In-situ gas reaction of thicker materials in environmental HVEM

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Environmental transmission electron microscopy (E-TEM) attracts recently a strong interest of materials researchers, particularly those of fuel cells and light metal batteries, because the actual chemical reaction processes with gases and liquids need to be clarified in real space and in atomic level, for which E-TEM is one of the best research tools. The resolution of E-TEM has attained sub-nm level with aberration correctors. However, the samples should be thin local edges of films and tiny particles due to limitation of transmission of electrons for ordinary TEM. E-TEM observations of thick samples of a few micron in gas environment, particularly using hydrogen and oxygen gas, become very important for cutting-edge materials technologies such as new battery development. 3D observation of samples is also necessary for clarifying morphologies of various active materials such as practical catalysts.

We have developed 1MV TEM/STEM equipped with an open-type environmental cell, which enables observation in 100 Torr atmosphere of hydrogen, oxygen, nitrogen, NO_x and carbon mono-oxide, named "Reaction Science HVEM"(RSHVEM)[1]. The higher transmission of electrons has realized the point-to-point resolution less than 0.2 nm even in gas-environment over 100 Torr. High-speed beam blanking system reduces irradiation effects of incident electrons, and realizes "in place observation" repeatedly with/without beams [1].

Figure 1(a) shows a front-view of the RSHVEM and Figure 1(b) is a top-view of the environmental cell in an objective lens as well as a cross-section of the system in Fig. 1(c). Figure 2 shows a recently developed non-exposure-transfer holder for Li-related battery materials.

Figure 3 shows in-situ observation of porous gold (Au) catalyst, whose inner (011) surface with zigzag atom arrangement enhances the catalytic reaction with carbon-mono oxide (CO) gas of 30 Pa[2]. Similarly we have succeeded in atomistic in-situ observation of oxidation process of copper particles located on a silica particle. The oxidation and reduction processes by oxygen and hydrogen gases were monitored quantitatively using in-situ EELS.

Figure 4 shows the world-first in-situ observation of "hydrogen brittleness" of copper(Cu)/silicon(Si) interface as well as in-situ measurement of stress/strain curves and critical force of 75 μN in mixed gas of hydrogen and nitrogen of 100 Pa[3]. We have extended this method to Ni_3Al structural materials[4].

The particular advantage of this E-HVEM is to in-situ observe nearly practical materials. Ordinary FIB thinning process is liable to change the samples from those as they are. Observation of Li-related battery materials is also available using the no-exposure-transfer holder in Fig. 2 [5] and liquid holders. Acknowledges are made to Prof. Muto, Drs. Fujita and Takahashi for kind collaboration of the present study.

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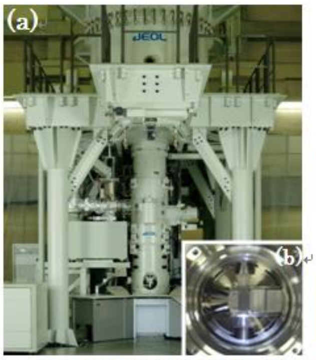
[5]N. Tanaka et al., AMTC Lett., 5(2016), 60.



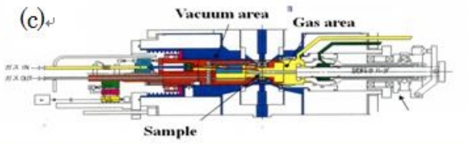


Fig. 1 : Front-view of 1MV E-HVEM(a), top-view of an e-cell in objective lens(b), and cross-section of the e-cell system (c).

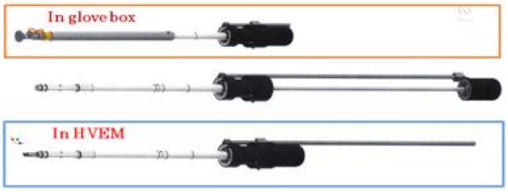


Fig. 2 : Non-exposure-transfer holder for E-HVEM for battery materials.

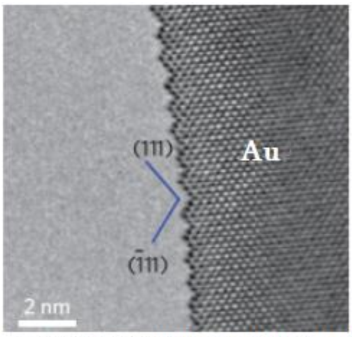


Fig. 3 : Atomic resolution in-situ observation of reconstruction of gold (011) surfaces by CO gas.

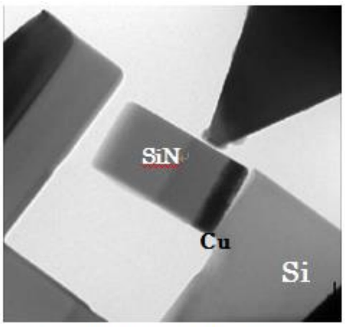


Fig. 4: In-situ TEM of fracture of Cu/Si interface in H_2+N_2 gas.