Development of a specimen holder and specimen preparation for in-situ observation of SOFC's reaction by environmental HVSTEM

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Solid oxide fuel cells (SOFC) have attracted attention as a promising power source in recent years. The performance of SOFC is influenced by microstructural changes and electrochemical reactions, especially, at triple phase boundaries (TPB), which are contact regions of a solid-electrolyte, electrodes and gases, are the most interest regions due to active sites of redox reactions[1]. Understanding the reactions at the interfaces have been attempted by cyclic voltammetry and scanning photoemission microscopy[2]. These approaches, however, cannot observe nano-scale reactions at TPB directly. For his purpose, we have developed a special specimen holder for 200kV electron microscopes[3]. The observation using an environmental high-voltage STEM (HVSTEM) which has a unique gas shielding mechanism is a powerful technique to understand chemical reactions[4][5]. In this study, to realize the detail in-situ observation at TPB in SOFC during the reaction, we have developed a specialized specimen holder for HVSTEM and established a specimen preparation technique by a focused ion beam (FIB) instrument. We will report the oxygen migration phenomenon during the reaction observed by electron energy loss spectroscopy (EELS) with HVSTEM.

Figure 1 shows the tip of the developed TEM specimen holder. The holder has three electrodes for heating and applying voltage to the specimen. A heater unit is a thin metal belt bridged between two electrodes (Fig.2). We adopted nickel-chromium (NiCr) as a heater material to suppress deformation during the heating in oxygen gas. The specimen which has a layered structure sandwiched yittria-stabilized zirconia (YSZ) layer between two platinum layers is mounted directly on the center of the heater belt. Connecting the electrode terminal of the heater unit to an electrode of the specimen using a gold thin wire, we can apply the external voltage to the specimen in TEM.

All the specimen preparation process (mounting to the heater, connecting the gold wire, thinning) is carried out by the FIB instrument (Fig.3). Firstly, we pick up a small volume from a SOFC bulk sample using micro-sampling technique. Then the sample picked up is mounted to

the heater and, the gold wire is connected to the top end of the specimen surface. The tip of the gold wire is processed beforehand so as to facilitate connection. Finally, the sample is thinned by the FIB. The TEM observation area is under 100 nm thick. If there is a deposit or damaged layer on the surface of the specimen, a short circuit occurs on the specimen surface by applying external voltage. In order to prevent electrical short circuit, we carefully cleaned with a weak ion beam to remove redeposits and damaged layers. We have established the specimen preparation method for observation of SOFC under heating and applying voltage in a gas atmosphere. The oxygen migration by applying voltage is observed in the mapping mode by STEM EELS.

Reference

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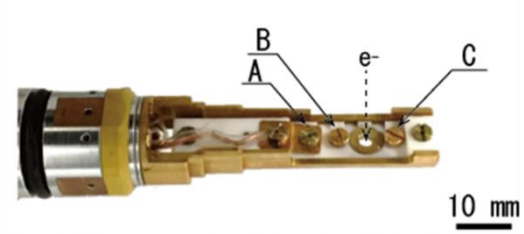

Fig.1 Photograph of the tip of the holder
A is the terminal for applying voltage
B and C are the terminals for heating

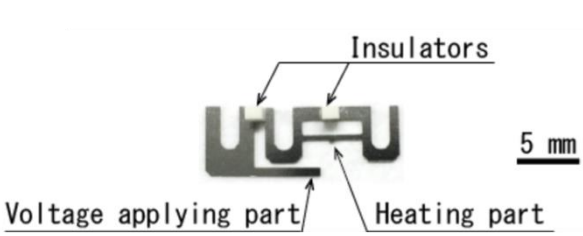

Fig.2 Photograph of the heater unit

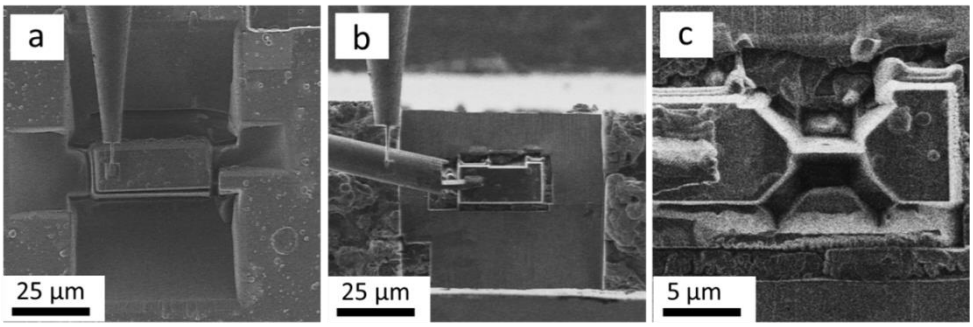

Fig.3 SIM images of specimen prepared by FIB method, (a)micro sampling (b)mounting and connecting Gold wire (c)thinning and cleaning