Innovation in Rechargeable Batteries and Battery Analysis
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ABSTRACT
Innovation in rechargeable batteries is urgently required to meet demands for application such as electric vehicles, renewable energy storage, and emergency backups. Next-generation rechargeable batteries include novel rocking-chair batteries, metallic lithium/sodium batteries, metal-air batteries, and flow cell systems. In order to improve battery performances and to bring innovation in rechargeable batteries, detailed knowledge on the battery reaction is indispensable. For clarifying the reaction mechanisms in details and proposing a guideline for the improvement, it is required to understand the heterogeneity (inhomogeneity), non-equilibrium and dynamic phenomena inside batteries under operating conditions. As an example, phenomena at electrode/electrolyte interface are elucidated by using surface-sensitive X-ray absorption fine structure analysis, X-ray photoelectron spectroscopy and nuclear magnetic resonance analysis. These analytical methods are applicable not only for the advanced LIB systems but also for totally innovative systems. Elucidating and understanding the reasons for the inactivity, slow kinetics and deterioration of LIB will be the key to open post LIB technology.

Keywords: Post Lithium Ion Batteries, In Situ Analysis, Synchrotron-Beam Aided Analysis, Nuclear Magnetic Resonance Analysis

1. Introduction
Lithium ion batteries (LIBs) and nickel metal hydride batteries have been successfully developed in the beginning of 1990s and both have drastically extended the battery markets. Especially LIB has been playing a main role of “Game Changing” in the area of information technology. Turning our eyes to mobility, electric vehicles employing rechargeable batteries are attracting so strong attentions. Since the disaster on March 11th 2011 in Tohoku area in Japan, batteries for electric power storage are in the spot-light. Higher performance batteries are urgently required to meet demands for application such as electric vehicles, renewable energy storage, and emergency backups.

Among battery performances, energy density is the most important requirement of today so as to supply power to electric vehicles for long driving distance or to smart phones for long working hours per charge. The ultimate energy density of LIBs is predicted to be 250 Wh kg\(^{-1}\), which is extremely high when compared with other battery systems but still insufficient to fulfill the present consumers’ demand. For large applications, cost and safety are the more serious issues, which are the issues of current LIB systems. Totally innovative battery systems are necessary to meet these requirements, and it probably takes a few decades before their commercial production. Consequently, material innovation in the LIB is required, in addition to the development of post LIBs.

In this article, a brief survey of current topics for next-generation rechargeable battery is first described, including advanced materials for LIBs, novel rocking-chair batteries, metallic lithium/sodium batteries, metal-air batteries, and flow cell systems. Then the importance of reaction analysis, in situ analysis in particular, is introduced in terms of battery innovation. Finally a few examples of recent results from the authors’ affiliations, with the aid of synchrotron-beam and nuclear magnetic resonance, are described and discussed.

2. Next-Generation Battery
2.1 Advanced materials for LIBs
Since the commercialization of LIBs, there has been extensive progress in the electrode material research to improve their performance. Among positive electrode materials, so called “lithium-excess manganates” have recently been explored with a capacity of 300 mAh g\(^{-1}\), which is twice as large as the capacity of conventional LiCoO\(_2\). The origin of the large redox capacity has...
not yet been clarified but could be related to oxygen species. Promising candidates for inexpensive iron polyanion compounds are LiFeBO$_3$, Li$_2$FeP$_2$O$_7$, Li$_2$FePO$_4$F, and Li$_2$FeSiO$_4$.

On negative electrodes, many alloys have been proposed and partially commercialized. Silicon and tin are the most attractive candidates because of their large capacity and resource abundance. Problems associated with large volume change on lithiation/delithiation are getting solved using nanotechnology.

2.2 Novel rocking-chair batteries

Besides LIBs illustrated in Fig. 1(a), there are some kinds of rocking-chair type batteries. Among them, sodium ion batteries are the current topics. Although sodium is heavier than lithium and shows less negative potential, which leads to lower energy density, its inexhaustible resource and the availability is appealing. On negative electrodes, many alloys have been proposed and partially commercialized. Silicon and tin are the most attractive candidates because of their large capacity and resource abundance. Problems associated with large volume change on lithiation/delithiation are getting solved using nanotechnology.

2.3 Batteries with metal negative electrodes

Metals as negative electrodes have been widely used in batteries such as zinc in dry cells and lead in lead-acid batteries. Metallic lithium and sodium are very attractive as negative electrodes because of their strong reducing power and lightweight. However, the irreversibility in dissolution/deposition reactions leads to limited cycle life and safety, and has hindered their use in practical systems except for the high temperature Na/S batteries. We should remember the failure of Li-MoS$_2$ rechargeable battery safety in 1980's and essentially no breakthrough has been brought about the metallic lithium electrode so then. Solid (both inorganic and polymer) electrolytes and ionic liquid would be applicable for improving the performance. When these metal electrodes become practically available, combination with positive electrode materials such as sulfur with a high capacity will lead to rechargeable batteries with high energy density. The use of conversion reactions such as FeF$_3$ and CoO is also attractive but still some issues are remaining before its practical use.

Magnesium has been also studied as the negative electrode and the cells with organic electrolyte solutions have been reported. Calcium systems are very limited. Strong coulombic interactions of these multi-valence ions with the electrodes/electrolytes hinder fast ionic transport and thus limit the practical capacity and rate performance.

2.4 Metal-air batteries

Metal-air batteries such as lithium-air and zinc-air batteries are widely studied as ultimately large capacity batteries. The main component in the cell is a metal negative electrode and a thin oxygen positive electrode using oxygen in the ambient atmosphere as the active material (air electrode). Oxygen is, needless to say, free, abundant and so an ideal active material.

Lithium-air system is attracting strong attentions in these years but there are many issues to be solved both in the air electrode and in the metallic lithium electrodes. When non-aqueous electrolyte is applied as shown in Fig. 1(c), problems reported so far include air inlet clogged with the insoluble discharge product Li$_2$O$_2$, limited rechargeability, and organic electrolyte incompatibility with humidity. The use of aqueous electrolyte as shown in Fig. 1(d) with lithium protecting solid electrolyte can partly solve the issues. Nevertheless, the difficulty in using metallic lithium electrodes has been practically unsolved as mentioned above.

Zinc-air, a representative aqueous air system, has a long history and is still attractive because of the large volumetric capacity and cost effectiveness. Although the primary battery is commercially available, rechargeable battery has suffered from the dendrite formation on zinc deposition and degradation of air electrode during charging. To escape from these difficulties, mechanical charging has been proposed where the fresh zinc electrode replaces the discharged electrode. An extensive study including the infrastructure is required for the mechanical charging system before its practical use.

2.5 Flow cell systems

Flow cell systems have recently been focused on as large energy storage systems because of its durability and size scalability (merely depending on the size of the flow solution tanks). The currently
developed systems mostly belong to the vanadium ion redox type, where V⁴⁺/V⁵⁺ and V²⁺/V³⁺ couples are employed in the aqueous solution. A new type of flow batteries was proposed that uses fine powder materials for LIB electrodes slurried in organic electrolytes.

3. Analysis for Battery Innovation

In order to improve battery performances and to bring innovation in rechargeable batteries, detailed knowledge on the battery reaction is indispensable. Batteries are generally sealed to avoid electrolyte leakage and undesirable reactions with humidity, and this makes reactions in batteries invisible. Accordingly, the battery reaction analysis is hardly employed under battery operation and has been limited so far mainly to destructive methods and at best to static modes with averaged images of the bulk materials such as electrodes and electrolytes themselves. For clarifying the reaction mechanisms in details and proposing a guideline for the improvement, it is required to understand the heterogeneity (inhomogeneity), non-equilibrium and dynamic phenomena inside batteries under operating conditions. Phenomena at electrode/electrolyte interface are good examples. They occur only during battery operation. In order to observe such phenomena a new analytical technology is required with a sufficient space resolution (of nanometer scale). Turning our viewpoint, the space scale of battery reactions ranges from nanometer to centimeter scales as illustrated in Fig. 2.

For further development of battery technology and leading to innovative batteries, it is essential to understand the battery reactions in wide time and space scales, namely, to develop advanced in situ analysis technology for batteries.

In situ electrochemical scanning probe microscopy and atomic force microscopy are a powerful tool to study surface morphology of the electrode. Other important laboratory techniques include Raman and Fourier-transformed infrared spectroscopy that enable to obtain vibration-related information during battery operation.

As large hardware facility analysis, synchrotron-X-ray beam is so strong that the light can pick out the reactions inside the batteries. That is, synchrotron-X-ray beam can penetrate laminate type batteries and thus we can elucidate the reactions inside the battery even in operation. Wide space ranges are available using beam-focusing and various detectors. With bright X-ray beam, an X-ray absorption fine structure (XAFS) spectrum or an X-ray diffraction (XRD) pattern can be measured less than 1 s. To detail the phenomena at the interface, XAFS clarifies the electronic and local structure of the element of interest. X-ray photoelectron spectroscopy (XPS) with hard X-ray is also promising as it enables to measure the solid electrolyte interphase (SEI) components without using destructive sputtering techniques. It also allows semi-quantitative analysis of SEI thickness.

Nuclear magnetic resonance (NMR) spectroscopy is also an attractive method with its element selectivity and high quantitativity. Although the space resolution is limited, the signal is highly sensitive to the environment of the element of interest and consequently is useful to analyze the local structure such as interface.

In the following section, some examples of the interface analysis are described.

4. Nano-Scale XAFS Analysis of Electrode Surface

As an example of electrode/electrolyte interface analysis, the surface of LiCoO₂ was examined using the depth-resolved (DR) XAFS method. A polycrystalline LiCoO₂ thin film electrode was used as a model electrode with a well defined surface. A film of 50 nm thickness was prepared on a platinum substrate using pulsed laser deposition at 873 K. As shown in Fig. 3(a), the fluorescence X-ray from the sample was detected by a pixel-array detector to provide information from the surface to the bulk with a fine space resolution of several nanometers. Delithiation from LiCoO₂ was examined to potential of 4.2 V and then to 4.4 V vs. Li/Li⁺, with using the XAFS spectra obtained for cobalt K-edge at around 7.7 keV.

Figure 4 shows the distances and Debye-Waller (DW) factors for Co-O bonds in Li₁ₓCoO₂ obtained by analyzing the extended X-ray absorption fine structure (EXAFS). During delithiation to 4.2 V, the Co-O distances shrank as expected for Co oxidation. The DW factors were unchanged in the bulk but increased at the surface with delithiation, suggesting that the delithiation took place first at the surface. When the potential was set at 4.4 V, there was further bond shrinkage in the bulk but no change in the bond distance at the surface, which shows that the surface was inactive for further oxidation. The DW factors now increased both in the bulk and at the surface. It has been well recognized that at this potential the reversibility of the Li₁ₓCoO₂ electrode is lost. The result of DR XAFS shows that instability starts at the surface. It is expected that surface coating could suppress this deterioration.
A newly developed surface sensitive XAFS method using total reflection [shown in Fig. 3(b)] is even surface sensitive and the information of 1–2 nm depth of the electrode can be obtained.23 With this method, the change at the top surface of the electrode can be clearly understood, in combination with the DR XAFS method.

5. Electrode Surface and SEI Analysis with XPS

The hard XPS method was applied to observe the LiCoO₂ surface and SEI formed on LiCoO₂ in contact with organic electrolyte solutions.24 As the SEI film sometimes grows up to several tens of nanometers, it is desirable to use a highly penetrative hard X-ray beam. For estimating the SEI film thickness, theoretical calculation was employed to obtain escape depths of photoelectron from various SEI components. For example, Fig. 5 shows the calculated escape depths of Co 2p₃/₂ photoelectron from LiF at various kinetic electron energy levels, which are useful to evaluate LiF film thickness formed on the LiCoO₂ electrode. The validity of this kind of calculation was proven by experiments using model SEI films.

Figure 6(a) shows the Co 2p₃/₂ photoelectron spectra from the LiCoO₂ composite electrode immersed in the organic electrolyte solution containing LiPF₆ as a solute. The decreased signal intensity suggested that the SEI was formed on the electrode. The F 1s photoelectron spectra shown in Fig. 6(b) indicated that the electrode had a signal at around 685 eV corresponding to LiF after electrolyte immersion, in addition to that at 688 eV for the fluorinated polymer binder. Since other possible organic SEI components that could show signals at C 1s spectra were insignificant, it was inferred that the SEI covering the LiCoO₂ was mainly LiF. Using Lambert-Beer’s law, the apparent signal intensity decrease in the Co 2p 3/2 is attributed to the formation of LiF of around 5 nm. It should be noted that the peak energy value of the Co 2p₃/₂ slightly shifted to lower binding energy levels with the immersion, suggesting that the surface cobalt species was somewhat reduced on immersion. When such an electrode was stored at 60°C, the film was grown up to 30 to 40 nm associated with the formation of some carbonate compounds.

The method described here can be applied to the observation of SEI film during charge/discharge and storage processes and hence should be useful in estimating important characteristics of batteries such as durability, rate capability and safety.
6. LiF Detection Using NMR

As described in the previous section, XPS is useful for detecting the existence of light elements in thin SEI films that are hardly detectable with the XRD or hard XAFS methods. However, the obtained binding energy values (for example of F 1s) are not always helpful in identifying the components, as several materials can have the same binding energy. This is also true for the NMR measurement when only a single component, such as \(^{19}\)F, is measured. Fortunately, \(^{7}\)Li is also a NMR active species and the correlation between \(^{19}\)F and \(^{7}\)Li can be used to show the existence of LiF. Namely, using the advantage of the environmentally sensitive NMR principle, the cross-polarization NMR method utilizing magnetization transfer from \(^{19}\)F to the adjacent \(^{7}\)Li can be detected. The signal shown in Fig. 7(c) measured in this way clearly indicates the formation of LiF on the LiCoO\(_2\) electrode.

Figures 7(a) and 7(b) show the \(^{7}\)Li spectra of LiF powder and the LiCoO\(_2\) electrode immersed in the organic electrolyte solution containing LiPF\(_6\) as a solute. As both LiF and LiCoO\(_2\) have the \(^{7}\)Li signals with chemical shifts at around 0 ppm, it is unclear whether LiF was formed on the LiCoO\(_2\) electrode or not. When the cross-polarization method is employed, only the \(^{7}\)Li species adjacent to \(^{19}\)F can be detected. The signal shown in Fig. 7(c) measured in this way clearly identifies the formation of \(^{7}\)Li on the LiCoO\(_2\) electrode. As the NMR method is applicable to light nuclei such as \(^{1}\)H and \(^{13}\)C and is highly quantitative, this method can greatly contribute to evaluation of SEI films. Other nuclei such as \(^{27}\)Si and \(^{27}\)Al are also attractive for applying the NMR method to various battery systems.

7. Summary

In this article, the importance of the reaction analysis for the battery innovation is emphasized, together with current trends for battery innovation. As examples of the analytical methods, surface-sensitive XAFS, XPS, and NMR analyses are introduced and some practical application studies are described. Although the application described here are limited to LIB, the technology are useful not only for the advanced LIB systems but also for totally innovative systems; elucidating and understanding the reasons for the inactivity, slow kinetics and deterioration of LIB will be the key to open post LIB technology.

Many researchers in academic institutions and industries must devote their power to the development of post LIBs, and the authors believe that the deep understanding of LIBs will help for this accomplishment, with a motto of “more haste, less speed.”

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References


Figure 7. \(^{7}\)Li NMR spectra of LiF (a), LiCoO\(_2\) electrode (b), and LiCoO\(_2\) electrode using \(^{19}\)F to \(^{7}\)Li cross polarization (c). Both (b) and (c) are from samples immersed in the organic electrolytes containing LiPF\(_6\).