

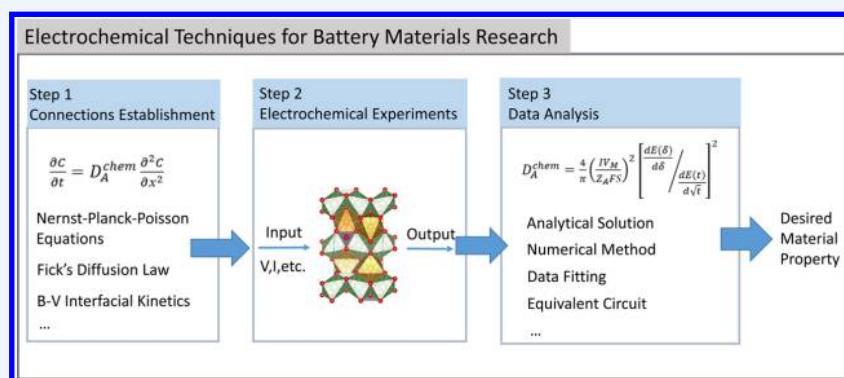
Electrochemical Techniques for Intercalation Electrode Materials in Rechargeable Batteries

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§ Supporting Information



CONSPECTUS: Understanding of the thermodynamic and kinetic properties of electrode materials is of great importance to develop new materials for high performance rechargeable batteries. Compared with computational understanding of physical and chemical properties of electrode materials, experimental methods provide direct and convenient evaluation of these properties. Often, the information gained from experimental work can not only offer feedback for the computational methods but also provide useful insights for improving the performance of materials. However, accurate experimental quantification of some properties can still be challenging. Among them, chemical diffusion coefficient is one representative example. It is one of the most crucial parameters determining the kinetics of intercalation compounds, which are by far the dominant electrode type used in rechargeable batteries. Therefore, it is of significance to quantitatively evaluate this parameter. For this purpose, various electrochemical techniques have been invented, for example, galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). One salient advantage of these electrochemical techniques over other characterization techniques is that some implicit thermodynamic and kinetic quantities can be linked with the readily measurable electrical signals, current, and voltage, with very high precision. Nevertheless, proper application of these techniques requires not just an understanding of the structure and chemistry of the studied materials but sufficient knowledge of the physical model for ion transport within solid host materials and the analysis method to solve for chemical diffusion coefficient.

Our group has been focusing on using various electrochemical techniques to investigate battery materials, as well as developing models for studying some emerging materials. In this Account, the principles of the aforementioned four electrochemical techniques and the corresponding analytical equations for calculating the chemical diffusion coefficients are first briefly summarized, followed by a discussion of the hidden assumptions for deriving these analytical equations and the resulting limitations in their implementation. To address these limitations, various corrections have been made in the literature. Nevertheless, the phase transition behavior, which is the typical feature for many intercalation materials, is barely considered. Here we retrospect our previous work on developing a two-phase model for describing the phase transition behavior of some intercalation compounds and discuss how to obtain the chemical diffusion coefficients based on the model, using LiFePO₄ as an example material. After that, we have a discussion on the methodology for using electrochemical techniques to investigate new material features. It is our hope that this Account can serve as a call for more endeavors into the development of novel electrochemical tools for battery research.

INTRODUCTION

It is crucial to develop high performance rechargeable batteries to meet the growing demand of energy storage. Currently, intercalation compounds are primary electrode choices for rechargeable batteries. In these materials, host atoms form a stationary framework in which guest ions occupy appropriate sites and

move between accessible sites. During charging or discharging, electroactive ions (H^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , etc.) are removed from or inserted into the host structure accompanied by the release or

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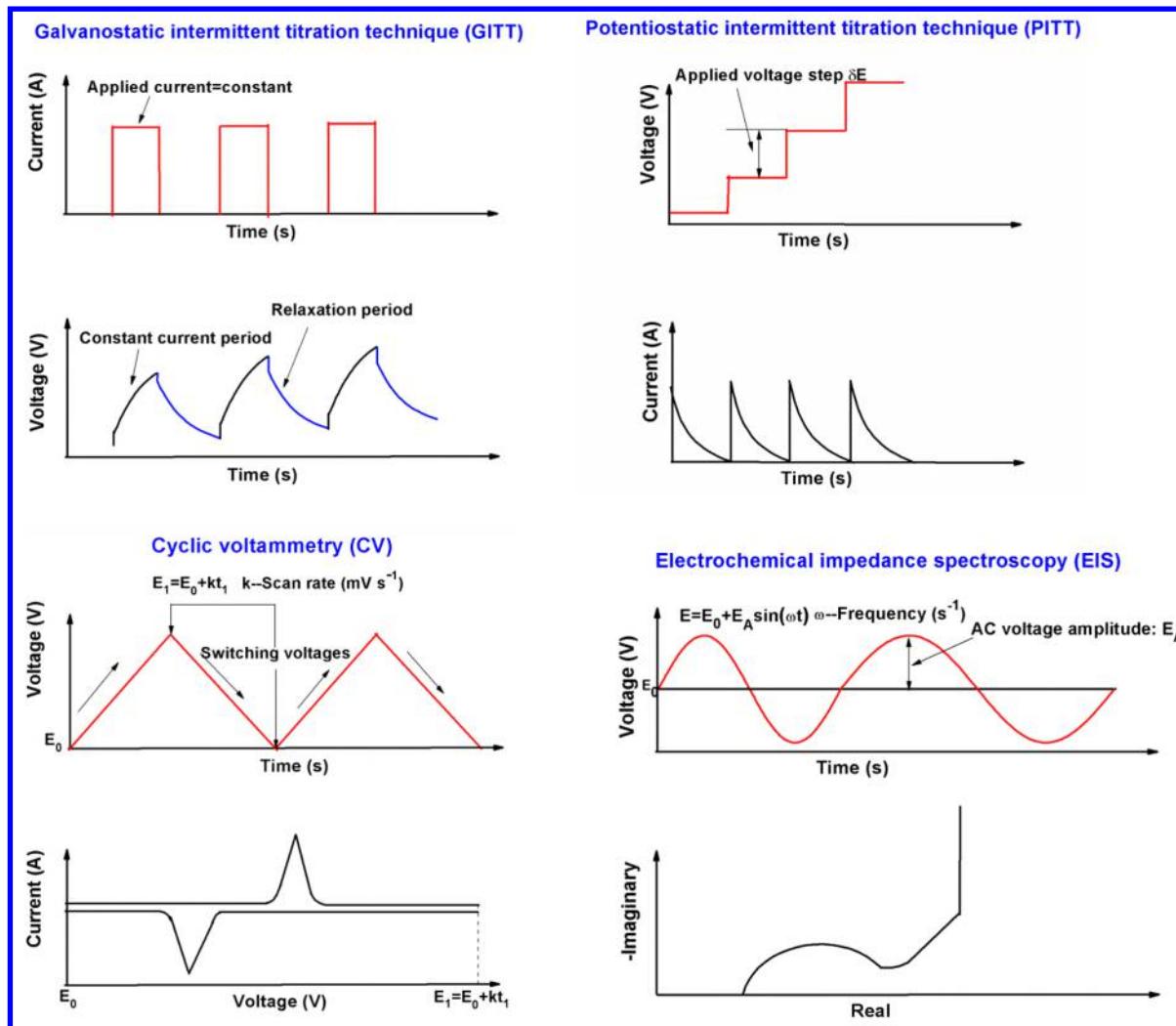


Figure 1. Schematic illustration of input signals and output results for GITT, PITT, CV, and EIS.

intake of electrons at the particular redox center (usually the d-orbital of the transition metals). The electrochemical performance of the intercalation compounds is highly dependent on their thermodynamic and kinetic properties. To develop new battery materials, it is of great importance to quantitatively evaluate these properties. Some of them, for example, open circuit voltage and ion storage capacity, are readily measurable. However, measurement of others can be nontrivial due to their implicit nature. One representative example is the chemical diffusion coefficient of the electroactive ion. It governs the transport of the electroactive ion inside the intercalation compounds and is one of the most critical kinetic parameters dictating the electrochemical performance of the intercalation compounds. Computationally, first-principles statistical mechanics have demonstrated great power toward understanding of Li transport in intercalation compounds.¹ Experimentally, several electrochemical techniques have been developed to measure this parameter in a variety of electrode materials, for example, the chemical diffusion coefficient of Li in alloy anodes,^{2,3} graphite,⁴ LiCoO₂,⁵ Li₃V₂(PO₄)₃,⁶ and Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂,⁷ and that of Na in olivine FePO₄.⁸ These experimental results have generated very valuable knowledge regarding understanding the electroactive ion diffusion in the host materials and provided useful insights for improving current materials. One attractive feature of electrochemical techniques is that the implicit chemical diffusion

coefficient can be connected with readily measurable electrical signals, voltage and current, with high precision. Nevertheless, appropriate physical models are essential to deciphering the collected data for quantifying chemical diffusion coefficient. A reliable quantification can only be achieved with a solid understanding of the ion transport process and the fundamental principles of the electrochemical techniques. Although these electrochemical techniques have found a great deal of applications in the field of battery research, the details, approximations, and limitations of these techniques are usually not transparent to those whose primary background is not electrochemistry. Inappropriate interpretation of data could give rise to spurious results, and large discrepancies were often reported from studies conducted by different authors.

Our group has been focusing on developing proper models for studying emerging materials, as well as adopting various electrochemical techniques to investigate the thermodynamic and kinetic properties of electrode materials.^{8–12} This Account mainly summarizes our contribution in developing models for studying phase transition intercalation materials, more specifically, measuring the chemical diffusion coefficient. We first briefly review major electrochemical techniques for quantifying the chemical diffusion coefficient with an emphasis on their conventional data analysis method. Then we discuss its limitations for phase transition intercalation compounds. After that, we

Table 1. Analytical Equations for Calculating the Chemical Diffusion Coefficient for GITT, PITT, EIS, and CV^a

	$t \ll L^2/D_A^{\text{chem}}$	$t \gg L^2/D_A^{\text{chem}}$
GITT ¹³	$D_A^{\text{chem}} = \frac{4}{\pi} \left(\frac{IV_M}{Z_A FS} \right)^2 \left[\frac{dE(\delta)}{d\delta} / \frac{dE(t)}{d\sqrt{t}} \right]^2$	$D_A^{\text{chem}} = \frac{ILV_M}{3Z_A FS} \frac{dE(\delta)}{d\delta} \frac{1}{E(t) _{t=0} - E(t=0)}$
PITT ¹³	$D_A^{\text{chem}} = L^2 \pi \left(\frac{I(t) \sqrt{t} dE(\delta)}{\Delta E} \right)^2$ $I(t)$ – transient current during the voltage step ΔE – magnitude of the voltage step	$D_A^{\text{chem}} = -\frac{d \ln I(t)}{dt} \frac{4L^2}{\pi^2}$ $\frac{d \ln I(t)}{dt}$ – slope of the plot of $\ln I(t)$ vs t
EIS ¹⁴	$D_A^{\text{chem}} = \frac{1}{2} \left[\frac{V_M}{\sigma Z_A FS} \frac{dE(\delta)}{d\delta} \right]^2$ σ – Warburg factor	$D_A^{\text{chem}} = \frac{V_M}{3FSRe(Z_d)} \frac{dE(\delta)}{d\delta} L$ $Re(Z_d)$ – the real part of the diffusion impedance
CV ¹⁵	$D_A^{\text{chem}} = \left(\frac{d_i_p}{d\sqrt{\nu}} / 0.446nFSC_A f^{0.5} \right)^2$ i_p – peak current during CV scan ν – scan rate $\frac{d_i_p}{d\sqrt{\nu}}$ – slope of the plot of i_p vs $\sqrt{\nu}$ n – number of electrons involved in the redox reaction C_A – initial concentration of A in B $f = \frac{nF}{RT}$	

^aNote: all undefined symbols have the same meanings as they do in eq 1.

introduce our two-phase model for phase transition intercalation materials and present the application of this model to interpret experimental results of LiFePO₄. Although we choose chemical diffusion coefficient as a representative example, it should be noted that the research methodology is generalizable toward other important thermodynamic and kinetic properties of electrode materials.

■ ELECTROCHEMICAL TECHNIQUES: THE CONVENTIONAL DATA ANALYSIS METHOD AND ITS LIMITATIONS

The underlying principle of most electrochemical techniques is that the system is driven away from equilibrium by manipulating current or voltage, and meanwhile the response of the other is recorded. The collected data is then analyzed with appropriate physical models for the desired parameters. Four electrochemical techniques are mostly used in battery research (Figure 1), namely, galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT),¹³ electrochemical impedance spectroscopy (EIS),¹⁴ and cyclic voltammetry (CV).¹⁵ When these techniques are applied to determine the chemical diffusion coefficient (D_A^{chem}) of electroactive ion A in the intercalation compound A_δB, the conventional data analysis method entirely relies on the analytical solutions of the one-dimensional diffusion equation with corresponding initial and boundary conditions. The resulting analytical equations for calculating the chemical diffusion coefficient are listed in Table 1. The physical model and governing equations adopted to derive these equations are quite similar. The major difference is the boundary condition at the interface between the electrode materials and electrolyte, which is dictated by the perturbing signals.²

Taking GITT as an example, during the electrochemical tests, a small constant current is imposed to the electrode for a short time interval to drive it off equilibrium, and then the current is removed to relax the system back to equilibrium. This process is repeated until the cutoff conditions are met. Meanwhile, voltage between the working electrode and reference electrode is

recorded during each constant current time interval and the following relaxation period.

With a one-dimensional diffusion model, it is shown that, at short time intervals, when the diffusion of electroactive species A inside host material B can be treated as semi-infinite, the chemical diffusion coefficient of A (D_A^{chem}) within host material B can be obtained as^{3,13}

$$D_A^{\text{chem}} = \frac{4}{\pi} \left(\frac{IV_M}{Z_A FS} \right)^2 \left[\frac{dE(\delta)}{d\delta} / \frac{dE(t)}{d\sqrt{t}} \right]^2 \quad t \ll L^2/D_A^{\text{chem}} \quad (1)$$

where I is the applied constant current, V_M is the molar volume of the electrode material, assumed to be constant during the electrochemical process, Z_A is the charge number of electroactive species A, F is the Faraday constant, S is the electrochemical active area between electrode material and electrolyte, $E(\delta)$ is the steady-state equilibrium voltage (i.e., open circuit voltage) of the working electrode (vs reference electrode) at the composition of A_δB, $E(t)$ is the transient voltage response of the working electrode during the constant current interval, and L is the characteristic length of the electrode material.

At longer time, that is, when $t \gg L^2/D_A^{\text{chem}}$, if $E(\delta)$ linearly changes with δ over the composition range involved in the current pulse, D_A^{chem} can be estimated from the extrapolated intercept at $t = 0$ ($E(t)|_{t=0}$) from the plot of $E(t)$ vs t as¹³

$$D_A^{\text{chem}} = \frac{ILV_M}{3Z_A FS} \frac{dE(\delta)}{d\delta} \frac{1}{E(t)|_{t=0} - E(t=0)} \quad t \gg L^2/D_A^{\text{chem}} \quad (2)$$

where $E(t=0)$ is the initial voltage of the working electrode after eliminating the ohmic drop when the current is turned on.²

Compared with eq 2, eq 1 is more regularly used for acquiring the chemical diffusion coefficient in the literature, because time for data acquisition is shorter for eq 1. Moreover, considering that the linear dependence of $E(\delta)$ on δ might not be fulfilled, especially for a long duration time of the current pulse, the validity of eq 2 is questionable in some cases. Since GITT

combines both transient and equilibrium measurements, besides the chemical diffusion coefficient, a series of kinetic and thermodynamic properties, including partial conductivity, thermodynamic enhancement factor, stoichiometry-dependent open circuit voltages, and free energy of formation, can be obtained.³ Compared with the potentiostatic method (PITT), one distinct advantage of GITT is that the interference of resistance polarizations (e.g., ohmic resistance and charge transfer resistance) is eliminated as long as these polarizations are fixed.

Generally, each electrochemical technique has its own advantages and pitfalls. Choice of electrochemical techniques is highly dependent on the actual requirements. In many cases, a combination of several techniques is required to give a comprehensive understanding of the processes.^{8,16} On the other hand, caution should be paid when applying the analytical equations to a new electrode material, because some assumptions made for deriving these equations may not comply with the physical reality. Some key assumptions are summarized as follows:

1. The electrochemical process is kinetically limited by the solid state diffusion of electroactive ions within the host material, and other kinetic processes (e.g., interfacial charge transfer and Ohmic resistance) are facile.
2. The electrode has dense and homogeneous thin film morphology or consists of particles with uniform and slab-like shape, and the current distribution in the electrode is uniform.
3. Transport of electroactive component into or within the host electrode material is one-dimensional and obeys Fick's second law of diffusion.
4. The chemical diffusion coefficient of the electroactive ion is concentration-independent during the period of each input signal.
5. There is no structure change, for example, phase transition, within the electrode material; that is, only one solid solution phase exists for the duration of each input signal.

When the analytical equations in Table 1 are employed for data analysis, care must be taken to ensure that these key assumptions are fulfilled. For electrode materials whose kinetics are not solely governed by the diffusion of the electroactive ion, appropriate modifications of the analytical equations have been made.^{17–19} Proper preparation of electrodes can ensure that the morphology and current distribution comply with assumption 2. Assumption 3 depends on the intrinsic nature of electrode materials. Meanwhile, the analytical solution for three-dimensional diffusion in spherical particles was also derived.²⁰ Assumption 4 can be satisfied by applying a small input signal for a short duration time provided the chemical diffusion coefficient is not strongly concentration-dependent.

Despite a large portion of intercalation compounds undergoing two-phase transition during charging and discharging,²¹ less attention has been paid regarding assumption 5 in practice. For these phase transition materials, assumption 5 cannot be met. In fact, the chemical diffusion coefficient in the two-phase domain is not defined in the physical model for deriving the analytical equations listed in Table 1. Thus, it is unreasonable to apply these equations to solve for the chemical diffusion coefficient at the two-phase region. However, in the literature this was happening and has generated much confusing or even misleading information. Indeed, when applying the analytical equations in Table 1 for phase transition materials, by default one

treats the two-phase domain similar to the solid solution phase and obtains an “apparent” chemical diffusion coefficient. According to the Gibbs phase rule, theoretical open circuit voltage should be constant, and the term $\frac{dE(\delta)}{d\delta}$ in the equations is zero at the two-phase domain. In practice, kinetic or thermodynamic effects cause small values of $\frac{dE(\delta)}{d\delta}$ at the two-phase region. As a result, the calculated “apparent” chemical diffusion coefficients often exhibit deep minima within the two-phase region,^{22–25} which are several orders of magnitude lower than those of the single phase region. Since the material is structurally composed of two phases, which usually do not show large variation of electroactive ion concentration and structure during the phase transition, it is highly doubtful to observe such a huge reduction in the chemical diffusion coefficient.

■ PHASE TRANSITION MATERIAL: A MIXED CONTROL TWO-PHASE MODEL

Since phase transition material is one important class of intercalation compounds,²¹ it is of great significance to develop a proper model to account for both ion transport and phase transition. In this regard, we have developed a one-dimensional mixed control model, which considers both ion diffusion and phase boundary movement in the presence of misfit strain between two coexisting phases. This mixed control model was applied to interpret GITT, PITT, and CV results for LiFePO₄^{26,27} a typical Li-intercalation phase transition cathode material.

Phase transition can take place by following different mechanisms. The mixed control model focuses on the transition process that occurs through nucleation and growth of a new phase within the parent phase (Figure 2). Electroactive

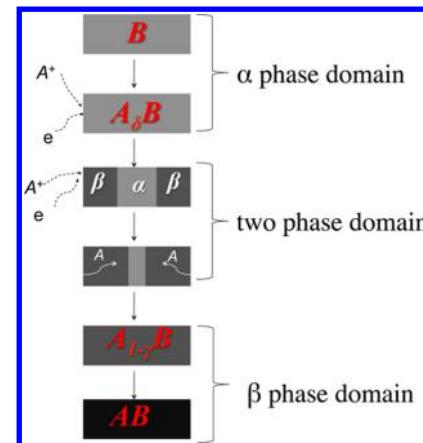


Figure 2. Evolution of phases during the electroactive component A insertion into the host material B.

component A initially inserts into host material B to form a solid solution phase α ($A_\delta B$, δ is the ion excess in the ion deficient phase, Figure 2). During ion insertion, stress and strain are usually generated in the α phase, which contribute to the chemical potential of the inserted components and hence affect the thermodynamics of the intercalation electrodes. It has been reported that stresses can alter both the open circuit voltage of Li–Sn and Li–Si battery systems and the solubility of Li in Si.^{28–31} The reported stress-potential coupling in lithiated Si can reach a magnitude of 100–120 mV/GPa.²⁹ When the ion insertion level reaches the solubility limit in the α phase, phase transition happens, and an ion rich β phase ($A_{1-\gamma}B$, γ is the ion

deficiency in the ion rich phase, Figure 2) is formed in the α phase matrix. Due to the lattice misfit between the α and β phases, the growth of the β phase inside the α phase results in the accumulation of strain/stress. Compared with theoretical system, which is infinitely large and stress-free, when the electrode particle size goes down, the energy penalties caused by the lattice misfit and the interface between the α and β phases increase the solubility of A in the α phase, causing the shrinking of the miscibility gap.^{32,33} Once the α phase completely transforms to the β phase, further inserted A will dissolve into the β phase and form a solid solution until it reaches its maximum solubility (assuming it corresponds to the formula of AB). Similarly, a reverse β phase to α phase transition will occur during ion extraction. If only elastic deformation occurs during the process, the measured open circuit potential would be the same between charging and discharging since insertion and extraction would follow the same stress path, analogous to loading and unloading. In practice, hysteresis, that is, the open circuit potential corresponding to ion extraction is higher than that of ion insertion, has been frequently observed in various materials, for example, LiFePO₄, Si, and some hydrogen storage materials.^{34–36} It is believed that such hysteresis loop is partially ascribed to the mechanical energy dissipation due to the plastic deformation.^{29,36}

If we only consider the growth of the β phase in consumption of the α phase, the α to β phase transition mainly involves two processes. First, electroactive components insert and diffuse from the particle surface to the phase boundary through the β phase. Second, the phase boundary migrates and the β phase layer grows simultaneously, which might result in a rearrangement of the lattice if the coexisting phases possess different structures. The free energy change, $\Delta G_{\alpha \rightarrow \beta}$, upon the α to β phase transition can be expressed as³⁷

$$\Delta G_{\alpha \rightarrow \beta} = \Delta G_{\alpha \rightarrow \beta}^{\text{chem}} + \Delta G_{\alpha \rightarrow \beta}^{\text{accom}} + \Delta G_{\alpha \rightarrow \beta}^{\text{surface}} \quad (3)$$

where $\Delta G_{\alpha \rightarrow \beta}^{\text{chem}}$ is the chemical free energy change on phase transition from unstrained α phase to unstrained β phase, $\Delta G_{\alpha \rightarrow \beta}^{\text{accom}}$ is the free energy change (called accommodation energy) caused by the volume difference between the coexisting two phases, which includes the contribution from elastic ($\Delta G_{\alpha \rightarrow \beta}^{\text{elastic}}$) and plastic ($\Delta G_{\alpha \rightarrow \beta}^{\text{plastic}}$) deformations ($\Delta G_{\alpha \rightarrow \beta}^{\text{accom}} = \Delta G_{\alpha \rightarrow \beta}^{\text{elastic}} + \Delta G_{\alpha \rightarrow \beta}^{\text{plastic}}$), and $\Delta G_{\alpha \rightarrow \beta}^{\text{surface}}$ is the surface and interface free energy changes associated with the phase transition.

The derivation of $\Delta G_{\alpha \rightarrow \beta}$ is presented in the Supporting Information. For the case that $\Delta G_{\alpha \rightarrow \beta}$ is sufficiently small, if the coupling between different coexisting processes can be neglected, irreversible thermodynamics indicate that the velocity (ν) of the interface during phase transition can be expressed as

$$\nu = M \times \Delta G_{\alpha \rightarrow \beta} \quad (4)$$

where M is the interface mobility. It is the velocity of the phase boundary under unit driving force and depends on interface coherence, strain/stress, and deformation of materials.³⁸

To construct the mixed control model, we assume that the motion of electroactive component A inside the coexisting phases is governed by Fick's second law of diffusion. The boundary condition at the interface between the electrode materials and electrolyte is determined by the perturbing signal. At the center of the electrode particle, the flux of the electroactive component is zero due to the symmetric condition. With one-dimensional diffusion along the x coordinate, at the interface separating the coexisting phases, besides eq 4, we also have

$$\nu = \frac{D_\alpha \frac{\partial C_\alpha}{\partial x} - D_\beta \frac{\partial C_\beta}{\partial x}}{C_\beta - C_\alpha} \quad (5)$$

where D_α/D_β and C_α/C_β are the chemical diffusion coefficient and concentration of the electroactive component in the α/β phase. Equations 4 and 5 indicate that the interface movement is jointly controlled by both ion diffusion and interface mobility. Under the local equilibrium assumption, $\Delta G_{\alpha \rightarrow \beta}$ becomes zero and thus the interface mobility M goes to infinity. Then, this mixed control model is reduced to classical diffusion-controlled moving boundary model.

■ INTERPRETATION OF GITT RESULTS OF LiFePO₄ BY THE MIXED CONTROL MODEL

We have characterized LiFePO₄ by using GITT (Figure 3), and applied the above mixed control model to interpret

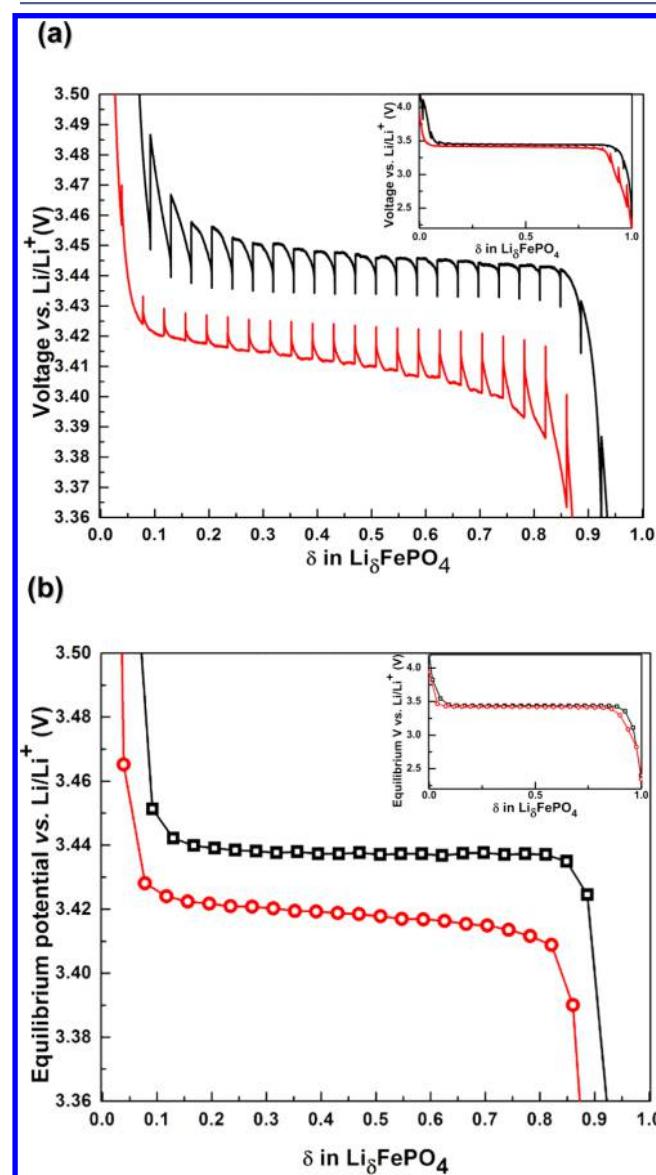


Figure 3. (a) Transient voltage response of LiFePO₄ during GITT. (b) Equilibrium potential of LiFePO₄ vs. Li/Li⁺ obtained from GITT.²⁶ Insets in panels a and b are the same plots in full scale. Reproduced with permission from ref 26. Copyright 2010 American Chemical Society.

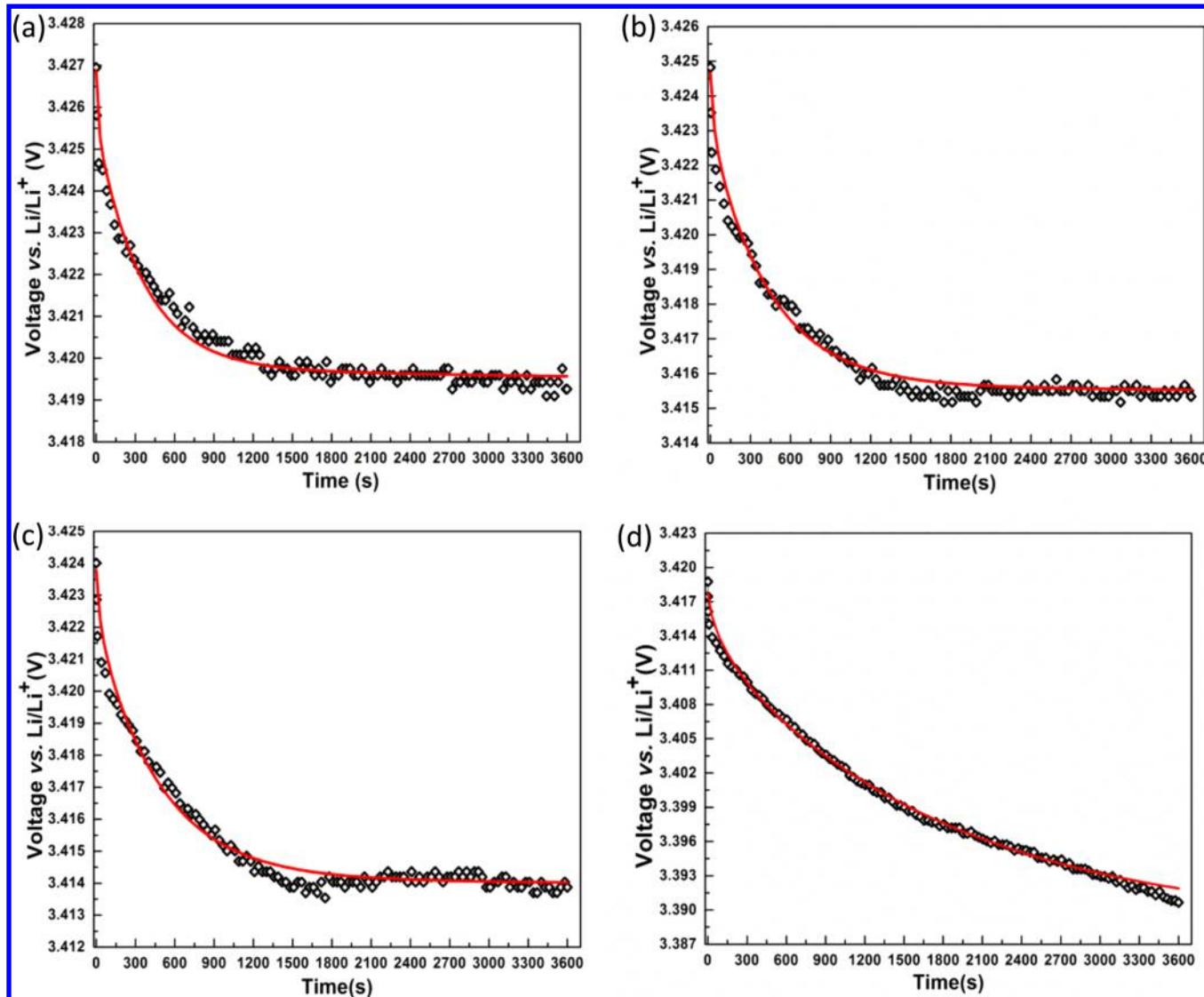


Figure 4. Transient voltage response of LiFePO_4 during GITT. Comparison of experimental data (black diamonds) and simulated results (red lines) by the mixed-control model at different state-of-discharge.²⁶ Reproduced with permission from ref 26. Copyright 2010 American Chemical Society.

the data. Regarding the charging–discharging mechanism of LiFePO_4 , several different models have been proposed.^{39,40} It is believed that phase separation is restricted under high charging–discharging rates, especially for nanosized LiFePO_4 .⁴¹ However, small currents are usually involved in GITT. Discussion of the exact phase transition mechanisms is beyond the scope of this Account. We believe that the physical picture involved in the mixed control model agrees with the phase transition process in LiFePO_4 to some extent, as demonstrated by our *in situ* TEM results of the electrochemical lithiation of microsized FePO_4 particles, which show that a sharp phase boundary between the coexisting phases migrates along the Li insertion direction.⁴²

Because it is difficult to obtain a closed form of analytical solution, the mixed control model is solved numerically. It is able to fit the transient voltage response of LiFePO_4 during the GITT test at various states-of-discharge (Figure 4). Through curve fitting, we have obtained the chemical diffusion coefficients of Li in the coexisting phases, which are plotted in Figure 5a. For comparison, we have also calculated the “apparent” chemical diffusion coefficients of Li by using eq 1. As shown in Figure 5a,

the “apparent” chemical diffusion coefficients in the two-phase domain are 4 orders of magnitude lower than those in the single-phase domains, consistent with discussion in the previous section and the results reported in the literature.⁴³ Such low values of “apparent” chemical diffusion coefficients in the two-phase domain cannot support the observed high rate performance of LiFePO_4 . By contrast, the chemical diffusion coefficients in the coexisting phases determined by the mixed control model are similar to the ones calculated from eq 1 in the single-phase regions. Since the chemical diffusion coefficients in the single-phase region obtained from eq 1 is considered to be reliable,^{4,44} this similarity validated the mixed control model.

As indicated in the mixed control model, besides the ion diffusion process, the migration of phase boundary is also dictated by the interface mobility. In addition to the chemical diffusion coefficient, the interface mobility of LiFePO_4 is also obtained by the mixed control model through curve fitting. The average value of the interface mobility is around $2.7 \times 10^{-15} \text{ m mol J}^{-1} \text{ s}^{-1}$ (Figure 5b), which is in the same order as the interface mobility of the martensite–austenite phase transition with a coherent interface at 350°C .⁴⁵

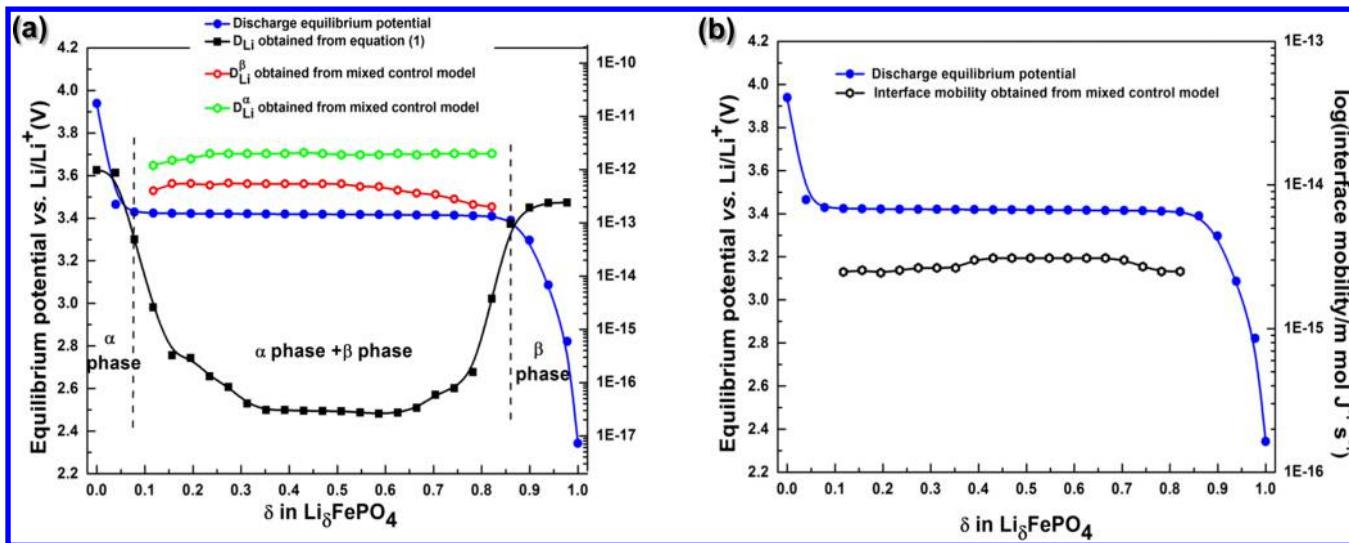


Figure 5. (a) Chemical diffusion coefficient of Li in LiFePO_4 determined from GITT results by eq 1 and the mixed control model. Note: the phase regions are arbitrarily marked. (b) Interface mobility of LiFePO_4 obtained from the mixed control model.²⁶ Reproduced with permission from ref 26. Copyright 2010 American Chemical Society.

Electrochemical Techniques for Battery Materials Research

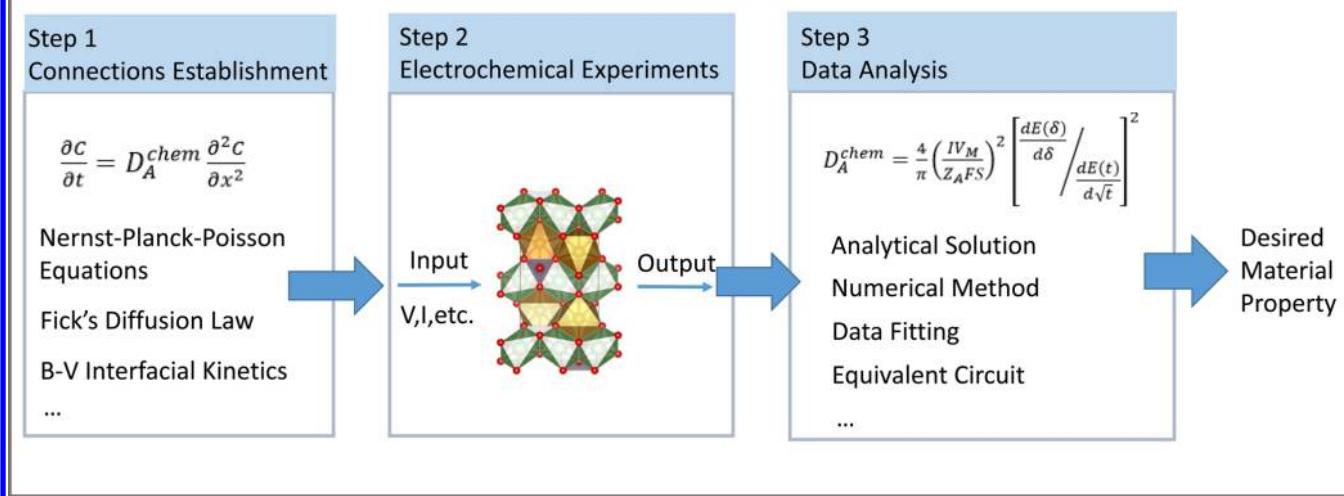


Figure 6. General methodology for using electrochemical techniques to quantify important properties of battery materials.

DISCUSSION

It is noteworthy that any physical model has assumptions and therefore limitations. For this reason, the mixed control model is limited to the intercalation materials whose phase transition processes satisfy the key assumptions adopted by the model, as presented in previous section and [Supporting Information](#). Our study serves as an example to demonstrate the procedure for developing model and method for electrochemical techniques in order to quantify important properties of emerging battery materials. Generally, the methodology of an electrochemical technique consists of three steps ([Figure 6](#)). First, Connections Establishment. One needs to build connections between the desired material properties and controllable variables in electrochemical tests (usually, current, voltage, time, and temperature). This requires a comprehensive understanding of the relevance between the electrochemical phenomena and the desired material properties. For some properties, for example, the

charge storage capacity and open circuit voltage, the connection is explicit. For implicit properties, for example, the chemical diffusion coefficient, it is necessary to model the electrochemical process in which the desired property is the core parameter. In some cases, time-domain modeling can be complicated, and frequency-domain description is favored. For example, analytical solution can be derived for measuring the ionic/electronic conductivity (resistance) of mixed conductive materials when the materials are excited by an AC input.^{46–48} Second, Electrochemical Experiments. One needs to design and conduct experiments to collect corresponding data. Special setup or sample preparation sometimes is necessary to perform the experiments. Third, Data Analysis. One needs to decipher the collected data to obtain the desired parameter. This can be done by substituting experimental data into suitable analytical solution of the physical model, if it can be derived. This approach is exemplified by the equations in [Table 1](#) and has been implemented extensively in the literature. If the analytical solution cannot be derived,

numerical methods are necessary as for the mixed control model we discussed above. Sometimes, this step can be realized by fitting the experimental data, if the desired parameter explicitly correlates with experimental results after model rearrangement. One example is the determination of the relative contribution of surface capacitive storage and bulk intercalation storage in cyclic voltammetry tests.⁴⁹ Another example is the calculation of conductivity and chemical diffusion coefficient in depolarization experiments.⁵⁰ For frequency-domain modeling, the analytical solutions are too complicated, and they are usually mapped onto the equivalent circuits for data interpretation.^{46,51,52}

To better utilize existing electrochemical techniques, it is suggested for researchers to read the original work and comprehend the physical models. It is necessary to understand any assumptions made in the model and try to comply with these assumptions by proper sample preparation or experimental conditions. However, if the studied material has an intrinsic feature that is not describable by the model, simply plugging in numbers into the analytical equations can generate unmeaningful results.

CONCLUSIONS

In this Account, we have reviewed major electrochemical techniques and the corresponding analytical equations for obtaining the chemical diffusion coefficient for intercalation compounds. These analytical equations were derived entirely based on the Fick's diffusion model, which only depicts the transport of electroactive ion but neglects the movement of phase boundary in phase transition materials. Therefore, they are unsuitable for studying phase transition materials. We developed a mixed control model to address this limitation and this model is applied to decipher the GITT results of LiFePO₄. Results have shown that the mixed control model is able to obtain more consistent chemical diffusion coefficient of Li in the two-phase domain of LiFePO₄. Notably, this model can also be applied to interpret the electrochemical data for other phase transition materials provided that their phase transition processes agree with the mixed control model. More importantly, the methodology discussed here is generalizable toward the further development of electrochemical techniques for other electrochemistry research.

Compared with the rapid advancement of computational methods toward understanding of ion transport in electrode materials, the progress of experimental techniques remains stagnant. Experimental evaluation of the chemical diffusion coefficient is challenging, because other parasitic kinetic processes, for example, interfacial charge transfer and phase transition, inevitably accompany the diffusion process and their influence can be enormous. Moreover, the solid-state ion diffusion process in intercalation compounds is strongly dependent on the crystal structure and chemistry. Therefore, it is impossible to develop a unified model for describing the ion transport in various intercalation materials. Specific models are usually necessary to account for particular occasions. Despite this, the importance of experimental techniques and the corresponding analysis method should never be overlooked for the reasons we discussed above. The community needs more advanced electrochemical tools for understanding the behaviors of new materials. As one old saying says “a workman must first sharpen his tools if he is to do his work well”. We hope this Account can serve as a call for more endeavors into the development of novel electrochemical tools for battery research.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.accounts.7b00031](https://doi.org/10.1021/acs.accounts.7b00031).

The derivation of the free energy change, $\Delta G_{\alpha \rightarrow \beta}$, upon the α to β phase transition ([PDF](#))

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