Atomic-level Observation of Platinum Dissolution and Re-deposition Using Liquid Electrochemical TEM

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A polymer electrolyte fuel cell (PEFC) is a promising energy source for fuel cell vehicles. Platinum nanoparticles are typical electrocatalysts used in PEFCs. While reduction of Pt usage and improvement in their durability are important subjects for developing advanced PEFCs, catalytic performance of Pt nanoparticles is degraded as repetitious operation of PEFC. Pt nanoparticles' surface area is decreased with a redox process promoting dissolution and re-deposition [1, 2]. To optimize material design and operating conditions of PTFCs, it is essential to understand the Pt dissolution and re-deposition mechanisms in real space.

To clarify the Pt dissolution and re-deposition behaviors relating with electrochemical potentials, we have developed an electrochemical TEM observation technique using a liquid flow cell TEM holder with electrical biasing capabilities (Poseidon, Protochips Inc.) and an environmental TEM with the Cs corrector (Titan ETEM, FEI Company)[3]. An electrochemical cell for simulating an activated PEFC environment was comprised of in-house developed MEMS chips and flowing electrolyte of 0.1 M aqueous solution of $HClO_4$. Pt polycrystalline thin film was deposited onto the MEMS chip as a model catalyst. We performed electrochemical measurements and dynamic TEM observations simultaneously.

Figure 1 shows configurations of the developed MEMS chip. The MEMS chip has a Pt electrode with a hole array pattern on a SiN viewing window which enables to observe an interface between Pt electrode and liquid at corners of SiN viewing windows. Figure 2 shows a low magnification TEM image of the viewing windows (Fig. 2(a)) and EELS spectra for cell thickness estimation (Fig. 2(b)). The MEMS chip enables to avoid bowing effect of SiN windows into a vacuum and achieve a cell thickness of ~110 nm which dramatically improved spatial resolution of a TEM image. Furthermore, we have employed the energy filter (GIF Tridiem, Gatan, Inc.) to eliminate innelastically scattered electrons blurring a TEM image. Figures 3 show a series of *in situ* energy filtered TEM images at an interface of polycrystalline Pt thin film electrode and 0.1 M $HClO_4$ electrolyte during a potential step voltammetry. Elevating the potential from 0.1 V_{RHE} to 1.2 V_{RHE} (Figs. 3(a), (b)), some part of Pt dissolved from its surface. On the other hand, putting the potential back to 0.1 V_{RHE} (Fig. 3(c)), Pt was re-deposited at a surface of Pt electrode. Thus, we have achieved an atomic-scale observation of electrochemical behaviour of a Pt catalyst in a liquid electrolyte for the first time. In conclusion, we believe that *in situ* liquid electrochemical TEM is a powerful tool to understand electrochemical behaviors of solid-liquid interfaces in atomic scale.
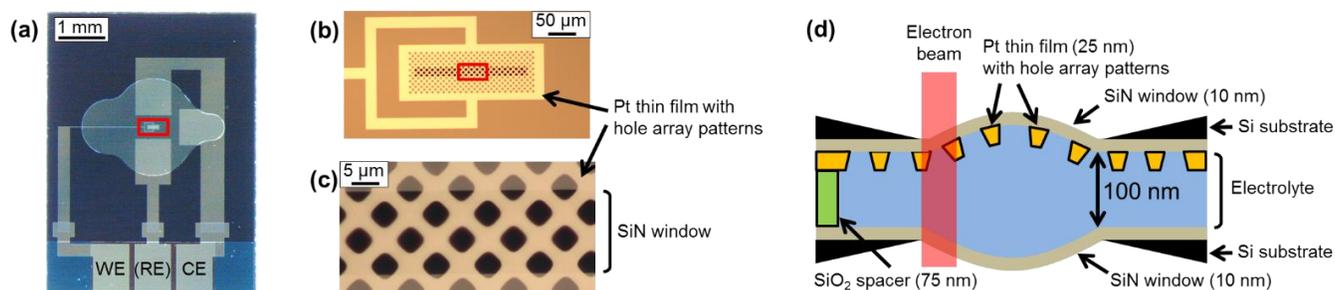
Figure 1. (a-c) Optical microscope images of a developed MEMS chip. (b), (c) Enlarged images correspond to the red rectangles in (a), (b), respectively. (d) A schematic cross section diagram of an electrochemical cell in a TEM chamber.
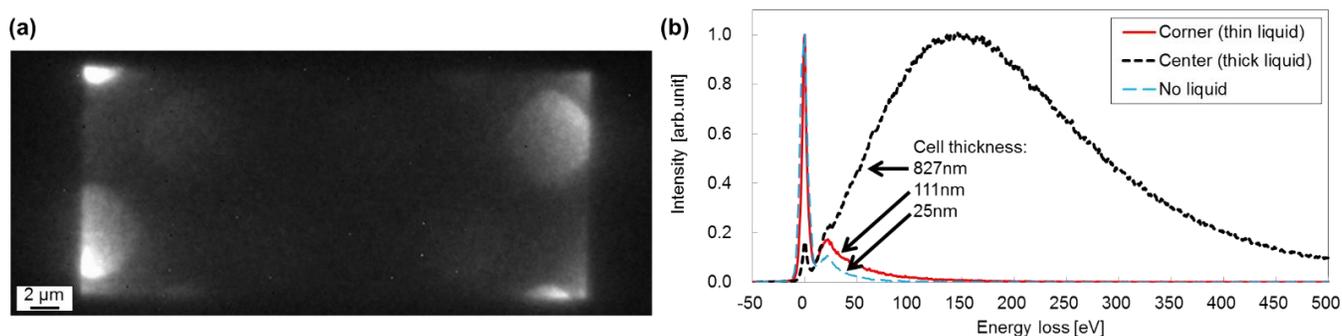

Figure 2. (a) A low magnification TEM image of the SiN viewing windows. The cell was filed with electrolyte. (b) EELS spectra obtained from a corner and a center of the viewing windows with electrolyte, and the viewing windows with no liquid, respectively. Each cell thickness was estimated as SiN thickness.
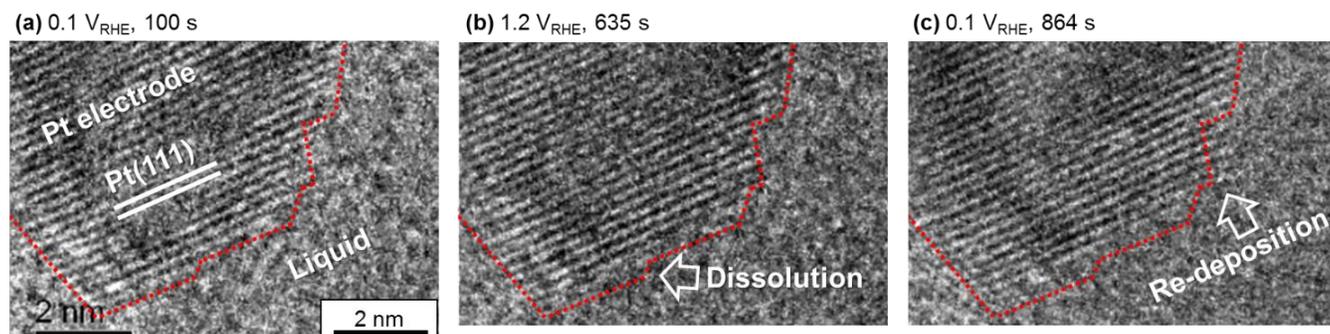

Figure 3. *In situ* energy filtered TEM images of Pt polycrystalline thin film electrode during a potential step voltammetry. The energy filter was set to zero loss with 30 eV slit width. The sequence of the applied potential was 0.1 V, 0.8 V, 1.0 V, 1.2 V and 0.1 V vs. RHE. Each potential was kept for 3 min. (a) Initial state at 0.1 V_{RHE}. (b) Oxidation state at 1.2 V_{RHE}. (c) Reduction state at 0.1 V_{RHE}.

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