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# *In situ* electron holography of electric potentials inside a solid-state electrolyte: Effect of electric-field leakage

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ABSTRACT

*In situ* electron holography is used to observe changes of electric-potential distributions in an amorphous lithium phosphorus oxynitride (LiPON) solid-state electrolyte when different voltages are applied. 2D phase images are simulated by integrating the 3D potential distribution along the electron trajectory through a thin Cu/LiPON/Cu region. Good agreement between experimental and simulated phase distributions is obtained when the influence of the external electric field is taken into account using the 3D boundary-charge method. Based on the precise potential changes, the lithium-ion and lithium-vacancy distributions inside the LiPON layer and electric double layers (EDLs) are inferred. The gradients of the phase drops at the interfaces in relation to EDL widths are discussed.



## 1. Introduction

Electron holography (EH) is an advanced transmission electron microscopy (TEM) technique for observing electromagnetic fields and atomic structures of materials at the micro/nanometer scale [1,2] that has been used widely for quantitative analysis of magnetic materials and semiconductor devices [3–8]. *In operando* EH observations of biased devices have also been performed, for example, observations of electric potential changes around *p*–*n* junctions in semiconductor devices [9–11] and magnetic fields around a carbon micro-coil [12].

Recently we reported the successful visualization of changes in local electric potential in the vicinity of electrode/solid-electrolyte interfaces in all-solid-state lithium-ion batteries (ASSLIBs) during charge-discharge cycling [13–15]. Such experiments provide important insights into electric-potential distributions in batteries, and promise to greatly improve our understanding of electrochemical reaction mechanisms at electrode/solid-electrolyte interfaces, thereby accelerating the development of more efficient and environmentally benign batteries [16]. However, electric potential distributions obtained by EH remain difficult to interpret, because the potential distributions depend on a variety of factors such as static-ion distributions and IR losses induced by transport of ions within and between the battery components. Furthermore, solid electrolytes are typically polycrystalline, and the large number of crystal grains of diverse orientations contributes to complex noise in the obtained phase images. To overcome these problems, in this study we observed an amorphous solid electrolyte in a simple capacitor (a configuration that does not generate diffraction phase noise). Such observations enable changes in static lithium-ion distributions in a solid electrolyte under an applied voltage to be analyzed directly and *in situ*.

In the field of electrochemistry, several models of electric-potential distributions around electrode/liquid-electrolyte interfaces, such as the Helmholtz model, the Gouy-Chapman model, and the Stern model [17], have been formulated. In these models, when a voltage is applied between two metal plates dipped in a liquid electrolyte, both cations and anions can move freely within the electrolyte to form “electric double layers” (EDLs) at the interfaces. Although dependent on the ion concentration, the width of each EDL is typically several nanometers or less. The potential within the liquid electrolyte is also usually assumed to be flat under equilibrium conditions. These models can explain electrochemical phenomena around the electrode/liquid-electrolyte interfaces well, and generally accepted as correct by electrochemists.

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In contrast, in a lithium-ion conductive solid electrolyte, only lithium ions ($Li^+$) can move in the host structure. Lithium vacancies can be considered to behave like anions, but their number and concentration is limited by the nature of the cation network of the electrolyte, particularly in terms of steric repulsion. Revealing the electric-potential distributions formed by the lithium ions and lithium vacancies is thus important for studying details of the reaction mechanisms in ASSLIBs and thereby deepening our understanding of fundamental solid-state electrochemical phenomena.

In order to interpret reconstructed phase images from *in situ* EH reliably, it is important to remember that electric fields spread three-dimensionally from the current-bearing specimen, and incident electrons pass through both the thin TEM specimen and these external (leakage) fields. The detected phase image is thus a projection of the three-dimensional (3D) potential and not just the potential distribution inside the specimen.

In this study, phase images of a thin-film capacitor comprising an amorphous solid electrolyte sandwiched between two electrodes were first obtained by *in situ* EH. Next, mathematical models of the TEM specimen were constructed assuming different potential profiles, and phase distributions including the effect of 3D electric leakage fields simulated numerically. Finally, the measured and simulated phase distributions were compared, and the potential models that gave the best match to the experimental phase distributions were taken as those closest to the actual potential distributions in the materials. To the best of our knowledge, this is the first time the effect of external fields on phase distributions from *in situ* EH has been explicitly included in the analysis. In the following sections, the experimental and simulation methods are described, and the results of the measurements and simulation (*i.e.*, electric potential distributions in the solid electrolyte) are presented. Based on these results, a model of lithium-ion and lithium-vacancy distributions in the solid electrolyte is used to interpret the observed electric-potential distributions.

## 2. Experimental and simulation methods

### 2.1. In situ EH measurement of phase distributions

A 400-nm-thick copper electrode was deposited on a titanium-buffer-film/glassy-carbon substrate by pulsed-laser deposition (PLD). Next, a 2400-nm-thick lithium phosphorus oxynitride ($Li_{3.3}PO_{3.8}N_{0.22}$; LiPON) solid-electrolyte layer was formed on the copper electrode by radio-frequency (rf) magnetron sputtering using the conditions reported by Bates et al. [18]. Another copper electrode (400-nm thick) was finally deposited on the LiPON layer by PLD. A small piece of this bulk specimen was loaded into an air-tight TEM holder (Hitachi High Technologies) having two electrodes for applying a voltage to the copper electrodes (See Fig. 1S). After tungsten was deposited on the specimen, a part of the specimen was thinned by focused gallium-ion beam (FIB) at room temperature from the direction indicated by the arrow in Fig. 1. The thickness of the thin region was about 100 nm. The FIB-damaged layer on the surface of the solid electrolyte, which generally has high electron conductivity, was carefully removed with a low acceleration voltage (0.3 kV) argon-ion beam until the original resistivity was recovered (See Fig. 2S). The glassy-carbon side was kept grounded, and a voltage was applied to the tungsten side.

The thin area enclosed by the dotted box in Fig. 1 was observed using an EH TEM (Hitachi HF3300EH, 300 kV). Interference fringes without Fresnel fringes were formed using two biprisms [19]. A constant voltage, $V_{Cu\text{-}Cu}$, of −2, −1, 1, or 2 V was applied to the copper electrode on the tungsten side, and holograms were recorded at each voltage. The phase images were reconstructed from holograms by the Fourier transformation method [20].

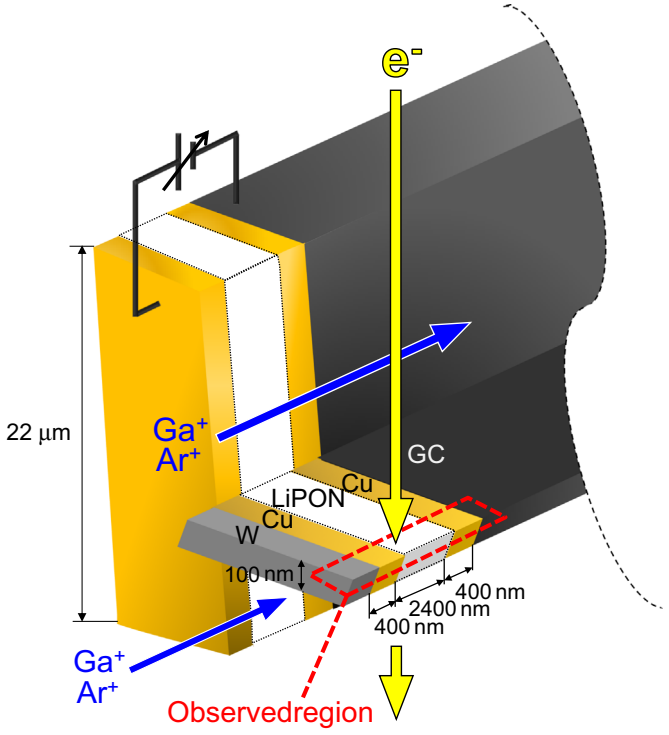


**Fig. 1.** Schematic of the specimen for *in situ* electron holography. The thin region for observation was prepared by focused-ion beam milling, and the damaged layers on the surface were carefully removed with a low-energy (0.3 kV) argon-ion beam.

Because copper and LiPON have different values of mean inner potential, even when the specimen is short-circuited a potential drop is present at the Cu/LiPON interface in our configuration. Although this mean inner potential drop may include the effects of differences in elemental distributions, crystal structure, and so on, it is not important in terms of the observed electrochemical behavior; the driving force for lithium ion transport is the potential change when a voltage is applied. To measure this potential change, the phase distribution of the short-circuited (0 V) specimen was subtracted from that of the voltage-applied specimen. This subtraction also cancels the effect of charging induced by emission of secondary electrons when the electronically insulating solid electrolyte is exposed to the incident electron beam, which otherwise overwhelms the signals from other interactions.

### 2.2. Computer simulation of phase distributions

The model of the Cu/LiPON/Cu sample used for simulating phase distributions is shown in Fig. 2(a). The simulated region consisted of a thin area (5 μm × 19 μm × 100 nm) protruding from a wall (height 22 μm) of Cu/LiPON/Cu; the thicknesses of the LiPON and copper layers were 2400 nm and 400 nm, respectively. These are the same values as those of the actual specimen shown in Fig. 1. Although in reality the specimen bulk extended far beyond the observed region, beyond the section of the bulk adjoining the thinned region its effect can be reasonably neglected.

An example of a potential profile inside the Cu/LiPON/Cu model along line A–B in Fig. 2(a) is shown in Fig. 2(b). To simplify the simulation, we assumed that the potentials in the copper electrodes and the LiPON electrolyte were flat and that the electric double layer (EDL) had a linear rather than curved potential slope. The electric potential within the specimen was also assumed to be uniform in the direction of the electron beam. In the first

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