

Electron Holography of Hetero-Interfaces between Metals and Solid Ionic Conductors

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1. INTRODUCTION

A solid oxide fuel cells (SOFC) is an expectable new energy source, which is operated at a high temperature. Its high electricity-generation efficiency is expected for a large scale generator. There are some problems to be solved, however, for general use. So called overpotential effect, that is drawable voltage decreasing from the expected value in a stable state as an operating current, is one of the problems required to be researched in detail. One of the origins of this effect is seemed to be the piling of oxygen ions near an anode and the lack of reserved oxygen ions near a cathode [1]. Inhomogeneous Oxygen ion distribution has been observed by Secondary Ion Mass Spectroscopy (SIMS) [2]. This observation, however, is only about the specimen which has been used, and it is a destructive observation, so we cannot detect dynamic phenomena. An external electric field applied to a solid ionic conductor moves carrier ions and courses the shift of the electrostatic potential in the electrolyte. If the specimen has an equal thickness, the electron phase shift measured by electron holography[3] reflects the electrostatic potential in the specimen, though the difference between mean inner potentials of adjacent materials has to be taken into account.

We report here the observation of the dynamical process of Oxygen anions and their vacancies with applying the external electric potential.

2. EXPERIMENTAL

In order to apply external voltage, a noble specimen holder for transmission electron microscopy has been developed[4]. The holder shown in Fig.1 has four electrodes, two of them are for heating the specimen and the other two are for applying it the voltage up to 5V. The cell sample was prepared by Pulse Laser Deposition (PLD) method on a Si wafer: a 30nm Pt film, a 3 μ m gadolinium doped ceria (GDC) layer and a 60nm Pt electrode and by a micro-sampling using a Focused Ion Beam (FIB) instrument for the cross-sectional observation. As shown in Fig.2, specimen was cut out from the wafer and mounted on the side edge of a thin Ta sheet. When the external potential will be applied, the specimen is connected with one of the electrodes on the specimen holder with an Au thin wire, and then an observed area was made a wedge shape of less than 5 degrees.

3.RESULTS AND DISCUSSION

The electron phase shift observed without an external potential is shown in Fig.3(a), which corresponds to a mean inner potential distribution. Figure 3(d) is its profile along the long side of the rectangular inserted in (a). The phases are reconstructed so as to be null in the vacuum area, and the plus phase-shifts in 3(d)-3(f) correspond to the positive potential. Applied extra voltage of -1.0V to the Pt electrode, the phase distribution and its profile are shown in Figs.3(b) and 3(e). Subtracting the phase distribution in 3(a) from that in 3(b) reveals a pure effect of external voltage on the electrostatic potential as shown in 3(c) and 3(f). Figures 4(a)–4(c) show differenced phase profiles when the external voltage was applied to the Pt electrode according to the process shown in 4(d). The difference between the phase applied -1.0V (point B in Fig.4(d)) and that before applied (point A) is shown in 4(a). The difference between the points C and A is in 4(b), and that between the points D and A is in 4(c).

The external voltage should increase the potential toward a positive electrode (rightward in Fig.4(a)) and decrease toward a negative electrode (rightward in 4(c)). However, the profiles of the phase difference show unexpected figures. The phase difference in Fig.4(a) shows that an electric double layer was formed at the interface due to the dielectric polarization with about 4nm thick, and that anions, i.e. oxygen ions, in the GDC were drawn toward the positive side and stacked in the area not so far from the anode about 20nm apart, and reduced the potential partially. In Fig.4(b), we can find that the electric double layer and the localization of anion were not recovered, even if the external voltage was removed. On the other hand, a voltage of +1V applied to the same electrode as in Fig.4(a) reversed the polarization of the electric double layer and vacancies of oxygen ion pilling near the interface can be recognized as a small hill of the potential around 6nm apart from the interface. The thickness of the double layer was about 3nm in this case. The difference between the thickness of the electric double layers shown in Fig.4(a) and 4(c) seems to be due to the poor resolution of electron hologram, about 3nm. However, the difference between relaxation lengths shown in these two figures is significant, and it may be due to the difference the order of applying the voltage or, may show characteristics of the electrolyte GDC and electrode Pt. In order to identify clearly the difference, more detailed examination will be required.

The thickness of the specimen has not been defined, nor is the exact value of the potential determined. It was the first time, however, to observe electric double layers at the interface and to confirm the localization of oxygen

ions caused by an external electric field in solid electrolytes, using the in-situ electron holography.

4. CONCLUSION

In order to observe the motion of oxygen anions in SOFCs, a new specimen holder and the method of specimen preparation have been developed. Electron holography has been utilized and electric double layers at the interface of the Pt electrode and the GDC electrolyte with external potential applied, and showed the inhomogeneous distribution of anions and ion vacancies.

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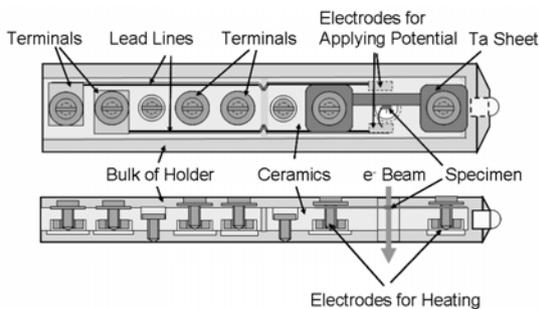


Fig.1: New specimen holder with four electrodes.

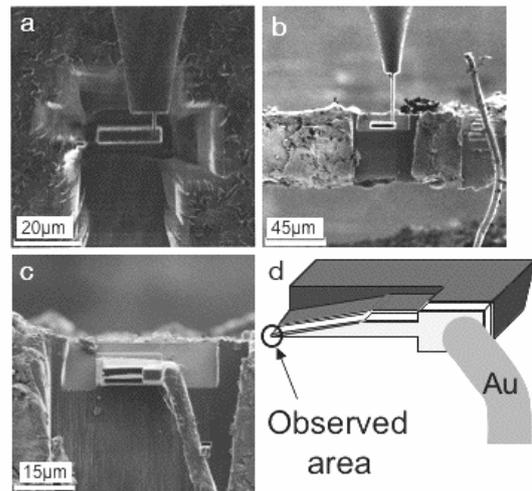


Fig.2: Specimen for TEM and electron holography is prepared by micro-sampling using an FIB, and mounted on the side edge of a Ta sheet.

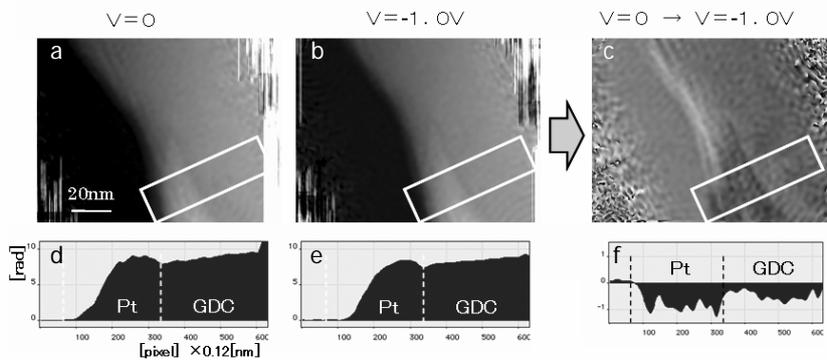


Fig.3: Reconstructed phase images (a):without an external field, (b): with applying -1.0V to the Pt electrode, (c):subtracted (a) from (b). Their line-profiles along the long sides of rectangular frames are (d), (e) and (f). They were averaged along the short sides of the frames.

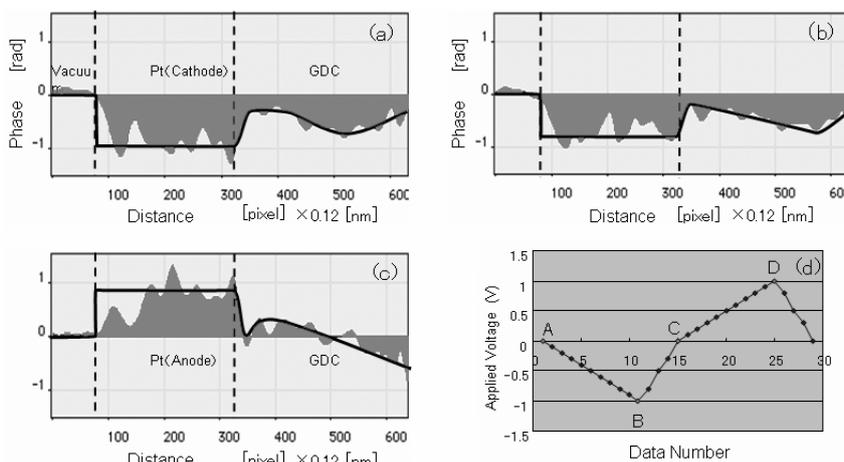


Fig.4: Phase differences between (a): those of -1.0V (point B in d) and 0 (point A), (b): those of 2nd. 0 (point C) and 1st.0 (point A), and (c): those of +1.0V (point C) and 0 (point A) show electric double layers and localization of oxygen anions. Solid envelopes correspond to electrostatic potential.