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Nano-scale simultaneous observation of Li-concentration profile and Ti-, O electronic structure changes in an all-solid-state Li-ion battery by spatially-resolved electron energy-loss spectroscopy

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HIGHLIGHTS

- SR-TEM-EELS visualizes the Li profile and changes of Ti and O electronic structure.
- Titanium and oxygen contribute to the charge compensation of the inserted Li.
- Picometer-scale expansion of the O—O distance due to the Li insertion is visualized.
- *In-situ*-formed negative electrode inserted by Li has an amorphous structure.
- Amorphous-electrode/solid-electrolyte interface reduces the interfacial resistance.

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ABSTRACT

All-solid-state Li-ion batteries having incombustible solid electrolytes are expected to be promising candidates for safe next-generation energy storage devices that have a long lifetime and high energy density. However, it is essential to address the large resistance of Li-ion transfer at the electrode/solid-electrolyte interfaces. A new concept electrode that is formed *in situ* from the Li_2O—Al_2O_3—TiO_2—P_2O_5-based glass-ceramic solid electrolytes with Si and Ge doping (LASGTP) produces atomic scale connection at the interfaces, which provides extremely low interfacial resistance. However, the formation mechanism and the reason for the low resistance are still unclear. Here we applied spatially-resolved electron energy-loss spectroscopy in a transmission electron microscope mode (SR-TEM-EELS) to visualize the nanometer-scale Li distribution and its effects on the electronic structures of other important elements (Ti and O). Local electron diffraction showed that the *in situ* formed electrode was an amorphous phase caused by the Li insertion. Picometer-scale expansion of O—O distance due to the Li insertion was also visualized in the electrode. These electronic and crystal changes and gradual Li distribution contribute to the low resistance and stable battery cycles.

1. Introduction

Lithium-ion batteries (LIBs) [1] are essential for numerous uses in business, industry, and daily life. However, conventional LIBs with flammable liquid electrolytes have some problems in terms of safety, reliability, lifetime, cost, and energy density. All-solid-state LIBs with incombustible solid electrolytes have enormous potential to overcome such problems [2]. However, the large interfacial resistance of Li-ion transfer at the electrode/solid-electrolyte interfaces prevents their practical use. Extensive efforts have been made to reduce the resistance at these interfaces [3–6]. One effective solution is an *in situ* formation of active electrode materials from the parent solid electrolytes [3,7–9]. Because the electrodes grow from the solid electrolytes, both materials probably become connected to each other at an atomic scale, leading to low

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interfacial resistance. Such electrodes were discovered in Li_2O–Al_2O_3–TiO_2–P_2O_5-based glass–ceramic solid electrolytes [8,9] (LATP, manufactured by OHARA Inc., Japan [10]). A negative electrode was formed *in situ* near the negative-side LATP/current–collector interface by decomposition with an excess Li-insertion reaction. The interfacial resistance was measured to be at most 100 Ωcm^2, which was much lower than that at a conventional deposited-electrode/solid-electrolyte interface, for example, 4000 Ωcm^2 at the $LiCoO_2$/LATP interface [11].

Electron holography (EH) was recently applied to visualize the local electric-potential distribution in a transmission electron microscope (TEM) [12], and the fabrication process of the *in-situ*-formed negative electrodes was dynamically observed during the battery reaction [11,13]. The electric potential gradually decreased in a 700-nm-wide region near the negative-side LATP during the charging process. However, EH can detect only local electric-potential change; thus, the structural growth mechanism is still unclear, as is the cause of the low interfacial resistance, the electronic structures of the negative electrodes, and the relationship between the local potential change and the Li concentration.

Here, we used spatially-resolved electron energy-loss spectroscopy in TEM mode (SR-TEM-EELS) [14,15] to directly visualize the nanometer-scale Li-concentration profiles around the *in-situ*-formed-negative-electrode/solid-electrolyte interface. The SR-TEM-EELS technique can also be applied to detect the precise electronic changes of other important elements, for example Ti and O included in the LATP, as chemical shifts of the EEL spectra. Some experimental reports have indicated that the transition metal (such as Ti) and O elements play significant roles when the Li-ions are inserted into some battery materials [16,17]. Those elements would contribute to the *in situ* formation of the negative electrodes and the redox reaction of the battery cycles. In this paper, we show the SR-TEM-EELS images of Li, Ti, and O around the *in-situ*-formed-negative-electrode/solid-electrolyte interface. Nano-scale simultaneous analysis of the images revealed not only a nanometer-scale Li profile but also a significant relationship of the above three elements in the Li insertion/extraction reaction: Ti^{3+}/Ti^{4+} electronic changes, the influence on Ti/O electronic hybridization orbits, picometer-scale expansion of O–O distances by Li insertion, and the relation with the electric potential observed by EH.

2. Experimental

2.1. Preparation of the all-solid-state LIB for TEM observation

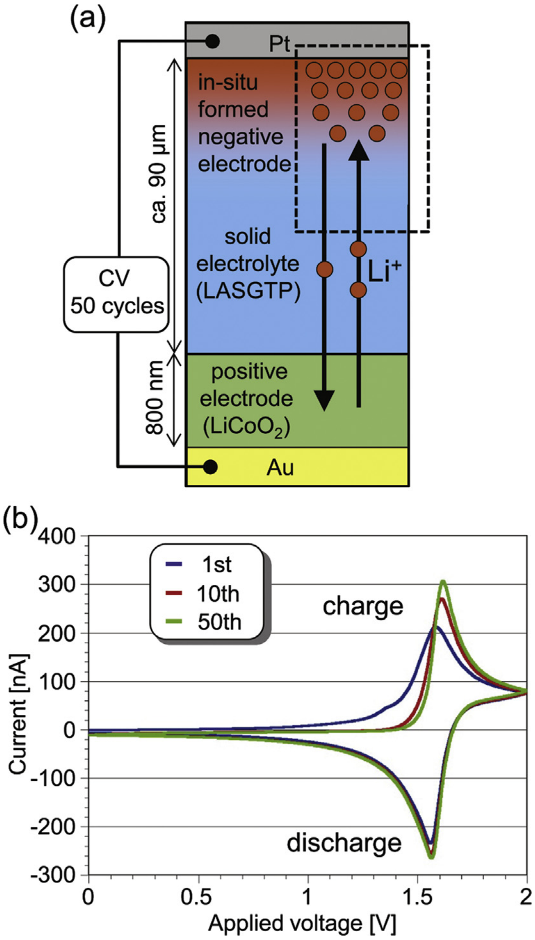

Fig. 1. All-solid-state LIB sample and its cyclic voltammogram. (a) Illustration of the prepared all-solid-state LIB cell. (b) Cyclic voltammogram (CV) measured in a vacuum with a sweep rate of 40 mV min^{-1}.

Fig. 1(a) illustrates the all-solid-state LIB sample we prepared for this study. A Si- and Ge-doped LATP sheet (LASGTP, 90 μm thick, by OHARA Inc.) was used as the solid electrolyte. The crystalline phases in the LASGTP glass matrix are composed of $Li_{1+x}Al_xGe_yTi_{2-x-y}P_3O_{12}$ (main-phase), $Li_{1+x+3z}Al_x(Ge,Ti)_{2-x}(Si_zPO_4)_3$ (sub-phase), and $AlPO_4$ [18]. The former two phases are sodium (Na) super ionic conductor (NASICON)-type structures. The 800-nm-thick film of the $LiCoO_2$ positive electrode was deposited at 873 K for 10 h on one side of the sheet by pulsed laser deposition (PLD), and then the gold (Au) was coated using a sputtering method onto the $LiCoO_2$ as the current collector. On the negative side, the platinum (Pt)-current-collector was directly deposited on the other side of the LASGTP. Small copper (Cu) plates were electrically connected on the current collectors using a silver paste, and then cyclic voltammetry (CV) was carried out for 50 cycles in a vacuum with a sweep rate of 40 mV min^{-1}. During the CV, the Li ions extracted from the $LiCoO_2$ charge around the LASGTP/Pt interface, which causes the irreversible formation of the *in-situ*-formed negative electrodes. Fig. 1(b) plots the CV curves at the 1st, 10th, and 50th cycles. Because the largest amount of Li insertion/extraction occurs at 3.93 V (vs. Li/Li^+) in the $LiCoO_2$ [19] and at 2.35 V (vs. Li/Li^+) in the negative electrode [8], the charge and discharge current peaks are clearly seen around the applied voltage of 1.6 V. This means that the Li-inserted region worked stably as the negative electrode even after 50 CV cycles. After the CV cycles, a small piece was lifted out from the negative side of the LIB sample by using a micro-sampling method in a focused ion beam (FIB) system (Hitachi, FB2100), and was thinned to a thickness of about 100 nm for TEM observation. To transfer the TEM sample from the FIB system to the TEM or an Ar glove box, the sample was put into an Ar environment covered by a glove bag in order to avoid air exposure.

2.2. Experimental set-up of SR-TEM-EELS

An experimental set-up of the SR-TEM-EELS system is shown in Fig. 2(a). The parallel electron beams are uniformly illuminated to the sample. Thus we can observe the TEM image at the bottom of the TEM column. A region of interest in the TEM image is selected with a rectangular slit on the front of the EELS system, and the energy-loss electrons resulting from inelastic scattering due to the battery sample are dispersed by a magnetic prism. The two-dimensional energy-dispersed plane is magnified by some lenses installed in the EELS system, and the plane is recorded by a charge-coupled-device (CCD) camera. A typical spectrum image is illustrated in Fig. 2(b). The horizontal and vertical axes correspond to