Theory of Electrochemical Kinetics based on Nonequilibrium Thermodynamics

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CONSPECTUS

Interest in electrochemistry is surging, driven by new applications in energy conversion, water treatment, materials processing, and biotechnology. As device dimensions shrink to the nanoscale, the rate-limiting step is often ion intercalation (i.e. reversible insertion) into a host solid for transport or storage. For example, oxygen intercalates into a ceramic electrolytes in solid oxide fuel

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cells, and lithium intercalates into carbon or metal oxide nanoparticles in Li-ion batteries. The standard phenomenological model for electrode kinetics is the Butler-Volmer equation, which fits the current-voltage relation in many situations and can be justified (in certain limits) by the Marcus theory of charge transfer. Existing theories, however, provide little guidance as to the form of the exchange-current prefactor to account for configurational entropy, elastic stress, phase transformations, and other non-idealities arising in ion intercalation.

These challenges are exemplified by the high-rate cathode material, $\text{Li}_x\text{FePO}_4$ (LFP), which has a strong tendency to phase separate into Li-rich and Li-poor phases believed to limit its performance. Phase separation was originally thought to occur as an isotropic “shrinking core” in each particle, but experiments later revealed striped phase boundaries along the active surface. Meanwhile, dramatic rate enhancement was attained with LFP nanoparticles, but no theory could predict the role of phase separation, far from equilibrium. In this Account, a general theory of charge transfer is described, which answers this question and provides a modeling framework for Faradaic reactions in ionic solids and concentrated solutions.

The theory is based on non-equilibrium thermodynamics. The Butler-Volmer and Marcus theories are reformulated in terms of activities and applied to lithium insertion in Li-ion batteries, electrocatalysis in solid oxide fuel cells, and charge transfer in ionic liquids. The Nernst potential and activation overpotential are defined variationally, consistent with Cahn-Hilliard (or Landau-Ginzburg) phase-field models. Unlike classical models, the reaction rate depends on concentration gradients, elastic strain, and surface tension, leading to many surprising conclusions for LFP nanoparticles. At low currents, “intercalation waves” travel across the active surface, but, above a critical current (close to the exchange current), phase separation is suppressed in favor of homogeneous intercalation. Similarly, in porous electrodes, stochastic phase-transformation fronts at low currents are broadened and stabilized at high currents. These complex phenomena can only be described by a unified theory of electrochemical kinetics, thermodynamics and transport.
Introduction

Motivation. Since the seminal work of J. A. V. Butler\textsuperscript{1} and M. Volmer,\textsuperscript{2} the equation that bears their names,

\[ I = I_0 \left( e^{-\alpha_c n e \eta / k_B T} - e^{-\alpha_a n e \eta / k_B T} \right) \]  \hspace{1cm} (1)

has become the standard phenomenological description of electrode kinetics.\textsuperscript{3–5} (Rather than using molar quantities, we define activities per particle and scale potentials to the thermal voltage, \( k_B T / e = RT / F \), where \( k_B \) = Boltzmann’s constant, \( e \) = elementary charge, \( T \) = temperature.) The Butler-Volmer (BV) equation relates the total current \( I \) due to the Faradaic reaction, \( O + n e^- \rightarrow R \), which converts the oxidized state \( O \) to the reduced state \( R \) and consumes \( n \) electrons, to the exchange current \( I_0 \) and overpotential \( \eta = \Delta \phi - \Delta \phi^{eq} \), where \( \Delta \phi \) is the interfacial voltage whose Nernst equilibrium value is \( \Delta \phi^{eq} \). For a simple single-step charge-transfer reaction, the anodic and cathodic charge-transfer coefficients \( \alpha_a \) and \( \alpha_c \) should satisfy \( \alpha_a = 1 - \alpha \) and \( \alpha_c = \alpha \) with a symmetry factor, \( 0 < \alpha < 1 \), although the same form is often fitted to more complicated experimental voltage dependence.

The microscopic theory of charge transfer,\textsuperscript{6} pioneered R. A. Marcus in 1956\textsuperscript{7,8} and honored by the Nobel Prize in Chemistry,\textsuperscript{9} provides partial justification for the BV equation and a means to estimate its parameters.\textsuperscript{3} The key quantity controlling \( I_0 \) and \( \alpha \) is the reorganization energy of the solvent upon charge transfer. The theory has been given a quantum mechanical basis by V. G. Levich, R. R. Dogonadze, A. M. Kuznetsov, J. Ulstrup and many others.\textsuperscript{6} Marcus theory has been widely applied to dilute solutions, where charge transfer occurs between isolated reactants, but provides little guidance on how to describe correlations in concentrated solutions.

In popular Li-ion battery models,\textsuperscript{5,10–13} excluded volume effects are described by an extra concentration factor,

\[ I_0(c) = k(c_{max} - c)^{\alpha_c} c^{\alpha_a} \]  \hspace{1cm} (2)

where \( c_{max} \) is the maximum concentration. The Nernst potential \( \Delta \phi^{eq}(c) \) is fitted to the battery open circuit voltage, and the chemical diffusivity \( D_{chem}(c) \) of Li in the solid is adjusted to fit
discharge data. In a thermodynamically consistent theory, however, these properties are not independent and should all derive from the lithium activity.

A more systematic approach could be based on non-equilibrium thermodynamics\textsuperscript{14,15} and phase-field models.\textsuperscript{16} A number of groups have recently made important progress in this direction for electrochemical systems\textsuperscript{17–25} and electrokinetic phenomena,\textsuperscript{26–34} but without consistently reformulating reaction kinetics. This Account summarizes my struggle to develop such a theory over the past five years,\textsuperscript{26,35–43} combining charge-transfer theory\textsuperscript{6} with concepts from statistical physics\textsuperscript{44,45} and non-equilibrium thermodynamics.\textsuperscript{14–16}

Advances in Li-ion batteries increasingly rely on controlling electrochemistry at the nanoscale.\textsuperscript{46–49} This trend is well illustrated by lithium iron phosphate, $\text{Li}_{x}\text{FePO}_4$ (LFP), which provided the motivation for my work. In the first LFP paper in 1997, Padhi et al.\textsuperscript{50} concluded that “the material is very good for \textit{low-power} applications” but “at higher current densities there is a reversible decrease in capacity that... is associated with the movement of a two-phase interface” (between Li-rich and Li-poor phases). Largely due to shrinking the particle size below 100nm, however, LFP has become the most popular \textit{high-power} cathode material,\textsuperscript{51,52} capable of 10 second discharge.\textsuperscript{53} Explaining this incredible reversal of fortune turned out to be a major scientific challenge.

We now understand that phase separation is strongly suppressed in LFP nanoparticles, to some extent in equilibrium,\textsuperscript{39,41,54} but especially under applied current,\textsuperscript{40,41,55,56} since reaction limitation,\textsuperscript{37} anisotropic lithium transport,\textsuperscript{57,58} elastic coherency strain,\textsuperscript{41,43,59,60} and surface energy\textsuperscript{40,61,62} are enhanced. At low currents, however, anisotropic nucleation and growth can also occur in nanoparticles,\textsuperscript{37,40,41,63} leading to stochastic multi-particle intercalation.\textsuperscript{42,64–66} These phenomena could not be described by traditional battery models,\textsuperscript{5,10} where the voltage plateau is fitted empirically and the phase boundary is artificially placed, as a spherical “shrinking core”.\textsuperscript{12,13} In order to develop a predictive model of intercalation in LFP nanoparticles,\textsuperscript{41} it was necessary to develop a phase-field theory of electrochemical kinetics,\textsuperscript{26,35,40} which is the focus of this Account.

**History of this Work.** I still remember the day in 2006 when my postdoc, Gogi Singh, brought me the paper of Chen et al.\textsuperscript{67} revealing striped phase boundaries in LFP, looking nothing
like a shrinking core. The images suggested phase boundary motion perpendicular to the lithium flux, which, I realized, could not be described by standard chemical kinetics, since the reaction rate would need to depend on concentration gradients. Our collaborator, G. Ceder, suggested adapting the CH model for bulk phase separation,\textsuperscript{20} but it took several years to achieve a consistent theory.

Our initial model predicted intercalation waves,\textsuperscript{36–38} but did not uphold the De Donder relation,\textsuperscript{44} as became clear from K. Sekimoto and D. Lacoste at ESPCI in Paris. It was there in 2007, while on sabbatical leave, that I first succeeded at generalizing BV kinetics to concentrated solutions. I spent the next year developing dynamical models of concentrated electrochemical systems,\textsuperscript{26} not only in batteries and fuel cells, but also induced-charge electrokinetics.\textsuperscript{68–70} In spring 2009, I synthesized the theory in lecture notes\textsuperscript{35,71} and published the generalized BV equation\textsuperscript{26} (Sec. 5.4.2).

The theory has enabled breakthroughs in modeling phase-separating battery electrodes. D. Burch used a thermodynamically consistent “Cahn-Hilliard-Reaction" model to study intercalation in nanoparticles\textsuperscript{39} (with $\alpha = 0$), without connections to the battery voltage. His Ph.D. thesis\textsuperscript{66} included early simulations of multi-particle phase separation and “mosaic instability".\textsuperscript{64,65} Simulations of galvanostatic discharge by P. Bai and D. A. Cogswell led to a theory of the suppression of phase separation in nanoparticles,\textsuperscript{40} first reported in 2010,\textsuperscript{72,73} which Cogswell extended for coherency strain.\textsuperscript{41} T. R. Ferguson did the first simulations of phase separation and voltage hysteresis in porous electrodes.\textsuperscript{42}

This Account provides an overview of the theory and its key predictions. A thermodynamic framework for reaction kinetics and diffusion is applied to Faradaic reactions, and the resulting BV model given microscopic justification via a reformulation of Marcus theory. The theory is then applied to Li-ion batteries, solid-oxide fuel cells, and ionic liquids. Finally, the theory is used to relate electrode kinetics to thermodynamic variational principles and applied to phase-separating battery materials.
Reaction Kinetics in Concentrated Solutions

**Nonequilibrium thermodynamics.** The theory begins with the diffusional chemical potential of species \( i \),

\[
\mu_i = k_B T \ln c_i + \mu_i^{\text{ex}} = k_B T \ln a_i
\]

where \( c_i \) is the concentration, \( a_i \) is the absolute chemical activity, \( \mu_i^{\text{ex}} = k_B T \ln \gamma_i \) is the excess chemical potential in a concentrated solution, and \( \gamma_i \) is the activity coefficient \( (a_i = \gamma_i c_i) \). In linear irreversible thermodynamics (LIT),\(^{14-16}\) the flux of species \( i \) is proportional to its chemical potential gradient,

\[
F_i = -M_i c_i \nabla \mu_i = -D_i \left( \nabla c_i + c_i \frac{\nabla \mu_i^{\text{ex}}}{k_B T} \right) = -D_i^{\text{chem}} \nabla c_i
\]

where \( D_i \) is the tracer diffusivity, \( M_i = D_i / k_B T \) is the mobility (using the Einstein relation), and \(-\nabla \mu_i^{\text{ex}}\) is the thermodynamic driving force beyond ideal diffusion (first term). The chemical diffusivity, \( D_i^{\text{chem}} \), differs from the tracer diffusivity by the thermodynamic factor,\(^5\)

\[
\frac{D_i^{\text{chem}}}{D_i} = 1 + \frac{c_i}{\gamma_i c_i} \frac{\partial \ln \gamma_i}{\partial \ln c_i} = 1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i}.
\]

By including the mean electrostatic energy \((z_i e \phi \text{ below})\) in the electro-chemical potential, this approach has been widely used to describe concentrated solutions in batteries\(^5,10,13,21-25\) and double-layer electrokinetic phenomena.\(^{26-34}\)

As shown in Eq. (4) and Eq. (5), the total flux has two contributions: (i) free diffusion driven by concentration gradients (Fick’s law), and (ii) migration induced by gradients in excess chemical potential. In probability theory, the former is the fundamental Wiener process, while the latter is a drift, described by Ito or Stratonovich differentials.\(^{45}\) In stochastic kinetics,\(^6,45,74\) the reaction complex makes random transitions between local minima in an energy landscape, \( U(x) \), which is independent of temperature and neglects many-body interactions. To account for thermal effects, transition state theory for solids\(^{75,76}\) introduces harmonic contributions to the many-body poten-
tial energy, analogous to “structural relaxation” in Marcus theory (discussed below). What is missing in this approach, however, is the effect of configurational entropy or other non-idealities contained in $\mu^{ex}(x)$, which may be obtained from finite-temperature molecular simulations.  

In a thermodynamically consistent formulation of reaction kinetics, therefore, the reaction complex explores a landscape of excess chemical potential $\mu^{ex}(x)$ between local minima $\mu_1^{ex}$ and $\mu_2^{ex}$ with transitions over an activation barrier $\mu^{\ddagger}$ (Figure 1(a)). Assuming long-lived states with rare transitions ($\mu^{\ddagger} - \mu_i^{ex} \gg k_B T$), the net reaction rate is given by

$$R = R_{1 \to 2} - R_{2 \to 1} = \nu \left[ e^{-(\mu^{\ddagger} - \mu_1)/k_B T} - e^{-(\mu^{\ddagger} - \mu_2)/k_B T} \right] = \frac{\nu (a_1 - a_2)}{\gamma^{\ddagger}}$$

(6)

which automatically satisfies the De Donder relation,  

$$\mu_1 - \mu_2 = k_B T \ln(R_{1 \to 2}/R_{2 \to 1}).$$

The frequency prefactor $\nu$ depends on generalized force constants, $k_i = \partial\mu^{ex}/\partial x_i$, or effective lengths $\ell_i = \sqrt{\frac{2\pi k_B T}{k_i}}$, at the saddle point and in one minimum (e.g. state 1, with a suitable shift of $\mu^{ex}_{\ddagger}$). Extending Kramers’ escape formula to $N$ reaction coordinates $x_1, \ldots, x_N$, we find

$$\nu = \frac{k^\parallel}{2\pi \zeta_f} \frac{\prod_{i=1}^N k_i^{min}}{\prod_{j=1}^{N-1} k_j^\perp} = \frac{D_f \prod_{i=1}^{N-1} L_i^\perp}{L^\parallel \prod_{i=1}^N L_i^{min}}$$

(7)

where $k_i^{min}$ are curvatures at the minimum (normal modes), $k_j^\perp$ are positive, transverse saddle curvatures, and $-k^\parallel$ is the negative saddle curvature parallel to the transition path. The rate increases with $k_i^{min}$ (due to faster vibrations and thus more frequent escape attempts) and $k_j^\perp$ (due to less time spent near the saddle), and decreases with $k_j^\perp$ (due to fewer trajectories captured with $k_B T$ of the saddle). The effect of $k_j^\perp$ from stochastic kinetics is missing in classical transition state theory, but it is often negligible in charge-transfer reactions, due to the Franck-Condon principle that electron transfer occurs suddenly when vibrational states overlap. In a liquid, the friction coefficient can be estimated by the Stokes-Einstein relation, $\zeta_f = \frac{k_B T}{D_f} \approx 6\pi \eta a$, where $\eta$ is the shear viscosity and $a$ is the molecular size.  

For the general reaction, $S_1 = \sum_i s_i M_i \to \sum_j s_j M_j = S_2$, the activities, $a_1 = \prod_i a_i^{s_i}$ and $a_2 = \prod_j a_j^{s_j}$, are equal in equilibrium, and the forward and backward reactions are in detailed balance.
Figure 1: Reaction kinetics in concentrated solutions. (a) The reaction complex moves in a landscape of *excess* chemical potential from state 1 to state 2 over a barrier (transition state). (b) Surface adsorption (or intercalation in a solid solution) from a liquid, where the transition state excludes $s > 1$ particle volumes as in Eq. (11), e.g. to accommodate the shedding of the solvation shell. (c) Activated diffusion on a surface (or in a solid solution), where the transition state excludes two particle sites and thus Eq. (13) reduces to Eq. (14).
(R = 0). The equilibrium constant is thus the ratio of the reactant to product activity coefficients:

\[
K = \frac{c_2}{c_1} = \frac{\prod_i c_i^{s_i}}{\prod_i c_i^{s_i}} = \frac{\prod_i \gamma_i^{s_i}}{\prod_j \gamma_j^{s_j}} = \frac{\gamma_1}{\gamma_2} = \frac{e^{(\mu_1^\text{ex} - \mu_2^\text{ex})/k_B T}}{e^{-\Delta G^\text{ex}/k_B T}}
\]

where \( \Delta G^\text{ex} \) is the excess free energy change per reaction. In order to describe reaction kinetics, however, we also need a model for the transition state activity coefficient \( \gamma_\text{\&} \), in Eq. (6)).

The subtle difference between total and excess chemical potential is often overlooked in chemical kinetics. Lai and Ciucci,\textsuperscript{23–25} who also recently applied non-equilibrium thermodynamics to batteries, start with the same flux relation, Eq. (4), but postulate a Faradaic reaction rate based on a barrier of total (not excess) chemical potential. The equilibrium condition (Nernst equation) is the same, but the rate (exchange current) is different and does not consistently treat the transition state. These concepts become more clear for adsorption phenomena without charge transfer, as we now illustrate.

**Surface or solid intercalation.** Consider surface adsorption from a liquid, or, equivalently, intercalation in the surface layer of a solid solution (Figure 1(b)). The standard approach in chemistry is to write the reaction as \( M + V_s \rightarrow M_s \), where \( V_s \) is a vacant surface site, and assume first-order kinetics,

\[
R = k[K c_M (1 - c) - c],
\]

where \( c \) is now the surface coverage (or solid filling fraction), \( K = e^{E_a/k_B T} \) is the equilibrium constant and \( E_a \) the adsorption energy. In detailed balance, \( R = 0 \), this implies a Langmuir isotherm, \( c^\text{eq} = K c_M/(1 + K c_M) \).

In our approach, rather than assigning a chemical identity to the vacancy, we consider the reaction \( M \rightarrow M_s \). In order to recover the Langmuir isotherm from the equilibrium condition, \( \mu_1 = \mu_2 \), we write diffusional chemical potentials for species \( M \) in the liquid, \( \mu_1 = k_B T \ln(K c_M) \) (as a dilute solution), and on the surface,

\[
\mu_2 = k_B T \ln \frac{c}{1 - c}, \quad \text{or} \quad \gamma = \frac{1}{1 - c}
\]
as a lattice gas, or ideal solid solution. We then consistently model $\mu^e$. For example, if the transition state has energy $E^\ddagger$ relative to the adsorbed state and excludes a volume $s \geq 1$ surface sites (not necessarily an integer), e.g. while shedding a solvation shell, then

$$\mu^e = E^\ddagger - sk_BT \ln(1 - c), \quad \text{or} \quad \gamma^\ddagger = \frac{e^{E^\ddagger/k_BT}}{(1 - c)^s}. \quad (11)$$

Plugging into Eq. (6), we obtain the reaction rate,

$$R = k \left[ KcM(1 - c)^s - c(1 - c)^s - 1 \right], \quad \text{where} \quad k = \nu e^{-E^\ddagger/k_BT}, \quad (12)$$

which differs from Eq. (9) if $s \neq 1$. In this simple case, for integer $s$, a similar form follows from Flory-Huggins kinetics with a higher-order vacancy reaction, $M + sV_s \rightarrow M_s + (s - 1)V_s$, but the general theory is needed for more complicated situations. For example, if adsorption occurs between disordered liquid and solid states, then the excluded volume cannot be treated as a distinct chemical species, but one could still use hard-sphere models for the excess chemical potentials in the present theory, as illustrated below.

**Surface or solid diffusion.** On a surface or in a solid solution, diffusion occurs by thermally activated hopping between adjacent sites (Figure 1(c)). The flux $F_i = -R/A_s$ through a cell area $A_s$ follows from Eq. (6) by linearizing $a_2 - a_1 \approx \Delta x \frac{\partial a}{\partial x}$. Comparing with Eq. (4), the tracer diffusivity is given by

$$D_i = \frac{\nu \Delta x^2 \gamma}{\gamma^\ddagger}, \quad (13)$$

In an ideal solid solution (Eq. (10)), the transition state excludes two sites ($s = 2$ in Eq. (11)) before and after the hop. The tracer diffusivity Eq. (13) then scales with the density of vacancies,

$$D_i = D_i^0 (1 - c), \quad \text{where} \quad D_i^0 = \nu \Delta x^2 e^{\Delta E^\ddagger/k_BT} \quad (14)$$

is the tracer diffusivity in a dilute solution. Due to a remarkable cancellation, the chemical diffu-
sivity (Eq. (5)) is constant,
\[ D_{i}^{\text{chem}} = \frac{D_i}{1 - c} = D_i^0 \] (15)
and equal to the dilute-limit tracer diffusivity of particles or vacancies. Nauman\textsuperscript{79} made thermo-
dynamic arguments to show that the \((1 - c)\) factor in Eq. (14) should appear in the Cahn-Hilliard
equation (discussed below), and here we see it follow from our reaction model Eq. (6). This factor
should also appear in the modified Poisson-Nernst-Planck equations for a solid solution.\textsuperscript{31}

**Butler-Volmer Kinetics in Concentrated Solutions**

For the general electrode reaction,
\[ S_1 = O^{z_O} + ne^- \rightarrow R^{z_R} = S_2 \] (16)
we write \(\mu_1 = \mu_O + n\mu_e\) and \(\mu_2 = \mu_R\), where charge conservation implies \(z_O - n = z_R\). We decom-
pose the electro-chemical potential into chemical and electrostatic contributions,
\[ \mu_i = k_B T \ln a_i + z_i e \phi_i = (k_B T \ln c_i + z_i e \phi_i) + \mu_i^{\text{ex}} \] (17)
where the term in parentheses describes an ion of charge \(z_i e\) in a mean potential \(\phi_i\) in a dilute
solution, and \(\mu_i^{\text{ex}} = k_B T \ln \gamma_i\) is the excess chemical potential. The electrostatic potential of the
electrode is \(\phi_e\), while that of the electrolytic solution is \(\phi\). The difference is the interfacial voltage,
\(\Delta \phi = \phi_e - \phi\).

The electric field \(E = -\nabla \phi\) at point is unique, so the potential \(\phi_i\) of species \(i\) depends its
position with respect to the interface. By definition, the electrons come from the electrode with
potential \(\phi_e\), but ions can exist in either position. In the most general Faradaic reaction (Figure 2(a)), the reduced and oxidized states can be split between the electrode and solution phases,
\(O^{z_O} = O^{z_O}_{(e)} + O^{z_O}_{(s)}\) and \(R^{z_R} = R^{z_R}_{(e)} + R^{z_R}_{(s)}\), if the electrode is a mixed ion-electron conductor. The
solution species, \(O^{z_O}_{(s)}\) and \(R^{z_R}_{(s)}\), are at potential \(\phi\) and electrode species, \(O^{z_O}_{(e)}\) and \(R^{z_R}_{(e)}\), are at poten-
Figure 2: Types of Faradaic reactions. (a) The most general reaction involving reduced and oxidized molecules, each split between the electrode and the electron-free electrolytic solution. (b) Redox reaction in solution. (c) Insertion or electrodeposition, where the reduced state lies inside or on the surface of the electrode, respectively.
tial $\phi_e$. Charge conservation implies $z_{Oe} + z_{Os} - n = z_{Re} + z_{Rs}$. The net charge $n_e e$ transferred from the solution to the electrode is given by

$$n_e = z_{Os} - z_{Rs} = z_{Re} - z_{Oe} + n.$$  \hspace{1cm} \text{(18)}$$

In this Account, we focus on situations where the oxidized state exists only in the solution ($z_{Oe} = 0$). In the simplest case of a redox reaction in solution (Figure 2(b)), there are no ions in the electrode and thus $n_e = n$. In electrodeposition, the reduced state is a neutral species on the surface ($z_R = 0$), so $n_e = n = z_O$. For cation insertion (Fig. Figure 2(c)), the reduced state is an intercalated ion, and the charge transferred across the interface is $n_e = z_O$.

In many cases, the interfacial charge transfer is equal to the number of electrons, $n_e = n$, and we can set $\phi_R = \phi_O = \phi$ without loss of generality, due to neutral reactants or products. Besides electrodeposition, we shall consider lithium ion insertion in a neutral crystal ($n_e = n = 1$, $z_R = 0$) and oxygen reduction in a solid electrolyte ($n_e = n = -z_R = 2$, $z_O = 0$). For this broad class of Faradaic reactions, the electrochemical potentials of the species in Eq. (16) are

\begin{align*}
\mu_O & = k_B T \ln a_O + z_{Oe} \phi \\
\mu_R & = k_B T \ln a_R + z_{Re} \phi \\
\mu_e & = k_B T \ln a_e - e \phi_e
\end{align*}

where $\mu_e$ is the chemical potential of electrons, or Fermi level. The electron activity $a_e = \gamma_e c_e$ accounts for the concentration of free electrons $c_e$ (density of states), as well as shifts in the Fermi level via $\gamma_e$, due to applied stress, phase transformations, donor or acceptor ions, etc. as illustrated below for semiconducting electrodes.

In equilibrium ($\mu_1 = \mu_2$), the interfacial voltage, $\Delta \phi = \phi_e - \phi$, satisfies the Nernst equation

$$\Delta \phi^{eq} = \frac{k_B T}{n_e e} \ln \frac{a_O a_R^n}{a_e}$$

\hspace{1cm} \text{(22)}$$
where $n_c = n$. Out of equilibrium, the current $I = neAR$ (where $A =$ electrode area) is related to the local (activation, or surface) over-potential,

$$\eta = \Delta \phi - \Delta \phi^{eq} \tag{23}$$

Specific models of charge transfer correspond to different choices of $\mu^e_x$.

In order to generalize Butler-Volmer kinetics, we approximate the mean electrostatic energy of the transition state as a linear combination of those of the initial and final states:

$$\mu^e_x = k_B T \ln \gamma^*_x + \alpha_a (z_O e \phi - n e \phi_e) + \alpha_c z_R e \phi \tag{24}$$

If, for consistency, the electric field is constant across the reaction coordinate $x$ from $x_R$ to $x_O$ past the transition state at $x_R < x^*_x < x_O$, then the transfer coefficients, $\alpha_a = 1 - \alpha$ and $\alpha_c = \alpha$, are related to the symmetry factor, $^4$

$$\alpha = \frac{x^*_x - x_R}{x_O - x_R} = \alpha_c = 1 - \alpha_a, \tag{25}$$

which acts as a Brønsted coefficient. $^6$

Substituting Eq. (22)-Eq. (25) into Eq. (6), we obtain the BV equation Eq. (1) with

$$I_0 = \frac{\nu neA (a_O e^a)^{1-\alpha} a_R^g}{\gamma^*_x} = \left[ \frac{\nu neA (c_O c_e^a)^{1-\alpha} c_R^g}{\gamma^*_x} \right] \left[ \frac{(\gamma_O \gamma_e^{\alpha})^{1-\alpha} \gamma_R^{\alpha} \gamma^*_x}{\gamma^*_x} \right] \tag{26}$$

The first factor is the classical formula,$^3-5$ but this is only valid for dilute solutions ($\gamma_O = \gamma_R = \gamma^*_x = \gamma_e = 1$). The second factor modifies the exchange current for concentrated solutions. In summary, the Faradaic current $I$ is related to the interfacial voltage $\Delta \phi$ and the various chemical activities $a_O$, $a_R$, $a_e$, and $\gamma^*_x$ by Eq. (1), Eq. (22), Eq. (23), and Eq. (26).
Marcus Theory for Concentrated Solutions

Just as we have reformulated the phenomenological Butler-Volmer model for concentrated solutions, so it is also possible to adapt the microscopic theory of charge transfer. The basic idea (Figure 3) is that the Faradaic reaction Eq. (16) occurs when the excess chemical potential of the reduced state, deformed along the reaction coordinate by statistical fluctuations, equals that of the oxidized state (plus \( n \) electrons in the electrode) at the same point. More precisely, charge transfer occurs randomly at somewhat lower energies due to quantum tunneling.\(^3,6\)

As a first approximation,\(^3,6\) we postulate harmonic restoring potentials for structural relaxation (e.g. shedding of the solvation shell from a liquid, or extraction from a solid) along the reaction coordinate \( x \) from the oxidized state at \( x_O \) to the reduced state at \( x_R \):

\[
\mu_1^{ex}(x) = k_B T \ln(\gamma_O \gamma^n_e) + z_O e \phi - ne \phi_e + \frac{k_O}{2} (x - x_O)^2 \quad (27)
\]

\[
\mu_2^{ex}(x) = k_B T \ln \gamma_R + z_R e \phi + \frac{k_R}{2} (x - x_R)^2 \quad (28)
\]

The Nernst equation Eq. (22) follows by equating the chemical potentials at the local minima, \( \mu_1(x_O) = k_B T \ln(c_O c_e^n) + \mu_1^{ex}(x_O) = k_B T \ln c_R + \mu_2^{ex}(x_R) = \mu_2(x_R) \) in equilibrium. The free energy barrier is set by the intersection of the excess chemical potential curves for the initial and final states,

\[
\mu^{ex}_{\pm} = \mu_1^{ex}(\bar{x}) = \mu_2^{ex}(\bar{x}), \quad (29)
\]

which is an implicit equation for the barrier position, \( x = \bar{x} \). Combining Eq. (23), Eq. (22), and Eq. (29) we obtain

\[
ne \eta - k_B T \ln \frac{c_R}{c_O c_e^n} = \frac{k_O}{2} (x_O - \bar{x})^2 - \frac{k_R}{2} (x_R - \bar{x})^2 = \mu_2^{ex}(x_R) - \mu_1^{ex}(x_O) = \Delta G^{ex} \quad (30)
\]

where \( \Delta G^{ex} \) is the excess free energy change per reaction. The overpotential is the total free energy
Figure 3: Above: The Faradaic reaction $O + ne^- \rightarrow R$ in concentrated electrolyte and/or electrode solutions. The reactants fluctuate in a landscape of excess chemical potential $\mu^{ex}$, shown along a favored reaction coordinate $x$. Charge transfer occurs whenever the oxidized state $O$ with $n$ free electrons or the reduced state $R$ reaches the transition state. Below: Illustration of these states for ion reduction by intercalation into a solid-solution electrode from a liquid electrolyte.
change per charge transferred,
\[ ne\eta = ne\Delta \phi - k_BT \ln \frac{a_Oa_R^2}{a_R} = \mu_2(x_O) - \mu_1(x_R) \equiv \Delta G \] (31)

where
\[ \Delta G = ne\eta = \Delta G^{ex} + k_BT \ln \frac{c_R}{c_Oc_e^n} \] (32)
is the thermodynamic driving force for the reaction. Note that in classical Marcus theory\(^3,9\) the overpotential is defined by \( ne\eta = \Delta G^{ex} \) without the concentration factors required by non-equilibrium thermodynamics. This is correct for charge-transfer reactions in bulk phases, e.g. \( A^- + B \rightarrow A + B^- \), because the initial and final concentrations are the same, and thus \( \Delta G = \Delta G^{ex} = \Delta G^0 \) (standard free energy of reaction). For Faradaic reactions at interfaces, however, the concentrations of reactions and products are different, and Eq. (32) must be used. The missing “Nernst concentration term” in Eq. (32) is also noted by Kuznetsov and Ulstrup (p. 219) in their quantum-mechanical theory of electrochemical kinetics.\(^6\)

Following Marcus, we solve Eq. (30) for \( x^\|_\tau \) and substitute into Eq. (29) in order to relate \( \mu^{ex}_\tau \) to \( \eta \). In the simplest case of symmetric relaxation, \( k_O = k_R = k \), we find,
\[ \mu^{ex}_\tau = k_BT \ln(\gamma_O\gamma_e^n) + z_Oe\phi - ne\phi_e + \frac{\lambda}{4} \left( 1 + \frac{\Delta G^{ex}}{\lambda} \right)^2 \] (33)
\[ = k_BT \ln \gamma_R + z_Re\phi + \frac{\lambda}{4} \left( 1 - \frac{\Delta G^{ex}}{\lambda} \right)^2 \] (34)

where
\[ \lambda = \frac{k}{2}(x_O - x_R)^2 \] (35)
is the “reorganization energy”. The barriers for the cathodic and anodic reactions are,
\[ \Delta G^{ex}_c = \frac{\lambda}{4} \left( 1 + \frac{\Delta G^{ex}}{\lambda} \right)^2 \] (36)
\[ \Delta G^{ex}_a = \frac{\lambda}{4} \left( 1 - \frac{\Delta G^{ex}}{\lambda} \right)^2 \] (37)
respectively. Substituting $\mu^{ex}_+$ into Eq. (6), the current $I = neAR$ is given by

$$I = I_0 e^{(ne\eta)^2/4k_BT\lambda} \left( e^{-\alpha ne\eta/k_BT} - e^{(1-\alpha)ne\eta/k_BT} \right)$$

(38)

which has a stronger nonlinear dependence on overpotential than in the Butler-Volmer equation. The exchange current,

$$I_0 = neAe^{-\lambda/4k_BT}(c_Oc^*_e)^{1-\alpha}c_R^\alpha$$

(39)

and symmetry factor,

$$\alpha = \frac{1}{2} \left( 1 - \frac{k_BT}{\lambda} \right)$$

(40)

are both related to the reorganization energy $\lambda$. In the typical case, $\lambda \gg k_BT$ (for thermally stable solvation), the symmetric factor is $\alpha \approx \frac{1}{2}$, and the current Eq. (38) is well approximated by the Butler-Volmer equation up to fairly large overpotentials, $|\eta| \ll k_BT ne \sqrt{\lambda/k_BT}$. Comparing Eq. (39) with Eq. (26), we can relate the reorganization energy to the activity coefficients defined above,

$$\frac{\lambda}{4} = k_BT \ln \frac{\gamma^*_O}{(\gamma_Oc^*_e)^{1-\alpha}c_R^\alpha} = (1 - \alpha)\Delta G^{ex}_c + \alpha\Delta G^{ex}_a$$

(41)

which is an average barrier for the cathodic and anodic reactions, weighted by the symmetry factor.

In a dilute solution, the reorganization energy $\lambda_0$ can be estimated by the classical Marcus approximation, $\lambda_0 = \lambda_i + \lambda_o$, where

$$\lambda_i = \sum_m \frac{k_m}{2}(q_{O,m} - q_{R,m})^2$$

(42)

is the “inner” or short-range contribution from structural relaxation (sum over normal modes) and $\lambda_o$ is the “outer”, long-range contribution from dielectric relaxation of the solvent. In the Born approximation, the latter is given by

$$\lambda_o = \frac{(ne)^2}{8\pi} \left( \frac{1}{a} - \frac{1}{R} \right) \left( \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$

(43)
for a Faradaic reaction at a flat metal electrode, where $\varepsilon$ is the (static) permittivity of the bulk solvent, $a$ is the radius of the solvation shell with (optical) permittivity $\varepsilon_{op}$, and $R$ is twice the separation of the ion from the electrode (charge-image distance). Since $\lambda_o = (0.5 - 1.0)n^2 \text{ eV} \gg k_BT$ for polar solvents at room temperature, the large barrier Eq. (32) implies that single-electron ($n = 1$), symmetric ($\alpha \approx \frac{1}{2}$) charge transfer is favored. Many quantum mechanical expressions for $\lambda_0$ are also available.\(^6\)

In a concentrated solution, we can use various models below to estimate the thermodynamic correction, $\gamma^c$, due to entropic and enthalpic effects in the transition state. The exchange current can then be modeled by Eq. (26) with

$$\gamma^e = \gamma^c e^{\lambda_0/4k_BT}.$$  \hspace{1cm} (44)

where $\alpha$ given by Eq. (40) with $\lambda = \lambda_0$. For example in surface adsorption, if the transition state excludes $s$ sites, $\gamma^c = (1 - c)^{-s}$, then Eq. (44) reduces to Eq. (11) with $E^c = \frac{\lambda_0}{4}$, consistent with Eq. (41). This approach provides a thermodynamically consistent way to model the combined effects of solvation, structural relaxation, enthalpy and entropy on charge transfer kinetics in a concentrated solution, ionic liquid or solid.

The compositional effects predicted by the general theory are crucial for deposition or intercalation reactions (Figure 4). Dilute solution approximations are widely used to model electrodeposition\(^80\) (Figure 4(a)), but our formulation of electrode kinetics enables the use of phase-field models (below), which are convenient for simulating electrodeposition\(^17,18,81–83\) with dendritic growth.\(^84–87\) With fixed interfaces, the general theory is also required for a thermodynamically consistent treatment of ion intercalation in solid solutions.\(^39–41\)

### Ion Intercalation in Solid Solutions

**Lithium insertion.** The canonical example is reversible lithium insertion, $\text{Li}^+ + e^- \rightarrow \text{Li}_x$, in a solid host\(^35,49\) (Figure 4(b)). Although lithium ions often remain charged after insertion, they
Figure 4: Examples of Faradaic reactions with non-ionic electrodes, $n_c = n$: (a) copper electrode-position, (b) lithium ion insertion in a transition metal oxide $M$ in a Li-ion battery, (c) oxygen reduction in a solid oxide fuel cell by gas adsorption on the electrode catalyst (LSM), followed by charge transfer and ion intercalation in the solid electrolyte (YSZ).

exist in neutral quasiparticle (polaron$^6$) states, $Li^+M^-$, coupled to reduced $M$ groups in the crystal. Lithium thus acts as a donor impurity, and in some cases, can cause metal-semiconductor transitions (see below). In transition metal oxides, the compensating electron usually resides on a metal ion, e.g. Fe$^{3+}$ $\rightarrow$ Fe$^{2+}$ in Li$_x$FePO$_4$, or on various dopants or surface coatings. In mixed ion-electron conductors, the separation of $Li^+$ and $M^-$ leads to diffuse charge near the interface and Frumkin corrections to the reaction rate, but we will focus on cases where local neutrality holds and thus $n_c = n$.

Motivated by LiFePO$_4$, consider a regular solution model$^{16,49,90}$ for the reduced state $R = \text{Li}$ with mole fraction $c$,

$$\mu_{Li} = k_B T \ln \frac{c}{1-c} + \Omega(1-2c) \quad (45)$$
where the first term is the configurational entropy and the second the enthalpy of mixing (setting \( \mu = 0 \) at half filling as a reference). The Nernst potential (Eq. (22)) is

\[
\Delta \phi(c) = \Delta \phi^0 - \frac{\mu_{Li}(c)}{e} + \frac{k_B T}{e} \ln a_e(c)
\]  

(46)

and, for insertion at the cathode, the open circuit voltage of the battery is \( V_O(c) = \Delta \phi(c) - \Delta \phi_{anode} \).

Suppose the transition state excludes \( s \) sites (where \( s > 1 \) accounts for the \( \text{Li}^+ \) solvation shell) and has reorganization energy \( \lambda_0 \), so that Eq. (44) implies \( E^{\mp} = \frac{\lambda_0}{4} \) in Eq. (11). The exchange current Eq. (26) then takes the form,

\[
I_0(c) = eA(a_+a_e(c))^{1-\alpha} c^\alpha (1-c)^{s-\alpha} \exp \left( \frac{4\alpha \Omega (1-2c) - \lambda_0}{4k_B T} \right)
\]  

(47)

where \( a_+ \) is the \( \text{Li}^+ \) activity in the electrolyte.

This example illustrates how our theory unifies charge-transfer reaction kinetics, equilibrium thermodynamics, and ion transport in a single thermodynamic framework. In contrast, existing porous electrode theories for Li-ion batteries \(^5,10,11,13\) contain thermodynamic inconsistencies. Doyle et al. \(^10\) assume the rate expression Eq. (2) for polymer insertion, \(^91\) which corresponds to Eq. (47) with \( a_+ = a_e = 1, \Omega = 0, \) and \( s = 1 \) (with \( \alpha_c = \alpha \) and \( \alpha_a = 1 - \alpha \) also reversed). The electrolyte activity a dilute solution, \( a_+ = c_+ \) has also been included, \(^13\) but all of these models are inconsistent with the use of concentrated solution models(\( a_+ \neq c_+ \)) to fit experimental data. Another common inconsistency is that the open circuit voltage, \( V_O(c) \), is fitted independently, when it should be related to the local activities of ions in solid solution Eq. (45) in both the Nernst equation, Eq. (46), and the exchange current density, Eq. (47). It is also inconsistent to model solid diffusion by Fick’s law with a fitted nonlinear diffusivity, rather than using ionic activity gradients in Eq. (4), consistent with \( V_O(c) \) and \( I_0(c) \).

**Semiconducting insertion electrodes.** The electron activity, \( a_e(c) \), generally depends on the local ion concentration. This effect is often negligible in mixed ion-electron conductors with \( a_e \approx 1 \), but it is important in semiconducting insertion electrodes with poor intrinsic electron
conductivity. Important examples include amorphous silicon (a-Si), a high-energy-density anode material,\textsuperscript{46,92,93} and tungsten bronze (Li\textsubscript{c}WO\textsubscript{3}), an electrochromic material.\textsuperscript{94–96} Since Li acts as an electron donor impurity, the density of free electrons increases with lithium filling as \( \rho_e = \rho_e^0 + c \rho_s p_d \), where \( \rho_s \) is the density of intercalation sites, and \( p_d \) is the probability that Li donates a delocalized electron to the conduction band. Assuming a simple free electron model in \( d \) dimensions, the electron activity is given by

\[
 a_e(c) \propto \exp \left( \frac{E_f(c)}{k_B T} \right), 
\]

in terms of the Fermi energy,

\[
 E_f(c) = \frac{\hbar^2 \alpha_d (\rho_e^0 + c \rho_s p_d)^{2/d}}{2m^*} 
\]

where \( m^* \) is the effective mass of electrons in the conduction band and \( \alpha_d \) is a constant (\( \alpha_1 = \pi^2 \), \( \alpha_2 = 2\pi \), and \( \alpha_3 = (3\pi^2)^{2/3} \)).

There are many interesting cases. For metals, we can set \( a_e \approx \) constant, due to the large density of intrinsic electron states, \( \rho_e^0 \gg \rho_s \). In the case of an ideal solid solution (Eq. (45) with \( \Omega = 0 \)) in a three-dimensional semiconductor (\( \rho_e^0 = 0, d = 3 \)), we recover the model of Raistrick and Huggins\textsuperscript{49,96} for the open circuit voltage of Li\textsubscript{c}WO\textsubscript{3} using Eq. (48) and Eq. (49) in the Nernst equation Eq. (46). In contrast to prior Butler-Volmer models of coloration dynamics in tungsten bronze,\textsuperscript{94,95} however, our theory shows how to consistently formulate insertion kinetics (Eq. (47)) and transport (Eq. (4)). The theory also predicts different lithium concentration dependence for electrode kinetics in anisotropic low-dimensional electron conductors, such as graphene flakes (\( d = 2 \)) and silicon or carbon nanotubes (\( d = 1 \)), which are increasingly used in battery electrodes.\textsuperscript{46,93}

In the preceding analysis, we have neglected diffuse charge (or space charge) in the solid, which is valid only once the doping by ion insertion has moved the Fermi level well into the conduction band (\( \Delta E \gg k_B T \)). In a more general treatment of the depleted/insulator state, intercalated ions and/or electron holes at potential \( \phi_e \) also participate in the reaction (Figure 2(a)). However, this
requires also describing electrostatics and transport (via Poisson-Nernst-Planck equations) in the electrode and electrolyte phases, as outlined below, and results in Frumkin corrections to Butler-Volmer kinetics.\textsuperscript{88,89}

**Solid oxide electrocatalysis.** To illustrate the theory for a multistep reaction, consider the oxygen reduction reaction, \( O_{2(g)} \rightarrow 2O_{(s)}^{2-} \), at the cathode of a solid oxide fuel cell (SOFC) (Figure 4(c)). Oxygen gas adsorption on the electrode catalyst, e.g. lanthanum strontium manganite (LSM) is followed by two charge transfer steps and ion intercalation in the solid oxide electrolyte, e.g. yttrium stabilized zirconia (YSZ).\textsuperscript{22,97–100} Similar concepts could be applied to multi-step hydrogen oxidation at the anode.\textsuperscript{101}

Assuming a Langmuir isotherm for surface adsorption and Nernst equations for charge transfer, equilibrium conditions for the three steps are:

\begin{eqnarray}
\text{Step 1:} & O_{2(g)} \rightarrow 2O_{ads}, & a_{O_2} = Kp_{O_2} = a_O^2 = \left( \frac{\Theta_O}{1 - \Theta_O} \right)^2 \quad (50) \\
\text{Step 2:} & O_{ads} + e^- \rightarrow O^{-}_{(s)}, & \Delta \phi_2^{eq} = \Delta \phi_2^0 + \frac{k_BT}{e} \ln \frac{a_{O_2} a_e}{a_{O^-}} \quad (51) \\
\text{Step 3:} & O^{-}_{(s)} + e^- \rightarrow O_{(s)}^{2-}, & \Delta \phi_3^{eq} = \Delta \phi_3^0 + \frac{k_BT}{e} \ln \frac{a_{O^-} a_e}{a_{O_{2}^-}} \quad (52)
\end{eqnarray}

where \( p_{O_2} \) is the partial pressure of oxygen. The theory can be applied to each step, but let us assume that step 2 is rate limiting. In that case, the first charge transfer sustains the over potential, \( \eta = \Delta \phi - \Delta \phi_2^{eq} \), while the second is in equilibrium, \( \Delta \phi = \Delta \phi_3^{eq} \).

Assuming \( s \) excluded sites in the transition state and plugging \( \Theta_O \) into Eq. (11), we obtain a Butler-Volmer equation for step 2,

\[ I = \left[ \nu eAe^{-E_i/k_BT} \left( a_e \sqrt{Kp_{O_2}} \right)^{1-\alpha} a_{O_2}^{\alpha} \right] \left( e^{-\alpha \eta / k_BT} - e^{(1-\alpha) \eta / k_BT} \right) \quad (53) \]

The equilibrium conditions for steps 1 and 3 determine the intermediate activity \( a_{O^-} \), which can be be eliminated in Eq. (53) to obtain a Butler-Volmer equation for the net reaction,

\[ I = \left[ \nu eAe^{-E_i/k_BT} (KP_{O_2})^{(2-\alpha)/4} a_{O_2}^{\alpha} a_{O_{2}^-}^{\alpha/2} \right] \left( e^{-\alpha \eta / 2k_BT} - e^{(2-\alpha) \eta / 2k_BT} \right) \quad (54) \]
where $E'_\pm = E_\pm + \frac{q}{2}(\Delta \phi^0_3 - \Delta \phi^0_2)$. The exchange current has the typical “volcano” dependence of electrocatalysis: The rate increases with $K_{PO_2}$ at low pressure and small adsorption energy, $E_a = k_B T \ln K$, as $(K_{PO_2})^{(2-\alpha)/4}$, but then decreases at high pressure or high adsorption energy due to surface saturation, as $(K_{PO_2})^{-s/2}$. For $\alpha = \frac{1}{2}$ and $s = 1$, the scaling exponents are $\frac{3}{8}$ and $-\frac{1}{2}$, respectively. The cathodic transfer coefficient is $\alpha_c = \alpha/2$, so, even if the rate limiting step is symmetric ($\alpha = \frac{1}{2}$), the net reaction appears to be asymmetric ($\alpha_c = \frac{1}{4}$).

**Ionic liquids.** As in ionic crystals, crowding effects are also important in solvent-free ionic liquids. Important examples include molten salts in liquid metal batteries\textsuperscript{102} and aluminum smelting\textsuperscript{103} and room-temperature ionic liquids (RTIL) in chemical synthesis\textsuperscript{104} and capacitive energy storage.\textsuperscript{105,106} In spite of liquid disorder, solid-solution models for the configurational entropy have been applied to RTIL,\textsuperscript{30,34,107} in which case Faradaic reactions could be described by the models above for ion intercalation in crystals. It is more natural to consider hard-sphere liquid models,\textsuperscript{26,28,29,108,109} although such models lose accuracy in highly charged double layers.\textsuperscript{26,110}

For identical hard spheres, the Carnahan-Starling equation of state\textsuperscript{111} (valid up to \( \approx 55\% \) volume fraction) corresponds to the excess chemical potential,

$$\frac{\mu_i^{ex}}{k_B T} = \ln \gamma_i = \frac{\Phi(8 - 9\Phi + 3\Phi^2)}{(1 - \Phi)^3}$$

which may be suitable for entropic effects in simple, high-temperature molten salts, such as NaCl.

For RTILs, which often have very different ion sizes, the extension for non-identical hard-sphere mixtures\textsuperscript{112,113} yields the following chemical potential of species $i$ in a mixture of $N$ species with diameters \( \{a_i\} \):

$$\ln \gamma_i = -\left(1 + \frac{2\xi_2 a_i^3}{\Phi^3} - \frac{3\xi_2^2 a_i^2}{\Phi^2} \right) \ln(1 - \Phi) + \frac{3\xi_2 a_i + 3\xi_1 a_i^2 \xi_0 + a_i^3}{1 - \Phi}$$

$$+ \frac{3\xi_2 a_i^2}{(1 - \Phi)^2} \left( \frac{\xi_2}{\Phi} + \xi_1 a_i \right) - \frac{3\xi_2^3 a_i^3}{\Phi^2} \frac{\Phi^2 - 5\Phi + 2}{(1 - \Phi)^3}$$

where $\xi_n = \sum_{j=1}^N \Phi_j a_j^{n-3}$, $\Phi_j$ is the volume fraction of species $j$, and $\Phi = \sum_{j=1}^N \Phi_j$ is the total
volume fraction of ions. If we assume that $s$ times the volume of the active ion of species $i$ is excluded in the transition state,

$$\gamma_i = \gamma_i^s e^{4\lambda_0/k_B T},$$

(57)

then the exchange current for the Faradaic reaction, $O_i + e^- \rightarrow R_j$ (converting species $i$ to $j$) is given by Eq. (26) with $\gamma_i$ and $\gamma_j$ from Eq. (55). This approach may give insights into the relative reactivity of ions of different sizes. Without a polar solvent, the reorganization energy $\lambda_0$ is smaller and can be comparable to $k_B T$, so asymmetric ($\alpha \neq \frac{1}{2}$) and multiple electron transfer ($n > 1$) may be possible, especially in molten salts at high temperature.

**Phase-Field Theory of Electrode Kinetics**

**Bulk phase-field models.** In a continuous, homogeneous, open system at constant pressure and temperature, the diffusional chemical potential is the derivative of the free energy with respect to composition. More generally, the it is the variational derivative of the free energy functional $F[c]$, which is the continuum analog of adding a particle and allowing the system to relax, e.g. by removing a vacancy in a crystal. To describe the free energy of an inhomogeneous system, Van der Waals added the “gradient energy” to the bulk integral over the volume $V$,

$$F[c] = \int_V \left[ \rho_s \bar{f}(c) + \frac{1}{2} \nabla c \cdot \kappa \nabla c \right] dV$$

(58)

where $\kappa$ is the symmetric, positive definite, “gradient penalty tensor”. For intercalation phenomena, we define the (Helmholtz) free energy $\bar{f}$ and filling fraction $c$ per crystal site, so we multiply by the site density $\rho_s$ to obtain the free energy per volume. The second integral is over the surface $S$ with surface tension $\gamma_s$ depending on the normal orientation $\hat{n}$. The chemical potential is given by

$$\mu = \frac{1}{\rho_s} \frac{\delta F}{\delta c} = \bar{g}'(c) - \frac{\nabla \cdot \kappa \nabla c}{\rho_s}$$

(59)

which depends on the curvature of the concentration profile.
This formulation of non-equilibrium thermodynamics was introduced in materials science by Cahn and Hilliard (CH) in 1958\textsuperscript{90,115–117} and forms the basis for modern phase field models.\textsuperscript{16} (In physics, similar models were introduced by Landau for second-order phase transitions\textsuperscript{118} and Ginzburg and Landau for superconductivity.)\textsuperscript{119} The gradient energy can be justified as the first term in the Taylor expansion of a nonlocal inhomogeneous free energy around the homogeneous state. If $\bar{f}(c)$ has multiple minima representing distinct stable phases, then the gradient term counteracts the tendency to phase separate and leads to a diffuse interface of width $\lambda$, whose concentration profile solves the Beltrami equation, $\mu =$ constant. In that case, we can also relate $\kappa$ to the inter-phasial tension, $\gamma$.

**Toward an electrochemical phase-field theory.** Building on earlier models of phase separation in ionic systems,\textsuperscript{120–122} there were several breakthroughs in 2004 that set the stage for my theory of electrochemical kinetics. Garcia, Bishop and Carter\textsuperscript{19} formulated variational principles for electromagnetically active systems, which unify the CH equation with Maxwell’s equations. In the same year, Guyer, Boettinger, Warren and McFadden\textsuperscript{17,18} introduced phase-field models to electrochemistry by representing a diffuse electrode/electrolyte interface with a continuous phase field, $\xi(x)$, varying between stable values 0 and 1. As in phase-field models of dendritic solidification,\textsuperscript{84–87} they used Landau’s quartic model, $\tilde{f}(\xi) \propto \xi^2(1 - \xi)^2$, to provide a double-welled homogeneous free energy ($c = \xi$ in Eq. (58)) to separate the electrolyte and electrode phases. They described the kinetics of electrodeposition\textsuperscript{18} (converting ions in the electrolyte to solid metal) by Allen-Cahn kinetics,\textsuperscript{123} linear in the thermodynamic driving force, $I \propto \Delta \mu$, but did not make connections with the Butler-Volmer equation or charge-transfer theory. Several groups have used this approach to model dendritic growth.\textsuperscript{81–83}

Also in 2004, Han, Van der Ven and Ceder\textsuperscript{20} first applied the CH equation to the diffusion of intercalated lithium ions in LFP, albeit without modeling reaction kinetics. Following Cahn and Hilliard\textsuperscript{90}, they used the regular solution model (Eq. (45)) with homogeneous free energy,

$$\tilde{f}(c) = k_B T \left[ c \ln c + (1 - c) \ln(1-c) \right] + \Omega c(1-c)$$ \hspace{1cm} (60)
where the terms (from left to right) represent the entropy of particles, the entropy of holes, and the enthalpy of particle-hole interactions. At high temperature, entropy dominates, and there is only one minimum at $c = \frac{1}{2}$ with maximal mixing. If $\Omega > 0$, then particles attract each other (and repel holes), and, below a critical temperature, $T < T_c = \frac{\Omega}{2k_B}$, there are two minima representing stable high-density and low-density phases, separated by a miscibility gap, or voltage plateau.\textsuperscript{25,40} Balancing terms in Eq. (58), the phase boundary width scales as $\lambda_i \approx \sqrt{\kappa/\Omega}$, and the inter-phasial tension as $\gamma_i \approx \sqrt{\kappa \Omega \rho_s}$.\textsuperscript{16,39,90}

These developments, followed by the observation of phase boundaries at LFP surfaces,\textsuperscript{67,124} led to the first phase-field theory of Faradaic reactions. The exponential (Tafel) dependence of the current on the overpotential, defined in terms of $\Delta \mu$ in Eq. (59), was first reported in 2007,\textsuperscript{36,37,125} but with a spurious pre-factor, noted by Burch.\textsuperscript{39,66} The complete theory, connecting the CH model to the BV equation and the battery voltage, appeared in 2009\textsuperscript{35,71} and later applied to LFP nanoparticles.\textsuperscript{40,41} For lithium intercalation, the reduced state has zero charge ($z_R = 0$), so the original CH functional Eq. (58) with $\tilde{f}(c)$ given by Eq. (45) was used to construct the electrochemical potential Eq. (59) in the Butler-Volmer and Nernst equations.

**Variational formulation of electrode kinetics.** For electrochemical kinetics, we consider the total Gibbs free energy $G$ of an open system, where the electrochemical potential is related to the cell voltage. For the general Faradaic reaction (Figure 2),

$$O + ne^- = \sum_i s_i O^{i^i} + ne^- \rightarrow \sum_j s_j R^{j^j} = R, \quad (61)$$

we define all the chemical activities $a_k$ and diffusional electrochemical potentials $\mu_k$ variationally:

$$\mu_O = k_B T \ln a_O + z_O e \phi_O = \sum_i \frac{s_i}{\rho_s} \frac{\delta G}{\delta c_i} \quad (62)$$

$$\mu_R = k_B T \ln a_R + z_R e \phi_R = \sum_j \frac{s_j}{\rho_s} \frac{\delta G}{\delta c_j} \quad (63)$$

$$\mu_e = k_B T \ln a_e - e \phi_e = \frac{1}{\rho_s} \frac{\delta G}{\delta c_e} \quad (64)$$
The Nernst voltage $\Delta \phi^{eq}$ is defined variationally by setting $\mu_R = \mu_O + n\mu_e$. According to Eq. (22), Eq. (23) and Eq. (32), the activation overpotential

$$\eta = \Delta \phi - \Delta \phi^{eq} = \phi_e - \phi - \frac{k_B T}{n_e} \ln \frac{a^0_{\text{R}}}{a_R} = \frac{\mu_R - (\mu_O + n\mu_e)}{n_e} = \frac{\mu_2 - \mu_1}{n_e} \quad (65)$$

is the change in total chemical potential of the Faradaic reaction per charge transferred ($n_c = n$). In this way, the diffusional electrochemical potentials $\mu_i = \frac{\delta G}{\rho_i \delta c_i}$ enter the Butler-Volmer (Eq. (1)) and Marcus (Eq. (38)) equations, as well as the exchange current Eq. (26).

The following free energy captures the essential physics of ionic materials: \cite{17,19,34,37,39–41,43}

$$G = \int_V \left[ \rho_s \left( f(\vec{c}) + \rho_e \phi \right) + \frac{1}{2} (\nabla \vec{c} \cdot \kappa \nabla \vec{c} - \nabla \phi \cdot \epsilon_p \nabla \phi + \sigma : \epsilon) \right] dV + \oint_S \gamma_s (\hat{n}, \vec{c}, \phi) dS \quad (66)$$

where $\vec{c}$ is the set of concentrations, $\epsilon_p$ the permittivity tensor, $\kappa$ the gradient penalty tensor, $\sigma$ the stress tensor, $\epsilon$ the strain tensor, $q_s$ the surface charge density, and $\rho_e = \sum_i z_i e c_i$ the bulk charge density (for ions and electrons, in the case of mixed conductors). The electrostatic potential acts as a Lagrange multiplier controlling the total ion densities\cite{19,41} while enforcing Maxwell’s equations. (See also the supporting material of Bazant et al.\cite{34}).

Mechanical deformation due to inserted ions can significantly affect charge-transfer kinetics.\cite{41} Assuming linear elasticity, the stress is given by Hooke’s law, $\sigma_{ij} = C_{ijkl} \epsilon_{kl}$, where $C$ is the elastic constant tensor. The lattice-preserving “coherency strain”:

$$\epsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \sum_m \epsilon_{ijm}^0 c_m \quad (67)$$

is the total strain due to compositional inhomogeneity (first term) relative to the stress-free inelastic strain (second term). In a mean-field approximation (Vegard’s law), each molecule of species $m$ exerts an independent strain $\epsilon_{jm}^0$ (lattice misfit between $c_m = 0, 1$).

In our theory, the Nernst voltage Eq. (22) and exchange current Eq. (26) depend on concentra-
Figure 5: Insertion kinetics in LFP nanoparticles. The low-energy phase boundary between FePO$_4$ and LiFePO$_4$ propagates as an “intercalation wave”$^{37,40,41,52,125}$ across the {010} facet, filling the crystal layer by layer, where the reaction rate (Eq. (70)) is enhanced by concentration gradients and elastic stress. [Reproduced from Bai, Cogswell, Bazant.$^{40}$]

...tion gradients and elastic stress via,

$$
\mu_i = \frac{\delta G}{\rho_s \delta c_i} = \left( \frac{\partial \tilde{f}}{\partial c_i} + \frac{\nabla \cdot \kappa \nabla c_i - \sigma : \varepsilon_i^0}{\rho_s} \right) + z_i e \phi = k_B T \ln a_i + z_i e \phi \tag{68}
$$

which leads new modes of ion intercalation (Figure 5). For ion insertion (Figure 3), we propose the general model,

$$
\gamma^\ast = (1 - c_i)^{-s} \exp \left[ \frac{1}{k_B T} \left( \frac{\lambda_0}{4} - \frac{\sigma : \varepsilon^\ast}{\rho_s} \right) \right] \tag{69}
$$

where $\varepsilon^\ast$ is the transition-state strain, $s \geq 1$ the number of excluded sites, and $\lambda_0$ the reorganization energy. For insertion in a regular solid solution, the exchange current is

$$
I_0 = \tilde{I}_0(c) \exp \left( \frac{\alpha (\nabla \cdot \kappa \nabla c) + \sigma : (\varepsilon^\ast - \alpha \varepsilon^0)}{\rho_s k_B T} \right) \tag{70}
$$

where $\tilde{I}_0(c)$ is the limit of zero stress and uniform concentration Eq. (47) and $\Delta \varepsilon = \varepsilon^\ast - \alpha \varepsilon^0$, is the “activation strain”.$^{126}$

**Conservation laws.** From the LIT flux Eq. (4), conservation of mass leads to the CH equation,

$$
\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{F}_i = \tilde{R}_i, \tag{71}
$$
where,

$$F_i = - \frac{D_i c_i}{k_B T \rho_s} \nabla \frac{\delta G}{\delta c_i}$$  \quad (72)

In our formulation, the tracer diffusivity $D_i$ is also defined variationally via Eq. (13). In the case of a solid solution, Eq. (14), this leads to the “modified CH equation”. The homogeneous reaction rate $\bar{R}_i$, describing bulk charge transfer reactions (e.g., water self-ionization), is often neglected, but could be described by our theory. The current density is also expressed variationally:

$$J = \sum_i z_i e F_i$$  \quad (73)

and enters charge conservation,

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot J = \sum_i z_i e \bar{R}_i = 0.$$  \quad (74)

Since elastic stress relaxes much faster than diffusion, mechanical equilibrium $\nabla \cdot \sigma = 0$ implies $\nabla \cdot \sigma = 0$.

Since the chemical potential involves two spatial derivatives (Eq. (59)), the CH equation is fourth-order and requires two boundary conditions at each interface. One relates the normal flux to the reaction rate

$$\hat{n} \cdot F_i = R_i$$  \quad (75)

where $R_i = 0$ for an inactive species and $R_i = \frac{J}{s_i z_i e}$ for an active species. The other is the “variational boundary condition”,

$$\left[ \hat{n} \cdot \kappa \nabla c_i \right] = \frac{\partial \gamma_s}{\partial c_i}$$  \quad (76)

(where $[X]$ denotes the jump in $X$ at an interface), which ensures continuity of the chemical potential and controls surface wetting and nucleation.

Electrostatics. In most models of electrochemical systems, the potential $\phi$ is determined implicitly by electroneutrality, $\rho_e = 0$, but here we allow for diffuse charge, which can alter reaction...
rates (the “Frumkin correction” below) and contribute to capacitive charge storage. The mean electrostatic potential $\phi$ in Eq. (66) is uniquely defined at each position in the microstructure. The potentials $\phi_O$, $\phi_R$ and $\phi_e$ refer to $\phi$ on appropriate sides of the interface where a Faradaic reaction occurs (Figure 2).

The potential is determined variationally by $\frac{\delta G}{\delta \phi} = 0$. Bulk variations lead to Poisson’s equation,

$$\nabla \cdot \mathbf{D} \equiv -\nabla \cdot (\varepsilon_p \nabla \phi) = \rho_e \tag{77}$$

and surface variations to the electrostatic boundary condition,

$$[\hat{n} \cdot \mathbf{D}] \equiv -[\hat{n} \cdot \varepsilon_p \nabla \phi] = \frac{\partial \gamma_s}{\partial \phi} \equiv q_s \tag{78}$$

where $q_s$ is the surface charge (per area), $\mathbf{D} = \varepsilon_p \cdot \mathbf{E}$ is the Maxwell displacement field and $\mathbf{E} = -\nabla \phi$ is the electric field. For ionic liquids, higher-order terms, such as $(\nabla^2 \phi)^2$, can be added to the free energy density to describe electrostatic correlations, and $\varepsilon_p$ becomes a differential operator.\textsuperscript{34}

Since the surface charge $q_s$ is not fixed at an electrode surface, another boundary condition is needed for Poisson’s equation Eq. (77), which relates the charge to the interfacial voltage $\Delta \phi = [\phi]$. In electrochemistry, it is usually assumed that $\Delta \phi$ is across the entire double layer, but as emphasized by Frumkin long ago,\textsuperscript{127} the diffuse part of the double layer outside the reaction plane must be excluded. Mathematical models of the Frumkin correction have recently been developed for solid electrolytes,\textsuperscript{128–130} liquid electrolytes\textsuperscript{88,130–132} and porous electrodes\textsuperscript{133–135} (See Biesheuvel et al.\textsuperscript{130} for a review.) Assuming that charge transfer occurs across a charge-free layer of thickness $h_s$ and permittivity $\varepsilon_s$ with constant electric field $\Delta \phi / h_s$, which could represent a Stern layer of electrode solvation\textsuperscript{88} or the radius of an ionic liquid molecule,\textsuperscript{34} the continuity of Maxwell displacement implies

$$\Delta \phi = \lambda_s \hat{n} \cdot \nabla \phi \tag{79}$$

where $\lambda_s = h_s \varepsilon_p / \varepsilon_s$ is an effective thickness of the Stern layer. The role of diffuse charge is con-
trolled by dimensionless parameter, \( \delta_s = \lambda_s / \lambda_D \), where \( \lambda_D \) is the Debye screening length.\(^{88,130,132,134}\) In the Helmholtz limit (\( \delta_s \to 0 \)), the double-layer is compact (at the molecular scale), and standard BV kinetics apply; in the Gouy-Chapman limit (\( \delta \to \infty \)) it is diffuse and acts like a semiconductor diode, where forward (or reverse) bias corresponds to electrostatic condensation (or repulsion) of the active ions.

**Ion Intercalation with Phase Separation**

**Size-dependent solubility.** It is well known that the spinodal gap of unstable compositions in a solid solution shrinks with decreasing particle size,\(^{117}\) as low energy long-wavelength fluctuations are prohibited. The miscibility gap also shrinks, since the relative cost of a phase boundary increases with the surface to volume ratio.\(^{136}\) Elastic coherency strain enhances both effects by increasing the energy penalty for phase separation.\(^{41,54,59}\)

The theory predicts novel effects of kinetics on solubility, due to ion exchange with the electrolyte reservoir.\(^{39,41}\) At constant voltage, the spinodal and miscibility gaps shrink with increasing exchange current,\(^{39}\) since fluctuations with fast reactions promote unfavorable concentration gradients. Experimental solubility data\(^{56}\) can be interpreted using a 1D Cahn-Hilliard-reaction (CHR) model,\(^{39,66}\) or a more accurate, 2D reaction-limited model with coherency strain.\(^{41}\)

**Intercalation waves.** In anisotropic crystals, ion intercalation dynamics can be limited by diffusion or reactions, independently in each direction.\(^{37}\) In LFP nanoparticles, the concentration tends to remain uniform in the [010] direction due to the fast diffusion\(^{57,137}\) and elastically unfavorable phase separation\(^{41}\) in short one-dimensional channels, unblocked by Fe anti-site defects.\(^{58}\) After [010] depth-averaging,\(^{37}\) the full CHR model reduces to a new, reaction-limited model on the active \{010\} crystal facet,

\[
\frac{\partial c}{\partial t} = J_0 f(\eta),
\]

(80)

(where \( J_0 = I_0 / A_s \) is the current per surface site), which is an electrochemical generalization of the Allen-Cahn equation\(^{16,123}\) (EAC) with with a nonlinear dependence on the variational overpoten-
where \( f(\eta) = I/I_0 \) can come from the BV (Eq. (1)) or Marcus (Eq. (38)) equations. For lithium insertion in a regular solution,\(^{40,41} \) the exchange current \( I_0(c, \nabla \cdot \kappa \nabla c, \sigma) \) is given by Eq. (70).

The theory has led to a paradigm shift in understanding insertion dynamics. In contrast to prior battery models, which assume a uniform reaction rate over the particle surface, limited by radial solid diffusion\(^{10,11,138} \) or a shrinking-core phase boundary,\(^{12,13} \) the EAC limit of the CHR model predicts reaction-limited intercalation waves (or “domino cascades”\(^{139} \)), sweeping across the active facet, filling the crystal layer by layer (Figure 5).\(^{37,40,41,125,140} \) Intercalation waves result from nucleation at surfaces or defects, or by spinodal decomposition,\(^{40} \) and trace out the voltage plateau at low current, as shown in Figure 6. Experimental evidence of one-dimensional nucleation and growth, consistent with the EAC theory,\(^{37,40} \) has recently been obtained by potentiostatic intermittent titration.\(^{63} \)

**Suppression of phase separation and quasi-solid solution.** The theory has led to some surprising conclusions about *electrochemically driven phase transformations*. Our first paper included a mathematical proof that traveling-wave solutions of the EAC equation only exist over a finite range of thermodynamic driven force,\(^{36,37} \) but the implications were difficult to grasp without the connection to the battery voltage. Once the generalization of BV kinetics was achieved,\(^{35,71} \) simulations and analysis revealed how phase separation is strongly influenced by the applied current.\(^{40,41} \) As suggested by Malik et al.\(^{55} \) based on bulk equilibrium free energy calculations, phase separation is suppressed during battery operation, but we now understand that the mechanism is due to surface reactions, far from equilibrium.

As explained by Bai et al.\(^{40} \), phase separation is suppressed, when the applied current approaches the exchange current. A linear stability analysis of the EAC model for BV kinetics with \( \alpha = \frac{1}{2} \) shows that concentration fluctuations of wavenumber \( k \) grow at a rate\(^{40} \)

\[
s(k; c, I) = - \sqrt{J_0 + \frac{I^2}{4}(\eta' + \kappa k^2)} + I \left( \frac{J_0}{J_0} + \frac{1}{2} \kappa k^2 \right) \tag{82}\]
Figure 6: Galvanostatic discharge into a single LFP cathode nanoparticle without coherency strain. Top: Linear stability (spinodal) diagram for the homogeneous state versus current $\tilde{I}$ (scaled to the exchange current at $X = 0.5$) and mean Li filling $X$. (a) Battery voltage versus state of charge ($X$) at different currents $\tilde{I}$. (b) Evolution of the concentration profile at low current $\tilde{I} = 0.01$ with insertion waves nucleated at the wetted [001] side facets. (c) Quasi-solid solution behavior close to the critical current $\tilde{I} = 0.5$, showing homogeneous filling ahead of the waves. [Reproduced from Bai, Cogswell, Bazant][40]
where \( \bar{\eta}(c) \) and \( \bar{J}_0(c) \) are the activation overpotential and exchange current density, respectively, in a homogeneous state of concentration \( c \) sustaining a current \( I \). The range of linear instability, \( s(c,I) > 0 \), predicted by Eq. (82) and Eq. (70) with elastic strain is shown in Figure 6(a).

The theory predicts a \textit{critical current}, of order the exchange current, above which phase separation by spinodal decomposition is impossible. Below this current, the homogeneous state is unstable over a range of concentrations (smaller than the zero-current spinodal gap), but for large currents, the time spent in this region is too small for complete phase separation. Instead, the particle passes through a transient \textit{quasi-solid solution} state, where its voltage and concentration profile resemble those of a homogeneous solid solution.

The suppression of phase separation predicted by the theory is very general. When nucleation is possible (see below), a similar current dependence is observed. As shown in Figure 6, the bulk crystal fills ahead of the surface-nucleated intercalation waves in the quasi-solid solution regime, while homogeneous filling occurs above the critical current. With elastic coherency strain included, the suppression of phase separation is analogous, but even stronger.\(^{41}\)

In the case of LFP, the critical current is an order of magnitude smaller than the exchange current.\(^{41}\) The surprising implication is that phase separation does not occur \textit{in situ} during normal battery operation, which helps to explain the high-rate capability and extended lifetime of LFP nanoparticles, due to larger active area and smaller elastic stresses. On the other hand, phase separation occurs at very low currents and can be observed in particles trapped at intermediate compositions for \textit{ex situ} measurements (Figure 7).

\textbf{Striped phase morphologies.} For quantitative interpretation of experiments, it is essential to account for the elastic energy. Even a simple elastic model can dramatically improve the inference of lithium diffusivity from intermittently titration with phase separation.\(^{141}\) Crystal anisotropy generally leads to striped patterns in equilibrium.\(^{41,43,59,60}\) Cogswell and Bazant\(^{41}\) showed that the stripe spacing

\[
\lambda_{\text{stripe}} = \sqrt{\frac{2\gamma L}{\Delta g}}
\]

follows from the balance between elastic energy, favoring short wavelengths at a stress-free bound-
Figure 7: Simulations of reaction-limited phase separation of a 500nm single crystal of Li$_{0.5}$FePO$_4$ into Li-rich (black) and Li-poor phases (white) in an electrolyte bath at zero current and zero pressure, consistent with *ex situ* experiments.\(^{67,124,142}\) (a) Coherent phase separation, where lithium insertion causes contraction along [001] ($c$) axis and expansion along the [100] ($a$) axis, leading to tilted interfaces aligned with {101} planes. (b) Loss of [001] coherency (e.g. due to microcracks\(^{67}\)) causes the phase boundaries to rotate to align with {100} planes. [Reproduced from Cogswell and Bazant\(^{41}\).]

In layered crystals, the lattice misfit can cause tension and compression in different directions, and Stanton and Bazant\(^{43}\) predicted that this could cause phase boundaries to tilt with respect to the crystal axes. For example, lithium insertion in LFP causes contraction of the iron phosphate planes in the [001] direction and expansion in the [100] and [010] directions.\(^{67}\) Cogswell quantitatively explained the experimentally observed phase morphologies\(^{124,142}\) and used the theory (Eq. (83)) to extract $\gamma$ and thus the gradient penalty $\kappa$. As shown in Fig. Figure 7, the new phase-field theory enables realistic simulations of reaction-limited phase separation for single particles at zero total current.
Surface wetting and nucleation. The theory also predicts how surface thermodynamics affects reaction kinetics. We have already mentioned the Frumkin effect of electrostatic amplification of the reaction rate, when active ions are attracted to the surface. Non-electrostatic attraction, or wetting, of the solid surface by intercalated ions can also dramatically affect the intercalation process. In Cahn’s theory, surface wetting is described by Eq. (76) with $\frac{\partial \gamma}{\partial c} < 0$. Using this boundary condition for the EAC equation Eq. (80), the nucleation of intercalation waves in LFP nanoparticles due to wetting of the \{100\} crystal facet can be simulated with coherency strain $^{41}$ (Figure 7) or without $^{40}$ (Figure 6). By combining surface wetting with elastic strain in the theory, the nucleation barrier in LFP (critical voltage past the equilibrium plateau to observe a sudden current) can be predicted as a function of particle size, in excellent agreement with experiments. The effect of surface wetting on intercalation kinetics may also be responsible for the surprising performance boost from phosphate-glass thin films on active nanoparticles of LFP $^{53}$ and Li$_x$CoO$_2$ $^{144}$

Mosaic Instability. The complex dynamics of ion intercalation in nanoparticles also affects the macroscopic response of a composite electrode. Using the CHR model $^{39}$ for a collection of particles in a reservoir of constant chemical potential, Burch $^{66}$ discovered what we called the mosaic instability, whereby particles filling uniformly at constant total current suddenly fill one-by-one. The mechanism is simple: As the particles enter the miscibility gap, the first to phase separate (due to random nucleation or spinodal decomposition) will suddenly lower its chemical potential and sustain a much larger current until it becomes full, at which point the current is shared by the others until the process repeats. Interestingly, in the CHR model, the smaller particles transform first, because diffusion brings the core concentration to the spinodal more quickly. In contrast, for reaction-limited particles, the larger ones are more likely to nucleate first.

Meanwhile, Dreyer et al. $^{64}$ described the mosaic instability and demonstrated it experimentally in two clever ways. They connected it to the zero-current voltage gap between charge/discharge cycles in LFP batteries, as well as the dynamics of an array of balloons connected to a single pressure line. Their theory $^{64,65}$ is similar to the “pseudo capacitor limit” of our models, where each particle maintains uniform (but time dependent) concentration, without internal phase separation.
Figure 8: Finite-volume simulations of macroscopic phase separation in a porous LFP cathode.\textsuperscript{42} (a) Voltage versus state of charge for slow charge/discharge and fast discharge. (b)-(d) Profiles of mean Li concentration in the solid at the red points in (a), showing narrow reaction fronts with mosaic instabilities, associated with voltage fluctuations. (e) Electrolyte Li concentration for fast discharge (d), showing diffusion limitation. [T. R. Ferguson]

**Porous electrodes.** The theory has recently been extended to porous electrodes undergoing phase transformations\textsuperscript{42} using classical porous electrode models to describe the electrolyte.\textsuperscript{145} Diffusion in the electrolyte provides a spatiotemporal bias for the mosaic instability, so that narrow fronts of stochastic particle phase transformations propagate away from the separator (discharge) or current collector (charge) at low current (Figure 8). The width of the reaction front separating low-density and high-density phases increases with current until the entire electrode becomes active, which is a macroscopic analog of the suppression of phase separation in nanoparticles.

The new theory can robustly predict experimental data for phase-separating porous electrodes for the first time without artificially fitting voltage plateaus or enforcing phase boundaries. Using the EAC regular-solution model for LFP\textsuperscript{40,41} in a porous electrode,\textsuperscript{42} the model can predict tiny voltage oscillations ($< k_B T / e = 25 \text{mV}$) and the limiting “voltage gap” at very low currents observed in experiments,\textsuperscript{64} which give way to a smoothly decaying voltage at high current\textsuperscript{53} (Figure 8). Nucleation is also crucial to consider at the porous electrode scale\textsuperscript{63} and can be naturally included in theory. Using a two-component regular solution model for graphite intercalation,\textsuperscript{35}
the theory is also able to fit experimental data for diffusion-limited intercalation of long graphite anodes\textsuperscript{146} with multiple reaction fronts of different colors corresponding to different stages of lithiation.

**Conclusion**

This Account describes steps to unify chemical kinetics with thermodynamics, electrostatics, and transport in electrochemical systems. The theory has shed light on rate processes in advanced Li-ion batteries with phase-separating nanoparticles. Other applications to energy conversion, such as electrocatalysis in solid oxide fuel cells and charge transfer in ionic liquids, may require incorporating diffuse charge\textsuperscript{34,89} and heat transfer\textsuperscript{147} in the general framework.

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