steps, we derive analytic solutions for the measured transient current associated with PITT, taking into account the effects of finite surface reaction rates. Using the analytic solutions, the diffusion coefficient, surface reaction rate, and the exchange current density can be determined simultaneously. An example of lithium diffusion in amorphous silicon thin-film electrodes is used to demonstrate the enhanced PITT approach.



1. INTRODUCTION

The potentiostatic intermittent titration technique (PITT) is a powerful technique to study the thermodynamic and transport properties of materials encountered in electrochemical processes. Because voltage and current can be controlled and measured precisely, PITT has become a commonly used electroanalytical method. Specifically, PITT has been used to measure the diffusion coefficient, D , of solutes in host materials as well as to obtain quasi-equilibrium voltage–capacity profiles of battery electrodes after it was first developed by Wen et al. to study LiAl alloys.^{1,2} Recently, PITT has been widely applied to characterize lithium diffusion in various lithium-ion battery (LIB) electrode materials, especially graphite negative electrodes^{3,4} and transition-metal oxide positive electrodes.^{5–11}

The original PITT theory was developed based on a thin-film geometry with diffusion across the thin electrode dimension.¹ Diffusion of only one species was allowed, and nucleation of new phases was not considered. Furthermore, the surface reaction rate was assumed to be infinitely fast; that is, surface reaction resistance was not considered. In practice, it has been challenging to apply PITT to electrochemical systems because many systems do not satisfy all of the assumptions. Therefore, several researchers have modified PITT to be applicable to various electrochemical systems. For instance, Markevich et al. analyzed the PITT theory in a phase-transformation region that involves slow nucleation and pointed out that D determined by PITT is less accurate than that by the galvanostatic intermittent titration technique (GITT).¹² Levi et al. studied the PITT of lithium-graphite in the two-phase regions using a two parallel diffusion paths model¹³ and a moving boundary model.¹⁴ In addition to

phase transformation, it has been realized that the resistance to surface reaction may affect the overall electrochemical behavior. For example, Montella considered possible limitations by insertion reaction kinetics and developed analytic solutions for PITT.¹⁵ Levi et al. developed approximate analytic solutions for PITT by considering Ohmic drop using a generalized dimensionless kinetic parameter (R_d/R_{external})¹⁶ and applied this technique to lithium diffusion in polymer electrode using a two-step refinement method.¹⁷ Churikov et al. considered phase transformation and surface resistance for lithium diffusion in multiple spheres and calculated D of lithium in LiFePO_4 by numerical fitting of parameters to experimental data.¹⁸ More recently, Delacourt et al. applied PITT to determine the lithium diffusion coefficient in LiFeSO_4F by using an analytic solution of diffusion in spheres with surface reaction resistance.¹¹

In this Article, we consider the influence of resistance to surface reaction in analyzing the diffusion of species within a host material during PITT for small potential-step excitations, and we provide analytic solutions to the concentration distribution and resulting current response. Using this simple analytic model of PITT, one can determine the diffusion coefficient and surface reaction rate (yielding the exchange current density) simultaneously. Using lithium diffusion in thin film amorphous silicon as an example, we show that the diffusion coefficient can be underestimated without considering the finite surface reaction rate. This enhanced PITT model is expected to be applicable to many

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systems, wherein diffusion and surface reaction resistance are both important phenomena.

2. THERMODYNAMICS AND ELECTROCHEMISTRY

We consider the electrochemical reaction at the electrolyte–electrode interface



representing the lithiation and delithiation of alloy-type LIB electrodes. Using the Butler–Volmer relation, we express the current density i at the electrode surface driven by the surface overpotential η_s ^{19,20}

$$i = i_0 \{ \exp[(1 - \beta)F\eta_s/(RT)] - \exp[-\beta F\eta_s/(RT)] \} \quad (2)$$

where i_0 is the exchange current density, β is the symmetry factor, F is Faraday's constant, R is the gas constant, and T is the temperature. The surface overpotential is given by $\eta_s = V - U$, where V is the applied surface potential of the electrode and U is the equilibrium potential. Our primary objective is to measure the Li diffusion coefficient and ensure accuracy by correcting for the intrusion of interfacial resistance on the measurement. Therefore, we consider a treatment wherein the potential is stepped from its initial equilibrium value to reach an effective steady state (to be denoted by subscript S) at the new potential value. Because the overpotential in a PITT experiment of the type we consider is small, eq 2 can be linearized about small η_s giving rise to what is commonly referred to as linear kinetics¹⁹

$$i = i_0 \frac{F}{RT} (V - U) \quad (3)$$

For sufficiently long times, the current and overpotential tend to zero and $U \rightarrow U_s = V$. For the PITT analysis, we consider small potential steps over which the lithium concentration within the host material does not deviate substantially from its initial value. Although i_0 and U are both concentration-dependent, they can be approximated using Taylor expansion about the final (equilibrated, steady-state) concentration C_s , as

$$i_0 = i_0|_s - \left. \frac{\partial i_0}{\partial C} \right|_s (C_s - C) + O(C - C_s)^2$$

$$U = U|_s - \left. \frac{\partial U}{\partial C} \right|_s (C_s - C) + O(C - C_s)^2$$

Discarding terms of order $(C - C_s)^2$ and higher, represented by $O(C - C_s)^2$, we obtain the following expression of the current–potential–concentration reaction

$$i = \left[i_0|_s - \left. \frac{\partial i_0}{\partial C} \right|_s (C_s - C) \right] \frac{F}{RT} \left[V - \left(U|_s - \left. \frac{\partial U}{\partial C} \right|_s (C_s - C) \right) \right] \quad (4a)$$

Again, discarding terms of $O(C - C_s)^2$ and higher and noting $U_s = V$ per the discussion above, we obtain

$$i = - \frac{F}{RT} (i_0|_s) \left. \frac{\partial U}{\partial C} \right|_s (C - C_s) \quad (4b)$$

A similar perturbation analysis can be employed to show that for small potential excitations Fick's law prevails for the Li

flux relation. The intercalate flux at the electrode surface is thus given by

$$N = \frac{i}{F} = -D \frac{\partial C}{\partial x}, \quad x = 0 \quad (5)$$

where D is the chemical diffusion coefficient associated with the concentration C_s . Using eqs 4a, 4b, and 5, we can write the interfacial boundary condition as

$$\frac{\partial C}{\partial x} + B \frac{(C - C_s)}{l} = 0, \quad x = 0 \quad (6)$$

where $B \equiv -l(i_0|_s)\partial U/\partial C|_s(DRT)$ is the electrochemical Biot number, a dimensionless parameter that is the ratio of diffusion resistance to that of the surface reaction,^{21,22} similar to the dimensionless parameters Λ ,^{15,16,23} α ,^{24,25} and j_0 ²⁶ from literature. For a PITT experiment such as what we investigate, B is a fixed value. A large B represents a fast surface reaction compared with diffusion and vice versa. Equation 6 is mathematically equivalent to the “radiation boundary condition” in heat transfer problems²⁷ and surface evaporation to a well-stirred environment.²⁸

3. ANALYTIC SOLUTIONS

To describe the diffusion of the guest within the host material consistent with the previous discussion, we recognize that for small overpotential excitations and deviations in C the diffusion equation can be linearized.²⁹ Therefore, we employ Fick's Second Law

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (7)$$

to describe the solid-state lithium diffusion through the thickness of a slab during the PITT analysis.

Initially, lithium is in equilibrium within the electrode

$$C = C_0, \quad 0 \leq x \leq l, \quad t = 0 \quad (8a)$$

The electrode is connected to the current collector at one end ($x = l$), and lithium cannot transport through the electrode and current collector interface. Therefore, we have a boundary condition

$$\frac{\partial C}{\partial x} = 0, \quad x = l, \quad t \geq 0 \quad (8b)$$

Using the analogy between heat conduction²⁷ and diffusion,²⁸ we can acquire the analytic solutions of concentration profile. The solution may comprise error functions or trigonometric series for short or long times, respectively.

The analytic solution of eq 7, with initial condition 8a and boundary condition 6 and 8b, is²⁷

$$\frac{C(x, t) - C_0}{C_s - C_0} = 1 - 2B \sum_{n=1}^{\infty} \frac{\cos \left[\lambda_n \left(1 - \frac{x}{l} \right) \right]}{(\lambda_n^2 + B^2 + B) \cos \lambda_n} \exp \left(-\lambda_n^2 \frac{Dt}{l^2} \right) \quad (9)$$

where λ_n ($n = 1, 2, 3, \dots$) are the positive roots of $\lambda \tan \lambda = B$. This solution converges quickly for long times ($Dt/l^2 \gg 1$). The solution can also be expressed in terms of error functions that

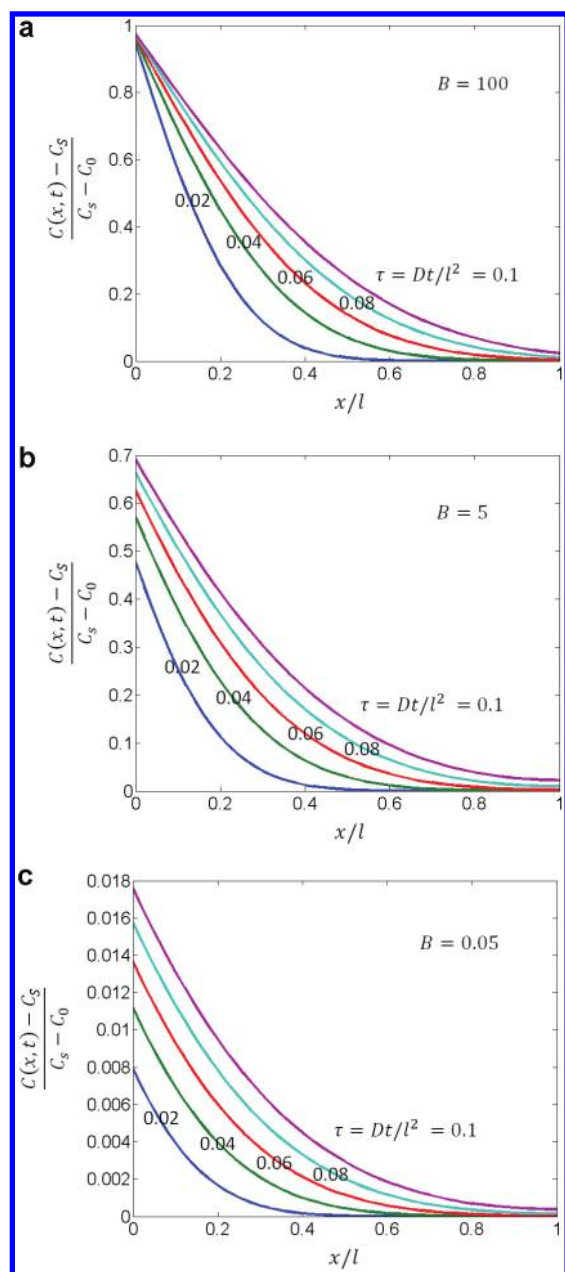


Figure 1. Concentration profiles under PITT operation at short times ($Dt/l^2 \ll 1$), for different electrochemical Biot numbers. (a) $B = 100$, (b) $B = 5$, and (c) $B = 0.05$.

converge rapidly for short times ($Dt/l^2 \ll 1$)²⁷

$$\begin{aligned} \frac{C(x,t) - C_0}{C_s - C_0} &= \operatorname{erfc} \frac{x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{2l-x}{2\sqrt{Dt}} \\ &- \exp\left(B\frac{x}{l} + B^2\frac{Dt}{l^2}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + B\sqrt{\frac{Dt}{l^2}}\right) \\ &- \exp\left(B\frac{2l-x}{l} + B^2\frac{Dt}{l^2}\right) \operatorname{erfc}\left(\frac{2l-x}{2\sqrt{Dt}} + B\sqrt{\frac{Dt}{l^2}}\right) \end{aligned} \quad (10)$$

Dimensionless concentration profiles in the electrode for various B values at short times ($Dt/l^2 \ll 1$) are plotted in

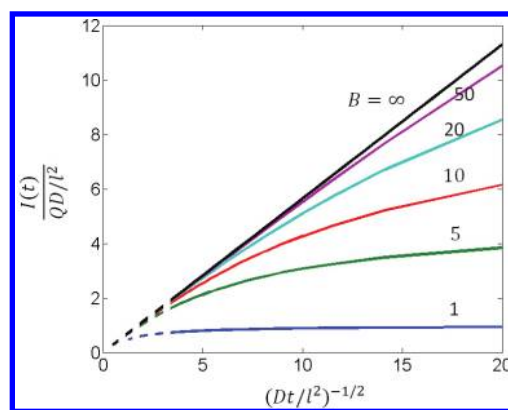


Figure 2. Dimensionless transient current versus time at short times with various electrochemical Biot numbers.

Figure 1. When the electrochemical Biot number is large, such as $B = 100$ in Figure 1a, the surface reaction is fast compared with the diffusion process. The concentration just inside the surface reaches C_s quickly. The concentration profile is similar to the case of infinitely fast surface reaction, as in the original PITT theory developed by Wen et al.^{1,2}

When the surface reaction rate is comparable to diffusion, such as $B = 5$ in Figure 1b, the concentration near the surface increases slowly to C_s . The characteristics of the concentration profile are between that which is obtained for constant concentration and constant flux boundary conditions. When the surface reaction is rate-limiting, such as $B = 0.05$ in Figure 1c, the concentration inside the electrode increases slowly. (Note the small range of concentration in Figure 1c.) In this case, the problem statement tends to that of constant flux diffusion.^{2,15,21,30} This can be further demonstrated by examining concentration profiles at longer time.

The electric current is related to the concentration gradient of solute at the electrode–electrolyte interface, as described by Fick's First Law. Neglecting higher-order terms, the short-time ($Dt/l^2 \ll 1$) transient current under potentiostatic operation corresponds to

$$I(t) = \frac{DQ}{l^2} B \exp\left(B^2 \frac{Dt}{l^2}\right) \operatorname{erfc}\left(B \sqrt{\frac{Dt}{l^2}}\right) \quad (11)$$

where we have employed the relation $C_s - C_0 = Q/(zFSl)$.² Here Q is the total charge transferred during the applied potential step $\int_0^\infty Idt$, S is the surface area of the electrode, and z is the charge number of the electroactive species ($z = 1$ for Li^+).

Comparing eq 11 with the traditional expression for the electric current under PITT operation (eq 15 in ref 2), we note that the electrochemical Biot number as well as the diffusion coefficient enters in the equation for the electric current. Furthermore, when the surface reaction is infinitely fast compared with diffusion or when B approaches infinity, we have

$$\begin{aligned} \lim_{B \rightarrow \infty} I(t) &= \lim_{B \rightarrow \infty} \frac{DQ}{l^2} B \exp\left(B^2 \frac{Dt}{l^2}\right) \operatorname{erfc}\left(B \sqrt{\frac{Dt}{l^2}}\right) \\ &= \frac{Q}{l} \sqrt{\frac{D}{\pi t}} \end{aligned} \quad (12)$$

This is the same as the current response to constant surface concentration condition (eq 15 in ref 2).

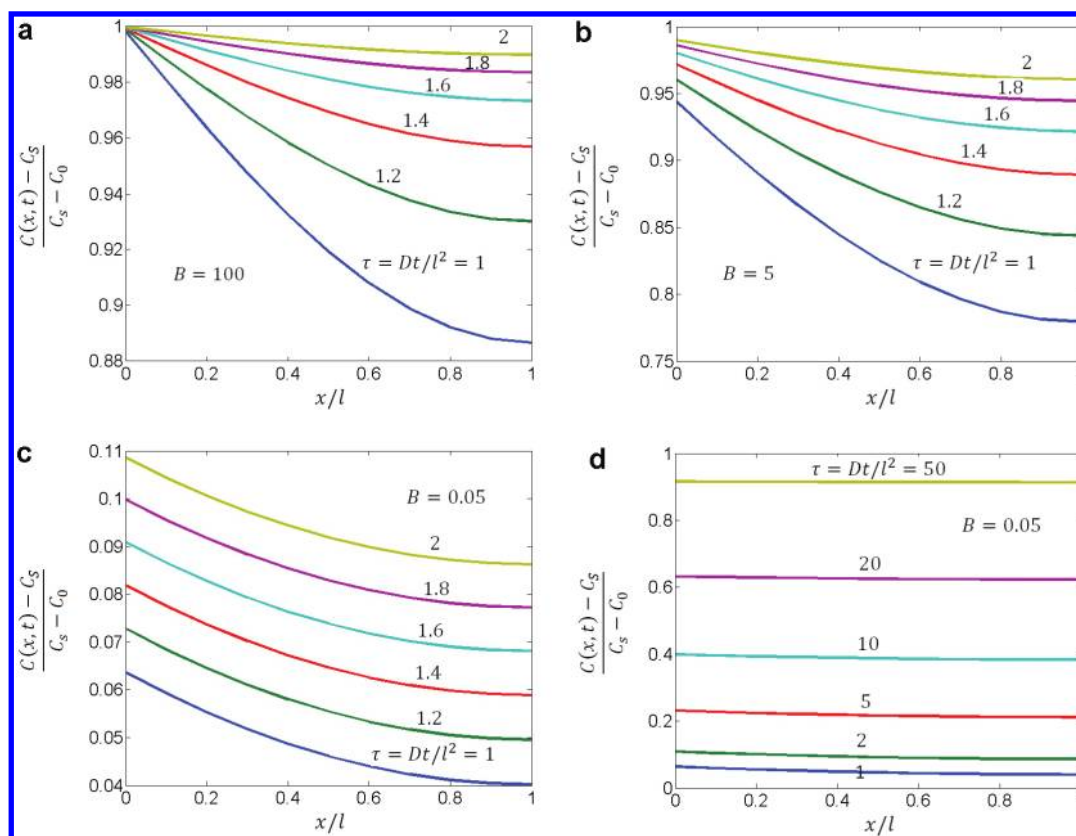


Figure 3. Concentration profiles under PITT operation at long times ($Dt/l^2 > 1$), for different electrochemical Biot numbers. (a) $B = 100$, (b) $B = 5$, and (c,d) $B = 0.05$.

Using eq 11, we plot the dimensionless transient current response versus $(Dt/l^2)^{-1/2}$ with various B in Figure 2. When B is infinitely large, the transient current for short times is a straight line with the slope equal to $(1/\pi)^{1/2}$, consistent with the constant surface concentration condition. As B decreases, the range of the linear region and the slope of the current versus $(Dt/l^2)^{-1/2}$ both decrease. Because the diffusion coefficient D is determined by the slope of the linear region in the original PITT theory, the diffusion coefficient D may be underestimated using the linear fitting method when B is finite or interfacial resistance is large, which is consistent with previous publications.^{15,31}

The concentration profile in the electrode with different B at long times ($Dt/l^2 \gg 1$) is plotted in Figure 3. When the surface reaction rate is facile relative to the diffusive process ($B = 100$ in Figure 3a), the concentration just inside the surface reaches the maximum concentration quickly, and the concentration profile is close to constant concentration condition. The concentration in the electrode quickly increases, and the dimensionless concentration reaches 0.9 when Dt/l^2 is greater than 1.1. Similar trends in concentration profiles can be found in figure 4 of ref 15, which illustrated the concentration evolution under diffusion-controlled processes.¹⁵ When surface reaction is comparable to the diffusion, such as $B = 5$ in Figure 3b, the concentration in the electrode increases slowly. The concentration just below the surface is smaller than unity at $Dt/l^2 = 2$, and the entire dimensionless concentration does not reach 0.9 until Dt/l^2 is greater than 1.4. When surface reaction is the rate-limiting process ($B = 0.05$ in Figure 3c,d), the concentration inside the electrode increases slowly. This is similar to the concentration profiles for galvanostatic (constant flux) operations.^{2,15,21,30}

Under this condition, concentration in the electrode increases quasi-uniformly to reach the maximum value (Figure 3d).

Substituting eq 9 into eq 5 and neglecting the higher-order terms, we find that the transient current at large times ($Dt/l^2 \gg 1$) can be expressed as

$$I(t) = \frac{2QD}{l^2} \frac{B^2}{(\lambda_1^2 + B^2 + B)} \exp\left(-\lambda_1^2 \frac{Dt}{l^2}\right) \quad (13)$$

Rearrangement of eq 13 yields

$$\ln[I(t)] - \ln\left(\frac{2QD}{l^2}\right) = \ln\left[\frac{B^2}{(\lambda_1^2 + B^2 + B)} \exp\left(-\lambda_1^2 \frac{Dt}{l^2}\right)\right] \quad (14)$$

Figure 4 shows the plot of $\ln[I(t)] - \ln(2QD/l^2)$ versus Dt/l^2 for various B values. The slope of the line is $-\pi^2/4$ when B is infinite. With decreasing B , the slope of the linear fit of the curve decreases. The intercept of the line is 0 only when B is infinity. With decreasing B , the intercept of the line is negative. Therefore, D can be underestimated by using the slope or intercept of $\ln[I(t)]$ versus t plot without considering the effect of surface reaction rate (cf. eq 16 in ref 2), in agreement with previous publications.^{15,31}

As $B \rightarrow \infty$, $\lambda_n \rightarrow ((2n-1)/2)\pi$, and we have

$$\begin{aligned} \lim_{B \rightarrow \infty} I(t) &= \lim_{B \rightarrow \infty} \frac{2QD}{l^2} \left[\frac{B}{B+1} \exp\left(-\lambda_1^2 \frac{Dt}{l^2}\right) \right] \\ &= \frac{2QD}{l^2} \exp\left(-\frac{\pi^2}{4} \frac{Dt}{l^2}\right) \end{aligned} \quad (15)$$

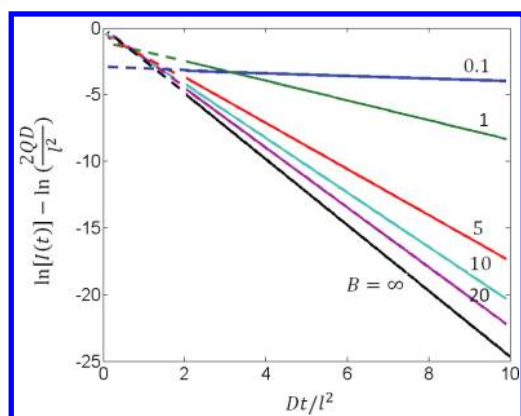


Figure 4. Dimensionless transient current versus time at long times with various electrochemical Biot numbers.

Equation 15 is the same as current response to constant concentration condition at long times (eq 16 in ref 2).

According to eq 14, D and B can be determined simultaneously from the linear plot of $\ln I$ versus t by solving three equations

$$\begin{aligned} -\lambda_1^2 \frac{D}{l^2} &= \text{slope} \\ \ln \left[\frac{2B^2 QD}{(\lambda_1^2 + B^2 + B)^2} \right] &= \text{Vertical Intercept (} \ln I \text{ axis)} \\ \lambda_1 \tan \lambda_1 &= B \end{aligned} \quad (16)$$

4. EXPERIMENTAL SECTION

Preparation. Amorphous Si thin films were deposited on Cu foil by means of E-beam evaporation. The Si working electrode (WE) was assembled into CR2032 coin cell with pure lithium metal (Alfa Aesar) as the counter electrode (CE). One piece of Celgard 3501 separator soaked with electrolyte (1 M LiPF₆ salt in 1:1 ratio of ethylene carbonate/dimethyl carbonate) was used in the coin cell.

Electrochemical Characterization. Electrochemical tests were conducted using a Bio-Logic potentiostat (VMP3) at room temperature. Before the PITT experiment, the coin cell was galvanostatically cycled four times between 1.0 and 0.3 V to form a substantially stable SEI layer and remove the influence of side reactions that are prevalent during the first couple cycles. The lower voltage limit of 0.3 V was chosen to ensure shallow cycling and prevent cracking in the Si thin films,³² which may affect diffusion behavior. Within each half cycle, the capacity was measured to be <20% of the theoretical capacity of Si (Figure 5). The PITT experiment was carried out during discharging from 0.395 to 0.390 V. Voltage was applied on the cell until the current fell below the equivalent of 1 mA g⁻¹ (about C/4200). The 1000 and 100 nm thick Si films were used for short-time and long-time evaluation of PITT, respectively.

5. RESULTS AND DISCUSSION

The diffusion coefficients D calculated by different methods are compared in Table 1. For testing the short-time nonlinear fitting method, PITT data were obtained during $t < 400$ s (Figure 6) using a 1000 nm thick Si film. For testing the long-time

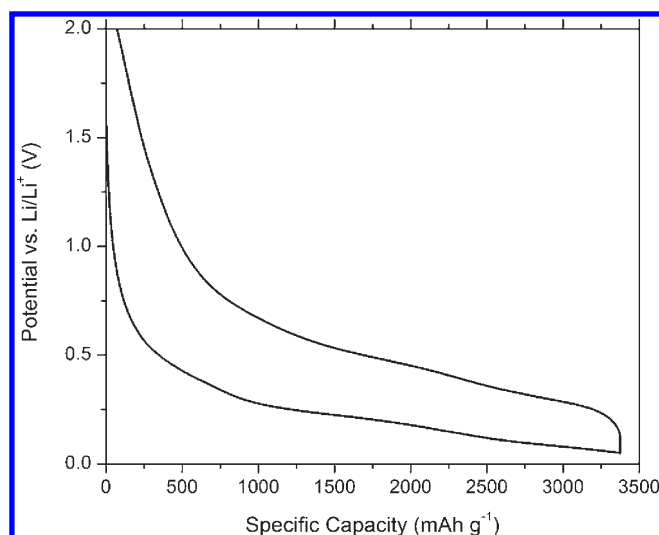


Figure 5. Potential–capacity profile of a 100 nm amorphous Si film under C/10 rate.

Table 1. Diffusion Coefficient of Li in Si Calculated by Different Methods

method	D (cm ² s ⁻¹)	B
short time (eq 11)	1.4×10^{-13}	49.4
short time linear fitting (eq 15 in ref 2)	1.1×10^{-13}	
long time (eq 16)	1.0×10^{-13}	45.7
long time (eq 16 in ref 2, slope)	7.7×10^{-14}	
long time (eq 16 in ref 2, intercept)	7.7×10^{-14}	

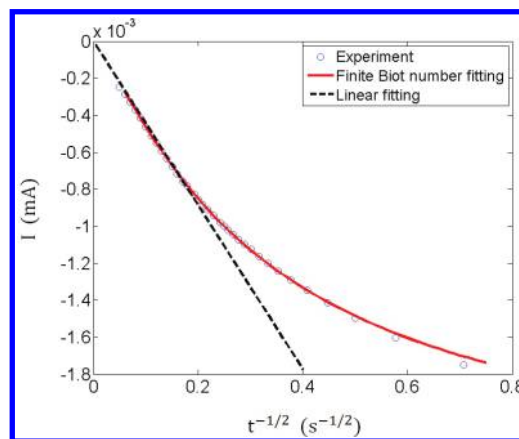


Figure 6. Plot of transient current versus $t^{-1/2}$ at short times for a 1000 nm thick Si film.

linear fitting method, PITT data were collected during $t > 600$ s (Figure 7) using a 100 nm thick Si film. The data points displayed are much fewer than the actual experimental data points so that the data and the fit can be discerned. For short times, D is calculated by a least-squares nonlinear fitting method (Curve Fitting Toolbox in Matlab) according to eq 11 and linear fitting according to eq 15 in ref 2. For long times, D is calculated by solving eq 16 with parameters obtained from Figure 7. As shown in Table 1, the diffusion coefficient of lithium in amorphous

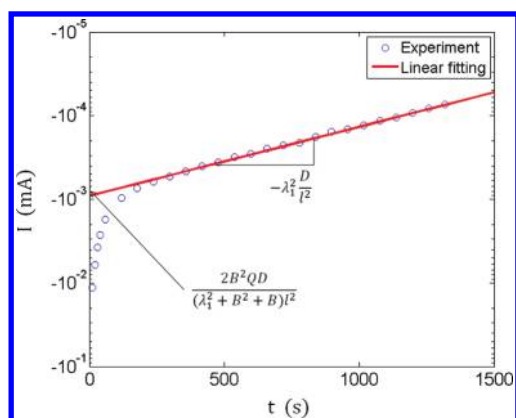


Figure 7. Exponential dependence of current on time at long times for a 100 nm thick Si film.

silicon at 0.390 V varies from 1.0×10^{-13} to $1.4 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. The electrochemical Biot number B is calculated to range from 45 to 50, which shows that both surface reaction and diffusion contribute to the system behavior. The lithium diffusion coefficient in amorphous Si using the traditional PITT theory are calculated to range from 0.7×10^{-13} to $1.1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, close to previously reported values.^{33–35} The lithium diffusion coefficient calculated by either eq 10 or eq 16 is larger than that calculated by the traditional short- and long-time linear fitting methods. The results suggest that the diffusion coefficient may be underestimated using the traditional methods when surface reaction rate is not infinitely fast or B is finite. Because the electrochemical Biot number is relatively large here, the system is biased to diffusion control, and the diffusion coefficients obtained considering the surface reaction rate are close to those using traditional methods. The diffusion coefficient calculated using traditional methods may be much smaller if the surface reaction is slow or if, more generally, B is smaller, such as can be the case for graphite electrodes.²¹

Furthermore, the exchange current density $i_0|_S$ can be calculated from the definition of the electrochemical Biot number in eq 6. Note that the dependence of equilibrium potential on concentration, $\partial U / \partial C|_S$, can be obtained separately by slow (quasi-equilibrium) cycling. In this work, we applied C/300 cycling of Si versus Li to obtain the equilibrium potential profile. The exchange current density of silicon electrodes during lithiation at 0.390 V is calculated to range from 0.07 to 0.13 mA cm^{-2} . It is interesting to note that this is nearly the same value as was obtained in the GITT experiment reported in figure 5 of ref 36 for a lithiated carbon electrode ($\sim 0.1 \text{ mA cm}^{-2}$ for fractional occupancies of lithium ranging from 0.3 to 0.75).³⁶

The surface reaction rate can be affected by the charge-transfer processes at the surface of the LIB electrodes. For negative electrodes of LIBs, it can also be affected by the presence of the solid electrolyte interphase (SEI). Properties of the SEI, including the chemical composition, thickness, stability, and mechanical properties, vary with electrode materials and the electrochemical environment. Surface modification, such as atomic layer deposition (ALD) coating and surface functionalization, may change the surface reaction rate. In general, we expect the surface reaction resistance to affect the electrochemical behavior of electrodes as well as the transient current response to potential steps.

6. CONCLUSIONS

We analyze the diffusion equation suitable for PITT when surface reaction resistance is important and derive analytic solutions for the concentration and transient current response. This treatment allows one to capture the additional influence of reaction resistance, relative to the conventional PITT analysis, in a single dimensionless group: the electrochemical Biot number B , which represents the ratio of diffusion resistance to that of the surface reaction. We show that the diffusion coefficient D can be underestimated using the traditional linear (I vs $t^{-1/2}$ for short times) and exponential fitting ($\ln I$ vs t for long times) methods without considering the influence of a finite surface reaction rate. Using this new method, we show that one can determine the diffusion coefficient and surface reaction rate simultaneously from a PITT measurement as well as the exchange current density. We implement the modified PITT to examine lithium diffusion in amorphous silicon thin-film electrodes. The modified PITT is applicable to LIB electrodes as well as other electrochemical systems wherein the measurement of diffusion and kinetic parameters characterizing surface reaction resistance (e.g., the exchange current density) is of interest.

■ ASSOCIATED CONTENT

S Supporting Information. Derivation of the electrochemical Biot number using equivalent circuit. This material is available free of charge via the Internet at <http://pubs.acs.org>

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■ LIST OF SYMBOLS

B	electrochemical Biot number
C	molar concentration
D	diffusion coefficient of the solute
e^-	electron
F	Faraday's constant
I	current
i	current density
i_0	exchange current density
Li^+	lithium ion
l	thickness of electrode
Q	total charge transferred during a potential step
S	surface area of electrodes
t	time
U	equilibrium potential
V	surface potential
x	thickness position
z	charge number of the electroactive species
β	symmetry factor

η_s surface overpotential
 λ_n n th positive roots of $\lambda \tan \lambda = B$
 τ dimensionless time

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