Nanocycles of Materials’ Transport studied by *in-situ* Electron Microscopy and Diffraction

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Abstract. A sub-50pm resolution electron microscope was applied for *in-situ* studies of ion transport in lithium ion battery and CO-oxidation catalyst. Lithium ions in LiM₂O₄ electrodes (M: transition metals) and titanium ions in Au/TiO₂ catalyst were enabled us to observe individually by ABF-STEM and TEM. Transport of lithium ions was seen, after *in-situ* observations, to induce structural transformation of the electrode materials that causes irreversible cycle of the battery reaction. Transport of the interstitial titanium ions results, due to oxygen gas for CO-oxidation, in modification of Au/TiO₂ interface structure. *In-situ* studies, thus, revealed materials’ transformation induced locally by ion/electron transport of the battery/catalyst system at high resolution and high contrast.

1. Introduction

It is of great interest to reveal ionic/electronic process in batteries and in catalysis, so as to manage utilization of their systems realizing the energy saving and resource saving. Ionic/electronic processes induce structural transformation of materials concerned, so that their cyclic process can often be irreversible, which affect efficiency and/or life-time of the system. As for rechargeable batteries, particularly for vehicles, one of issues is long lifetime [1-3]. Charge-discharge cycles change the interface structure between electrode materials and electrolyte irreversibly [4-6], which is thought to deteriorate the battery lifetime. As the shorter charging time causes the faster deterioration, we need nano-scale understanding of the issue. Lithium ion transport, then, is fundamental process at lithium ion battery electrodes. For nano-scale study of the change-discharge process, transmission electron microscopy (TEM) is one of powerful methods [7].

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Furthermore, in-situ TEM observation could give rich information about local structure change of cathode and/or anode materials during battery reaction, as demonstrated by Huang et al [8-10]. They revealed anisotropic swelling of Si nanowire anode during lithiation by in-situ TEM observation [11]. However, electrochemical measurement such as cyclic voltammetry has not been performed simultaneously with the structural observation. Simultaneous in-situ observation is really inevitable for nano-scale understanding and realization of long-life batteries against rapid-charging.

On the other hand, in titanium dioxide (TiO$_2$)-based catalysis, substrates of titanium dioxide (TiO$_2$) and other transition-metal oxides are widely as metal nanoparticle catalysts [12]. Gold nanoparticle catalysts for low-temperature CO oxidation (2CO + O$_2$ → 2CO$_2$) [12] are especially attractive for applications in air purification and reduction of environmental burdens. The catalytic activity in gas environments depends on the morphology [13,14] and electronic structure [13,14] of contacts between metal nanoparticles and the oxide support. The morphology and electronic structure change via strong metal-support interaction (SMSI) [13-17], which causes complication in understanding the catalytic reaction path. The SMSI at Au/TiO$_2$ caused by the reaction between interstitial Ti ions and adsorbed O$_2$ molecules [13,14]. In-situ electron microscopy, therefore, might give certain information about SMSI, when interstitial titanium ions could be detected directly. In-situ study at high resolution is a mean to find reaction path of CO-oxidation, via SIMS.

2. Experimental

In-situ studies were done using an aberration corrected electron microscope achieving a sub-50pm resolution, R005 microscope [18]. The microscope is fitted with two aberration correctors for probe forming and for image forming, both of which are operated simultaneously for STEM-TEM imaging. The microscope, equipped with a cold field emission emitter of a tungsten <111> tip, is daily used at accelerating voltages of 300, 200, or 80 kV [18].

For in-situ observation of lithium ion transport, we developed a specific specimen holder which has enabled us to observe a current-voltage relation of a LiMn$_2$O$_4$-nanowire[19]-based lithium ion battery and structure change of the nanowire simultaneously[20]. Structure observations were done by STEM imaging (ABF and/or HAADF) and TEM with diffraction images.

For study of CO-oxidation catalysis, gold nanoparticles deposited on TiO$_2$, we developed a specimen holder with gas injection nozzles opening at the specimen surface. Specimens of Au/TiO$_2$ were prepared in a separate vacuum chamber, just before the in-situ observation: A TiO$_2$ (rutile) crystal was crushed into pieces and annealed at 1170 K for 1 hour at 10$^{-4}$ Pa, and characterized by CL (cathode luminescence). The gas pressure at the Au/TiO$_2$ specimen could increase/decrease within one second from the base pressure of 2x10$^{-5}$ Pa up to 100Pa.

3. Results and Discussion

3.1 Individual lithium ion imaging in LiV$_2$O$_4$ and LiMn$_2$O$_4$ crystal by STEM

Structure change is discussed in relation to the current-voltage relation of a model LIB. At excess or deficient concentration of lithium ions, spinel electrodes exhibited local disorder. The bulk LiMn$_2$O$_4$ crystal forms different phases: X-ray analysis [21-22] shows that the crystal is in the cubic spinel phase for x=1, but in the tetragonal phase for x=2. We observed as-grown LiMn$_2$O$_4$ nanowires by the R005 microscope. High resolution ABF (annular bright field) images shown in figure 1(a) and (b) demonstrate that lithium ions can be detected discriminating from the Mn and/or O columns. In addition, the images clarify the termination of the surface layer. Comparing the observed images with the model structure, the as-grown nanowires had the cubic-spinel structure. Such as-grown LiMn$_2$O$_4$ nanowires were used for nanowire-based model battery.
3.2 In-situ observation of nanowire-based lithium ion battery

For simultaneous observation of cyclic voltammetry (CV) and the nanowire cathode (ILE) interface, we fabricated nanowire batteries as illustrated in figure 2: The nanowire electrode has generally thick bundles consisting of short LiMn$_2$O$_4$ nanowires. Figure 3(a) shows the CV of a “single” nanowire battery. The pair of double current peaks in figure 3(a) corresponds to the 4V battery reaction (vs Li/Li$^+$), where the lithium concentration change between $x=1$ and $x\sim0$ of Li$_x$Mn$_2$O$_4$. The battery looks like figure 3(b), and a single LiMn$_2$O$_4$ nanowire looks in TEM images like figure 3(c). In general, LiMn$_2$O$_4$ nanowires in our batteries maintained the cubic structure during charge process. In the discharge process, the cubic structure changed into the tetragonal phase, which was restored the cubic phase in the next charge cycle.
It is interesting that the LiMn$_2$O$_4$ nanowire was completely restored into the cubic phase from the tetragonal phase without fracture. This behaviour is different from the reported case of LiMn$_2$O$_4$ particles, which were damaged due to the tetragonal formation [23]. The observed reversible phase transformation without fracture supports that LiMn$_2$O$_4$ nanowires are promising as a cathode material improving the life-time of LiMn$_2$O$_4$ crystals based batteries.

![Image](image1)

**Figure 3.** (a) Typical cyclic voltammogram of the nanowire-battery. Horizontal axis is the voltage vs Li/Li$^+$ and the vertical axis is the current, I, passing through the Li$_x$Mn$_2$O$_4$ nanowire. The concentration, x, changes from two (at V=2 for the discharged state) to nearly zero (at V=5 for the charged state). (b) photo-image of a developed LiMn$_2$O$_4$ nanowire battery. (c) TEM image of a part of the nanowire, which shows that a “single” nanowire only bridges the platinum electrode and ionic liquid electrode (ILE).

### 3.3 Individual interstitial titanium ion imaging by TEM

Interstitial titanium (Ti) ions can be contained in our prepared Au/TiO$_2$ specimens. Figure 4(a) illustrates the view of TiO$_2$ crystal from the [110] direction. Interstitial Ti ions can occupy cation sites at the center of oxygen octahedrons [24-28]. As illustrated in figure 4(c), *titanium ions occupying the iv-site (“iv-Ti ions”) can be detected by TEM*. In figure 4(b) of a TEM image of TiO$_2$, a titanium ion is recognizable at the edge, which is adsorbed on the lateral (001) surface. In order to visualize interstitial Ti ions inside the edge, we simulated TEM images of TiO$_2$ columns with the iv-Ti ions, and those without them to derive the intensity given by a “single” iv-Ti ions in a column. Intensity calculations of the Ti-columns and Ti-O columns (see figure 4(a)) were agreed with experimental images, and also that a single iv-Ti ion gives a definite intensity. Furthermore, the intensity is doubled when two iv-Ti ions locate in the same atomic column [29].

High resolution TEM images of wedge-shaped TiO$_2$ specimens with Au particles were obtained (figure 5(a)). The atomic columns of the Ti-O, Ti-only and O-O are imaged as bright dots, similarly to figure 4(c). We determined thicknesses of the observed Ti-only columns from comparison with the calculation. In order to find “residual” image intensity at the iv-Ti sites, a “background-free” image was processed from figure 5(a) by subtracting the calculated image intensity without iv-Ti ions: The background-free image is shown in figure 5(b). As marked by rhombus, the residual intensity at the center of each rhombus, tells interstitial Ti ions occupying iv-Ti sites. Figures like figure 5(b) gives local distribution of interstitial Ti ions. The iv-Ti ions had high density at around Au/TiO$_2$ periphery, and deficient in the TiO$_2$. On the other hand, they are rather homogeneous in TiO$_2$ specimens without Au deposit [29].
3.4 In-situ study on titanium ions while oxygen gas injection on Au/TiO$_2$

Following discussions on SIMS, O$_2$ gases induce diffusion of Ti ions in Au/TiO$_2$ and TiO$_2$ (110) surface. In figure 6(a), our Au/TiO$_2$ specimens were found to have a specific phase at the perimeter of the Au/TiO$_2$ interface. As shown in figure 6(b), the specific phase grew extensively by exposing to O$_2$ gas at 100 Pa into a pillar which has a chemical composition of Ti$_{1-x}$O$_2$ ($x > 0$). Thus, in-situ TEM observation gave an evidence of Ti ion diffusion from substrate to surface by exposing to O$_2$. This observation, together with those in section 3.3, seems to suggest a possible scenario of Au/TiO$_2$ catalysis: In relation to O$_2$ gas exposure, interstitial Ti ions accumulate at the perimeter/interface of Au/TiO$_2$, providing new active sites which promote the O$_2$ adsorption and dissociation for the CO oxidation through electron donation.

![Figure 4](image4.png)

**Figure 4.** (a) Illustration of TiO$_2$ crystalline structure, and (b) configuration of an interstitial site of titanium ions, $iv$ site. Bright dot indicated by an arrow in (c) is an adsorbed ion, presumably, $iv$-Ti ion on the top surface.

4. Summary

A sub-50pm resolution electro microscope, R005, was applied for in-situ studies using a nanowire lithium ion model battery. Although the LiMn$_2$O$_4$ nanowire cathode was changed locally into the tetragonal phase while 4V reaction (vs Li/Li$^+$), the cathode was restored to cubic phase without any fracture to continue cyclic charge-discharge process. No fracture while cubic-tetragonal transition is promising for the long-life-time battery with LiMn$_2$O$_4$ nanowire cathode. The microscope was also used for study of Au/TiO$_2$ model catalyst of CO-oxidation. Interstitial titanium ions in TiO$_2$ substrates with gold nanoparticle (Au/TiO$_2$) were detected, and are found to be accumulated at Au/TiO$_2$ periphery in coincident with Ti$_{1-x}$O$_2$ pillar formation at the periphery.

![Figure 5](image5.png)

**Figure 5.** (a) Transmission electron microscope (TEM) image of Au/TiO$_2$, from [110] direction. (b) the same TEM image as (b), after the subtraction of simulated background intensity for each unit column. The colored rhombus indicates the position and the number of $iv$-Ti ions. Orange, green and light blue represents one, two and three ions, respectively. Yellow rhombus represents interstitial Ti ions at Au/TiO$_2$ interface / perimeter.
In conclusion, transport of ions results in structural transformation at nano-micron scale. In-situ studies revealed materials’ transformation, which is induced by interplay between charge and mechanical balances, at high resolution and high contrast.

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