Developments of Ultra High-Resolution/HV/3D ETEMs and their Applications in Materials Science

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The invention of differential pumping systems[1-4] and membrane type environmental cells has enabled us to achieve high-resolution transmission electron microscopy (HRTEM) of samples while they are immersed in a gaseous environment. Many successful *in-situ* HRTEM observations have already been reported using such environmental transmission electron microscopy (ETEM) since 1997[1]. ETEM will be of much interest for research into the latest nm-sized catalysts, ceramics and biomedical materials, particularly in next few years.

For maturing of the ETEM technique, we have recently developed/installed two types of advanced ETEM in Nagoya University and the Japan Fine Ceramics Center. One has a retractable differential pumping E-cell, which was designed for minimizing the missing wedge to improve the accuracy of electron tomography. The ideal acceleration voltage for 3D ETEM is in the range of 800-1000 kV for thick specimens (300nm to 10μm) of real devices in materials science [4]. Another major demand for ETEM is in catalysis. Spatial and time resolution and stability of the HRTEM were explored for dynamic observation of single atom behavior, needed for understanding chemical reactions. The ultra high-resolution ETEM made by alterations to a TITAN ETEM (FEI) gives real-time video recording with information transfer out to 0.1nm, time-resolution below 0.2 seconds and accelerating voltage range from 80kV to 300kV. In the present talk, we report an *in-situ* gas study and three-dimensional analysis using a newly developed 1MV 3D ETEM (JEM-1000KRS, Nagoya Univ/JEOL, Fig.1) and an ultra high-resolution ETEM (JFCC/ FEI, Fig. 2).

Figure 3 shows a 3D tomogram of a carbon micro-coil prepared by the CVD method from acetylene gas and nickel powder on graphite substrates[5]. More than 100 images were recorded at 1MV using a 360 degree single-axis rotation holder. The image reconstruction was performed by software using the SIRT method (JEOL). Sections from the 3D reconstruction clearly show the cross-section of the fiber, which provides information about the CVD growth of the coil.

Figure 4 shows Pt single atoms visualized using 300kV aberration corrected ETEM. Pt/a-carbon is a typical electrode catalyst for a proton exchange membrane fuel cell (PEMFC). Fig. 4(a)-(d) are selected area captured (SAC) images from the original video, which can be downloaded from (http://sirius.cirse.nagoya-u.ac.jp/~kenta/jem2011/index.html)[6]. These *in-situ* observations with single atom resolution first clarified that dispersed single atoms like the one arrowed (i) could not maintain their position even with Pt-carbon bonding because of heating by the 300kV accelerated electrons with 40-60 A/cm^2 of local current density. Furthermore, several atoms on the edge of a Pt-nanoparticle, which are indicated by arrow (ii), moved between particles. One particle shrinks while the other grows - particles will try to minimise their surface area and surface energy. These results indicate that *in-situ* aberration corrected TEM observation is useful for visualizing and identifying the sintering mechanisms due to coalescence and Ostwald ripening [6].

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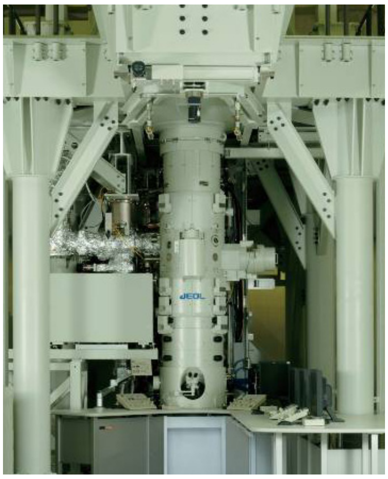

Fig. 1: Environmental HV-(S)TEM with 3D tomography and EELS in Nagoya University

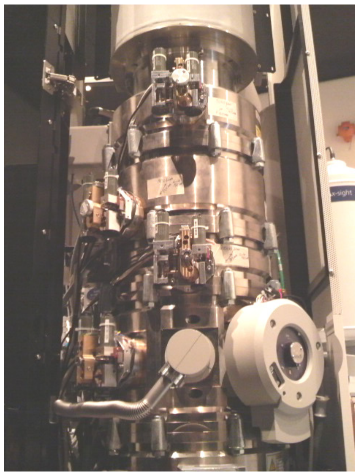

Fig. 2: Environmental ultra high-resolution TEM in JFCC

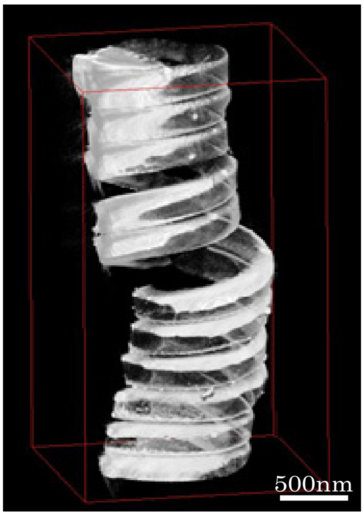

Fig. 3: 3D electron tomography of a carbon micro-coil by 1 MV TEM, showing that the cross-section of the fiber is a kind of square.

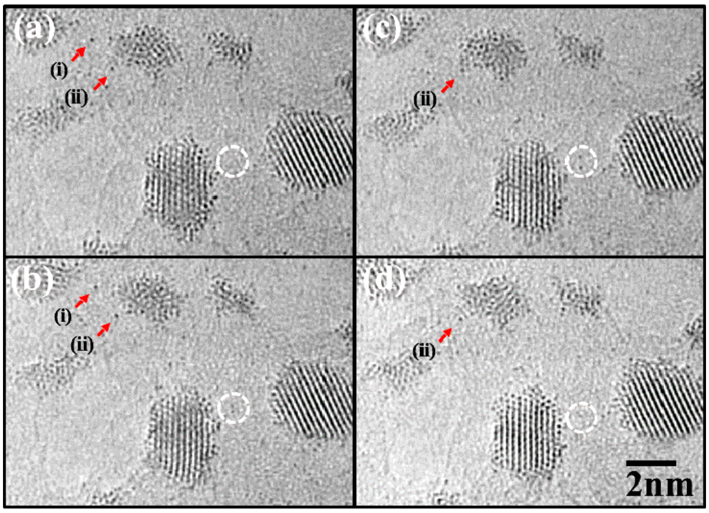

Fig. 4: 300kV high-resolution ETEM images of platinum atoms and clusters on a carbon film as the model sample of a proton exchange fuel cell. (a)-(d) are frame images from the video record with separation of one second.