The Role of Phase Transformation in the Rate Performance Limited Li$_x$V$_2$O$_5$ Battery Cathode

by

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Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of
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Abstract:
It has recently been reported that the rate performance of Li$_x$V$_2$O$_5$, a widely studied candidate Li-ion battery cathode material, can be significantly improved through a variety of particle size reduction techniques, (e.g. nanotemplating). It is widely believed that the microscale mechanism responsible for this improvement in rate performance is a reduction in the Li$^+$ diffusion path length. Yet, the experimentally observed discharge performance of Li$_x$V$_2$O$_5$ cathode films comprised of active material particles of varying sizes (between films) and subject to variable rates of discharge deviates sharply from results predicted by Fickian scaling laws.

In a crystalline Li$^+$ insertion host the incorporation of ionic volume commensurate with electrochemical discharge often leads to phase transformation. While the consequent phase coexistence is largely responsible for the high energy densities reported in many crystalline insertion hosts, its effect upon rate performance, (or power density), is not well understood. Recently, researchers identified facilitated phase boundary motion as the mechanism responsible for improved high-rate performance in one nanoscaled insertion compound. The preservation of a coherent phase boundary between differentially lithiated, coexistent end-member phases that would normally relax the interfacial strain associated with biphasic volumetric mismatch by forming incoherent phase boundaries, they reasoned, lead to the observed improvement in high-rate performance.

A number of discrete structural and electrochemical signatures have subsequently been identified that are believed to correlate with facilitated phase-boundary-motion in nanoscaled insertion hosts. These equilibrium signatures, which include; enhanced Li$^+$ solubility in end-member phases, decreased volumetric mismatch between coexistent end-member phases, increased interfacial strain between coexistent end-member phases, and reduced cycling hysteresis, have been identified in the dimensionally graded Li$_x$V$_2$O$_5$ system, suggesting that rate performance in this system may, in fact, also be gated by sluggish phase boundary motion.

Finally, a non-equilibrium experimental technique, (modified GITT), designed to identify regimes in which phase-boundary motion is rate-limiting, is described. This modification entails the suppression of several assumptions governing the conventional application of the GITT technique to kinetic parameter extraction, namely, the use of “small” current pulses and the violation of the implicit monophasic constraint. It is observed that this variable rate-technique can identify regimes of phase boundary motion control in dimensionally graded Li$_x$V$_2$O$_5$. Further, it is proposed that this technique might allow the microscale phenomenology of rate-limiting phase evolution to be modeled.

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Chapter 1: Introduction

According to a recent report issued by the Pacific Northwest National Laboratory concerning the conversion of the U.S. light duty fleet to plug-in hybrid vehicles (PHEVs), “up to 84% of U.S. cars, pickup trucks and sport utility vehicles (SUVs) could be supported by the existing U.S. electric power infrastructure... without any additional investments in generation, transmission and distribution capacities.” [1] While the full environmental benefits of PHEV fleet conversion are ultimately constrained by the means of electricity production, (currently 49% of the electricity in the U.S. is generated by coal power plants), the report estimates that PHEV fleet conversion could result in an immediate 27% reduction in total greenhouse gases. [2] Fundamental to this analysis is the assumption that PHEVs will provide significantly increased energy efficiency due, in part, to their use of regenerative braking in which a vehicle’s kinetic energy (which would otherwise be dissipated as heat during braking) is converted into electrical energy which can then be stored in the vehicle’s rechargeable batteries. While the nickel metal hydride (NiMH) batteries currently employed in production (non plug-in) hybrid vehicles are capable of meeting this rate-performance intensive requirement, they lack the energy density needed to sustain the long-range (64 km/40 miles) electric-only performance that is seen as essential in a commercially viable PHEV.[3] Consequently, auto manufactures are now looking at Li-ion technologies which provide more than twice the energy density of the next-best NiMH batteries.[4]

Since the introduction of the first consumer-grade rechargeable Li-ion batteries in the mid 90’s, researchers have been searching for chemistries and processing routes that would improve upon many of the apparent limitations in those early Li-ion battery systems.[5] While operational safety, cyclability and life-cycle toxicity rightly rank amongst the most pressing research subjects, a fundamental concern, as regards the implementation of Li-ion battery technology in PHEVs, is the significant loss of useful capacity at charge/discharge rates appropriate to the power requirements of vehicles which employ regenerative braking. [6] Recently, the LiFePO₄ system, which had initially been dismissed as a candidate cathode chemistry due to its intrinsically poor electronic and ionic conductivity has been the subject of vigorous research, resulting in the commercialization of several high power batteries for power tool applications.[7, 8]
Yet, despite this and other recent advances a number of fundamental questions remain regarding performance limiting mechanisms in the lithium intercalating compounds currently utilized in Li-ion batteries.

For many years it was widely believed that sluggish Li$^+$ diffusion in the bulk cathode material was the primary cause of poor high rate performance in most Li-ion batteries.\[9\] Consequently, a significant share of battery cathode research has focused upon shortening the diffusive path length via dimensional reduction. And while approaches including ballistic deposition, nanotemplated growth, and sol-gel processing have indeed yielded significantly improved rate performance in some systems, the underlying microscale mechanisms responsible for those improvements remain poorly or incompletely understood, especially in systems that exhibit predominantly biphasic behavior during charge and discharge.[10-12]

More recently a number of researchers have begun to investigate the role played by phase transformation itself in sluggish charge/discharge kinetics. In particular, spectroscopic studies of dimensionally graded LiFePO$_4$ suggest that particle size reduction might relax volumetric strain constraints correlative with the relative facility of phase boundary motion, leading to significantly enhanced rate performance.[13] This thesis intends to pursue a similar line of inquiry, with the aim of corroborating and expanding upon these findings in similarly dimensionally graded Li$_x$V$_2$O$_5$ particles. To this end, this work will begin with a survey of previously reported experimental work regarding the potentially rate-limiting role played by phase boundary motion in a variety if Li$^+$ intercalating compounds. The objective of this literature survey is twofold: 1) to validate the claim that phase boundary motion can indeed limit rate performance in Li$^+$ intercalating compounds and, 2) to enumerate a set of electrochemically and spectroscopically accessible signatures believed to correlate with variations in the kinetics of phase boundary motion, (and more broadly rate performance), as a function of active material particle size. Next, this work will document the experimentally observed variation of these signatures in the dimensionally graded Li$_x$V$_2$O$_5$ system, with the aim of validating the central thesis of this work, namely, that the reduction in active material particle size leads to enhanced rate performance via the mechanism of facilitated phase boundary motion. Finally, this thesis will elaborate upon a heretofore unreported
electrochemical signature of phase boundary motion rate-limited intercalation kinetics, derived of a simple modification to the standardized GITT technique.

**Battery Overview**

A conventional Li-ion secondary battery consists of a Li\(^{+}\) intercalating anode (typically carbon-based), a lithium salt-doped, non-aqueous liquid electrolyte and a Li\(^{+}\) intercalating transition metal oxide or transition metal phosphate cathode as depicted in Figure 1-1. A mixed powder architecture comprised of finely distributed carbon particles, (added to enhance electronic conductivity between the semi-conducting active material and the aluminum current collector), and a polymeric binding agent, (added to ensure the mechanical integrity of the cathode film), is often employed in cathode fabrication. Upon discharge Li\(^{+}\) ions diffuse from the anode through the ionically conducting, electronically insulating electrolyte and into the cathode where they occupy interstitial sites without undergoing chemical reaction. Concurrently, electrons travel from the anode, though an external circuit, (delivering energy to an external load) and into the cathode where they locally charge compensate the oxide environment surrounding the intercalated Li\(^{+}\) ion, (partially or completely reducing the neighboring active transition metal species).

---

**Figure 1-1:** A schematic of a rechargeable lithium battery upon discharge
The driving force for reaction is the difference in electrochemical potential between Li\(^{+}\) ions at the surface of the anode material and Li\(^{+}\) ions at the surface of the transition metal oxide or transition metal phosphate cathode material. This difference in electrochemical potential is manifest macroscopically as a potential under equilibrium conditions as expressed in Equation 1-1,

\[
V(x) = \frac{\mu_{Li}^{\text{positive}}(x) - \mu_{Li}^{\text{negative}}}{zF}
\]

\textit{Equation 1-1}

Where \(x\) represents the degree of intercalation at the cathode (the chemical potential at the negative electrode, or anode, is assumed here to be invariant, corresponding to a lithium metal anode), \(F\) is the Faraday constant and \(z\) is the magnitude of the charge transported by the Li\(^{+}\) ion, (in this case equal to 1).

In a generalized \(Li_xMO_y\) system the following half-cell reactions obtain during discharge:

At a Li metal anode:

\[
\text{Li} \rightarrow y\text{Li}^{+} + ye^{-}
\]

\textit{Equation 1-2}

At a lithiating carbon anode.

\[
\text{Li}_y\text{C} \rightarrow \text{C} + y\text{Li}^{+} + ye^{-}
\]

\textit{Equation 1-3}

At a transition metal oxide cathode:

\[
y\text{Li}^{+} + \text{Li}_x[(2-x)\text{M}^{n+}, x\text{M}^{(n-1)+}]\text{O}_y + ye^{-} \rightarrow \text{Li}_{x+y}[(2-x-y)\text{M}^{n+}, (x+y)\text{M}^{(n-1)+}]\text{O}_z
\]

\textit{Equation 1-4}

where \(x\) corresponds to the degree (or mol fraction) of Li\(^{+}\) present in the cathode at the onset of intercalation, \(y\) corresponds to the mol fraction of Li\(^{+}\) transported from the anode to the cathode during a discharge event, \(M\) corresponds to the transition metal species, and \(n\) corresponds to the initial valence state of the transition metal ion. The reverse reactions obtain during charging.
In a typical Li-ion battery the transition metal species undergoes a valence shift of up to plus or minus 1 during charge or discharge respectively. While larger valence shifts in the transition metal species are readily achievable and in fact, in principle, desirable, in practical crystalline systems larger valence shifts (which in the Li-ion system correspond to larger degrees of lithium intercalation) often give rise to irreversible structural transformations in the oxide material, resulting, in many cases, to significant loses in cycling capacity.[14]

For a monophasic system, that is a system that does not undergo first order phase transformations during charge or discharge, the cell's equilibrium open circuit potential will vary monotonically with the degree of lithium intercalation as can be seen in Figure 1-2 which depicts typical discharge behavior in an amorphous LiₓV₂O₅ battery.

![Figure 1-2: Characteristic discharge profile for an amorphous V₂O₅ aerogel based composite electrode. Reproduced from Passerini et al. [15]](image)

Conversely, in a system that undergoes first order phase transformations, the galvanostatic discharge profile will exhibit both monotonic variations as well as, under equilibrium conditions, flat plateaus as evident in the quasi-equilibrium discharge profile for the crystalline LiₓV₂O₅ battery system shown in Figure 1-3.
Thermodynamically these plateaus are known to correspond to biphasic regimes in which the concentration or degree of intercalation in coexistent end member phases remains invariant, with Li⁺-rich phases growing at the expense of Li⁺-poor phases during discharge and Li⁺-poor phases growing at the expense of Li⁺-rich phases during charge. This behavior can be understood by reference to a schematic, pseudo-binary free energy plot, in which, at equilibrium, a system with a composition between the common tangents of the free energy curves corresponding to the stable end-member oxides can lower its energy by phase separating into Li⁺-poor and Li⁺-rich phases, with the relative composition of either phase given by the tangent connecting the minima of those free energy functions. [Figure 1-4] The driving force for this phase separation is commonly believed to derive from a combination of electrostatic interactions between the intercalated Li⁺ ions and structural strain induced by the incorporation of additional ionic volume. [17]
Figure 1-4: Highly Schematic representation of the variation in cell potential and commensurate bulk concentration profiles as a function of the degree of Li$^+$ intercalation in a generic biphasic cathode.

As can be seen on the right hand side of Figure 1-4, the coexistence of differentially lithiated phases is manifest microscopically as a discontinuity in Li$^+$ concentration within the bulk active material. Presently the effects of phase boundary formation and phase boundary motion upon intercalation kinetics remain incompletely understood. The next section will provide an overview of the battery performance metrics germane to developing a more complete understanding of the proposed role played by phase transformation in lithiating cathodes.

**Battery Metrics**

In assessing the suitability of a given Li-ion battery system to a given application it is necessary to consider a number of different performance metrics. A system that offers excellent cycle life, for example, may not meet the power requirements of a given application. Conversely, a system with excellent power density may offer unsatisfactory energy density, as is the case with the lead-acid and NiMH systems mentioned above. Differentiating between these metrics therefore is
an essential part of materials selection and system design. The following section will provide an overview of the metrics most relevant to the needs of high power applications.

**Cycle Life**

Cycle life is defined as the number of charge/discharge cycles over which a given battery system can continuously provide the required energy and/or power for a given application. The cycle life depends significantly upon the depth of discharge or the degree to which a given system can be reversibly intercalated and deintercalated. Outside of those limits a system might undergo irreversible transformations that will adversely affect the system’s performance upon subsequent cycling.

**Intercalation Capacity**

Intercalation capacity describes the quantity of a given ion (in this case Li⁺) that can be reversibly inserted into and extracted from the host transition metal oxide or transition metal phosphate electrode. This metric, which is conventionally expressed in units of mAh/g or Ah/kg (or somewhat more schematically as a fraction per formula unit of active material), depends primarily upon the structural stability of the intercalation host to Li⁺ insertion, and along with the degree of insertion dependant discharge potential bounds the theoretical performance of a given system.

**Energy Density**

Energy density describes the amount of electrical energy that can be reversibly extracted from the battery. Depending upon the application, energy density is expressed on a mass basis (Wh/kg) or on a volumetric basis (Wh/L) either of which may be defined in terms of gross system properties (total system mass or volume) or a specific active material’s properties (molar mass or volume). The theoretical energy density of a given system is defined as the product of system’s equilibrium discharge potential (V) and intercalated capacity (Ah/kg). The phase transforming chemistries discussed in this work are especially well-suited to high energy density applications as the biphasic plateaus provide, during quasi-equilibrium cycling, invariant potential throughout the biphasic regime leading to enhanced high-potential capacity. In practical systems, the theoretical capacity is never fully accessed, due, in part, to irreversible, parasitic side reactions.
involving the electrodes and liquid electrolyte. At non-equilibrium rates of discharge ohmic losses and other kinetic factors such as bulk ionic diffusion, charge transfer kinetics, electronic conductivity and, as will be discussed more fully in this work, phase transformation kinetics, become manifest, resulting in diminished energy density.

**Power Density**

Power density describes the maximum rate at which a battery can deliver electrical energy and can likewise be expressed on a mass (W/kg) or volumetric basis (W/L). This figure captures the kinetic processes within the battery and is constrained by any of a number discrete or correlated activated processes within the battery. The metric is defined as the product of the cell’s non-equilibrium discharge potential (V) and its maximum useful discharge rate (A/kg). In the battery literature, galvanostatic rates are often reported in terms of C-rate, with a C-rate of 1C corresponding to full charge or discharge of the specified active materials in 1 hour, a C-rate of 2C corresponding to discharge in 30 minutes and a C-rate of C/2 corresponding to discharge in 2 hours. While the C-rate convention accurately portrays the per unit active material mass response of these systems, it fails to account for variations in real surface area (as opposed to the geometric surface area) of a particular cathode architecture, complicating comparisons between the dimensionally graded systems under consideration in this work. This document will briefly address the implications of this approach to quantifying rate-performance in Chapter 4.

**Optimizing Li-ion Batteries for High Rate Performance**

The theoretical energy density of a particular Li-ion system, under equilibrium conditions, is completely determined by thermodynamic properties intrinsic to the relevant active materials. The cell’s open circuit potential at a given state of charge is fixed by the electrodes’ composite redox potential while the cell’s equilibrated intercalation capacity is a function of the thermodynamic stability of the constituent electrode phases.

Conversely, power density, while circumscribed by the equilibrium properties of a given chemistry, is to a much greater extent a function of net system composition and architecture. Poor high rate performance can potentially derive from any number of
kinetically slow processes. These processes include ionic conduction in the bulk solid active material or liquid electrolyte, electronic conduction in the bulk active material, charge-transfer reactions at the electrode/electrolyte interface or electrode/current collector interface or, as will be argued in this work, sluggish phase boundary motion and/or phase nucleation. Thus, for high rate performance a battery system must be optimized so as to minimize the combined effects of each of these potentially rate-limiting mechanisms.

During non-equilibrium rates of discharge a battery’s open circuit potential will deviate from equilibrium according to Equation 1-5 below,

\[ \Delta E = E_{\text{cathodic}} - E_{\text{anodic}} - IR - \eta_{\text{cath}} - \eta_{\text{anode}} - \eta_{\text{mass trans}} \]  

*Equation 1-5*

where \( E_{\text{cathodic}} \) and \( E_{\text{anodic}} \) refer to the equilibrium redox potentials of the cathodic and anodic species respectively, \( IR \) refers to ohmic losses associated with electronic transport in the anode and cathode species, \( \eta_{\text{cath}} \) and \( \eta_{\text{anode}} \) refer to overpotentials associated with charge transfer reactions at the cathodic and anodic interfaces and \( \eta_{\text{mass trans}} \) refers to the overpotential associated with mass transport limitations in the electrolyte and electrode species.[18] Mitigating the effects of each of these terms is critical to achieving high rate performance.

Poor electronic conductivity, a characteristic of many of the ceramic materials employed as Li-ion battery cathodes, and the primary source of IR losses, is routinely enhanced via carbon coatings, the incorporation of metallic or transition metal dopants within the active oxides, and/or dimensional reduction (resulting in decreased conduction path lengths within the oxide particles). [7, 8, 19, 20] Kinetic losses associated with Faradaic processes at the electrode/electrolyte interfaces, \( \eta_{\text{cath}} \) and \( \eta_{\text{anode}} \) in the expression above, can be minimized by choosing electrode/electrolyte pairs that have intrinsically high catalytic activities for reaction and by maximizing the electrode/electrolyte surface area at the electrodes. Approaches to surface area maximization include, as mentioned above, mechanical milling, ballistic or sputter deposition, and the supercritical drying of sol-gels to form high surface to volume aerogels and xerogels.
The rate at which Li\(^+\) can be intercalated into the active materials, the principal source of the \(\eta_{mass\;trans}\) term in a liquid electrolyte system, depends upon the active material chemistry and particle geometry. *Ab initio* studies of layered oxide structures indicate that activation energy of Li\(^+\) hops is determined by a combination of repulsive interactions between host cations and the intercalating species and the size of the interstitial sites through which the migrating Li\(^+\) must pass. [21] Diffusion penetration time, defined as \(L^2/D\) (where D is the diffusion coefficient and L is the diffusion favored dimension) scales with particle size.

A final, and less well-described, contributor to poor high-rate performance is the rate of phase nucleation and phase boundary motion in systems that undergo phase transformation during intercalation. The effects of these processes are manifest through the \(\eta_{mass\;trans}\) term though their quantification escapes or complicates conventional approaches to parameterizing kinetic processes within the active electrode particles. It has been suggested by recent work that phase-boundary motion rate limited materials can be kinetically enhanced through nanoscaling of the active material particles, resulting in the relaxation of the strain constraints responsible of phase transformation itself. [13] One observable manifestation of this effect is the enhanced end-member Li\(^+\) solubility observed in nanoscale systems which has been reported to correlate with a reduction in the volumetric mismatch between coexisting phases. [22, 23]

**Description of Thesis**

The next chapter provides an overview of relevant literature, beginning with a survey of recent work describing the evolving understanding of the role played by phase transformation in high-rate intercalation processes and continuing with an introduction to recent approaches to rate-performance optimization in phase transforming battery cathodes, including a variety of particle size reduction techniques. The chapter concludes with an overview of the Li\(_x\)V\(_2\)O\(_5\) cathode chemistry. Chapter 3 describes experimental techniques and synthesis strategies that are employed in the fabrication and quantification of the systems under consideration. Chapter 4 describes the dimensionally graded Li\(_x\)V\(_2\)O\(_5\) system, beginning with a systematic assessment of the various rate enhancing mechanisms expected to scale with particle size in these systems, and concluding with a
plausibilization of the proposed rate limiting role of phase boundary motion. Chapter 5 introduces a novel application of the GITT technique commonly used to determine kinetic parameters as well as equilibrated energy density. Finally, Chapter 6 summarizes the accomplishments of this thesis and provides recommendations future research.

References


17. "what goes here 3?"


19. "what goes here 4?"


Chapter 2: Literature Review

This chapter summarizes past findings germane to the methods and materials employed in this dissertation. It begins with a survey of rate-performance in a variety of Li-ion intercalating compounds, highlighting the structural, electrochemical and kinetic features common to the species under consideration. It continues with a summary account of a widely cited attempt to identify and model rate-limiting processes in one of those compounds, LiFePO$_4$, that employs a simplified phase transformation geometry. Next, it describes a more detailed account of phase-nucleation energetics that illustrates the shortcomings of the highly simplified phase transformation geometry employed by that model. The following section will elaborate upon addition experimental evidence regarding the phenomenology and potentially rate-limiting effects of phase evolution in Li-ion intercalating compounds, paying particular attention to reported spectroscopic and electrochemical signatures of phase nucleation and/or phase boundary motion limited intercalation kinetics. Finally, it describes the transition metal oxide, vanadium oxide, and its history as a lithium battery cathode.

Phase Transformation in Li-ion Intercalating Compounds

Rate Performance in Li-ion intercalating electrodes

Li-ion intercalating compounds can be sorted into one of two general classes, phase transition materials such as LiFePO$_4$ and Li$_{4/3}$Ti$_{5/3}$O$_4$, and phase transformation-solid solution materials such as LiCoO$_2$ and LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$. [1] Phase transition compounds are characterized by extensive potentiodynamic plateaus in which differentially lithiated end-member phases of fixed composition shrink or grow at one-another’s expense during charge and discharge. Phase transformation-solid solution compounds, on the other hand, are characterized by potentiodynamically contiguous regimes of biphasic plateaus and monotonic sloping, the later corresponding to a monophasic host in which Li$^+$ composition (and, assuming Nernstian kinetics, cell potential) vary linearly with the degree of charge or discharge. Examples of both types of materials are depicted in Figure 2-1.
As might be expected, rate performance in these compounds varies considerably from chemistry to chemistry as can be readily seen in Figure 2-2. Ma et al., attempt to correlate these “characteristic” variations in rate performance with electroanalytically and spectroscopically derived material’s parameters. Using scanning electron microscopy (SEM), galvanostatic intermittent titration (GITT) and electrochemical impedance spectroscopy (EIS), the authors evaluated the particle size, equilibrium discharge profile, and electronic and ionic conductivities for each of the four systems, the results of which are shown in Table 2-1.
Table 2-1: Electronic/ionic conductivities and rate functional discharge capacities for the intercalation hosts depicted in Figure 2-1. Reproduced from Ma et al. [1]

These experimentally derived parameters were then order-ranked and compared against observed rate-performance, and the relative contribution of each potentially rate-limiting mechanism was assessed. Ma et al. conclude from this analysis that a given chemistry’s rate capability is controlled primarily by phase transformation kinetics (a subject we will return to later), or, in the absence of phase-transformations, (as in the case of the phase transformation-solid solution compounds) Li-ion diffusion. The authors rationalize this finding by reference to the observed correlation between the volumetric misfit between coexistent phases in the biphasic regimes of the phase transition materials (~0% in \( \text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4 \) and 6.8% in \( \text{LiFePO}_4 \) ) and the dissimilar contractions of their biphasic plateaus (and consequent intercalation capacity) as a function of increasing rates of discharge.
Yet, while Ma et al.'s analysis is intuitively compelling, absent a more detailed account of the phenomenology and kinetics of phase transformation itself, their conclusions regarding the role of phase transformation in rate performance must be considered provisional.

**Modeling the Kinetics of Li-ion Intercalation in Biphasic Systems**

In 2004 Srinivasan and Newman published a discharge model of the LiFePO$_4$ battery system. Their objective was to rationalize 3 characteristic signatures commonly associated with poor high-rate performance in the LiFePO$_4$ battery, namely: “(i) a drop in utilization with increasing current density; (ii) a decrease in midplateau potential with increasing current density; and (iii) a slope in the discharge curves at higher current densities” as shown in Figure 2-3. [2] It bears mentioning that all three signatures can be readily discerned in the discharge profiles depicted in Figure 2-2.

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**Figure 2-2: Voltage Profiles of (a) Li$_{4/3}$Ti$_{5/3}$O$_4$ (b) LiFePO$_4$ (c) LiCoO$_2$ (d) LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ at different C-rates. Reproduced from Ma et al. [1]**
Figure 2-3: Characteristic variations in experimental discharge performance for the LiFePO₄ battery. Reproduced from Srinivasan et al. [2]

Unlike many previous attempts to model variable-rate discharge performance in Li⁺ intercalating compounds, the model employed by Srinivasan and Newman explicitly incorporates the well-documented coexistence of Li⁺-rich and Li⁺-poor phases (nominally LiFePO₄ and FePO₄ respectively) during discharge. To account for the fact that “(i) the active material has two phases and (ii) there is bulk utilization of the material”, the authors invoke a shrinking-core geometry in which a spherically symmetric Li⁺-rich shell of uniform thickness surrounds a Li⁺-poor core, with the Li⁺-rich shell growing at the expense of the Li⁺-poor core during discharge as shown in Figure 2-4.
Figure 2-4: Schematic representation of shrinking-core model. Reproduced from Srinivasan et al. [2]

Importantly, this model does not include a phase boundary motion energy term, assuming instead that the motion of the boundary itself is facile. This feature of the model is manifest in the assumption that the interface between the coexisting phases is at equilibrium at all rates of intercalation as demonstrated by boundary condition employed at the phase interface

\[ c_s = c_{eq} \text{ at } r = r_i(t) \]

Equation 2-1

Where \( c_s \) is the time/position dependant concentration within the bulk active material particle, \( c_{eq} \) is the concentration of the lithium-rich phase (assumed to be in equilibrium with the Li\(^+\)-deficient phase) and \( r_i \) is the time dependant position of the interface itself. Further, as will be discussed in greater detail below, it ignores observed volumetric variations between the coexisting phases despite a reported 6.8% increase in unit cell volume upon lithiation. [3] As a result, the decrease observed in high-rate discharge capacity is ascribed largely to sluggish Li\(^+\) diffusion (or “Diffusion resistance”) within discrete end-member phases as shown in Figure 2-5.
While this phenomenological simplification allows them to plausibly characterize the kinetic contributions of other potentially rate limiting mechanisms such as charge-transfer and ohmic resistances and to closely model the discharge performance of LiFePO$_4$ system across a wide spectrum of discharge conditions (Figure 2-6), the shrinking-core assumption itself has since been called into question by a number of researchers owing to a combination of theoretical, electrochemical and microstructural inconsistencies observed elsewhere.

Figure 2-5: Contributions to deviations from equilibrated discharge performance. Reproduced from Srinivasan et al. [2]
Problematic assumptions of the Shrinking Core model

A Thermodynamic Critique of the Shrinking Core Phase Transformation Geometry

In a recent work Meethong et al. argue against the plausibility of the shrinking core model on two grounds. First, they argue that the circumferential shell of uniform thickness implied by the model requires that “the first infinitesimal increment in (new phase volume) requires a finite interfacial area (the sphere area) for the spherical shell configuration”. [4] Meethong et al. suggest instead a more plausible nucleation geometry, one in which a phase transformation proceeds from a finite spherical cap of infinitesimal extent. They develop this alternative geometry further by exploring the relative phase-transformation energies implied by either model.

Thermodynamically, the molar free energy of coexisting phases in the absence of elastic energy can be described by Equation 2-2.

\[ ZF \Delta \phi = -\Delta \mu_i \]

Equation 2-2
Where $Z$ represents the magnitude of the charge on the diffusing species (in this case equal to 1), $F$ represents Faraday’s constant, $\Delta \phi$ represents a difference in electrical potential and $\Delta \mu$ represents the difference in chemical potential of the Li$^+$ ions at the surface of the coexisting phases. This relationship can be represented schematically in the form of a plot of chemical potential ($\mu$) vs. degree of intercalation ($x$) as shown in Figure 2-7 below.

![Figure 2-7: Schematic representation of variations in free energy as a function of degree of intercalation in a biphasic cathode. Reproduced from Meethong et al. [4]](image)

Meethong et al. next consider the energetics necessarily entailed by a shrinking core account of phase transformation in which, “the geometry of the two interfaces within the particle does not permit sliding (e.g. a spherical shell surrounding a sphere of one phase)” In this case the elastic energy stored at the interface due to the volumetric discontinuity between the isostructural phases (a feature ignored by the shrinking core model) gives rise to an increase in the system’s potential energy, introducing an additional term to the molar free energy equation as shown in Equation 2-3 below:
\[ ZF \Delta \phi = -\Delta \mu_f + \frac{V_M}{C} \frac{\partial u_{\text{elastic}}}{\partial V_f} \]

Equation 2-3

Where \( V_f \) is the volume fraction of the new phase in a total volume \( V_T \), \( C \) is the number of Li\(^+\) ions necessary to convert the old phase into the new phase, \( V_M \) is the molar volume of the old phase and \( u_{\text{elastic}} \) is the elastic energy per \( V_T \). By employing the shrinking core assumption and approximating the particles as spheres an exact solution for the \( u_{\text{elastic}} \) term can be calculated as shown in Equation 2-4 below:

\[ u_{\text{elastic}} = \frac{\left( \frac{\Delta V_M}{\Delta V_M^f} \right)^2 \cdot EV_j \cdot (V_f - 1)}{9(1 - \nu)} \]

Equation 2-4

where \( \Delta V_M = V_M^\text{II} - V_M^\text{I} \) is the difference in molar volume between the coexistent phases. Meethong et al. conclude from the foregoing analysis that the shrinking core model does not accurately describe the phenomenology of phase evolution for two reasons; 1) the onset of phase transformation entails, as mentioned above, an implausible nucleation geometry, and 2) there are alternative transformation geometries that are energetically favorable as depicted in Figure 2-8 below.
Yet while this proposed spherical cap nucleation geometry is energetically favorable for the reasons given above, there is scant spectroscopic evidence to support it. Still, the larger point remains: the phenomenology of phase evolution is not well-represented by the shrinking core model, thereby reopening the question of whether or not kinetic processes in phase transforming electrodes can be modeled without invoking a more plausible account of phase transformation geometries and kinetics. In fact Srinivasan and Newman clearly anticipated this possibility, stating that “further understanding of the phase evolution is needed in order to refine the model”. [2] As such, the following sections will consider additional experimental and analytical evidence describing the phenomenology and kinetics of phase transformation observed in a variety of Li⁺ intercalating compounds.

**Spectroscopic Evidence of Phase Transformation Limited Kinetics**

While spectroscopic evidence of phase transformation in Li⁺ intercalating compounds has appeared in the literature for years, it was not until quite recently that researchers began to investigate its effects upon discharge kinetics. Wagemaker et al. offered early evidence of the role phase transformation might play in their Li-7 MAS
NMR study of the Li$_x$TiO$_2$ anatase-titanate couple. Probing the site-hopping activities of Li$^+$ ions in chemically intercalated biphasic compounds of Li$_x$TiO$_2$ they observed a significant increase in local activation energies associated with Li$^+$ diffusion across the anatase-titanate phase boundary as depicted in Figure 2-9 below. [5] The observation of this energetic feature has several interesting implications. Firstly, it calls into question the suitability of conventional non-local or macroscale electroanalytic techniques for determining kinetic parameters in biphasic materials, (a subject we will return to in Chapter 5). The activation energies Wagemaker, et al determined for Li$^+$ site hopping in end member phases (.2eV and .09eV in the anatase and titanate phases respectively) differ significantly from the .5eV activation energy for Li$^+$ diffusion derivable from macroanalytic techniques such as GITT and PITT. Secondly, it suggests the possibility that phase boundary motion itself might be a rate limiting mechanism in biphasic intercalation compounds as the .5eV figure derived macroanalytically closely matches the activation energy Wagemaker et al found for Li$^+$ hopping across the anatase-titanate phase boundary.

![Figure 2-9: Activation energies for Li$^+$ diffusion in the Li$_x$TiO$_2$ system. Reproduced from Wagemaker et al. [5]](image)

Chang et al. have observed a similar deviation from equilibrium phase-structure-stoichiometry relations in the LiFePO$_4$/FePO$_4$ couple during moderate rate (C/10 - 1C) charge/discharge experiments. [6] Performing in situ synchrotron X-ray diffraction on electrochemically cycled mixed powder electrodes, Chang et al. observed a significant discrepancy between the expected phase population and the measured electrochemical signature. As can be seen in Figure 2-10, the appearance of second phase (LiFePO$_4$)
diffraction peaks were absent throughout almost the entire electrochemically biphasic discharge plateau in some experiments.

![Diffraction Peaks](image)

**Figure 2-10:** Coupled in situ diffraction and electrochemical cycling profiles for electrochemically cycled LiFePO₄. Reproduced from Chang et al. [6]

The authors attribute this discrepancy to two factors: 1) slow nucleation kinetics in the second phase, and 2) strong localized charge interactions which maintain a two-‘‘phase’’ interface between Li⁺-rich and Li⁺-lean domains which are, respectively, stabilized and energetically differentiated mainly by the coulombic interaction energy difference.

**Electrochemical Evidence of Phase Transformation Limited Kinetics**

**Impedance Techniques**

Hong et al, have employed a variety of electroanalytic techniques including Electrochemical Impedance Spectroscopy (EIS) to investigate the role of phase transformation in the LiFeMgPO₄ system.[7] A typical EIS experiment involves subjecting an electrochemically active system to a small AC perturbation over a wide range of frequencies (.01- 10,000Hz) at a fixed DC potential (corresponding, in monophasic regimes, to a narrow range of Li⁺ intercalation). If the magnitude of the AC perturbation is small (typically 5-10mV), the cell polarization should meet the linearity requirement for accurate EIS measurement. The advantage to this technique relative to
other electrochemical techniques is that it allows the rates of individual kinetic steps to be determined, provided that the time constants associated with those steps are resolvable. Yet, as Hong notes, the equilibrium potential hysteresis induced by phase transformation is often in the range of 10-30mV, as a result of which, phase transformation events go undetected by low magnitude AC perturbations. [8] By increasing the magnitude of the AC perturbation to 30mV (in excess of the 18mV two-phase potential hysteresis value Hong determined using GITT) Hong et al observe that, in biphasic regimes, an additional feature becomes manifest in the impedance plot. This feature, which they describe as an impedance loop, is evident only in two phase regimes and entirely absent in single phase regimes as shown in Figure 2-11.

Figure 2-11: Impedance curves for single (lower plots) and biphasic (upper plots) regimes following charge (left hand plots) and discharge (right hand plots) to 50% material utilization at AC amplitudes of 5, 10 and 30mV. Reproduced from Hong et al. [7]
Hong et al. develop an equivalent circuit comprised of three elements connected in series to model the EIS response curves, as depicted in Figure 2-12. In the equivalent circuit, resistance $R_S$ is used to simulate the contact resistance, electronic resistance in the electrode, and ionic conductive resistance in the electrolytes. The $(CPE1)-(RI)$ parallel components are used to simulate the impedance of the bulk electrode, and the $CPE_{ct}$ component paralleling the resistance $R_{ct}$ represents the impedance of the charge-transfer reaction with $W$ representing diffusion impedance. The phase transformation is simulated by an inductance $L$ paralleled with a resistance $(R_2)$. Hong et al. conclude from the foregoing that in otherwise kinetically fast materials (that is materials in which ionic, electronic and charge transfer processes are not rate-limiting) phase transformation plays an important role at high rates of discharge.

![Model Circuit](image)

Figure 2-12: Model Circuit. Reproduced from Hong et al.[7]
Potentiostatic Techniques

Another common electroanalytic technique employed by battery electrochemists is potential step chronoamperometry or PSCA. In a typical PSCA experiment an electrochemical cell is driven from equilibrium by stepping to a potential slightly positive or negative of the current equilibrated state, (a fuller account of which will be provided in Chapter 3). While this technique is often employed to extract kinetic parameters (when used in an intermittent manner roughly analogous to the GITT technique) the step magnitude of a single PSCA experiment can also be specified so as to fully transgress a known biphasic plateau. A number of researchers have fit the results of such large-step PSCA experiments to the Johnson–Mehl–Avrami equation to determine the geometry and rate-limiting mechanism of biphasic intercalation reactions. Allen et al., for example, advance the case of phase transformation rate-limited discharge kinetics in their study of the LiFePO$_4$ system. In their work they perturbed the system potentiostatically and analyzed the resultant chronoamperometric response using the Avrami-Johnson-Mehl-Erofeev (AJME) equation shown below.[9]

\[ f = 1 - \exp(-kt)^n \]

Equation 2-5

Where $f$ represents the volume fraction of the second phase, $k$ is a rate constant parameter, $t$ is time and $n$ is an exponent whose value depends upon the geometry of the transformation. Depending upon the value of the Avrami exponent the growth geometry can be determined to be either 1, 2 or 3-dimensional. By linearizing the response curve at three different temperatures Allen et al. determined the diffusion to be 1-dimensional, as shown in Figure 2-13. This finding is consistent with studies to be described later in this work.
Figure 2-13: Linearization of potentiostatic pulse responses at various temperatures for LiFePO$_4$. Reproduced from Allen et al. [9]

Allen et al. next proceed to determine the rate-limiting mechanism in this system by expanding the Avrami exponent as follows

$$n = a + bc$$

Equation 2-6

Where $a$ corresponds to the nucleation index (reflecting the time dependence of nuclei growth), $b$ corresponds to the dimensionality of the growth, and $c$ is a growth index dependant upon the rate-limiting step of the transformation process ($c=1$ in the case of phase boundary motion limited control, $c=1/2$ in the case of diffusion control). If $b$, is taken to be 1 (corresponding to the 1-dimensional growth result derived above) “the only possible values for $a$ and $c$ leading to $n=1$ are 0 and 1 respectively” corresponding to phase-boundary controlled kinetics. While Allen et al. seem reasonably confident in their findings, it bears mentions that the values for $a$ and $c$ determined above are not, in fact, the only mathematically possible values.[10] As such it is necessary to independently verify the transformation feature indicated by its index.

The Geometry of Lithium Intercalation and Phase Growth

Laffont et al. have investigated the dimensionality of Li$^+$ diffusion and phase growth in the nanoscale LiFePO$_4$/FePO$_4$ system. [11] In their work they employ a
combination of high-resolution transmission electron microscopy (HRTEM) and high-resolution electron energy loss spectroscopy (HREELS) to probe the chemical and valence states of the LiFePO$_4$/FePO$_4$ couple along a particle on the nanometer scale. They observed that regardless of whether or not the biphasic particles were obtained via intercalation or deintercalation (that is, irrespective of cycling history), the particle always consisted of a FePO$_4$ “core” surrounded by a LiFePO$_4$ “shell” as depicted in Figure 2-14.

Figure 2-14: Phase population in fractionally intercalated LiFePO$_4$. White represents the LiFePO$_4$ phase, black the FePO$_4$ phase and red the phase interface. Reproduced from Laffont et al. [11]

To address this apparent discrepancy with the isotropic shrinking core model employed by Srinivasan and Newman, Laffont et al. propose a 1-dimensional Li$^+$ diffusion model (consistent with the AJME results described above and the computational findings described below) and develop an alternative phase transformation model in which Li$^+$ insertion and extraction takes place by progressive filling and emptying of Li channels during intercalation and deintercalation respectively as shown in Figure 2-15.
This 1-dimensional intercalation mechanism suggested by Laffont et al. was confirmed by Ouyang et al. utilizing first-principles calculations. [12] The results obtaining from GGA for the activation energy for Li\(^+\) diffusion in LiFePO\(_4\) along the \(a\) and \(c\) axes (which correspond to the \(c\) and \(b\) axes respectively in Laffont et al.’s representation) are shown in Figure 2-16.

Figure 2-16: Energy change as a function of direction in LiFePO\(_4\). Reproduced from Ouyang et al. [12]

Further confirmation of Laffont et al.’s conclusions regarding the dimensionality of Li\(^+\) diffusion and phase growth in LiFePO\(_4\) appear in Chen’s spectroscopic study of
phase transformations in that system. [13] Chen et al. utilized TEM and HRTEM to investigate lattice mismatch in large, hydrothermally grown LiFePO$_4$ crystals that had been chemically lithiated by stirring in a solution of bromine in acetonitrile. Edge dislocations, a structural defect commonly associated with lattice mismatch between contiguous phases, are clearly visible along the $c$ axis in the left hand image in Figure 2-17. Fourier transforms of subsequent HRTEM images (not shown) probing regions on either side of the dislocation zone yield lattice data that closely corresponds to the well-resolved lattice parameters for the LiFePO$_4$ and FePO$_4$ phases.

Figure 2-17: TEM images showing domains in the Li$_{0.8}$FePO$_4$ crystal aligned with the $c$ axis. Reproduced from Chen et al. [13]
Chen et al. attribute these features of the TEM images to the formation of strong dislocation stress fields in the $ac$ plane upon delithiation. As $Li^+$ diffusion is energetically constrained to the $b$ axis (iterating the computational and experimental results mentioned above), the $ac$ plane is favored for phase boundary growth as depicted schematically in Figure 2-18.

![Figure 2-18: Schematic representation of the phase transition zone in the LiFePO$_4$ system. Reproduced from Chen et al. [13]](image)

The observation of anisotropic diffusion and phase growth is not limited to the LiFePO$_4$/FePO$_4$ couple. Iriyama et al., investigating the phenomenology of phase transformation in the $Li_xMoO_3$ system (a 2-dimensional system like $Li_xV_2O_5$) reported the absence of discrete phase boundaries at the onset of a phase transformation in electrochemically biphasic materials. [14] From TEM studies of chemically lithiated particles they observed, in lieu of a clear phase front, randomly distributed, deeply penetrating lattice expansions which could be dimensionally correlated to the $Li^+$-rich end member phase as shown in Figure 2-19 below. Coupled ex-situ x-ray diffraction experiments, which indicated a delayed onset of second phase growth in the electrochemically biphasic regime (similar to the results reported by Chang, et al. for the LiFePO$_4$ system described above) were rationalized in terms of this random distribution
of Li-rich material, the second phase remaining “invisible” to x-ray diffraction until the randomly arrayed galleries had multiplied sufficiently to become “visible” to x-radiation.

Figure 2-19: TEM micrographs of Li\(^+\) intercalation in MoO\(_3\). Reproduced from Iriyama et al. [14]

**Preliminary Conclusions Regarding the Phenomenology of Phase Transformation in Li\(^+\) Intercalating Compounds**

To this point we have considered both theoretical and experimental accounts of phase transformation in a variety of phase transition and phase transformation-solid solution Li\(^+\) intercalation hosts. While no single account of the phenomenology of phase transformation in these systems completely determines to role phase transformation might play in discharge kinetics, a preponderance of the evidence presented so far strongly argues against the simplified, “diffusion-resistance” limited, shrinking core geometry presented at the beginning of this chapter. In the following section we will consider a mechanistic account of the phase transformation process in a dimensionally graded LiFePO\(_4\) system that expressly situates rate-limited discharge kinetics at the phase boundary, with a view to expand upon and generalize those findings in subsequent chapters of this work.

**The Effects of Nanoscaling on Phase Transformation**

Quite recently a number of researchers have reported significantly modified insertion thermodynamics in nanoscaled transition metal oxide and transition metal phosphate systems. Wagemaker et al., revisiting the anatase-titanate couple, observed
both a significant increase in the Li$^+$-poor end-member’s single phase solubility as well as, below a particle size of about 120nm, the appearance of a new Li$_x$TiO$_2$ phase, (dubbed Li$_1$TiO$_2$), that was isostructural with the Li$^+$-poor end-member as shown in Figure 2-20.[15]

![Phase diagram](image)

**Figure 2-20:** Phase diagram for the LiTiO$_2$ anatase system showing variations in single phase Li$^+$ solubility and phase coexistence as a function of particle size. Reproduced from Wagemaker et al. [15]

Wagemaker et al. present the following account of variations in Gibb’s Free energy as a function of particle size to rationalize their observations. They proceed by augmenting the standard $\Delta G_{\text{mix}}(x)$ expression with a surface energy term

$$\Delta G_{\text{mix}}(x) = (x_2 - x_1)^{-1}((x_2 - x)G_1 + (x - x_1)G_2) - G(x) + A(x)\gamma_A/\nu_\text{Li}V$$

Equation 2-7

Where $x_1$ and $x_2$ are the composition limits of the end member phases, $G_1$ and $G_2$ are the free energies in the Li$^+$-poor and Li$^+$-rich phases respectively, $G(x)$ is the free energy for the solid solution state, $A(x)$ is the degree of intercalation dependant interfacial surface area, $\gamma_A$ the surface energy due to strain, $\nu_\text{Li}$ the molar volume of inserted Li$^+$ and $V$ is the
volume of the particle. Between the end-member solubility limits (that is when \( x_1 < x < x_2 \)) \( \Delta G_{\text{mix}} \) will be negative, favoring phase coexistence. As particle size decreases, according to the above expression, the energetic contribution from the strain energy term will increase (\( A(x) \) scales with \( r^2 \) while \( V \) scales with \( r^3 \) where \( r \) is the particle radius) destabilizing two phase coexistence in smaller particles and resulting in enhanced solubility in the anatase phase. An unexpected outcome of this energetic account is that below a particular particle dimension the single phase domain size in the biphasic regime is isovolumetric with particle size, suggesting that below a particular particle size a given particle is entirely monophasic, with the balance of coexistent phases distributed between discrete nanoscale particles. This feature of Wagemaker et al.’s analysis is depicted graphically by restating the \((\alpha + \beta)\) notation in Figure 2-20 (corresponding to intraparticle biphasicity) as \((\alpha) + (\beta)\) below a particle size of ~50nm.

Meethong et al. report similar thermodynamic enhancements to end-member single-phase solubility (or biphasic miscibility) in an XRD study of the nanometrically graded LiFePO\(_4/\)FePO\(_4\) insertion couple as show in Figure 2-21.[16]

![Figure 2-21: Variations in phase miscibility as a function of particle size and temperature in the LiFePO\(_4\) system where Sample A has a particle size of 42nm, Sample B a size of 34 nm and Sample C a size of 113nm. Reproduced from Meethong et al. [16]](image-url)
This increase in end-member solubility (or nonstoichiometry) has important electrochemical consequences. As Meethong et al. demonstrate, the potentiodynamic profiles for dimensionally graded particles at quasi-equilibrium rates of charge and discharge (C/50-C/100) exhibit more gradual variation between monophasic and biphasic regimes with decreasing particle size, as shown in Figure 2-22. While such variations in discharge performance are commonly ascribed to kinetic effects, Meethong et al argue that, for the nanoscale particle, this more gradual sloping is a direct consequence of enhanced end-member nonstoichiometry. To confirm this hypothesis the authors perform a simple PITT experiment (not shown) which confirms that sample NC (the nanoscale particle) indeed exhibits greater electrochemically induced nonstoichiometry than sample AC.

Figure 2-22: Variations in cell potentiodynamics for 40nm (sample NC) and 113nm (sample AC) LiFePO₄ particles during quasi-equilibrium rates of discharge. Reproduced from Meethong et al. [16]
In a follow-up paper the same group observed that strain within end-member phases in the biphasic regime in nanoscale particles was significantly increased relative to sub-microscale particles, a feature which they attributed to a relaxation of the strain boundary conditions in nanoscale particles, as shown in Table 2-1. [4] Larger scale particles, they argue, relax excess strain by undergoing phase transformation at smaller and larger degrees of end-member lithiation respectively, resulting in lower interfacial strain but higher lattice mismatch between coexistent phases. Nanoscale particles on the other hand, maintain a coherent interface, resulting in enhanced local strain but more facile phase-boundary evolution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LFP</th>
<th>FP</th>
<th>Strain (%)</th>
<th>Crystalline Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A*</td>
<td>a (Å)</td>
<td>b (Å)</td>
<td>c (Å)</td>
<td>V (Å³)</td>
</tr>
<tr>
<td></td>
<td>10.266</td>
<td>5.979</td>
<td>4.706</td>
<td>288.85</td>
</tr>
<tr>
<td></td>
<td>9.860</td>
<td>5.829</td>
<td>4.774</td>
<td>274.38</td>
</tr>
<tr>
<td>Sample B**</td>
<td>LFP</td>
<td>FP</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.308</td>
<td>5.997</td>
<td>4.670</td>
<td>290.53</td>
</tr>
<tr>
<td></td>
<td>9.854</td>
<td>5.815</td>
<td>4.787</td>
<td>274.31</td>
</tr>
<tr>
<td>Sample C***</td>
<td>LFP</td>
<td>FP</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.329</td>
<td>6.007</td>
<td>4.691</td>
<td>291.02</td>
</tr>
<tr>
<td></td>
<td>9.827</td>
<td>5.794</td>
<td>4.783</td>
<td>272.36</td>
</tr>
</tbody>
</table>

Table 2-2: Variation in lattice parameter, unit cell volume and interfacial strain in dimensionally graded, partially discharged LiFePO₄ cathodes where Sample A has a particle size of 42nm, Sample B a size of 34 nm and Sample C a size of 113nm. Reproduced from Meethong et al. [4]

This last result, Meethong et al. argue, explains the significant enhancement in rate performance they and others have observed in nanoscale LiFePO₄ particles. As shown in Figure 2-23, the 40nm particles (NC) exhibit 50% greater discharge capacity at high rates (10C) of discharge than the 113nm particles (AC). This result, they argue, is at variance with Fickian scaling laws which attribute increased rate performance with decreased particle size to reductions in the diffusive path-length. And while the diffusive path length is indeed reduced in these nanoscale particles, that feature alone cannot account for the total increase in rate performance. Rather, the improved rate performance is believed to derive principally from the enhanced end-member nonstoichiometry which
results in reduced lattice mismatch between coexistent phases and facilitated phase boundary motion across a coherent phase interface. The necessary corollary to this finding is that phase transformation, as suggested by Ma and others, is rate-limiting in microscale phase transition compounds.

![Graph showing variations in discharge capacity for galvanostatically discharged 40nm (NC) and 113nm (AC) LiFePO₄ particles.](image)

**Figure 2-23**: Variations in discharge capacity for galvanostatically discharged 40nm (NC) and 113nm (AC) LiFePO₄ particles. Reproduced from Meethong et al. [16]

While the preceding section makes a compelling case for phase transformation limited discharge kinetics in Li⁺ intercalating compounds, as argued by Ma and others, work remains to be done, specifically as regards the quantification of the kinetic impediment imposed by phase transformation in microscale particles. The remainder of this chapter will discuss the LiV₂O₅ system, preparing the ground for a more detailed account of the interaction between phase boundary motion kinetics and particle size in that system.
The Vanadium Oxide System

The Structure of V$_2$O$_5$

Vanadium pentoxide (V$_2$O$_5$) was selected as a model system for this work due to its stability, relative safety, low cost, ease of synthesis, and high energy density. V$_2$O$_5$ crystallizes into an orthorhombic structure characterized by parallel layers of edge and corner sharing VO$_5$ square pyramids aligned perpendicular to the $c$ axis, as shown in Figure 2-24. During electrochemical cycling, Li$^+$ ions intercalate into and deintercalate from the galleries between these layers along the $ab$ plane. Concurrently, vanadium atoms located in the vicinity of the intercalated Li$^+$ ions are reduced from V$^{5+}$ to V$^{4+}$ during discharge and oxidized from V$^{4+}$ to V$^{5+}$ during charge.[17]

![Figure 2-24](image)

**Figure 2-24:** Showing a) the layered structure of V$_2$O$_5$ and b) the five-fold V-O coordination. Reproduced from Li et al. [18]

The four equatorial V-O bond lengths in crystalline V$_2$O$_5$ are approximately 2Å, while the fifth, apical bond is somewhat shorter, 1.54Å, corresponding to a double bond. [19]

The V$_2$O$_5$ structure can alternatively be described in terms of distorted VO$_6$ octahedra, with a considerably longer sixth V-O bond (2.81Å) in the $c$-direction maintained by weak electrostatic interactions as shown in Figure 2-25.
The Electrochemistry of V_2O_5

During quasi-equilibrated galvanostatic discharge microscaled Li_xV_2O_5 particles undergo a series of structural modifications commensurate with variations in the system’s potentiodynamic response, the later of which is depicted in Figure 2-26 below.

At the onset of discharge only the Li-poor \( \alpha \)-V_2O_5 phase is present. At considerably less than 0.1 Li\(^+\) per formula unit of V_2O_5 the galvanostatic profile deviates from a smooth downward slope (characteristic of a monophasic regime) into a flat plateau, indicative of the nucleation of a second phase, \( \varepsilon \)-Li_xV_2O_5. These two structurally similar phases, depicted in Figure 2-27, coexist until between 0.3-0.4 Li\(^+\) per formula unit of V_2O_5 has been intercalated into the particle, at which point the galvanostatic profile sharply deviates from the flat, biphasic plateau and follows a steep downward slope.
At approximately 0.5 Li\(^+\) per formula unit V\(_2\)O\(_5\), another Li\(_x\)V\(_2\)O\(_5\) phase (\(\delta\)-Li\(_x\)V\(_2\)O\(_5\), shown in Figure 2-28) nucleates and the galvanostatic profile flattens again until approximately 0.9 Li\(^+\) per formula unit V\(_2\)O\(_5\) has been intercalated. Beyond 1.0 Li\(^+\) per formula unit V\(_2\)O\(_5\), (corresponding to a potential of 2.5V vs. lithium metal) a number of other phase transformations take place, all of which are known to result in structurally irreversible changes in the system, thereby restricting its utility as a reversible cathode material to the 3.6-2.5V range. [19]
In addition to these structural effects, the insertion of Li\(^+\) ions into V\(_2\)O\(_5\) has other kinetic consequences. As the battery is discharged V\(^{5+}\) ions present in the neat oxide are reduced to V\(^{4+}\) by Li\(^+\) charge compensating electrons from the anode. Electronic conduction, which occurs via electron hopping between V\(^{4+}\) and V\(^{5+}\) ions increases with the amount of V\(^{4+}\) present in the oxide. At an insertion ratio of 0.02 Li\(^+\) per formula unit V\(_2\)O\(_5\), (or 1% V\(^{4+}\) per formula unit), for example, the oxide’s conductivity is 4 × 10\(^{-5}\) S/cm while at 0.2 Li\(^+\) per formula unit V\(_2\)O\(_5\) (or 10% V\(^{4+}\)) the conductivity increases to 2 × 10\(^{-3}\) S/cm. \[^{[21]}\] Other reports put the conductivity of unlithiated V\(_2\)O\(_5\) at ~1.0 x 10\(^{-3}\) S/cm, increasing to approximately 1.0 x 10\(^{-2}\) S/cm at 20% lithiation (Li\(_{0.2}\)V\(_2\)O\(_5\)) and falling to 1.0 x 10\(^{-4}\) S/cm in fully lithiated LiV\(_2\)O\(_5\). \[^{[22]}\] Concurrently, the diffusion coefficient for Li\(^+\) ions in the bulk host material, (both within single phases and between structurally distinct phases), evolves. Mui et al, have demonstrated this feature of the Li\(_x\)V\(_2\)O\(_5\) system using the galvanostatic intermittent titration technique (GITT). \[^{[23]}\] Their results are show in Figure 2-29.

\[ y\text{Li}^+ + \text{Li}_x\text{V}_2\text{O}_5 + ye^- \rightarrow \text{Li}_{x+y}\text{V}_2\text{O}_5 \]

\[^{\text{Equation 2-8}}\]

Figure 2-29: Showing the evolution of the diffusion coefficient in Li\(_x\)V\(_2\)O\(_5\) as a function of degree of intercalation. Diffusion values determined using GITT are only valid in the single phase (\(\alpha, \varepsilon\) and \(\delta\)) regimes. Reproduced from Mui et al. \[^{[23]}\]

The overall reaction for the insertion of lithium into vanadium oxide particles during discharge is:

\[ y\text{Li}^+ + \text{Li}_x\text{V}_2\text{O}_5 + ye^- \rightarrow \text{Li}_{x+y}\text{V}_2\text{O}_5 \]

Or, with the valence state of vanadium taken into consideration:
The reverse reactions obtain during charge.

**Rate performance in the microscale Li$_x$V$_2$O$_5$ system**

With an average open circuit potential of 3.3 V and a theoretical intercalation capacity of 147 mAh/g, V$_2$O$_5$ has long been considered a strong candidate material for Li-ion secondary cells. One factor that hampers the practical applications of V$_2$O$_5$, though, is the significant capacity fading observed during cycling. This capacity fading has been variously attributed to low electronic conductivity, poor Li$^+$ diffusivity and structural collapse during long term cycling. Another characteristic of the Li$_x$V$_2$O$_5$ chemistry that limits its broader application is its relatively poor rate performance, as depicted in Figure 2-30 at various rates for discharge ranging from C/15 to 4.5C.
Figure 2-30: Characteristic variations in discharge performance as a function of discharge rate for a CVD prepared LiV$_2$O$_5$ thin film (800nm) battery. Reproduced from Lantelme et al [24]

This rate performance limitation will be addressed in the next section, which briefly surveys recent innovations in materials processing approaches intended to enhance rate capability in the Li$_x$V$_2$O$_5$ system.
Nanostructured V$_2$O$_5$

As mentioned at various points in this work, it is widely believed that rate performance in many Li$^+$ ion intercalating compounds is constrained by bulk Li$^+$ diffusion. As such a number of researchers have attempted to improve rate performance in these materials through particle size reduction, effectively decreasing the diffusion penetration time as expressed by the $\tau = L^2/D$ relationship mentioned in chapter 1. To this end a number of different approaches have been employed, including ballistic deposition, supercritical drying of sol-gels to produce high surface to volume xerogels and aerogels, high energy ball-milling and nanotemplated growth. [25-29] As this work employs the later technique exclusively to achieve nanoscale materials, it alone will be described in detail.

Simply, template based synthesis of nanostructured materials entails deposition of the material of interest within the pores of a microporous template membrane. Patrissi et al, have employed this technique to prepare nanostructured V$_2$O$_5$. [28] In their work they seek to enhance the volumetric energy density of nanotemplated V$_2$O$_5$ by chemically etching the template membrane prior to template synthesis in order to increase its porosity. Etching was performed by submersing commercial template membranes into a NaOH bath for two minutes before removal and quenching in deionized water. The etched templates were then dried under vacuum at room temperature for 1 hour. The dried template was then placed on a Pt foil (to serve as the current collector) and a V$_2$O$_5$ precursor was applied to the membrane. The assembly was then hydrolyzed in the side arm of a glove box for 10 hours. Finally, the polycarbonate membrane was removed by heating in air at 70°C for 2 hours and then placing the assembly into an oxygen plasma. The resulting films, which were comprised of V$_2$O$_5$ fibrils approximately 250nm in diameter, were then assembled into three electrode cells and cycled galvanostatically at various rates, the results of which can be seen in Figure 2-31.
Figure 2-31: Discharge performance of nanostructured V2O5 at various C-rates. Reproduced from Patrissi et al. [28]

Comparing the discharge performance of 250nm thick nanotemplated V2O5, (as depicted in Figure 2-31), with the results shown for microscale (approximately 800nm thick film) V2O5 in Figure 2-30 it is clear that the nanostructured material offers far superior rate performance. In the prior work, a factor of 70 increase in discharge rate results in a potentiodynamic profile that shows clear evidence of rate limitation, whereas, in Patrissi et al’s work, the nanostructured V2O5 retains its quasi-equilibrated potentiodynamic features upon a factor or 400 increase in discharge rate (despite an evident loss of capacity). This finding is largely consistent other results characterizing the performance enhancement associated with nanoscaling in the Li_xV_2O_5 system. [29, 30] It bears mentioning that Patrissi et al. attribute this enhancement entirely to reduction in the Li^+ diffusion path length, a conclusion whose validity is the principal subject of this work.

Summary and Introduction to the Next Section

This work investigates the role of phase transformation in rate-limited Li^+ ion intercalation compounds. The Li_xV_2O_5 cathode has been selected as a model system for
this investigation. A survey of the literature demonstrates that, while progress has been made, the phenomenology and kinetic consequences of phase transformation in these systems is not entirely well understood. A recent attempt to model rate performance in the LiFePO\textsubscript{4} system fails to capture the apparent complexity of the phase transformation process and, as a result, fails to properly address the potentially rate-limiting effects of these events. Thermodynamic, spectroscopic and electrochemical evidence strongly suggest that phase transformation may in fact be rate-limiting in a number of Li\textsuperscript{+} ion intercalating compounds and that the nanoscaling of intercalation hosts may allow for these limitations to be bypassed (though there is some debate regarding the microscale mechanism responsible for this improvement). The next chapter will survey the analytical techniques employed in this research.

References

7. Hong, J.; Wang, C. S.; Kasavajjula, U., Kinetic behavior of LiFeMgPO\textsubscript{4} cathode material for Li-ion batteries. *Journal of Power Sources* 2006, 162, (2), 1289-1296.


Chapter 3: Processing and Characterization Techniques

This chapter describes the materials processing and characterization techniques employed in this research. The first section presents two approaches to particle size reduction used in this work. The second section provides details on cathode film preparation and electrochemical cell assembly. The final two sections describe the electrochemical and spectroscopic techniques employed in characterizing the active material particles, cathode thin films and full cells, providing theoretical background where appropriate.

Particle Size Reduction

In order to investigate the role of particle size on end-member solubility and phase boundary kinetics two approaches to particle size reduction were employed in this work; mechanical ball milling and nanotemplating.

Ball Milling

Nanoscale V$_2$O$_5$ powder was prepared by ball-milling. The starting material (10 mesh V$_2$O$_5$, 99.2%, Alfa Aesar) was placed in a 500 ml Nalgene bottle with zirconia milling media (weight ratio of active material to milling media 1:20) and acetone. Milling was carried out on a standard roller-mill for times ranging from 4-24 hours at a high rate of revolution. Once milling was complete the V$_2$O$_5$/acetone mixture was poured into a glass crystallizing dish in a fume hood where acetone was allowed to evaporate for 24 hours before powder recovery and hand grinding in an agate mortar. Ground powders were transferred to a ceramic crucible and placed in a furnace where they were calcined in air at 300°C for 6 hours. Processed powders were then deposited onto a glass slide for x-ray diffraction to confirm phase purity. Using XPS and XRD Guimarães et al. have shown nanoparticulate V$_2$O$_5$ prepared by ball-milling to be single phase and free of chemical impurities. [1]

Nanotemplating process

The nanotemplating process described in the work was developed by Dr. Elsa A. Olivetti and co-workers at the Massachusetts Institute of Technology. [2] Co-assembled nanocomposite materials were obtained by first dissolving 5 wt % POEM-b-PBMA, (a
microphase-separated, block polymer with a domain periodicity of ~35 nm), in acetone. Varying amounts (20-60 wt%) of the precursor vanadyl triisopropoxide, VO(OC3H7)3 (VO-(OiPr)3, Gelest), were added to the polymer solution, and the resulting solutions were stirred for 30 min. To catalyze the sol-gel process, deionized water was added, maintaining the mole ratio of H2O/V at 40:1. After stirring for 1 h the solutions were solvent cast into Teflon dishes and dried in air at room temperature under glass Petri dishes to slow the evaporation process. After air-drying for at least 48 h, films were heated under vacuum at 80 °C overnight to remove residual solvent. This procedure is represented schematically in Figure 3-1.

Figure 3-1: Scheme for growth of vanadium oxide in situ in the polymer domains to prepare composite films. Reproduced from Olivetti. [2]

To remove the templating polymer the dried films were heated at 400°C in Argon and then again at 400°C in air, which resulted in some particle coarsening (10nm to 60nm) but ensured a high concentration of 5+ vanadium.

**Cathode Film Preparation**

V2O5 powders of various particle sizes were hand mixed in an agate mortar with 10 weight percent Carbon Black (Super P) and 10 weight percent polyvinylidene fluoride (PVDF) purchased from Kynar. 1 gram of the mixed powder was then placed in a small glass vial with approximately 200 weight percent 1-methyl-2-pyrrolidinone (NMP) purchased from Sigma Aldrich. The vial was sealed and placed into an oven at 100°C for
15 min to accelerate dissolution of the PVDF. Once fully dissolved the resultant slurry was blade cast onto Al foil taped to a large glass slide to ensure uniform thickness in the final film. The cast film was allowed to evaporate in a fume hood for 24 hours before being placed in a vacuum oven at 110 degrees for 1-2 hours. Individual cathodes were punched from the cast film using an 11mm punch and transferred to a glove box for final cell assembly.

**Electrochemical Characterization Techniques**

**Cell Preparation**

Test cells were assembled in an argon-filled glove box with moisture levels below 6.0 ppm. The two-electrode cells used in galvanostatic cycling, GITT and PITT measurements consist of stainless steel plugs as current collectors within PTFE sleeves sealed with brass lids as shown schematically in Figure 3-2. 0.7 mm thick lithium foil, purchased from VWR Scientific, was used as an anode and Celgard 1240 was used as a separator. 1 M LiPF₆ dissolved in a 50/50 wt% mixture ofethylene carbonate (EC) and ethyl methyl carbonate EMC (EM Industries, Inc.) was used as an electrolyte. The fully assembled cells were wrapped in ParaFilm and housed in plastic containers to prevent moisture from altering measurements.

![Schematic of coin cell housing used in battery testing. Reproduced from Olivetti.][1]

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[1]: Figure 3-2: Schematic of coin cell housing used in battery testing. Reproduced from Olivetti. [2]
Tests were performed as indicated on either a Solartron 1286 or 1287 potentiostat (Solartron Analytical, Oak Ridge, TN) and controlled by a PC running CorrWare (Scribner Associates, Inc., Southern Pines, NC) or a MACCOR 4000 Series 32 Channel system. Impedance spectroscopy was measured using a frequency response analyzer (Solartron 1255, Solartron Analytical, Oak Ridge, TN), coupled to a potentiostat (Solartron 1287, Solartron Analytical, Oak Ridge, TN) and controlled by a PC running commercially available software (Zplot, Scribner Associates, Inc., Southern Pines, NC).

**Galvanostatic Cycling and Fractional Intercalation**

Rate performance was measured by galvanostatic discharge experiments. Cells were initially held at 3.6V vs. metallic lithium for 1 hour before discharging at a C/20 rate (based up active material mass) to ensure electrochemical homogeneity between cells and to correct for any variations in cell assembly that might result in the electrochemical isolation of active cathode materials. Following two more full cycles at a C/20 rate individual cells were discharged at rates of C/10, C/5, C, 5C and 10C for up to 20 cycles in cycling experiments. For fractional intercalation experiments the same conditioning steps were following, followed by C/20 galvanostatic discharge to pre-specified degrees of intercalation. Fractionally intercalated cells were then allowed to dwell at OCP for 4 hours to ensure that cells were well-equilibrated prior to disassembly and rinsing with anhydrous acetonitrile in an Ar-filled glove box.

**Galvanostatic Intermittent Titration (GITT)**

The GITT or galvanostatic intermittent titration technique, first described by Weppner and Huggins in 1977, is commonly employed to probe diffusion kinetics and establish equilibrium cycling performance. [3] This technique involves the application of fixed current $I_o$ for a specified interval $\tau$, the product of which is equivalent to some small fixed increment of the full range of Li$^+$ intercalation, typically 0.1-1.0%. In a GITT experiment the application of a current pulse will induce a time-varying potential, $E(t)$, response as depicted in Figure 3-3 below (in the case of a charging current).
Figure 3-3: Galvanostatic stimulus and potentiodynamic response vs. time for the GITT technique. $\Delta E_t$ is the transient potentiodynamic response. $\Delta E_s$ is the steady state change in the equilibrated cell potential.

If the pulsing current is sufficiently small, values for the diffusion coefficient ($D_{chem}$) can be extracted from the potentiodynamic pulse response curves, provided that a) the diffusion coefficient does not change during the galvanostatic increment, b) the diffusion process can be approximated by a simple 1-D geometry c) Fickian dynamics obtain and d) the pulse duration is short enough that the particle behaves as a single phase, semi-infinite solid throughout the experiment. [4] This last constraint is captured by the following expression:

$$\tau \ll L^2/D$$

Equation 3-1

where $\tau$ is the pulse duration, $L$ is the diffusion path length (the radius, for example, of a spherical particle) and $D$ is the diffusion coefficient. In a diffusion limited, monophasic system that satisfies the above constraints the potential ($E$) will vary linearly with the square root of time.

However, it has been observed that deviations from linearity in this relationship across the full potential range (that is, including both monophasic and biphasic regimes) subject to high current pulsing (C and 5C rates) can be correlated with the phase state of the active material. Further, as will more fully developed in Chapter 5, these deviations from linearity seem to exhibit behavior characteristic of phase nucleation and growth.
Potentiostatic Intermittent Titration (PITT)

The PITT or potentiostatic intermittent titration technique, also developed by Weppner and Huggins, differs from the GITT technique in that the perturbing force is a potential step and the response is a time-varying current. [5] Solving Fick’s second law, subject to the appropriate boundary conditions, allows both the concentration and current profiles as a function of time to be calculated in terms of the diffusivity. The diffusivity can then be backed out of the following expression, known as the Cottrell equation, which describes a diffusion-controlled reaction at a planar electrode [6]

\[ I(t) = zFs(cs - c_o) \left( \frac{D_{PITT}}{\pi t} \right)^{1/2} \]

Equation 3-2

Where \( I(t) \) is the chronoamperometric pulse response, \( z \) in the magnitude of the charge on the diffusing species, \( F \) is Faraday’s constant, \( s \) is the cross-sectional surface area of the cathode, and \( (cs - c_o) \) is the difference in concentration at the cathode surface at times \( t \) and \( t_o \) respectively which should be constant due to the constant potential boundary condition. [4] As values of \( c_s(t) \) are impossible to measure experimentally, its value is estimated by integrating the total charge transferred over time (\( \Delta Q \)) once the system has completely equilibrated following a potential step as follows

\[ \Delta Q = \int_{0}^{t} I(t) dt = zFnV_M (cs - c_o) \]

Equation 3-3

Where \( V_M \) denotes the molar volume of the Li\(^+\) intercalating species.

While PITT is commonly employed to determine kinetic parameters and establish equilibrium potentiodynamic response (in a manner analogous to the GITT technique described above) in this work PITT is utilized primarily to determine the single phase capacity (or solubility limit) in end-member phases. PITT is preferred to GITT for this type of experiment as the \( V_2O_5 \) system undergoes a first-order phase transition at low degrees of Li\(^+\) intercalation (0.01-0.1 Li\(^+\) per formula unit \( V_2O_5 \)). The current pulsing
employed in the GITT technique inherently leads to an increase in overpotential, which could introduce hysteresis effects due to the nucleation of a second, Li⁺-rich, phase. [7]

**Potential Step Chronoamperometry (PSCA)**

PSCA is a variant of the PITT technique in which a small single potential step is specified so as to circumscribe the potential regime of interest, (for example, a phase transition in a biphasic compound). Chronoamperometric response data can then be fitted to one of a number of different models to determine the rate-limiting mechanism within a particular intercalation regime. Levi et al. have applied both Cottrell and moving boundary models to chronoamperometric response data to determine regimes of kinetic control in phase-transforming graphitic intercalation electrodes. Their results are shown in Figure 3-4.

![Figure 3-4: Chronoamperometric curve for graphite electrode discharged potentiostatically across a biphasic plateau.](image)

**Electrochemical Impedance Spectroscopy (EIS)**

Impedance measurements involve subjecting an equilibrated electrochemical system to small ac potential perturbations (typically 5-10mV) across a wide range of frequencies (10kHz-0.01Hz). If the various relaxation processes (charge transfer, bulk
ionic diffusion, etc.) are time-separable the electrical behavior of a battery can be modeled by discrete circuit elements such as resistors or capacitors in series and/or parallel where each of these elements represents a physical processes occurring within the cell. [9]

Impedance measurements were performed using a three electrode cell, as shown in Figure 3-5 with an electrolyte of 1 M LiPF₆ dissolved in a 50/50 wt% mixture of ethylene carbonate (EC) and ethyl methyl carbonate EMC. Lithium metal was used both as a reference electrode (RE) and counter electrode (CE). The working electrode (WE) consisted of a V₂O₅ mixed powder cathode that was prepared according to the methods described above and cast onto a Au-coated glass slide. The three electrode cell was assembled in an Argon filled glove box prior to testing. Argon was pumped continuously through a fourth port (not shown) in the cell to prevent reactions between cell components and air.

![Figure 3-5: Schematic representation of a 3-electrode cell used in electrochemical impedance spectroscopy.](image)
EIS was also performed on pure, dimensionally graded V_2O_5 pellets using blocking electrodes. Pellets with a diameter of 9.5mm and varying thicknesses were prepared by die-pressing loose powders at 250MPa for 10 min. The pellets were then coated with Ag paste and sandwiched between stainless steel blocking electrodes. EIS measurements were conducted over a frequency range of 32MHz-1Hz with a sine wave amplitude of 50mV. Values for the electronic conductivity of additive free bulk oxide power were calculated using an equivalent circuit model proposed by Jamnik and Maier.[10]

**Ex situ Characterization Techniques**

**X-Ray Diffraction**

For X-ray diffraction structural analysis, fully assembled cells were subject to three galvanostatic conditioning cycles at C/20 before being discharged at a C/20 rate for a time commensurate with a predetermined degree of Li^+ intercalation. Discharged cells were then transferred to an Ar-filled glove box (H_2O < 6ppm) where they were carefully disassembled. Cathode films were rinsed 3 times with anhydrous acetonitrile (99.8%, Alfa Aesar) and allowed to dry overnight before removal from the glove box. Fractionally intercalated mixed powders were then scraped from the Al foil onto a glass slide using a razor blade. The polymer bound powders were then finely chopped using the same razor blade and deposited onto the center of a Vaseline coated zero background sample slide. 10 wt% corundum powder (NIST SRM 676) was mixed into a batch of pure, microscale V_2O_5 powder for use as an internal standard. X-ray patterns were obtained using a Rigaku RTP500RC instrument with a rotating anode and CuK_α radiation and were slow-scanned at 0.15°/min over a 2θ range from 10 to 80°. The structural parameters were refined by Rietveld analysis using PANalytical X’Pert HighScore Plus software.

**Electron Spectroscopy**

Scanning electron microscopy (SEM) was performed on uncycled cathode films. The samples were mounted with carbon tape onto aluminum posts. The microscopy was performed on a JEOL 6320FV Field-Emission High-resolution SEM at 1 kV.
BET

The surface area of the samples was determined using the Brunauer, Emmet and Teller technique on a Micrometrics ASAP2020 instrument. Prior to the measurement, the samples underwent degassing for 2 hours under flowing nitrogen at 100°C.

References

Chapter 4: Equilibrium Signatures of Phase Transformation Controlled Rate Performance in Dimensionally Graded V\textsubscript{2}O\textsubscript{5}

This chapter describes variations in the electrochemical performance of Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} cathode films as a function of the active material particle size employed in the mixed power cathode assembly. It begins by comparing the spectroscopic features of the three particle sizes under consideration and continues with a demonstration of the correlation observed between enhanced high rate capacity and reduced particle size. In the following sections, it systematically considers the various kinetic consequences normally ascribed to size-scaling in Li\textsuperscript{+} intercalating compounds, and assesses their role in the rate-limited discharge performance observed in the Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} system. It concludes with a consideration of the role phase boundary motion is believed to play in limited high-rate performance in Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} battery cathodes.

Particle Size and Structural Analysis

Three dimensionally distinct batches of V\textsubscript{2}O\textsubscript{5} particles were prepared according to the size reduction techniques described in Chapter 3. The three materials are designated as follows: as-received V\textsubscript{2}O\textsubscript{5} (AR), 24 hour ball-milled V\textsubscript{2}O\textsubscript{5} (BM24) and nanotemplated V\textsubscript{2}O\textsubscript{5} (NT). Prior to film deposition and full cell assembly neat V\textsubscript{2}O\textsubscript{5} particles were subject to XRD analysis to confirm phase purity and to investigate possible variations in structural parameters between dimensionally graded materials. As shown in Figure 4-1, all three samples appear to be single phase V\textsubscript{2}O\textsubscript{5} (unidentified peaks, common to all three samples, are designated by an asterisk). While it has been reported in earlier work that up to 15\% of the vanadium atoms in the NT sample have been reduced from the V\textsuperscript{5+} valence state (characteristic of the fully oxidized α-V\textsubscript{2}O\textsubscript{5} phase) to V\textsuperscript{4+} as a result of template burnout in a reducing environment, no evidence of the structurally distinct ε-Li\textsubscript{x}V\textsubscript{2}O\textsubscript{5} phase (commensurate with vanadium reduction at very low degrees of lithium incorporation) is observed in the diffraction results.[1]
Rietveld analysis was also performed to determine lattice parameters. Variations in lattice parameters, referenced to the as-received (AR) form of V$_2$O$_5$, are included to simplify comparison between dimensionally graded particles. The results of this analysis are shown in Table 4-1. Li et al. and others have predicted highly anisotropic Li$^+$ diffusion in Li$_x$V$_2$O$_5$ using computational simulations. [2, 3] Mui et al. have confirmed these findings in differentially oriented, sputter-deposited V$_2$O$_5$ thin films. [4] As such it bears mentioning that all three samples show consistent variations in peak intensity throughout the diffraction spectra, indicative of textural uniformity as a function of particle dimension.

Table 4-1: Lattice parameters for uncycled, dimensionally graded V$_2$O$_5$ particles.

<table>
<thead>
<tr>
<th></th>
<th>AR</th>
<th>BM24</th>
<th>ΔAR/BM24</th>
<th>NT</th>
<th>ΔAR/NT</th>
</tr>
</thead>
<tbody>
<tr>
<td>a lattice (Å)</td>
<td>3.5588</td>
<td>3.567129</td>
<td>0.998</td>
<td>3.5598</td>
<td>1.000</td>
</tr>
<tr>
<td>b lattice (Å)</td>
<td>11.5026</td>
<td>11.52219</td>
<td>0.998</td>
<td>11.5013</td>
<td>1.000</td>
</tr>
<tr>
<td>c lattice (Å)</td>
<td>4.3663</td>
<td>4.377262</td>
<td>0.997</td>
<td>4.36953</td>
<td>0.999</td>
</tr>
</tbody>
</table>
The BET technique was employed to determine specific surface area in samples BM24 and NT, (instrument constraints did not allow for BET analysis of microscale sample AR). [5] The results of BET experiments can readily be translated into particle size data though the relationship depicted in Equation 4-1. [6]

\[ d = \frac{6}{\rho S_{BET}} \]

**Equation 4-1**

Where \( d \) is the particle size, \( \rho \) is the density of V₂O₅ and \( S_{BET} \) is the BET surface area. As written, Equation 4-1 assumes a spherical particle morphology. At large particle sizes this approximation is inappropriate, owing to the platy particle geometry seen for sample AR in Figure 4-2. For smaller particles (samples BM24 and NT) the spherical approximation is more reasonable. Results of BET experiments and particle size calculations for samples BM24 and NT, (assuming a density of 3.37 g/cm³), are show in Table 4-2. [7]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM24</td>
<td>9 m²/g</td>
<td>200nm</td>
</tr>
<tr>
<td>NT</td>
<td>200 m²/g</td>
<td>30nm</td>
</tr>
</tbody>
</table>

Table 4-2: Specific surface area and average particle size as determined by BET for samples BM24 and NT.

To confirm the results from BET and to determine particle size for sample AR, SEM has been used. Due to the semi-conducting nature of V₂O₅, SEM experiments were performed on uncycled, mixed powder films as the introduction of a conductive additive is necessary to prevent charge build-up on the sample surface during electron bombardment. SEM results, which suggest particle sizes of 1-2μm, 200-300nm and 30-70nm for samples AR, BM24 and NT respectively, are shown in Figure 4-2, Figure 4-3 and Figure 4-4.
Figure 4-2: SEM micrograph of sample AR. Scale bar is 1\(\mu\)m

Figure 4-3: SEM micrograph of sample BM24. Scale bar is 1\(\mu\)m
Figure 4-4: SEM micrograph of sample NT. Scale bar is 100nm

As the forgoing results clearly demonstrate all starting materials are pure-phase $\alpha$-V$_2$O$_5$ with particle sizes ranging from 1-2µm, 200-300nm and 30-70nm for sample AR, BM24 and NT, respectively.

**Rate Performance as a Function of Particle Size in Li$_x$V$_2$O$_5$ Mixed Powder Cathodes**

In order to minimize the variations between cells not attributable to particle size scaling, cathode films comprised of the three active material particle sizes under consideration were prepared by the same technique and utilizing the same weight ratios of active and non-active material in the cathode thin films. In each case films comprising 10 weight percent Carbon Black (Super P) and 10 weight percent PVDF were blade cast onto heavy duty Al foil before being punched into 11mm diameter cathode disks for assembly in an argon-filled glove box. Full cell batteries were then assembled according to the protocol described in Chapter 3.
To determine equilibrium performance two-electrode cells were held at 3.6V for 1 hour prior to being discharged and charged three times at a C/20 rate (based upon active mass and assuming a theoretical capacity of 147mAh/g) between 3.6V and 2.5V. Following this conditioning step, cells were held again at 3.6V for four hours before being galvanostatically titrated in increments of approximately 1mol% Li\(^+\) per formula unit V\(_2\)O\(_5\) at a C/20 current. Cells were allowed to relax for up to four hours between each titration step to allow for full cell equilibration. Results from this experiment (shown in Figure 4-5) verify that all three systems can, upon equilibrium cycling, nearly fully access the specified theoretical capacity. Further, aside from apparent variations in the extent of \(\alpha\)-Li\(_x\)V\(_2\)O\(_5\)/\(\varepsilon\)-Li\(_x\)V\(_2\)O\(_5\) and \(\varepsilon\)-Li\(_x\)V\(_2\)O\(_5\)/\(\delta\)-Li\(_x\)V\(_2\)O\(_5\) phase coexistence, the titration profiles indicate that three cathode films exhibit highly similar equilibrium potentiodynamic response.

![Figure 4-5: Galvanostatic titration of dimensionally graded V\(_2\)O\(_5\) full cells](image)

To investigate rate performance each cell was first cycled 3 times at a C/20 rate to ensure that charged cells were well-equilibrated and that any subsequent irreversibilities associated with electrode-electrolyte reaction were minimized. Subsequent C-rate calculations were based upon the quasi-equilibrated discharge capacities of the third
discharge to correct for any apparent capacity loses associated with active material isolation or errors in dry weighing of cathode films. The dimensionally graded cathodes were then discharged at the following C-rates, C/10, C5, C, 5C (not shown) and 10C. Figure 4-6, Figure 4-7, and Figure 4-8 show variations in discharge performance as a function of particle size for the three systems.

![Figure 4-6: Variation in capacity as a function of discharge rate for sample AR.](image)

![Figure 4-7: Variation in capacity as a function of discharge rate for sample BM24](image)
Referring back to the characteristic signatures of poor high-rate performance articulated by Srinivasan and Newman in Chapter 2, (namely, “(i) a drop in utilization with increasing current density; (ii) a decrease in midplateau potential with increasing current density; and (iii) a slope in the discharge curves at higher current densities”) it appears that all three characteristic deviations from equilibrium performance are systematically minimized with decreasing particle size. Of particular note is the enhanced relative utilization observed with decreasing particle size, (a signature that Srinivasan and Newman attributed to “diffusion resistance” in their work), as summarized in Figure 4-9. As can be seen in that figure all three systems exhibit a decrease in intercalation capacity (relative to C/10 discharge capacities) with increasing rates of discharge, though the rate of decrease clearly increases as a function of increasing particle size. Implicit in this somewhat oversimplified rate-performance criterion, (which disregards phase-state specific contributions to the final intercalation capacity), is the relative increase in potentiodynamic extent of the biphasic plateaus as a function of decreasing particle size. This feature, Ma et al. argue, (as summarized in Chapter 2 of this work), is believed to be indicative of facilitated phase boundary motion, a hypothesis that will be considered more carefully in the subsequent sections of this Chapter.

**Figure 4-8: Variation in capacity as a function of discharge rate for sample NT.**
Figure 4-9: Capacity retention as a function of discharge rate for dimensionally graded Li$_x$V$_2$O$_5$ full cells. C-rate axis is logarithmic. $R^2$ figures describe the fitness of the logarithmic trend line.

**Rate Limiting Mechanisms in Dimensionally Graded Intercalation Compounds**

Particle size reduction in Li$^+$ intercalating compounds is expected to enhance rate performance through the following three mechanisms 1) increased surface area to volume ratio which entails a higher electrode/electrolyte contact area leading to higher charge/discharge rates, 2) enhanced Li$^+$ ion diffusion due to reduced path lengths for Li$^+$ transport, and 3) increased e$^-$ conductivity due to decreased path lengths for electronic transport. [8] A fourth, less well documented mechanism, (and the subject of the present work), is facilitated phase nucleation and/or phase boundary motion, ascribed to improved strain accommodation within the bulk particle. [9] In order to credibly advance the case of phase boundary motion limited kinetics in the Li$_x$V$_2$O$_5$ system it is essential to first consider the effects of these other mechanisms, beginning with the increased surface area to volume ratio.
Increased Electrode/Electrolyte Rates of Reaction

Comparing rate performance at equivalent real (as opposed to gravimetric) current densities provides some insight into the relative effect of the increased electrode/electrolyte surface areas commensurate with particle size reduction in the Li$_x$V$_2$O$_5$ system. As shown in Figure 4-10, which compares the rate performance of sample AR discharged at a C/10 rate and sample NT discharged at a rate of 10C (a 2 order of magnitude increase in gravimetric current density), both systems show comparable discharge responses up to approximately 60 mAh/g, (notwithstanding the uniform depression of the NT discharge profile relative to the AR discharge profile, a feature likely attributable to the significantly enhanced net cell ohmic resistance in the higher current experiment). Given the approximately 1.5 order of magnitude increase in active material specific surface area illustrated above, it is reasonable to expect that cells discharged at comparably scaled gravimetric current densities (and absent significantly increased surface occlusion by carbon particles) would exhibit highly similar discharge profiles, assuming both the relative invariance in interfacial charge transfer resistances and the absence of other rate-limiting mechanisms. [10] Yet, as shown in Figure 4-10, the discharge profile of sample NT deviates significantly from that of sample AR above ~60mAh/g, a capacity commensurate with the Li$^+$ saturation of the $\varepsilon$-Li$_x$V$_2$O$_5$ phase and the onset of $\delta$-Li$_x$V$_2$O$_5$ phase nucleation. This highly localized variation in discharge performance, coincident with 2$^{nd}$ phase nucleation, suggests that the mode of kinetic control has transferred from a charge transfer mechanism to a phase boundary motion mechanism, consistent with the hypothesis put forth in this work.
Enhanced Li$^+$ Diffusivity

As first mentioned in Chapter 3 of this work, the rate of Li$^+$ diffusion within a given intercalation host can be characterized by subjecting the system to “small” galvanostatic or potentiostatic pulses and fitting those pulse responses to parameterized expressions derived of solutions to Fick’s second Law. Assuming 1-D diffusion, an assumption justified by highly anisotropic diffusion observed both experimentally and computationally in the Li$_x$V$_2$O$_5$ system, (as described above), the diffusion penetration time can be simply characterized by Equation 4-2

$$\tau = \frac{L^2}{D}$$

Equation 4-2

Where $\tau$ is the diffusion penetration time, $L$ is the diffusion path length (the radius, for example, of a spherical particle) and $D$ is the diffusion coefficient. Assuming a constant diffusion coefficient for Li$^+$ in all V$_2$O$_5$ phases of $2.5 \times 10^{-12}$ cm$^2$/s (a rough average of monophasic diffusion coefficients reported elsewhere and reproduced in Chapter 5 of this work), the characteristic diffusion penetration time, $\tau$, will vary as a function of particle size as shown in Table 4-3: Characteristic diffusion time as a function of particle size,
where “upper” and “lower” subscripts designate the limits of particle sizes observed for each particle system in the first part of this chapter. [4, 11] The calculated diffusion times can then be converted into C-rates, which will, in this simplified approach, establish lower bounds on the current rates at which diffusion limitations will begin to effect discharge performance, (excluding variations in the midplateau potentials previously ascribed to generalized ohmic and/or charge transfer limitations).

Table 4-3: Characteristic diffusion time as a function of particle size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle Size (nm)</th>
<th>T (seconds)</th>
<th>t (minutes)</th>
<th>t (hours)</th>
<th>C-Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR_upper</td>
<td>2000</td>
<td>10000.00</td>
<td>166.67</td>
<td>2.78</td>
<td>1/3</td>
</tr>
<tr>
<td>AR_lower</td>
<td>1000</td>
<td>2500.00</td>
<td>41.67</td>
<td>0.69</td>
<td>1.5</td>
</tr>
<tr>
<td>BM24_upper</td>
<td>300</td>
<td>225.00</td>
<td>3.75</td>
<td>0.06</td>
<td>16</td>
</tr>
<tr>
<td>BM24_lower</td>
<td>200</td>
<td>100.00</td>
<td>1.67</td>
<td>0.03</td>
<td>36</td>
</tr>
<tr>
<td>NT_upper</td>
<td>70</td>
<td>12.25</td>
<td>0.82</td>
<td>0.01</td>
<td>294</td>
</tr>
<tr>
<td>NT_lower</td>
<td>30</td>
<td>0.25</td>
<td>0.02</td>
<td>0.00</td>
<td>14400</td>
</tr>
</tbody>
</table>

Considering only the upper limit values of particle size show in Table 4-3, rate performance should, under the assumption of diffusion-limited discharge kinetics, remain largely unaffected up to 1/3C, 16C and 294C for samples AR, BM24 and NT respectively. Yet, as is clearly evident in the respective rate-performance results shown above, discharge performance, as characterized by the signatures of poor high-rate performance articulated by Srinivasan and Newman, violates this assumption. This suggests that diffusion is can not, in fact, be the rate-limiting mechanism in these systems.

Enhanced Electronic Conductivity

As mentioned in chapter 2 of this document, the electronic conductivity of pure V$_2$O$_5$ is reported to range between $1.0 \times 10^{-3}$ – $4.0 \times 10^{-5}$ S/cm. DC sweeps of unlithiated, pelletized particles yielded conductivities of $2.5 \times 10^{-5}$ and $4.9 \times 10^{-5}$ S/cm for samples AR and BM24, respectively. Due to the very small yield of the nanotemplating process similar conductivity experiments were not possible for the NT material. As such direct comparison between the three systems could not be performed. Instead, variations in rate performance between the two tested samples (AR and BM24) are compared against Cu-doped V$_2$O$_5$. Coustier et al. have reported conductivities of up to $1.0 \times 10^{-2}$ S/cm in the Cu$_{0.1}$V$_2$O$_5$ system, an order of magnitude larger than the largest reported value for V$_2$O$_5$. 

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Wei et al. subsequently investigated the effects of Cu doping upon rate performance in the V$_2$O$_5$ system. Their results are shown below in Figure 4-11.

![Graph showing variations in galvanostatic discharge performance for pure V$_2$O$_5$ and Cu$_{0.04}$V$_2$O$_5$ subject to calcining for 5 hours at 300°C (Sample-A) and 600°C (Sample-B) respectively. Reproduced from Wei et al. [13]](image)

As can be readily observed, the rate performance of the Cu-doped systems is in fact slightly inferior to that of the undoped material, suggesting that the enhanced conductivity (Wei et al. did not directly investigate electronic conductivity, though they did detect an increase in the concentration of V$^{4+}$ cations in the unlithiated material using X-ray absorption near edge spectroscopy (XANES). This increase in the concentration of V$^{4+}$ is expected to enhance conductivity in a manner analogous to that observed at low degrees of lithiation as described in Chapter 2) is offset by some other kinetic feature of the material.
Complementing their electrochemical experiments, Wei et al. performed SEM on the Cu-doped materials. They observed that Sample-A had a particle size of roughly 300 nm while Sample-B had a particle size of 1-2 μm, consistent with the size variation in the AR and BM24 materials employed in this work. Comparing the rate performance of V$_2$O$_5$ samples AR and BM24 at C/5, (roughly equivalent to the current employed by Wei et al.), with the rate performance of the electronically enhanced Cu$_{0.04}$V$_2$O$_5$ materials, as shown in Figure 4-12, it seems clear that variations in rate performance between these electronically distinct systems are in fact more likely due to variations in particle size and/or active surface area. Of particular note are the marked similarities between variations in the extent of the biphasic plateaus and variations (or lack thereof) in the monophasic slopes as a function of particle size. If, in fact, as Wei et al. and others contend, enhanced electronic conductivity leads to improved rate performance, the effects of as much as an order of magnitude increase in conductivity should overwhelm variations attributable to particle size scaling. Whatever small variations exist between the doped and undoped systems are more likely attributable to subtle variations in cathode composition, cell assembly and experimental protocols.

![Graph showing galvanostatic discharge (C/5) performance](image)

**Figure 4-12:** Variation in galvanostatic discharge (C/5) performance for samples AR and BM24. Inset depicts discharge performance of Cu-doped materials against the same range of potential and intercalated capacity. Reproduced from Wei et al. [13]
The Role of Phase Transformation in Intercalation Kinetics

In the absence of a more compelling account of rate-performance limitations in the Li$_x$V$_2$O$_5$ system an alternative hypothesis must be considered. Following on the work of Meethong et al. and others the effect of phase transformation on discharge kinetics will be considered in the following sections.

Enhanced End-Member Solubility

Meethong et al. observed a significant increase in end-member Li$^+$ solubility as a function of decreased particle size in the LiFePO$_4$ system, an effect, they argued, that accounts for the significantly improved rate performance in nanoscaled LiFePO$_4$. [14] Equilibrium phase diagrams for the pseudo-binary Li$_x$V$_2$O$_5$ system (shown in Figure 4-13) suggest an upper bound on the solubility of Li$^+$ in the microscale α-Li$_x$V$_2$O$_5$ end-member phase of between 9 and 13mol% Li$^+$. [15, 16] Other reports have put the limit of Li$^+$ solubility in the α-Li$_x$V$_2$O$_5$ phase as low as 3mol%, consistent with findings reported below. [17]

Figure 4-13: Phase diagrams for the Li$_x$V$_2$O$_5$ system. Reproduced from Delmas et al. (left) [15] and Murphy et al. (right) [16].

To investigate the effect of particle size on end-member α-Li$_x$V$_2$O$_5$ Li$^+$ solubility a variety of experimental approaches were employed, beginning with quasi-equilibrium
(C/50) galvanostatic discharges. As before each cell was discharged 3 times at a C/20 rate prior to discharge at a C/50 rate, as shown in Figure 4-14. C/100 discharges (not shown) were also performed to ensure that the C/50 discharge profiles were representative of quasi-equilibrium behavior.

![Figure 4-14: C/50 discharge curves for AR, BM24 and NT samples.](image)

As shown in Figure 4-15, the inflection points in the C/50 galvanostatic profiles, characteristic of the onset of 2nd phase nucleation, shift to larger degrees of lithiation with decreased particle size. Relative specific energy densities were estimated by integrating the potential vs. capacity curves between 3.6V (slightly positive of OCP) and the potential corresponding to biphasic equilibrium for each of the three cells up to 3mol% Li per formula unit V₂O₅ (as shown in the inset in Figure 4-15). Significantly, these calculations systematically underestimate increases in specific energy density as a function of decreasing particle size due to the increasing magnitude of the ΔV term with increasing particle size. The origin of this variation in biphasic potential is likely ohmic in nature, despite the low discharge current, as it is not reproduced in the titration results shown in Figure 4-5.
Figure 4-15: Variation in C/50 discharge profiles at onset of $\varepsilon$-V$_2$O$_5$ phase nucleation. Inset shows integrated capacity between OCP and 3mol% intercalated Li$^+$. 

In order to confirm that this feature in the galvanostatic profile is indeed associated with the delayed onset of phase transformation and not attributable to other kinetic processes in the cathode, two complementary analytic approaches are adopted. To verify the single phase capacity of Li-poor end member phases PITT was employed. PITT is preferred in this case to GITT owing to the fact that GITT can induce phase transformation even at relatively low discharge currents. [14] PITT, on the other hand, can be parameterized so as to avoid inducing a phase transformation by setting the terminal potential slightly above the observed biphasic plateau value. The results of those experiments are shown in Figure 4-16.
To further confirm the apparent increase in single-phase solubility, that is to verify that Li$^+$ incorporation is throughout the bulk phase and at not simply at the surface, X-ray diffraction was used to investigate the phase characteristics of the three systems. Each cell was first subject to the three C/20 discharge/charge cycles. Cells were then held at 3.6V for 4 hours to ensure monophase homogeneity before discharging at C/20 to predetermined degrees of intercalation. After the cells had rested at OCP for 24, hours the cells were carefully disassembled in an argon-filled glove box and the cathode films were removed and rinsed with anhydrous acetonitrile and left to dry overnight. Dry cathode powder was then scraped from the Al substrate and deposited onto a zero background diffraction slide coated with petroleum jelly to keep the powders in place during the experiment. The results for discharge to 0.1 Li$^+$ per formula unit V$_2$O$_5$ (or 10mol% lithiation) are shown in Figure 4-17 below. As is clear in the micrographs, the nanotemplated powder manifests single phase behavior (consistent with the findings from the C/50 and PITT experiments) while as-received and 24-hour ball-milled particles show evidence of varying degrees of phase transformation, consistent with the relative solubilities of Li$^+$ reported above for the $\alpha$-Li$_x$V$_2$O$_5$ phase.
Referring back to Figure 4-5 it can be clearly seen that the extent of the entire \( \alpha\)-Li\(_x\)V\(_2\)O\(_5\) \(\leftrightarrow\) \(\varepsilon\)-Li\(_x\)V\(_2\)O\(_5\) plateau is significantly increased as a function of decreasing particle size. This suggests that the solubility effects of dimensional reduction are not restricted to the \(\alpha\)-Li\(_x\)V\(_2\)O\(_5\) phase but, in fact, extend throughout the intercalation regime as the onset of \(\delta\)-Li\(_x\)V\(_2\)O\(_5\) phase nucleation also occurs at greater degrees of Li\(^+\) intercalation (~65mol% in sample AR, ~70mol% in sample BM24 and approaching 80mol% in sample NT) as a function of decreased particle size. This finding suggests, at a minimum, that increased end-member solubility is proportionally related to improved rate performance. The following sections will provide more detail on a possible mechanistic relationship between this variation in single phase solubility and facilitated phase transformation kinetics.

**Decreased Volumetric Mismatch between Coexistent Phases**

Another apparent consequence of particle size reduction that has been observed in this work is a variation in the unit cell volumes of coexistent end-member phases within biphasic regimes. To investigate this effect X-ray diffraction experiments were performed upon the dimensionally graded systems at comparable degrees of phase transformation, (as opposed to comparable degrees of lithiation, owing to variations in the degree of lithiation commensurate with the onset of phase transformation as demonstrated above). In this experiment, cells were subject to the same conditioning steps applied earlier and subsequently discharged to the midpoint (determined by galvanostatic titration) of the \(\alpha\)-Li\(_x\)V\(_2\)O\(_5\) \(\leftrightarrow\) \(\varepsilon\)-Li\(_x\)V\(_2\)O\(_5\) biphasic regime. Cathodes were extracted, rinsed and allowed to dry.
overnight in an argon filled glove box before the experiment. As shown in Table 4-4 the
difference in unit cell volume for coexistent phases (the $\varepsilon$-Li$_x$V$_2$O$_5$ volume is divided by
half for comparison purposes) is quite similar for the AR and BM24 samples. In the
nanoscale system, on the other hand, the volumetric mismatch has been reduced to 25%
of the value of the larger particle size systems. This variation in the degree of volumetric
mismatch is somewhat surprising, given the more consistent variation of structural
properties as a function of particle size seen above, and suggests, perhaps, that certain
scaling effects are magnified below a certain particle size as has been suggested
elsewhere. [18]

Table 4-4: Variations in volumetric mismatch between coexistent phases in
dimensionally graded V$_2$O$_5$ particles. Samples AR and BM24 are discharged to
15mol% Li$^+$ while sample NT is discharged to 25mol%, the midpoint in the $\alpha$-
Li$_x$V$_2$O$_5$/\varepsilon-Li$_x$V$_2$O$_5$ biphasic plateau.

<table>
<thead>
<tr>
<th></th>
<th>AR15</th>
<th>AR15</th>
<th>BM2415</th>
<th>BM2415</th>
<th>NT25</th>
<th>NT25</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>3.56507</td>
<td>4.477544</td>
<td>3.56548</td>
<td>4.47581</td>
<td>3.58262</td>
<td>4.48121</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.48519</td>
<td>11.42783</td>
<td>11.4889</td>
<td>11.42968</td>
<td>11.45985</td>
<td>11.4285</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.39564</td>
<td>7.131641</td>
<td>4.39252</td>
<td>7.131195</td>
<td>4.43269</td>
<td>7.13139</td>
</tr>
<tr>
<td>Vol (Å$^3$)</td>
<td>179.9817</td>
<td>364.9162</td>
<td>179.9327</td>
<td>364.8111</td>
<td>181.9898</td>
<td>365.2235</td>
</tr>
<tr>
<td>Delta Vol</td>
<td>1.38</td>
<td>1.37</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Similar experiments probing the volumetric mismatch between the $\varepsilon$-Li$_x$V$_2$O$_5$ and
$\delta$-Li$_x$V$_2$O$_5$ phases yield similar results, as shown in Table 4-5. Interestingly the NT $\varepsilon$-
Li$_x$V$_2$O$_5$ phase could not be indexed to the same crystal system as the AR and BM24 $\varepsilon$-
Li$_x$V$_2$O$_5$ phases, suggesting that the nanoscaling of V$_2$O$_5$ may have more significant
structural consequences than has been considered to this point. A further point that bears
mentioning is that the variations in volumetric misfit observed as a function of particle
size are strikingly consistent between biphasic couples with misfit decreasing by 1-5%
between the AR and BM24 $\alpha$-Li$_x$V$_2$O$_5$/\varepsilon-Li$_x$V$_2$O$_5$ and $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$ couples and
by 75-79% between the BM24 and NT $\alpha$-Li$_x$V$_2$O$_5$/\varepsilon-Li$_x$V$_2$O$_5$ and $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$
couples.
Table 4-5: Variations in volumetric mismatch between coexistent phases in dimensionally graded V$_2$O$_5$ particles. Samples AR and BM24 and NT are discharged to 65mol% Li$^+$, the midpoint in the ε-Li$_x$V$_2$O$_5$/δ-Li$_x$V$_2$O$_5$ biphasic plateau.

<table>
<thead>
<tr>
<th></th>
<th>AR65</th>
<th>AR65</th>
<th>BM2465</th>
<th>BM2465</th>
<th>NT65</th>
<th>NT65</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ε-V$_2$O$_5$</td>
<td>δ-V$_2$O$_5$</td>
<td>ε-V$_2$O$_5$</td>
<td>δ-V$_2$O$_5$</td>
<td>ε-V$_2$O$_5$</td>
<td>δ-V$_2$O$_5$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.56398</td>
<td>3.602624</td>
<td>4.534098</td>
<td>3.3528</td>
<td>4.606495</td>
<td>3.575694</td>
</tr>
<tr>
<td>c (Å)</td>
<td>7.14567</td>
<td>11.25693</td>
<td>7.136432</td>
<td>11.98455</td>
<td>7.142269</td>
<td>4.665472</td>
</tr>
<tr>
<td>Vol (Å$^3$)</td>
<td>370.7026</td>
<td>402.1575</td>
<td>368.5009</td>
<td>398.2485</td>
<td>373.2181</td>
<td>379.2694</td>
</tr>
<tr>
<td>Delta Vol</td>
<td>7.82</td>
<td>7.47</td>
<td>1.60</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reduced Potential Hysteresis

Another distinctive feature of many biphasic intercalation compounds is the appearance of potential hysteresis between charging and discharging potentiodynamic profiles. Pyun, et al. have reported the presence of potential hysteresis in graphite electrodes that contain two stage phases. [19] The appearance of potential hysteresis in such biphasic systems, they argue, is a manifestation of an energetic asymmetry in the biphasic state as represented by the following expression for the chemical potential of Li$^+$

$$\mu_{Li^+} = \mu_{Li^+}^0 + U_{int}$$

**Equation 4-3**

Where the right hand side of the equation represents the chemical potential of Li$^+$ in the strain free state augmented by an interaction energy ($U_{int}$) that captures the volumetric strain effects of Li$^+$ phase boundary site-hopping as shown below

$$U_{int} = \frac{4(1+\nu)Gb^2\varepsilon Sin\theta}{3(1-\nu)s}$$

**Equation 4-4**

Where $\nu$ is Poisson’s ratio, $G$ is the modulus of elasticity in shear, $b$ is the Burgers vector, $\theta$ is the angle between the straight line from the dislocation core to the intercalated Li$^+$ atom, and $s$ is the distance between the dislocation core and the intercalated ion. The $\varepsilon$
term represents strain associated with the introduction or removal of a Li\(^+\) ion from the 2\(^{\text{nd}}\) phase and is defined as follows

\[ \varepsilon = \frac{(a' - a)}{a} \]

Equation 4-5

Where \(a'\) and \(a\) are the radii of the intercalated ion and the lattice hole respectively. The geometric components of Equation 4-4 are represented schematically in Figure 4-18 which portrays Li\(^+\) intercalation and phase transformation in the graphite system, but can, in generality, be understood to represent phase transformation processed in any 2-dimensional, phase transforming intercalation host.

![Diagram of phase boundary in lithiated graphite](image)

**Figure 4-18: Schematic representation of the phase boundary in lithiated graphite. Reproduced from Pyun et al. [19]**

During intercalation the strain term (\(\varepsilon\)) will be positive due to the excess volume associated with the intercalated ion (\(a'\) in Equation 4-5), and the \(U_{\text{int}}\) expression will evaluate to a positive number, indicative of a repulsive interaction between the intercalated ion and the compression side of the phase boundary dislocation core. Conversely, during deintercalation the \(U_{\text{int}}\) term will be negative.
Potential hysteresis within biphasic regimes, they argue, is a manifestation of this energetic asymmetry. During discharge the magnitude of $\Delta \mu$ (the difference in electrochemical potential between Li$^+$ at the anode interface and Li$^+$ at the cathode) will be augmented by the interaction energy $U_{int}$ effectively depressing the cell potential with respect to the unstrained state. During charge, the negative $U_{int}$ term will reduce the magnitude of the $\Delta \mu$ term, effectively elevating the cell potential relative to the unstrained state.

As the particle size of the intercalation host decreases the molar volume of the Li$^+$ poor end-member phase in a biphasic couple has been observed to increase. This increase in molar volume effectively increases the dimension of the lattice hole ($a$ in Equation 4-5), reducing the magnitude of $U_{int}$ through the strain term in Equation 4-4. As a consequence, cell potential during discharge will be observed to increase as a function of reduced particle size as can be seen in Table 4-7. As such, facilitation of phase boundary motion should be manifest by a decrease in the magnitude of the potential hysteresis at comparable rates of discharge and charge. It has been observed in the Li$_x$V$_2$O$_5$ system that the magnitude of potential hysteresis in the $\alpha$-Li$_x$V$_2$O$_5$/$\varepsilon$-Li$_x$V$_2$O$_5$ and $\varepsilon$-Li$_x$V$_2$O$_5$/$\delta$-Li$_x$V$_2$O$_5$ couples, at a C/50 discharge rate, is functionally dependent upon particle size as shown in Table 4-6. It bears repeating that the $\Delta$Volume for these microscale biphasic couples is 1.6% and 10.2% respectively. Meethong et al. observed a similar variation of .006 V in the hysteresis of the LiFePO4 system as a function of reduced particle size.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Discharge Plateau ($a/\varepsilon$)</th>
<th>Charge plateau ($a/\varepsilon$)</th>
<th>Hysteresis ($a/\varepsilon$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>3.39973 V</td>
<td>3.40621 V</td>
<td>0.00694 V</td>
</tr>
<tr>
<td>BM24</td>
<td>3.39998 V</td>
<td>3.40586 V</td>
<td>0.00588 V</td>
</tr>
<tr>
<td>NT</td>
<td>3.40354 V</td>
<td>3.40515 V</td>
<td>0.00161 V</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Discharge Plateau ($\varepsilon/\delta$)</th>
<th>Charge Plateau ($\varepsilon/\delta$)</th>
<th>Hysteresis ($\varepsilon/\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>3.32032 V</td>
<td>3.24118 V</td>
<td>0.03791 V</td>
</tr>
<tr>
<td>BM24</td>
<td>3.20411 V</td>
<td>3.24075 V</td>
<td>0.03664 V</td>
</tr>
<tr>
<td>NT</td>
<td>3.21011 V</td>
<td>3.24066 V</td>
<td>0.03055 V</td>
</tr>
</tbody>
</table>
Cycle Life

It has been argued that poor cycle life in the V₂O₅ system is due to so-called “electrochemical grinding”, in which the strain associated with lattice expansions and contractions commensurate with Li⁺ ingress and egress respectively give rise to crack formation and propagation within the bulk active material particles. These cracks can result in material fracture and electronic isolation. It was anticipated that the relaxation of strain constraints via particle size reduction would lead to improved cyclability in nanoscale materials. As can be seen in Figure 4-19, which portrays relative cycling capacity as a function of cycle number, this is not the case. While the initial decrease in capacity is indeed reduced with decreasing particle size, the relative capacity in nanoscale V₂O₅ appears to continue to slightly decrease with increasing cycle number.

![Figure 4-19: Relative capacity as a function of cycle number at 5C discharge rate for dimensionally graded cathode films.](image)

Summary

In this chapter evidence has been offered suggesting that phase transformation, not bulk Li⁺ diffusion, is the proximate cause of rate-limited performance in the LiₓV₂O₅ battery cathode. A variety of potentially rate-limiting mechanisms have been considered and ultimately dismissed owing to apparent inconsistencies between their proposed scaling effects and observed variations in rate performance in dimensionally graded
mixed powder systems. An alternative hypothesis, phase-transformation-limited discharge kinetics, has been considered, and its plausibility supported by structural and energetic features of the equilibrated and quasi-equilibrated system. In the following chapter additional non-equilibrium evidence will be considered that will reinforce the likelihood of phase transformation based kinetic limitations.

References

Chapter 5: Non-equilibrium Signatures of Phase Transformation Controlled Rate Performance in Dimensionally Graded Li$_x$V$_2$O$_5$

This chapter considers additional evidence of phase-transformation-limited rate performance in the Li$_x$V$_2$O$_5$ system. It begins by describing atypical response profiles in microscale Li$^+$ intercalating systems subject to conventional, electroanalytical experiments. It continues with a more complete introduction to the galvanostatic intermittent titration (GITT) technique commonly employed to identify kinetic parameters in these compounds. It concludes by describing a simple modification to the GITT technique that allows for the ready identification of phase-nucleation and/or phase-boundary-motion kinetically limited regimes in Li-ion intercalating electrodes.

Atypical Electrochemical Pulse Response in Li$^+$ Intercalating Compounds

During discharge a typical Li-ion intercalating compound exhibits, depending on the specific chemistry, varying degrees of microstructural evolution. Monophasic systems, such as amorphous Li$_x$V$_2$O$_5$, typically exhibit lattice expansions and contractions that evolve proportionally with the extent of lithiation. Predominantly biphasic intercalation compounds like LiFePO$_4$ and Li$_x$V$_2$O$_5$, on the other hand, are characterized by extensive intercalation regimes within which coexistent phases of fixed composition, (and correspondingly fixed lattice dimensions) shrink and grow at one another’s expense during intercalation and deintercalation. Many of these materials are known to manifest significant volumetric mismatch between coexistent phases, (6.8%, 1.6% and 10.2% in the FePO$_4$/LiFePO$_4$, α-Li$_x$V$_2$O$_5$/ε-Li$_x$V$_2$O$_5$ and ε-Li$_x$V$_2$O$_5$/δ-Li$_x$V$_2$O$_5$ couples, respectively).[1, 2] Commonly, the end-member species in these biphasic couples, (depending, as demonstrated in Chapters 2 and 4, on particle dimensions), exhibit a narrow range of single phase Li$^+$ solubility at either extreme of the biphasic plateau. In this regime the rate and extent of Li$^+$ incorporation can be readily modeled using Fick’s second Law, (shown for one-dimensional diffusion below)
\[
\frac{\partial c_i(x,t)}{\partial t} = D \times \frac{\partial^2 c_i(x,t)}{\partial x^2}
\]

Equation 5-1

Where \( c_i \) is the concentration of Li\(^+\) ions at the surface of the active material particle, \( D \) is the diffusion coefficient, (assumed here to be independent of the degree of lithiation), \( t \) is time and \( x \) is the linear extent of Li\(^+\) intercalation from the electrode/electrolyte interface. [3] Assuming constant diffusivity, a reasonable assumption over small degrees of lithiation, and a semi-infinite solid particle, (valid for all single phase particles at short enough times), this equation can be employed to extract values for \( D \) from galvanostatic or potentiostatic pulse data (GITT or PITT respectively). [4] In the absence of coexisting phases (as in the case of partially or fully monophasic intercalation compounds such as LiCoO\(_2\) or amorphous V\(_2\)O\(_5\), respectively) these techniques can be employed to determine whether or not bulk Li\(^+\) diffusion is indeed rate-limiting in a given intercalation host.

Conversely, in the presence of multiple phases these techniques yield ambiguous results due, in part, to variations in the linear extent of the monophasic end member phases, (particularly at the onset of 2\(^{nd}\) phase nucleation), which effectively violates the semi-infinite assumption. Further, while the invariance of \( D \) in a single-phase regime over a narrow intercalation step might be plausible, within a biphasic regime it is unclear which of two coexistent diffusion constants is being measured. In fact, when applied to biphasic systems in which the value of \( D \) for end member species is well-resolved, the GITT technique yields significant deviations from either end member value (as shown for the Li\(_x\)V\(_2\)O\(_5\) system in Figure 5-1), exhibiting, depending upon the system and the publication, orders of magnitude increases or decreases in the estimated values of \( D \). Mui et al., ascribe these deviations to the relative flatness of the steady state (or quasi-equilibrium) potentiodynamic profile in the biphasic regimes, as captured by the \( dE/dl \) term in the closed-form solution to the 1-D form of Fick’s second Law, (Equation 5-7, to be discussed more fully below). [5]
Similarly, PITT, when applied to biphasic regimes, often manifests response characteristics that are systematically inconsistent with the monophasic assumptions underlying its application. Meethong et al., for example, have employed this technique to investigate the kinetics of phase transformation in the LiFePO$_4$ system. [2] Considering cathodes comprised of dimensionally graded, doped and undoped LiFePO$_4$ particles (samples NC and AC, with particle sizes of 43nm and 114nm, respectively), they subjected full cells to 10mV potentiostatic pulses over the full range of Li$^+$ intercalation. Their results, reproduced in Figure 5-2, clearly indicate distinctive galvanodynamic response profiles. In the case of sample NC, potentiostatic steps induce current responses characteristic of diffusion control, with a large onset currents followed by a rapid, monotonic decay. The current response in sample AC, on the other hand, is characterized by a small onset current followed by a gradual rise over 4 hours to a maximum value which is clearly inconsistent with the expected $I(t) \propto t^{-1/2}$ (see Equation 3-2) response behavior for a system under diffusion control. The authors attribute this disparity in pulse response to variations in the overpotential required to initiate phase nucleation in either sample (15mV and 30mV in samples NC and AC respectively).
Figure 5-2: Galvanodynamic pulse response in dimensionally graded LiFePO$_4$ cathodes. Reproduced from Meethong et al. [2]

**Atypical Galvanodynamic Signatures in Dimensionally Graded Li$_x$V$_2$O$_5$**

Given the significant variation in galvanodynamic responses observed in the dimensionally graded LiFePO$_4$ system subject to small magnitude potential steps, it seems worthwhile to consider the response of V$_2$O$_5$ subject to a similar testing protocol. McGraw et al. have observed a similar galvanodynamic response in 300 nm thick, pulse laser deposited (PDL) Li$_x$V$_2$O$_5$ films subject to 30 mV potential steps from 3.45-1.5 V as shown in Figure 5-3. It should be noted that the “atypical” response profiles reproduced below did not occur in either the α-Li$_x$V$_2$O$_5$/ε-Li$_x$V$_2$O$_5$ or the ε-Li$_x$V$_2$O$_5$/δ-Li$_x$V$_2$O$_5$ biphasic couples. Rather this behavior was observed only in the δ-Li$_x$V$_2$O$_5$/γ-Li$_x$V$_2$O$_5$ and the γ-Li$_x$V$_2$O$_5$/ω-Li$_x$V$_2$O$_5$ biphasic couples both of which lie outside of the Li$^+$ intercalation regime investigated in this study. Unit cell volumes for the respective monophases derived from DFT calculations indicate a large degree of volumetric misfit between coexisting end-members in this regime, (7.20% and 12.78% for the δ-Li$_x$V$_2$O$_5$/γ-Li$_x$V$_2$O$_5$ and γ-Li$_x$V$_2$O$_5$/ω-Li$_x$V$_2$O$_5$ couples, respectively), though, contrary to the couples previously described, the monophasic unit cell volumes are observed to decrease with increasing degree of lithiation. [6]
Potentiodynamic Signatures of Phase Transformation in Dimensionally Graded LiₓV₂O₅: The Variable Rate GITT Technique

This section will introduce the standard GITT technique and describe modifications to this technique which may provide further insight into the proposed rate limiting role of phase transformation in the LiₓV₂O₅ system. It begins with a validation of the technique under model specified conditions. The effects of systematically increasing the magnitude of the pulse current, (in violation of the “small” current constraint assumed...
in the standard model), will then be considered, (first in the monophase regime and then in the biphasic regime). Finally, variations in the variable-rate potentiodynamic response as a function of both particle size and pulse rate will be considered.

**Validation of the standard GITT technique in the monophasic \( \varepsilon-V_2O_5 \) phase**

As mentioned above, GITT can be employed to extract kinetic parameters from intercalation compounds, provided that the assumptions governing its application are satisfied. In this case Fick’s second Law (Equation 5-1) can be solved by prescribing the following initial and boundary conditions (assuming one-dimensional diffusion):

\[
c_i(x,t = 0) = c_o \quad (0 \leq x \leq L) \quad \text{Equation 5-2}
\]

\[-D \frac{\partial c_i}{\partial x} \bigg|_{x=0} = \frac{I_o}{S_z q} \quad (t \geq 0) \quad \text{Equation 5-3}
\]

\[- \frac{\partial c_i}{\partial x} \bigg|_{x=L} = 0 \quad (t \geq 0) \quad \text{Equation 5-4}
\]

Where Equation 5-2 represents the assumption that the system is fully equilibrated at the onset of the current pulse, (with the concentration of \( Li^+ \) invariant throughout the particle bulk), Equation 5-3 captures the presumed time independent \( Li^+ \) flux at the surface of the particle and Equation 5-4 expresses the semi-infinite boundary condition assumed to obtain over the duration of the experiment. At times \( t << \frac{L^2}{D} \) the full solution can be approximated by the following expression.

\[
\frac{dc_i(x = 0,t)}{d\sqrt{t}} = \frac{2I_o}{S_z q \sqrt{D \pi}} \quad (t << \frac{L^2}{D}) \quad \text{Equation 5-5}
\]

Neglecting changes in molar volume with composition and expanding by \( dE \) yields the following expression for the time dependence of the cell potential during a galvanostatic step.
Rearranging the terms in Equation 5-6 to solve for \( D \), the diffusion coefficient, yields Equation 5-7 below.

\[
\frac{dE}{d\sqrt{t}} = \frac{2V_{ul}I_a}{SFz_i \sqrt{D\pi}} \frac{dE}{d\delta} \quad (t << \frac{l^2}{D})
\]

**Equation 5-6**

\[
\tilde{D}_{\text{GITT}} = \frac{4}{\pi} \left( \frac{V_{ul}I_a}{SFz_i} \right)^2 \left[ \frac{(dE_a)}{(d\delta)} \right]^2 \left[ \frac{(dE_p)}{(d\sqrt{t})} \right]^2
\]

**Equation 5-7**

As a first step in exploring the application of a variant of this technique to the biphasic regime, the model was validated by performing GITT experiments on microscale (as-received) \( \text{Li}_x\text{V}_2\text{O}_5 \) within the monophasic regime at “small” currents (C/20). Cells were held at 3.6V for 1 hour prior to cycling once at a C/20 rate. Cells were held again at 3.6V for 4 hours before the first galvanostatic pulse. Cells were subsequently titrated at a C/20 rate for 180 seconds, commensurate with an intercalation increment of 0.25% after which they were again held at OCP for 4 hours to ensure full cell equilibration. Data reproduced in Figure 5-4 corresponds to a single titration step in monophasic \( \varepsilon\)-\( \text{Li}_x\text{V}_2\text{O}_5 \) (the narrow \( \text{Li}^+ \) solubility limits of microscale \( \alpha\)-\( \text{Li}_x\text{V}_2\text{O}_5 \) make it difficult to access via this technique). The potentiodynamic response curve (the \( dE/d\sqrt{t} \) term in Equation 5-7) is shown in blue in that figure. Parameters derived experimentally or taken from the literature were then supplied to Equation 5-7 to solve for the diffusion coefficient, \( D \). Excellent correspondence between the experimental data and the model (red dots in Figure 5-4) was observed, yielding a diffusion coefficient of \( 2.5 \times 10^{12} \) cm\(^2\)/s, well within the range of values reported elsewhere in the literature. While the application of a one-dimensional model to an inherently multi-dimensional system might seem inappropriate, the high degree of diffusional anisotropy reported by Braithwaite et
al. and others in computational simulations and coupled electrochemical/spectroscopic experiments in Li$_x$V$_2$O$_5$ would seem to validate this approach. [5, 8-10]

![Graph showing potentiodynamic pulse response in monophasic Li$_x$V$_2$O$_5$. Blue line is experimental data. Red dots are model fit.](image)

**Figure 5-4: Potentiodynamic pulse response in monophasic ε-Li$_x$V$_2$O$_5$. Blue line is experimental data. Red dots are model fit.**

Somewhat surprisingly, violations of the monophasic constraint, (or, equivalently, simultaneous violations of both the semi-infinite boundary condition and the assumed invariance of $D(x)$), while leading to orders of magnitude variations in the derived kinetic parameters (as seen in Figure 5-1 above), seem, at small pulse magnitudes, to exhibit transient (the $dE/d\sqrt{t}$ term in Equation 5-7) response profiles (as shown in Figure 5-5) consistent with monophasicity. Assuming, as proposed by this model, that diffusion control is maintained throughout the duration of the current pulse, potentiodynamic response (as opposed to the steady state variation in cell potential given by $dE/d\delta$ term in Equation 5-7) should vary linearly with the square root of time in a monophasic system, as shown in Equation 5-6. Yet, as shown in Figure 5-5 and Table 5-1, linearity in the $E$ vs $\sqrt{t}$ relationship is observed in both monophasic and biphasic regimes subject to “small” current GITT experiments, the later of which clearly violates the assumptions underlying the application of this technique.
Figure 5-5: Plots of $E$ vs. $\sqrt{t}$ taken a midpoint in monophasic and biphasic regimes respectively for $Li_xV_2O_5$ sample AR titrated at C/20. Monophase $\delta$-$V_2O_5$ not shown.

Table 5-1: GITT pulse slope and corresponding $R^2$ values for 5 phase states in $Li_xV_2O_5$ titrated at C/20.

<table>
<thead>
<tr>
<th>Phase State</th>
<th>E vs. $\sqrt{t}$ slope</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.001490313</td>
<td>0.9900</td>
</tr>
<tr>
<td>$\alpha-\epsilon$</td>
<td>0.000985222</td>
<td>0.9929</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.003521127</td>
<td>0.9982</td>
</tr>
<tr>
<td>$\epsilon-\delta$</td>
<td>0.000626174</td>
<td>0.9841</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.027777778</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Further examination of Equation 5-7 suggests a possible explanation for both the orders of magnitude variation in derived values of the diffusion coefficient throughout the intercalation spectrum (as shown in Figure 5-1) as well as the unexpected linearity in $E$ v. $\sqrt{t}$ response profiles within biphasic regimes. In biphasic regimes the $dE/d\delta$ term, which characterizes variations in the steady-state slope within the titrated regime, is factors and even orders of magnitude lower than the corresponding value in monophasic regimes due to the invariance in the $Li^+$ chemical potential (and, correspondingly, the cell potential) expected at the surface of a biphasic particle (as illustrated in Figures 2-7 and 2-8). This relative invariance leads, through the $dE/d\delta$ term in Equation 5-7, to significant depressions in the derived kinetic parameters. Mui et al. have investigated this
phenomenon by performing a “sensitivity analysis” on the variable terms that appear in Equation 5-7, as shown in Figure 5-6, which depicts the relative variation in the two variable terms as a function of degree of intercalation in sputter deposited Li$_x$V$_2$O$_5$. [5]

\[ \text{(c)} \]

\[ \text{(d)} \]

**Figure 5-6**: Variation in $dE/d\delta$ and $dE/d\sqrt{t}$ as a function of degree intercalation in Li$_x$V$_2$O$_5$.

As can be clearly seen, the $dE/d\delta$ term varies by several orders of magnitude over the intercalation spectrum, effectively depressing the derived kinetic parameters shown in Figure 5-1. Variations in $dE/d\sqrt{t}$ term, on the other hand, (which are effectively suppressed by variations in the orders magnitude larger $dE/d\delta$ term in equation 5-7) likely reflect variations in the true kinetic properties of the tested materials. The unexpectedly “diffusive” character of biphasic microscale Li$_x$V$_2$O$_5$ (as manifest in the linear $E$ v. $\sqrt{t}$ pulse responses depicted in Figure 5-5) can be therefore be understood to reflect the true kinetic character of that system, a finding consistent with the analysis represented in Table 4-3 which suggests that, at the tested current rate, the system is indeed operating
under diffusion control. Mui et al. further suggest that the $dE/d\nu$ term in Equation 5-7 might therefore be profitable employed as a “metric to express the facility for mass transport and phase transformation” throughout the intercalation spectra, an approach that will be developed further in the foregoing analysis.

**Relative Invariance of Monophasic Pulse Response at “large” Pulse Currents**

As mentioned above, application of the GITT technique is properly restricted to monophasic systems in which the magnitude of pulsed current is “small” and particle dimensions and pulse durations satisfy the following constraints:

$$t \ll \frac{L^2}{D}$$

Equation 5-8

Where $t$ is pulse duration, $L$ is the relevant particle dimension and $D$ is the diffusion coefficient. [4] It has been observed, though, that the violation of this “small” current pulse constraint does not necessarily lead to significant deviations in the derived kinetic parameters within the monophasic regimes of a phase transforming material, as shown in Figure 5-7 below, which compares E vs. $\sqrt{t}$ responses at two current pulse magnitudes (C/5 and 1C) in monophasic, microscale $\text{Li}_x\text{V}_2\text{O}_5$. As before cells were held at OCP for 4 hours following each galvanostatic increment to ensure homogeneity within lithiated particles.

![Figure 5-7: E vs $\sqrt{t}$ for α (blue), ε (green) and δ (red) $\text{Li}_x\text{V}_2\text{O}_5$ monphases at C/5 and 1C galvanostatic pulse rates.](image)

As shown in Table 5-2, $R^2$ values for each of the three single phase regimes at current pulses of C/5 and 1C indicate a high degree of linearity in the E vs. $\sqrt{t}$ response curves. It
should be noted that derived values of $D$ are consistently a factor of $\sim 5/3$ higher at a rate of 1C than at C/5 or C/20. Comparing both sides of Equation 5-6, the value of $I_0$, which corresponds to current magnitude, increases by a factor of 5 while the value and $dE/d\sqrt{t}$ increases by only a factor of $\sim 3$. This is likely a manifestation of increased ohmic resistance associated with the higher current rates.

Table 5-2: E vs. $\sqrt{t}$ slope and $R^2$ values for sample AR titrated at C/20, C/5 and C in the monophasic regimes

<table>
<thead>
<tr>
<th>C-rate</th>
<th>C/20</th>
<th>C/5</th>
<th>1C</th>
</tr>
</thead>
<tbody>
<tr>
<td>phase</td>
<td>E vs. $\sqrt{t}$</td>
<td>$R^2$</td>
<td>E vs. $\sqrt{t}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.0015</td>
<td>0.9900</td>
<td>0.0015</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.0035</td>
<td>0.9982</td>
<td>0.0035</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.0278</td>
<td>0.9994</td>
<td>0.0276</td>
</tr>
</tbody>
</table>

Variations in Variable Rate GITT Response as a Function of Particle Size

To this point potentiodynamic response profiles in both monophasic microscale materials subject to “large” pulsing currents as well as biphasic microscale materials subject to “small” pulsing currents have been considered. In each case, despite variations in the derived kinetic parameters associated with each experiment, we have observed an unexpected linearity in the material’s E vs. $\sqrt{t}$ response, characteristic of diffusion control, (a finding generally consistent with the analysis summarized in Table 4-3 of this document). It has been suggested above that this response may in fact be representative of the true kinetic character of the systems under investigation. As such, this approach has been extended to dimensionally graded material in hopes of demonstrating, electrochemically, the differential manifestation of phase-boundary motion control in these materials.

As before, dimensionally graded mixed powder $V_2O_5$ cathode films (samples AR, BM24 and NT with active material particles sizes of 1-2µm, 200-300nm and 10-60nm, respectively) were prepared by the same technique and in the same mass ratios. Each system was subject to three different galvanostatic pulse rates corresponding to C/20, C/5 and 1C at fixed increments of lithiation (1% per pulse). Figure 5-8 depicts full-sweep galvanostatic response profiles at two current rates (C/5 and C) above GITT response.
profiles corresponding to the same discharge rate at the midpoint in the ε-Li₂V₂O₅/δ-LiₓV₂O₅ biphasic plateau. Consistent with results shown above in Table 5-2, at C/5 all three systems manifest potentiodynamic response curves similar to the monophasic model pulse response, (as demonstrated by the linearity of E vs. √t plots shown in Figure 5-9). Similarly, all three systems at C/5 show comparatively flat ε-Li₂V₂O₅/δ-LiₓV₂O₅ biphasic plateaus and relatively good capacity retention.

At the 1C rate, on the other hand, the microscale sample (AR) shows significant ε-Li₂V₂O₅/δ-LiₓV₂O₅ biphasic sloping in the full potentiodynamic sweep as well as a pronounced depression at the onset of the galvanostatic titration pulse. Submicro and nanoscaled samples, (BM24 and NT, respectively), on the other hand, show considerably less potentiodynamic sloping in the full sweep profiles and roughly linear E vs. √t titration responses.

Figure 5-8: Potentiodynamic sweeps and biphasic galvanostatic pulse response curves for samples AR, BM24 and NT at C/5 (left hand plots) and 1C (right hand plots)
Figure 5-9: Linearizations of galvanostatic pulse responses for samples AR, BM24 and NT at C/5 (left hand side) and C (right hand side) 

As can be seen in Table 5-3, (which quantifies the results presented in Figure 5-9), all three samples show linear $E$ vs. $\sqrt{t}$ response at the C/5 rate. At the 1C rate, on the other hand, the $E$ vs. $\sqrt{t}$ response for sample AR is clearly non-linear.

Table 5-3: $E$ vs. $\sqrt{t}$ slope and $R^2$ values for samples AR, BM24 and NT titrated at C/5 and 1C.

<table>
<thead>
<tr>
<th>System</th>
<th>C-Rate</th>
<th>C/5 $E$ vs. $\sqrt{t}$</th>
<th>$R^2$</th>
<th>C $E$ vs. $\sqrt{t}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>0.0006</td>
<td>0.9862</td>
<td>-0.0034</td>
<td>0.7722</td>
<td></td>
</tr>
<tr>
<td>BM24</td>
<td>0.0012</td>
<td>0.9983</td>
<td>0.0047</td>
<td>0.9989</td>
<td></td>
</tr>
<tr>
<td>NT</td>
<td>0.0009</td>
<td>0.9672</td>
<td>0.004</td>
<td>0.9903</td>
<td></td>
</tr>
</tbody>
</table>

This clear deviation from GITT model pulse response within the $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$ biphasic regime in the microscale system at 1C, combined with the sharp deviation from equilibrium galvanostatic full sweep performance observed in the $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$ biphasic regime in this system at the same current rate suggest that, at this current rate, the system is no longer under diffusion control. Rather, given that the microscale system does not exhibit deviations from GITT model pulse response in any of the other tested phase states at this current rate, it is reasonable to conclude that the presence of the highly volumetrically mismatched $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$ biphasic couple, (as characterized in Table 4-5), is responsible for these deviations. Further, the fact that these deviations from model pulse response are not observed in either of the other systems under consideration within the $\varepsilon$-Li$_x$V$_2$O$_5$/\delta-Li$_x$V$_2$O$_5$ regime at comparable current rates suggests that phase boundary motion is, in fact, enhanced by particle size
reduction in the Li$_x$V$_2$O$_5$ system through the mechanism of reduced biphasic volumetric mismatch.

**Signatures of Phase Evolution in Biphasic Regimes using Variable Rate GITT**

While potentiodynamic responses at “large” (5C) GITT currents reveal relatively little deviation from model response in the monophasic regimes of the microscale (AR) material, significant deviations in pulse response were observed in the ε-Li$_x$V$_2$O$_5$/δ-Li$_x$V$_2$O$_5$ couple subject to “large” current pulsing. As shown in Figure 5-10 the evolution of phase population in this system seems plausibly correlated with variations in the current pulse response at the 5C rate. At the onset of phase transformation (0% lithiation in Figure 5-10), the entire potentiodynamic profile is significantly depressed relative to its monophase analog. With an increasing degree of lithiation the initial potential depression sharpens into a peaked feature, while at even higher degrees of lithiation the right side of the potentiodynamic profile begins to adopt a more conventional GITT response contour, (while retaining the onset peak). Finally, near the end of the transformation regime, the curve, while still peaked at the onset of the current pulse, is clearly adopting a more typical “diffusive” tail.

![Figure 5-10: Variation in potentiodynamic response as a function of degree of ε-Li$_x$V$_2$O$_5$/δ-Li$_x$V$_2$O$_5$ phase transformation for sample AR at 5C current.](image)

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Significantly, these features were not observed in the $\alpha$-Li$_x$V$_2$O$_5$/\(\varepsilon\)-Li$_x$V$_2$O$_5$ biphasic couple at this or any other particle size or tested current rate. This is likely due to the relative magnitudes of the volumetric mismatches between the respective co-existent phases, (1.6% and 10.2% in $\alpha$-Li$_x$V$_2$O$_5$/\(\varepsilon\)-Li$_x$V$_2$O$_5$ and $\varepsilon$-Li$_x$V$_2$O$_5$/\(\delta\)$-\alpha$-Li$_x$V$_2$O$_5$ couples, respectively), a structural feature which has been singled out by Ma et al. and others as the source of phase transformation limited kinetics in Li$^+$ ion intercalating compounds. [11] Further, these features were not observed, (as can be seen in Figure 5-11, which depicts 5C GITT pulse response in the $\varepsilon$-Li$_x$V$_2$O$_5$/\(\delta\)$-\alpha$-Li$_x$V$_2$O$_5$ biphasic couple in the nanoscale (NT) system), in any other system within the $\varepsilon$-Li$_x$V$_2$O$_5$/\(\delta\)$-\alpha$-Li$_x$V$_2$O$_5$ biphasic regime. Finally, it bears mentioning that the relatively extreme deviations from model pulse response observed during 5C GITT discharge pulsing in the microscale (AR) system were largely absent on charging, suggesting an energetic asymmetry between the intercalation and deintercalation reactions as described in Chapter 4 of this work.

![Figure 5-11: Variation in potentiodynamic response as a function of degree of $\varepsilon$-Li$_x$V$_2$O$_5$/\(\delta\)$-\alpha$-Li$_x$V$_2$O$_5$ phase transformation for sample NT at 5C current.](image-url)
Levi et al. have observed a similar feature in galvanostatically titrated graphite electrodes, as shown in Figure 5-12, though paradoxically, this feature was only evident at slow current pulsing and entirely absent from high current experiments. They attribute this feature of the pulse response to phase nucleation as depicted in the Figure 5-12.

![Figure 5-12: Potentiodynamic response at “slow” current pulsing across the LiC$_{12}$/LiC$_6$ intercalation peak in graphite. Reproduced from Levi, et al. [12]](image)

While the elaboration of a detailed mechanistic model which might permit the tracking of phase evolution consistent with the observed deviations from model response behavior in variable rate GITT technique is beyond the scope of the present work (see Chapter 6 for some preliminary observations on this topic), it seems clear that this approach bears further scrutiny. As of this writing, no single macroanalytical approach captures the proposed rate-limiting mechanism observed in these systems. PITT, while useful for identifying the presence of phase transformation behavior, is limited in that in necessarily steps across the entire biphasic regime in one experiment (due to the relative invariance of cell potential throughout a biphasic regime). The proposed modification of the GITT technique, on the other hand, if properly parameterized might allow for, not only the identification of phase transformation limited behavior, but further, provide some insight into the phase nucleation/evolution process through the entire biphasic plateau.
Summary

This chapter has considered two electroanalytic approaches to identifying phase transformation rate limited behavior in the Li$_x$V$_2$O$_5$ system, PITT and GITT. Both techniques show a clear correlation between particle dimensions and observed signatures of phase transformation. Nanoscaled materials, which show markedly superior cycling performance, show little evidence of phase transformation limited kinetics within the current regimes considered, while microscale materials show clear evidence of phase transformation limited kinetics at moderate currents. A modification to the standard GITT technique is proposed that might allow for the parameterization of phase transformation kinetics and the tracking of phase boundary motion.

References


Chapter 6 : Contributions of Dissertation

This chapter provides a summary of the findings of this study, synthesizing the conclusions from the previous two chapters and providing potential future directions for subsequent work.

General Conclusions

This thesis investigated the role of phase transformation on cycling kinetics in dimensionally graded mixed powder Li$_x$V$_2$O$_5$ cathodes. It began by considering a variety of potential rate-limiting mechanisms as described in the literature and proceeded by comparing the expected variation in performance as a function particle size with results observed in the dimensionally graded Li$_x$V$_2$O$_5$ system. Particle size reduction is expected to have four kinetic consequences; 1) an increase in the effective active material surface area which may facilitate enhanced rates of electrode/electrolyte reaction by lowering areal current densities 2) a decrease in the diffusion path length which should lead to faster bulk incorporation 3) an increase in bulk electronic conductivity and 4) at sufficiently small scales, a relaxation of strain constrains associated with Li$^+$ incorporation, phase nucleation and boundary motion (here generalized as phase transformation).

The effect of the first, increased surface area, was clearly observed in the reduction of discharge profile depression with decreased particle size at accelerated rates of discharge, though this effect is not believed to contribute significantly to variations in net cell capacity. The second effect, decreased path length, did not appear to significantly alter cell discharge performance as demonstrated by the large discrepancy between expected scaling effect and observed cell performance. The third effect, increased electronic conductivity, while incompletely analyzed due to the limited availability of the nanotemplated particles, is not expected to significantly alter cell performance in this system. The fourth effect, facilitated phase transformation, was unambiguously observed though a variety of structural, thermodynamic and kinetic variations which, in most cases, scaled consistently with reduction in particle dimensions. Those variations include, increased end-member solubility, decreased equilibrium cycling hysteresis, decreased volumetric mismatch, and deviations from expected PITT and GITT response behavior.
While no single experimental technique completely resolves the question of whether or not phase transformation is in fact rate-limiting, a preponderance of the evidence presented strongly indicates that phase-transformation does indeed control intercalation kinetics in this biphasic material at moderate to high rates of discharge.

Finally, a modification to the standard GITT technique was proposed that, if well-modeled, might lead to further insights into the phenomenology of phase transformation itself. While the development of such a model is beyond the bounds of this work, a point of departure is suggested in the following section.

**Suggested Directions**

**Additional Work with Particle Size Reduction**

As Meethong et al. Wagemaker et al. and others have noted, the nanoscaling of lithiating compounds such as LiTO$_2$ and LiFePO$_4$ leads to an increase in end-member solubility or, looked at from another vantage, a decrease in the biphasic miscibility gap. [1, 2] As they have suggested, it is interesting to consider the dimensional limits of this modification. Wagemaker has observed that below 50nm, phases in biphasic Li$_x$TiO$_2$ material are distributed between rather than within particles, while Meethong has considered the possibility of further reducing or completely eliminating the miscibility gap in sufficiently dimensionally reduced LiFePO$_4$ particles. As regards the Li$_x$V$_2$O$_5$ system, Patrissi et al., Chan et al. and Li et al. have observed very high rate performance in nanoscale Li$_x$V$_2$O$_5$ (significantly higher than those seen in this work), absent a systematic analysis of the manifold signatures herein ascribed to the phase transformation process [3-5]. As such it would be interesting to consider precisely those metrics in Li$_x$V$_2$O$_5$ prepared according to these techniques to further validate the proposed role phase transformation plays in discharge performance and to investigate the limits of this effect.

**Proposed Modification of GITT Boundary Conditions**

While the proposed variable rate GITT technique seems to provide some useful qualitative insight into rate limiting mechanisms in biphasic systems, it would be far more useful if quantitative information could be extracted from this technique. While this work does not pretend to resolve this matter, it suggests an approach that might lead in
that direction. Essential to modifying the conventional approach to titration analysis in biphasic materials, is a reformulation of the boundary conditions employed. Wang et al. have proposed the following model to describe the phase transformation process, as depicted in Figure 6-1.

Figure 6-1: Schematic representation of phase transformation and Li$^+$ concentration distribution with the LiFePO$_4$ cathode. Reproduced from Wang et al. [6]
They further propose the following modifications to the initial and boundary conditions employed to solve the diffusion equation that take into account the presence of rate-limiting phase transformation processes in intercalation electrodes. [6]

\[ C(x, t = 0) = C_{a\beta} \quad (0 \leq x \leq L) \quad \text{Equation 6-1} \]

\[ D \frac{\partial C}{\partial x}_{x=0} = \frac{I_0}{F} \quad (t \geq 0) \quad \text{Equation 6-2} \]

\[ C = C_\beta = \frac{1}{2} \left[ C_{\beta a} + C_{a\beta} + \sqrt{(C_{\beta a} - C_{a\beta})^2 - \frac{4C_{\beta a} D}{MRT(1 - A \times (1 - x_i(t))^2)}} \right] \quad \text{Equation 6-3} \]

\[ \frac{dx_i(t)}{dt} = \frac{D}{(C_{\beta a} - C_\beta)} \left( \frac{\partial C}{\partial x} \right)_{x=x_i(t)} \quad \text{Equation 6-4} \]

Where \( C \) corresponds to the concentration of lithium inside the active material particle, \( C_{a\beta} \) corresponds to the limiting \( Li^+ \) concentration of the Li-poor phase, \( C_{\beta a} \) corresponds to the limiting \( Li^+ \) concentration of the Li-rich phase, \( C_\beta \) corresponds to the actual interface concentration of the Li-rich phase, \( D \) corresponds to the lithium diffusion coefficient in the Li-rich phase, (which is assumed to be independent of concentration), \( x_i(t) \) corresponds to interface position, and \( i \) corresponds to the reaction current applied on the particle surface. Of particular note are the inclusion of parameters \( M \) and \( A \) which characterize the interface mobility, (which depends upon the degree of coherence at the interface and the buildup of stresses and deformations), and the energy associated with the volume change, respectively. In the limiting case of fast interface mobility, \( (M \rightarrow \infty) \), \( C_\beta \) will be equal to \( C_{\beta a} \) and the system of equations corresponds to the diffusion-control case described by Srinivasan and Newman. [7]

As the proposed system of equations yield highly accurate model fits to experimental data it would be interesting to consider the application of these conditions
to the proposed modification to the GITT technique. Unfortunately, as these equations do
not yield closed-form solutions, numerical methods are necessary, methods which lie
beyond the scope of the present work.

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