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Hierarchical Spatiotemporal Analyses of Reactions Using Synchrotron Radiation and the Design of Next-Generation Energy Conversion Devices

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ABSTRACT

To improve the performance of electrochemical devices such as batteries and fuel cells, it is essential to understand reaction hierarchies over wide temporal and spatial ranges. To this end, *operando* measurement techniques have been developed that enable analysis of the electrode/electrolyte interface of the reaction site, phase transitions of active materials, and macro reactions within real electrodes over various spatial and temporal scales. These analytic techniques pioneer a new way of performing kinetic analysis by introducing axes of space and time into reaction analyses, and are applicable to various types of electrochemical devices. Moreover, a magnesium rechargeable battery featuring the merits of high theoretical energy density, high safety, and easily acquirable raw materials was developed by employing these *operando* analytic techniques.

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1. Introduction

Electrochemical energy conversion devices such as lithium ion batteries, solid oxide fuel cells, and polymer electrolyte fuel cells are expected to become widely used for energy storage in electric vehicles and smart grid communities.¹ Understanding of the reaction hierarchies of such electrochemical devices over wide temporal and spatial ranges is essential background knowledge to improve their performance. Because the reactions in these devices are complicated and proceed in a nonequilibrium state, the kinetic factors and degradation mechanisms that govern them are not yet fully characterized. Figure 1 shows a schematic image of the elementary reactions in lithium ion batteries (LIBs) arranged along spatial and temporal scales. The main reaction for LIBs is the charge transfer reaction at the electrode/electrolyte interface, where lithium ions and electrons react with each other and after which lithium ions are stored in active materials. To achieve a more efficient reaction site and improve storage capacity for practical use, composite electrodes

consisting of active materials, carbon, and a binder are widely used. In practice, a battery pack is used as energy storage device. For the further improvement of battery performance, it is essential to characterize each elementary reaction mechanism and enhance these reactions. This article reviews *operando* measurement techniques using synchrotron X-ray radiation that were developed to observe reaction phenomena directly in electrochemical devices under operating conditions.

2. Interface between Electrode and Electrolyte

The reaction site in LIBs is a nanometer-scale interface between the electrode and electrolyte.² At the interface, the electrochemical potential difference between the electrode and lithium ions in the electrolyte should be compensated. This causes a potential drop around the interface, forming a space-charge layer at the electrode side and an electrical double layer at the electrolyte side. This results in anomalous transport properties at the interface, which differ from bulk properties. The space-charge layer is expected to exist at the interface between the solid-electrode and liquid electrolyte system in LIBs. Therefore, controlling the interface is an essential step towards significantly improving both the durability and the reaction kinetics of such batteries.³ The lifetime of LIBs is primarily limited by parasitic reactions that occur at the electrode/electrolyte interface,⁴ and deterioration at the positive-electrode/electrolyte interface, in particular, has been demonstrated in recent years to be an important factor affecting this lifetime.^{5,6} Therefore, observing the interface seems to be a quite important means to gain knowledge for improving battery performance. The scale of such an interfacial region is speculated to be on the order of a few nanometers, which is assumed to be approximately the Debye length. This scale indicates that the structural and chemical information should be tracked with a resolution of a few nanometers to reveal the phenomena of the electrode/electrolyte interface precisely.

For the analysis of the electrode/electrolyte interface, a well-defined flat surface is essential and thus the use of a thin film is

Figure 1. (Color online) Schematic image of elementary reactions in lithium ion batteries arranged along spatial and temporal scales.

Figure 2. (Color online) (a) Co *K*-edge XAS spectra and (b) TRF-XAS spectra of LiCoO₂ before and after electrolyte immersion. Absorption edge energy change during charge-discharge for (c) bulk LiCoO₂ and (d) surface LiCoO₂.⁷

suitable. Surface X-ray diffraction and X-ray reflectivity measurements of the interfacial structure under operating conditions have been reported.^{10,11} Although these methods are useful for investigating the interface, they hold the disadvantage of being unable to detect amorphous structures or electronic structure changes. Among the few methods that can be used to analyze the behavior at the interface of a flat thin-film electrode at a nanometer-scale spatial resolution, *operando* total-reflection fluorescence X-ray absorption spectroscopy (TRF-XAS) has risen to prominence as a potent technique for analyzing the electronic structure at the electrode/electrolyte interface under real battery operating conditions.^{7,8} This section introduces observations of interfacial phenomena between the electrode and electrolyte in LIBs obtained using TRF-XAS.

The reflective index of X-rays is just slightly smaller than unity. Therefore, a highly collimated X-ray beam applied to a flat surface at an angle smaller than the critical angle will be totally reflected.⁹ Such a beam penetrates the sample to a depth of only a few nanometers. In this condition, only atoms at the very surface of the electrode are excited and only the surface information is extracted. Considering the density of LiCoO₂ thin-film electrodes and the energy of Co *K*-edge XAS, the calculated critical angle of total reflection (θ_{TR}) of LiCoO₂ was determined to be 0.28° and the corresponding penetration depth to be 6.8 nm. When the incident angle was set at 0.2°, the penetration depth was estimated to be ~3 nm. The bulk information is obtained by setting the incident angle to be larger than the critical angle of total reflection; in this condition, the penetration depth has been estimated to be greater than 100 nm. For LiCoO₂ film of approximately 50 nm, information from the whole of the film can be obtained.

The surface structure of LiCoO₂ changes drastically when liquid organic electrolyte contacts it. Figure 2(a) and (b) show normalized Co *K*-edge TRF-XAS spectra obtained from the bulk and the surface before and after electrolyte soaking.⁷ While the bulk XAS spectra were unchanged by electrolyte soaking, the surface XAS spectra were significantly changed in contrast. The energy level shifted toward lower energy in the surface XAS spectra, which was attributable to a reduction of the Co ions at the surface of the LiCoO₂ electrode by contact with electrolyte. As the bulk XAS spectra were unchanged by electrolyte soaking, the reduction of Co

ions must have occurred within a depth of a few nanometers from the surface of the electrode. Such nanoscale phenomena cannot be observed by conventional bulk techniques. The reduction of Co at the electrode surface was confirmed by theoretical calculations.¹⁰

The oxidation and reduction properties of a LiCoO₂ surface during charge-discharge show hysteresis compared with the corresponding properties of the bulk. Figure 2(c) and (d) show the absorption energy at the normalized intensity of 0.5 in the XAS spectra under various potential conditions. The bulk XAS spectra shifted continuously toward higher (Co oxidation) and lower (Co reduction) energy levels as electrochemical charging and discharging proceeded, respectively. In the case of the bulk, the energy returned back to the original position after charge and discharge, suggesting that the LiCoO₂ bulk keeps its layered structure and shows good electrochemical reversibility. However, the behavior at the surface was essentially irreversible, in contrast to the good reversibility in the bulk. Although it appears that the surface Co²⁺ species formed during the electrolyte soaking process were oxidized during the charging, the reduction was insufficient.

Reduction at the surface forms a space charge layer at the LiCoO₂ surface. LiCoO₂ is a semiconductor with a relatively small band gap of ~1.5 eV.¹¹ The energy level of the bottom of the LiCoO₂ conduction band is sufficiently low to allow electron transfer from the electrolyte to the electrode. The reduction and the subsequent distortion of the local structure occur via this electron transfer. The changes in the electronic structure at the surface are related to the initial deterioration of the LiCoO₂ electrode. In addition, during the Li-ion extraction process, further deterioration occurs due to additional distortion of the local structure at the LiCoO₂ surface, as shown in Fig. 3(a).^{7,12}

Some methods for controlling interfacial reactions between the electrode and electrolyte have been investigated: they are shown as numbered in Fig. 3(b). (1) LiFePO₄ electrodes can stabilize the electronic structure at the electrode/electrolyte interface.¹³ The energy level at the bottom of the LiFePO₄ conduction band is much higher than that of the LiCoO₂. Thus, fewer electrons are transferred to reduce the electrode at the surface, and the space charge layer at the LiFePO₄ ends up being much smaller than that at the LiCoO₂. (2) Oxide coating such as MgO and ZrO₂ improves cyclability,

Figure 3. (Color online) (a) Schematic illustrations of changes in electronic structure at the LiCoO₂/electrolyte interface. (b) Methods for controlling interfacial reactions between the electrode and electrolyte.

especially at high potentials.^{8,14,15} Direct contact of LiCoO₂ with the electrolyte decreases space charge layer formation, but the magnesium ion serves as a pillar and stabilizes the layered structure of LiCoO₂ in delithiated states at the interface at high potentials. (3) Deterioration of the positive electrodes can be reduced by using electrolyte additives such as vinylene carbonate (VC).¹⁶ The formation of a layer of decomposed VC molecules at the LiCoO₂/electrolyte interface stabilizes the LiCoO₂ surface. *Operando* TRF-XAS has clearly shown that surface reduction is suppressed by these three controlling methods.

3. Phase Transition Dynamics

Phase transitions in active materials are accompanied by lithium insertion and extraction. The crystal structure during charge-discharge has generally been investigated through static measurements, in which thermodynamically stable states are characterized.¹⁷ In addition, the diffusion path of lithium ions, the dominant factor governing a battery's rate capability, has also been analyzed.^{18–20} Under real battery operating conditions, however, the crystal phase dynamically changes during lithium extraction/insertion. The dynamic phase transition is one of the critical parameters determining rate capability because the charge-discharge process of LIBs proceeds under nonequilibrium conditions. This section describes studies that have revealed the transient state of electrode materials under battery operation.

The polyanionic compound LiFePO₄ has been used as a model material to investigate phase transition dynamics. Its phase transition reaction proceeds in a two-phase manner between Li-rich Li_{1–*x*}FePO₄ (LFP) and Li-poor Li_{*β*}FePO₄ (FP).²¹ Strictly thermodynamically speaking, the crystal structure should remain unchanged between the two phases during the two-phase reaction. Electrode materials, however, react under nonequilibrium conditions, which can cause different phenomena from those expected from strictly thermodynamic calculations to occur. The transient phase change during battery operation have been tracked experimentally, and *operando* time-resolved X-ray diffraction (XRD) measurements have been performed to detect the transient state changes of LiFePO₄.

The transition behavior of the crystalline phase was assessed through XRD measurements. Figures 4(a) and (b) show XRD data collected during a 1 C charge reaction for 60 nm and 1000 nm LiFePO₄, respectively.²² Before in situ XRD measurements, the cell was charged slowly to 3.35 V, which is just below the plateau potential of LiFePO₄/FePO₄. This treatment can avoid the single

Figure 4. (Color online) Time-resolved X-ray diffraction pattern of (a) 60-nm and (b) 1000-nm Li_{*x*}FePO₄ particles during a galvanostatic charge reaction at a charge rate of 1 C. Reprinted with permission from ref. 22. Copyright 2013 American Chemical Society.

phase reaction for the LFP phase from influencing the results. For materials of this composition, only a merged peak at 19.15° from LFP (211) and (020) is observed. During the charge reaction, new peaks appear at 19.5 and 19.9° that correspond to FP (211) and (020), respectively. This result indicates that the two-phase reaction proceeds according to the 1 C charge rate. In the *operando* time-resolved XRD measurements shown in Fig. 4(a), the peaks of LFP (211) and (020) appear to shift and broaden during the two-phase reaction, in contrast to ex situ XRD measurements that show constant peak position and full width at half maximum (FWHM).²³ The peak shift is clearly observed especially for the diffraction of FP (020) in 60-nm LiFePO₄. The peak width and peak position estimated from Gauss function fitting can be used to discuss phase transition phenomena at the crystal size level.

The peak position shift is mainly related to the transient change of the lattice constant. The calculated lattice constants for both phases from the (020) reflection as a function of *x* in Li_{*x*}FePO₄ are plotted in Fig. 5(a). The *x* value represents the overall average concentration of lithium in the following formula Li_{*x*}FePO₄, which is estimated from the electrochemical charge current. At approximately *x* = 0.9, where the FP phase starts to form, the lattice constant *b* in the FP phase is much larger than that in the equilibrium phase, regardless of particle size. During further lithium extraction, the lattice constant *b* in FP decreases markedly to *x* = 0.6 and then gradually approaches the equilibrium value. On the other hand, the change of lattice constant *b* in the LFP phase appears dependent on particle size. For large-particle LFP, the lattice constant *b* is almost the same as the initial value and decreases slightly as lithium extraction proceeds. The lattice constant *b* of the 60-nm LFP gradually decreases with lithium extraction. However, the change in

Figure 5. (Color online) (a) Lattice constants of LFP and FP as a function of lithium concentration x estimated from the electrochemical charge current during a galvanostatic charge reaction at a charge rate of 1 C. (b) Gibbs free energy diagram for the two-phase reaction between LFP and FP. Reprinted with permission from ref. 22. Copyright 2013 American Chemical Society.

the lattice constant is much smaller than that observed for FP, and the degree of the decrease in lattice constant b in FP at the end of the charge reaction is also greater for the smaller particles.

The present results can be explained by using the Gibbs energy diagram shown in Fig. 5(b). In a two-phase coexistence system, the phase change can be expressed by two Gibbs free energy curves and the common tangent. When the lithium ion is extracted from the solution limit of $\text{Li}_{1-\alpha}\text{FePO}_4$, phase separation between LFP and FP can occur. The chemical potential line of this stage is expressed by the tangent line of $\text{Li}_{1-\alpha}\text{FePO}_4$. The initial lithium concentration of the FP phase formed in a $\text{Li}_{1-\alpha}\text{FePO}_4$ particle is located at the intersection between the tangent lines of the Gibbs energy curve for LFP at $\text{Li}_{1-\alpha}\text{FePO}_4$ and the Gibbs energy curve for FP. This is because the driving force for FP formation is generated only for $\beta' > x > \beta$, and the lithium concentration should change continuously from $x = 1 - \alpha$ to $x = \beta$ during the charge reaction. That is, the formation of two thermodynamically stable phases ($\text{Li}_{1-\alpha}\text{FePO}_4$ and $\text{Li}_\beta\text{FePO}_4$) is delayed under nonequilibrium conditions during battery operation. The instantaneous phase corresponds to $\text{Li}_{\beta'}\text{FePO}_4$, which has a larger lithium concentration than the thermodynamically stable $\text{Li}_\beta\text{FePO}_4$.

However, when the charge-discharge reaction of LiFePO_4 is performed at a rate of 10 C, the transient state is quite different to this well-known two-phase reaction. Figure 6 shows the change in XRD peak during five charge-discharge cycles at a rate of 10 C with a relaxation period between cycles.²⁴ Before charging, a peak at 19.15 degrees was observed, which corresponds to diffraction by the (211) and (020) planes of LFP. The charge reaction causes the appearance of peaks at 19.50 and 19.87 degrees, which are attributable to the (211) and (020) planes of the FP phase, respectively. What is remarkable is that, in addition to the diffraction peaks in the thermodynamically expected phases, an unknown peak

Figure 6. (Color online) Time-resolved XRD patterns for Li_xFePO_4 during galvanostatic charge-discharge cycles at a charge rate of 10 C. The diffraction peaks of LiFePO_4 (211) and (020) at 19.15 degree overlap, whereas those of FePO_4 at 19.50 and 19.87 degrees do not. Reprinted with permission from ref. 24. Copyright 2013 American Chemical Society.

appears at 19.35 degrees during the first discharge and subsequent charge-discharge reactions. The appearance of the new peak can be seen more clearly in the individual diffraction patterns acquired during the first discharge and the second charge. The lattice constant of the b -axis is estimated as $b = 5.936\text{--}5.945$ Å. According to Vegard's law, this range of lattice constants corresponds to Li_xFePO_4 ($x = 0.61\text{--}0.66$). It should be noted here that these peaks slightly shift during electrochemical cycling, yielding some uncertainty in the calculated lattice constants. Despite such uncertainty, the lattice constants are almost entirely consistent with the reported values of thermally formed metastable solid solutions of Li_xFePO_4 with lithium mole percentage of 0.6–0.75.^{25,26} Therefore, the new peaks observed during the charge-discharge reaction are believed to derive from the electrochemically formed Li_xFePO_4 ($x = 0.6\text{--}0.75$) solid solution phase.

The results from *operando* time-resolved XRD measurements represent experimental evidence in favor of the existence of a nonequilibrium phase transition path between FP and LFP. When the reaction potential of the discharge process is just below the equilibrium potential between the FP and LFP phases, a direct phase transition from FP to LFP should occur. This situation is essentially a quasi-static phase transition. The rate-determining step in the phase transition of Li_xFePO_4 is then expected to be the nucleation reaction.²³ The large lattice mismatch between FP and LFP (+3.6% and −1.8% in the b and c axes, respectively) gives rise to a large interfacial energy, which in this case means that the quasi-static phase transition can make only a small contribution to current flux. A reaction potential much lower than the equilibrium potential would be required for a discharge process with large current flux, leading to a much lower discharge potential than at equilibrium. The reaction potential from the FP to the Li_xFePO_4 phase is lower than the equilibrium potential between the FP and LFP phases, because the Li_xFePO_4 phase is not thermodynamically stable. In this regard, an applied electrochemical driving force with large current flux can be employed to overcome this potential difference.

The rate-determining step of the phase transition between FP and LFP is reported to be nucleation of the formed phase.²³ Nucleation energy is equivalent to the change in free energy for the formation of the new phase, interfacial energy, and strain energy. The lattice mismatch between the FP and Li_xFePO_4 phases is considerably lower (+2.5% and −0.66% in the b and c axes, respectively) compared with the mismatch between the FP and LFP phases. This

Figure 7. (Color online) Cross-sectional two-dimensional mapping of X-ray absorption energy at Fe K-edge in LiFePO₄ composite electrodes. Current collector is located at the bottom side.

reduced lattice mismatch may be a preferable condition to enact in order to decrease the strain and interfacial energies, and thus the nucleation energy. Therefore, the nonequilibrium phase transition path can make a large contribution to optimize the behavior of a system with large current flux by acting as a bypass route.

4. Analysis of Reaction Distribution

It is well known that the morphology of composite electrodes influences the electrochemical performance of batteries. To improve the performance of LIBs in practical use, it is necessary to tune parameters of composite electrodes such as porosity, compounding ratio and thickness.^{27–30} However, even though much research has been performed in the field of LIB development, the most calibration of composite electrodes has been performed on an empirical, trial-and-error basis to date because the factors determining composite electrode performance are not rigorously and theoretically understood. From a practical standpoint, it is quite essential to scientifically develop a principled design guide for composite electrodes. In composite electrodes, electrons and lithium ions are supplied from current collectors and the electrolyte side, respectively. In their conduction paths, there are a number of internal resistances inherent in the composite electrode. The electronic conduction is influenced by metric and film resistances in aluminum, and by carbon and surface resistances in active materials. The ionic conduction is impeded by ionic resistance in the electrolyte and pores in composite electrodes, and by solid state diffusion in active materials. Since the electrode reaction occurs preferentially in regions with lower resistance, the reaction distribution might vary along the depth direction within composite electrodes, especially in large-scale LIBs. This section introduces several analyses of reaction distributions in composite electrodes and discusses the factors behind them.

Figure 7 shows the cross-sectional reaction distribution mappings of the electrodes with different porosities discharged with the nominal composition of Li_xFePO₄ approaching $x = 0.45$ at a rate of 10 C. The color change from blue to red represents that a decrease in absorption energy corresponding to the discharge reaction taking place. Therefore, the transition from blue to red in the color bars indicates that the discharge reaction proceeds. Low porosity electrodes seem to undergo an inhomogeneous reaction. When the porosity of the electrode is 44%, and 36%, the reaction occurs preferentially at the electrode/electrolyte interface. However, a uniform reaction is achieved when the porosity is 56%.

The impact of porosity on cross-sectional reaction distribution can be attributed to effective ionic and electronic conductivities. In order to measure these, we have developed a method for simultaneous measurement of electronic and ionic conductivities in composite electrodes based on the reported principle.³¹ Figure 8 shows the effective ionic conductivities for various porosity composite electrodes. The electronic conductivity is at least 10

Figure 8. Effective ionic conductivity as a function of porosity in LiFePO₄ composite electrodes.

times higher than the ionic conductivity, which implies that the contribution of the ionic conduction to the electrochemical performance is dominant. For high-porosity electrodes, the effective ionic conductivity is almost constant; for electrodes having porosities of less than 47%, the ionic conductivity decreases. This result indicates that the effective ionic conductivity decreases due to the narrow and distorted ion diffusion paths within the composite electrode and the pores of the electrode. The narrow and distorted pores impede movement of Li ions and produce a concentration gradient within the composite electrode, consequently leading to large concentration polarization, especially at the end of discharge reaction.

Low porosity causes composite electrodes to exhibit large polarization in high-rate discharge reactions and decreases their capacity. In these electrodes, the discharge reaction occurs preferentially at the top surface of the electrode, at the electrolyte side. Further, low porosity results in low effective ionic conductivity. Ionic conduction in the composite electrodes is the primary factor governing LIB performance. Controlling the ionic conductivity of composite electrodes is an important means to further improve the performance of LIBs.

5. Summary and Outlook

This article introduced synchrotron-based *operando* X-ray measurement techniques, which enable analysis of the electrode/electrolyte interface of the reaction site, phase transitions of active materials, and macro reactions within real electrodes over various spatial and temporal scales. This analytic technique is a dramatic step forward in that it pioneers a new way of performing kinetic analysis by introducing axes of space and time for reaction analyses.

Figure 9. (Color online) Charge-discharge profiles of ion-exchanged MgFeSiO₄. Three-electrode cells using a Mg metal counter electrode and a silver reference electrode were used. The electrolyte was 0.5 M magnesium (trifluoromethylsulfonyl)imide (Mg(TFSI)₂) in acetonitrile (solvent).³³

Figure 10. (Color online) Schematic illustration for the recent development of magnesium rechargeable battery.

Knowledge of reaction mechanisms obtained through these techniques has been utilized to develop novel magnesium rechargeable batteries.

Magnesium rechargeable batteries are poised to become viable alternatives for large-scale energy storage devices in smart grid communities and electric vehicles.³² However, their energy density is low, limited mainly by the cathode materials. Ion-exchanged MgFeSiO_4 is a material that can help to realize a high-energy-density battery system: it demonstrates a high reversible capacity exceeding 300 mAh g^{-1} as shown in Fig. 9.³³ The electronic and crystal structure changes during the charging and discharging process, which is a manifestation of the insertion and extraction of magnesium in the host structure. A proposed system that combines ion-exchanged MgFeSiO_4 with a magnesium bis(trifluoromethylsulfonyl)imide–triglyme electrolyte (shown in Fig. 10 as the 4th generation magnesium rechargeable battery) confers a low-cost and practical rechargeable magnesium battery with high energy density that is free from corrosion and safety problems. This summarized research has uncovered excellent possibilities for practical applications of magnesium rechargeable batteries, and its results are momentous in that they provide a starting place for the development of new electrochemical energy conversion devices.

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