Single Atom Behavior of Platinum on a Carbon Film Using Aberration Corrected In Situ ETEM Imaging

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Platinum nanoparticles on amorphous carbon (Pt/a-carbon) is a typical electrode catalyst for a Proton Exchange Membrane Fuel Cell (PEMFC) [1]. Recently, a Pt/TiO_2–Carbon catalyst has been synthesized for such a PEMFC [2]. The importance of reducing the size and increasing the density of the Pt nanoclusters on anatase titanium dioxide to enhance catalytic activity in such systems has attracted strong interest.

Pt nanoparticles were deposited using an argon ion sputter-coating machine on 5nm thick amorphous carbon films prepared by chemical vapor deposition from CH_4 and C_2H_4 gases. The samples were characterised using a spherical aberration corrected environmental TEM (Titan ETEM, FEI Company) in different gas atmospheres including N_2, O_2, H_2 and CO in addition to conventional high vacuum of 10^{-6} Pa.

Figure 1 shows the spherical aberration corrected environmental TEM, which was installed in the Japan Fine Ceramics Center. The instrument has dedicated gas environmental/camera systems such as a plasma cleaner, bake out heaters, a direct pumping line and a high-speed CCD camera (Orius, Gatan) for dynamical visualization of single atoms. The dynamic high-resolution ETEM made by alterations to the Titan ETEM (FEI) gives real-time videos recorded with the information transfer out to 0.1nm, time-resolution below 0.2 seconds and 80kV - 300kV for acceleration voltage. These high spatial/time resolutions enable us to study the dynamic behavior of single atoms and clusters, which are known to be active species in electrochemical reactions in the PEMFC.

Figure 2 is a Selected Area Captured (SAC) image from the original video. Dots with sharp contrast moving between particles were successfully visualized. By such a transfer of the surface atoms one particle shrinks while the other grows. This result indicates that *in-situ* AC-TEM observation is useful for visualizing and identifying sintering mechanisms such as coalescence and Ostwald ripening [3]. Figure 3 shows AC-TEM images of Pt/a-carbon. Fig. 3(a) and (b) were taken at 300kV, and show Pt nanoparticles 1.6nm and 2.4nm in diameter, respectively. Figures 4(a) and (b) are intensity line profiles measured between points (i) and (ii) in Fig. 3(a) and (b). Black arrows show intensities of a single Pt atom and a bi-atom. Figure 5 shows surface atom behavior. These SAC images and the original video were also obtained with 300kV. It is reasonable to conclude that 300kV AC-TEM video images are better than those at 200kV for visualizing metal single atoms and bi-atoms on amorphous carbon because the signal to noise is improved and the background carbon film contrast is reduced.

In this study, we achieved single atom imaging of platinum on amorphous carbon using 300kV AC-TEM and studied the behavior of Pt atomic species

dynamically. Single atoms, clusters (<1nm) and nanoparticles (<3nm) were successfully visualized in the same region at the same time. The time resolution (0.2s) is similar to that reported in a previous *in-situ* AC-STEM study [4]. Our time resolution will hopefully be improved by reducing the exposure time and optimizing and local current density to still maintain adequate signal.

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References

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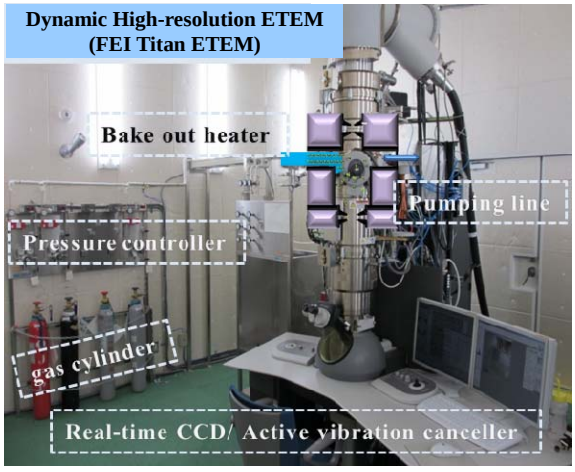

Fig. 1. Dynamic high-resolution ETEM in JFCC.

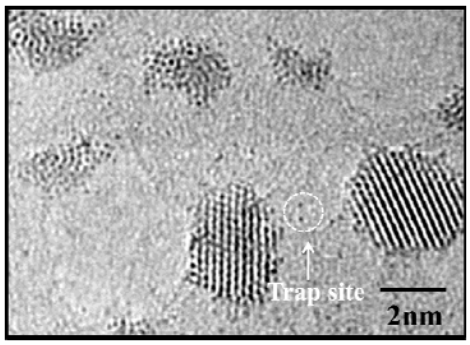

Fig. 2. SAC image of Pt/a-carbon.

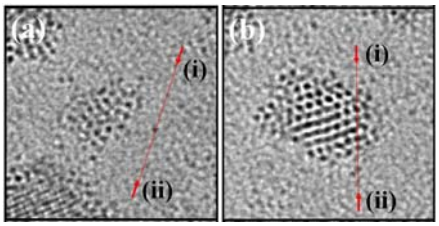

Fig. 3. AC-TEM images of Pt nanoparticles.

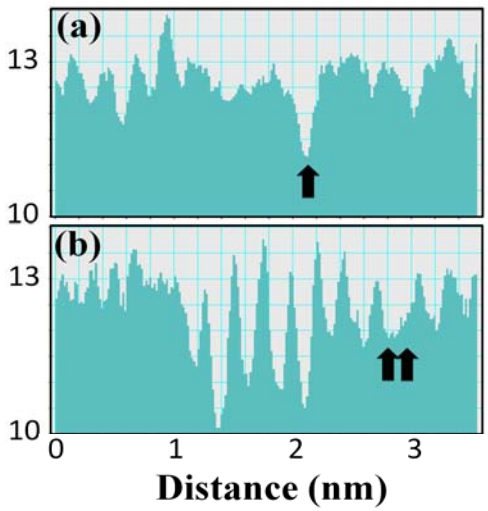

Fig.4 Intensity line profiles corresponding to the 3.5nm distances shown in Fig. 1(a) and (b), extracted using the Digital Micrograph software.

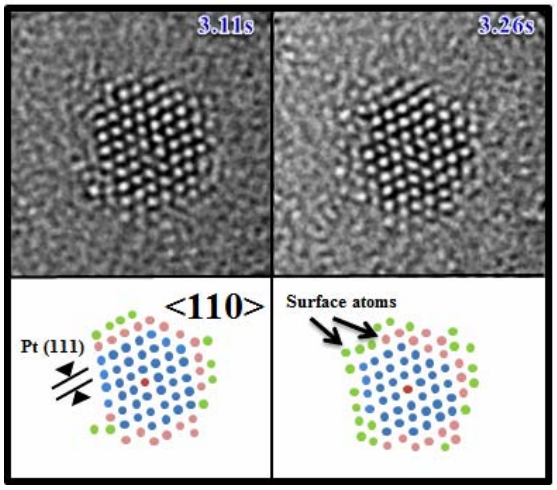

Fig. 5: SAC image of a Pt nanoparticle obtained 3.11 and 3.26s after the start of EM observation.