

## Dynamic AC-ETEM observation of deactivation processes of platinum electrode catalysts in a proton exchange membrane fuel cell

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There have been reports of the challenges of designing platinum carbon (Pt/C) electrode catalysts for proton exchange membrane fuel cells (PEMFC). Pt/C electrode catalysts deactivate much faster on the cathode (in moisturized O<sub>2</sub>) than on the anode (in H<sub>2</sub>). The main deactivation processes of the Pt/C electrode catalyst system have been reported previously - platinum particle sintering, platinum dissolution, carbon support corrosion, carbon mono-oxide corrosion and detachment from the carbon support. These degradation processes were indicated by structural changes shown in electron micrographs and through electrochemical measurements. *Ex-situ* and *in-situ* microscopy to show the dynamic behaviour of the fuel cell catalyst is very valuable to improve understanding of the degradation mechanisms and thus improve robustness. The first atomic resolution environmental transmission electron microscopy (ETEM) [1] has proven to be one of the most efficient tools for *in-situ* visualisation of the deactivation of heterogeneous catalysts in a reactive gas atmosphere at the nanometer scale [2].

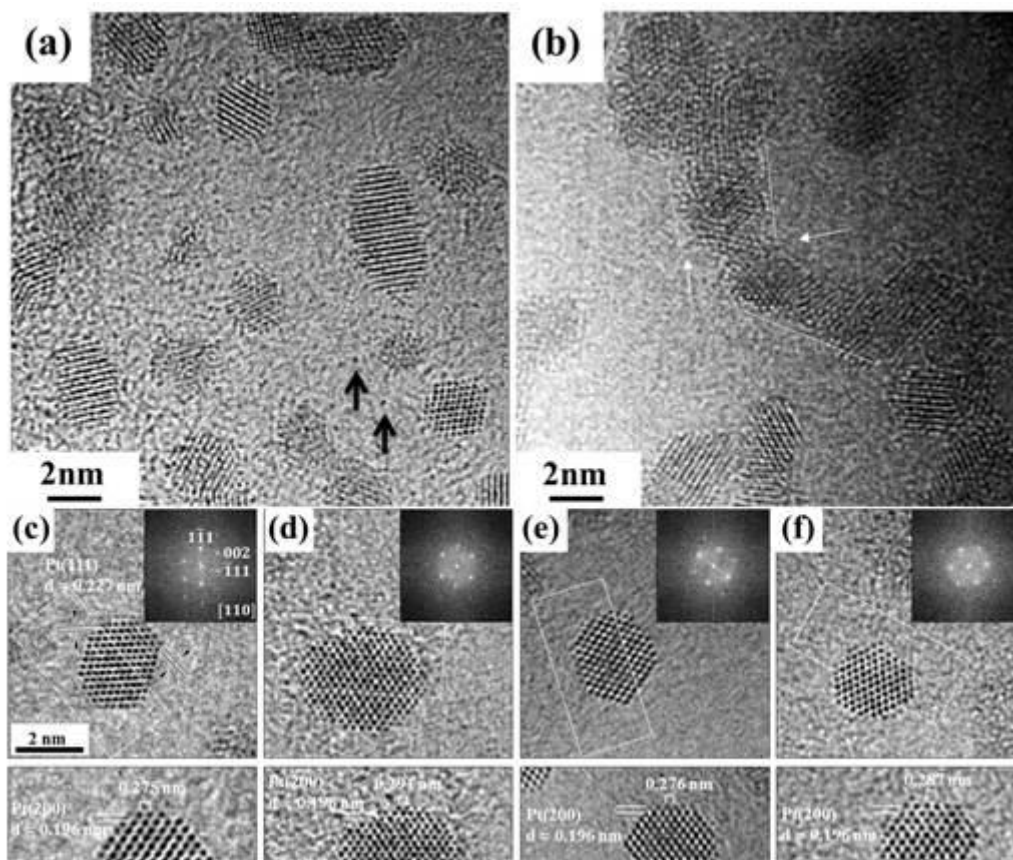
To understand the influence of moisture and oxygen on the deactivation of the Pt/C catalysts in PEMFCs [3-6], spherical-aberration-corrected environmental (scanning) transmission electron microscope (AC-ETEM) [7-9] and humidifier system (wet-ETEM) [10] were applied with a high-speed CCD camera. Structural changes in the Pt/C electrode catalysts were dynamically recorded in moisturized Nitrogen. Mass spectrometry confirmed the moisture content (between 5 to 30 %) of oxygen gasses passed through a humidifier. The migration speeds of platinum nanoparticles were carefully evaluated in moisturized oxygen, pure oxygen and hydrogen atmospheres respectively (Fig.1a and b). Surface atomic structures of Pt nanoparticles in hydrogen (99.99999 %), carbon mono-oxide (99.95 %) [5], nitrogen (99.9998 %) and pure oxygen (99.99995 %) environments were carefully evaluated (Fig.1c to f). Specific surface areas were also estimated using recorded ETEM movies to correlate the nanoscale microscopy images with the macroscopic catalytic activity in the device structure. The Pt/C showed considerable structural weakness in a moisturized O<sub>2</sub> atmosphere. Comparable results obtained by wet-ETEM from advanced Pt/C-TiO<sub>2</sub> catalysts (oxide composite supports), which were quantity-synthesized by photocatalytic reaction also suggested ways to improve oxygen reduction reaction (ORR). *In-situ* heating experiment visualised influences of such supporting materials on the sintering process of Pt nanoparticles (Fig.2).

In the presentation, the deactivation processes such as oxidation, hydroxylation and hydrocarbonation of carbon supports are visualised in atomic scale and then structural robustness of electrode catalysts in a cathode environment of the fuel cell are discussed from a view point of life time usage of the PEMFCs. Dynamic movies are presented with critical designs of *in-situ* microscope equipment such as differential pumping, humidifier system and heating/electrochemical holders to clarify importance of on-going modifications of ETEMs and next developing issues.

### References

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**Figure 1.** Morphology of the Pt NPTs in pure nitrogen (a), moisturised nitrogen (b). HRTEM images of the Pt/a-Carbon in H<sub>2</sub> atmosphere (a), CO atmosphere (b), N<sub>2</sub> atmosphere (c) and O<sub>2</sub> atmosphere (d) of  $1 \times 10^{-2}$  Pa at RT and their FFT patterns as an inset.



**Figure 2.** Dynamic ETEM observation of Pt/C Catalysts in 0.01 Pa of hydrogen at 423 K (a, d), 573 K (b, e), 723 K (c, f). The average particle sizes for Pt NDs and NCs are shown in (d-f).

