

ETEM observation of Pt/C electrode catalysts in a moisturized cathode atmosphere

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Abstract. There have been reports of challenges in designing platinum carbon (Pt/C) electrode catalysts for PEMFC. Pt/C electrode catalysts deactivate much faster on the cathode (in moisturized O₂) than on the anode (in H₂). To understand influences of moisture and oxygen on the deactivation of the Pt/C catalysts in proton-exchange-membrane fuel cells (PEMFCs), spherical-aberration-corrected environmental transmission electron microscopy (AC-ETEM) was applied with a high-speed CCD camera. Structural changes of the Pt/C electrode catalysts were dynamically recorded in moisturized nitrogen, oxygen and hydrogen. The mass spectrometry confirmed the moisture content (between 5 to 30 %) of nitrogen driving gas through a humidifier. Coalescence of platinum nanoparticles (D = 3.24 nm) was carefully evaluated in pure N₂ and moisturized N₂ atmosphere. The Pt/C showed considerable structural weakness in a moisturized N₂ atmosphere. Comparable results obtained by AC-ETEM in different gas atmospheres also suggested ways to improve the oxygen reduction reaction (ORR). In this paper, the deactivation process due to moisture (hydroxylation) of carbon supports is discussed using for comparison the movement of platinum nanoparticles measured in moisturized nitrogen and pure nitrogen atmospheres.

1. Introduction

In recent years, proton exchange membrane fuel cells (PEMFC) and direct methanol/oxygen fuel cells (DMFC) [1] have shown great promise as new energy technologies because of their low operating temperature, fast start-up and potential for miniaturization. However, several breakthroughs are still needed to enable widespread use in electric automobiles. PEMFCs and DMFCs typically consist of bipolar plates, electrodes, a membrane separator and an electrode catalyst, and one of the biggest challenges is the synthesis of robust electrode catalysts [2].

PEMFCs use platinum nanoparticles on carbon black (Pt/Carbon) as the electrode catalyst for both the anode and cathode regions [3]. But it is now well established that degradation of the carbon support at the cathode limits the lifetime of Pt/Carbon catalysts and thus the performance of the PEMFC. The main degradation processes of the Pt/Carbon 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 [4,5]. 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 help to improve robustness. Environmental transmission electron microscopy (ETEM) [6], which was first reported in 1997, 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 [7-9].

Here we report a progressive gas injection system for studying the dynamic behaviour of the heterogeneous catalyst in moisturized environmental conditions. The gas injection system was firstly applied to the Pt/Carbon electrode catalysts of PEMFC, then typical sintering of Pt nanoparticles in moisture is presented.

2. Experimental Procedure

Pt nanoparticles were deposited by sputtering (Ar Ion Sputter E-1030, Hitachi) on a 5 nm amorphous carbon film prepared by chemical vapour deposition (CVD coater NC5 Turbo, Enomoto AV) using methane (CH_4) and ethene (C_2H_4) as precursor gases. Mica sheets (G250-2, Agar Scientific) were used as substrates for the growth of the amorphous carbon film. CVD and ion sputter deposition were carried out at room temperature (288–300 K). Pt/a-carbon was characterised by dynamic aberration-corrected ETEM (Titan ETEM, FEI Company) in nitrogen (N_2 , 99.9998%) or moisturized nitrogen gas atmosphere of 10^{-2} Pa. These gases were introduced from cylinders into the sample area. Gas inlet needle valve positions and the pumping rate of the differential pumping ETEM were set to known locations for achieving equilibrium partial pressures between 10^{-5} to 100 Pa in the sample area [10]. The focused electron beam ($1800\text{A}/\text{cm}^2$, illuminating a $20\text{ nm} \times 20\text{ nm}$ sample area) was used to heat the sample and is also considered to create ionized gas molecules around the sample during imaging [11,12].

3. Results and discussion

Figure 1 shows the modified gas injection system. A hot stirrer kept the temperature of the humidifier at 370K. A PTFE boiling stone provide continuous moisture into the driving N_2 gas bubbled through the humidifier. A thermostatic chamber at 473K was used to introduce the moisturized gases to the differentially pumped E-cell through a needle valve. The mass spectrometry confirmed the moisture content of the nitrogen driving gas through the humidifier, the thermostatic chamber and the E-cell. The partial pressures of N_2 and H_2O at the E-cell were 9.17×10^{-3} Pa and 2.90×10^{-3} Pa respectively and the moisture content in the E-cell chamber was estimated to be 23.8 %. Water injection systems have been reported in previous works, such as a window type wet cell by T. Yaguchi et al. [13] and direct injection by one of the present authors [14]. However, those systems could not measure accurately the moisture content at the sample. Our present system enables the differential pumping E-cell to achieve a wet environment and directly measures the moisture content by Q-mass spectroscopy.

We present an application of the WetTEM (moisturised gas environmental transmission electron microscopy) for the Pt/Carbon electrode catalysts. Structural weaknesses of the Pt/Carbon in the cathode atmosphere have been a big issue to improve PEMFC for a long time. Our earlier study had clarified one main deactivation mechanism of Pt nanoparticles sintering due to carbon supports shrinking in an oxygen atmosphere [15]. Pt nanoparticles sintering in pure nitrogen (N_2 , 99.9998%) and moisturized nitrogen gas atmospheres were compared to study the influences of water synthesis at the PEMFC cathode.



Figure 1. (a) Humidifier on the hot stirrer, (b) Thermostatic chamber and (c) gas injection and differential pumping line of the ETEM.

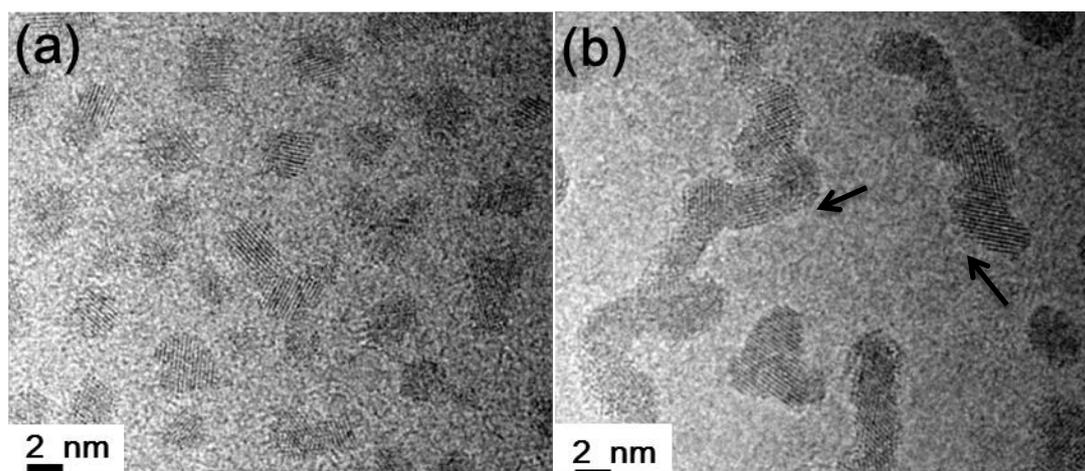


Figure 2. (a) SAC image at 230s of a movie obtained from the Pt/Carbon samples in pure N₂ environment. (b) SAC image at 40s of a movie obtained from the Pt/Carbon in 23.8% moisturized N₂ environment.

Sintering and migration of Pt nanoparticles observed in moisturized N₂ atmosphere was much faster than in a pure N₂ atmosphere as shown in the Selected Area Captured (SAC) images of Figure 2. Fig. 2(b) shows connected Pt nanoparticles which were typically observed in wet condition. The damage and shrinkage of the carbon support is not the reason for the connections because the granular pattern of the carbon support is still seen to survive. White contrast surrounding the Pt connections (arrowed in Fig. 2(b)) also indicates that the carbon films became thinner at the Pt/Carbon interface; presumably because of hydrocarbon desorption. We consider that physical adsorption of water and hydroxylation of the carbon surface is a main reason for the higher mobility of Pt nanoparticles in a moisturized N₂ atmosphere. The present in-situ observations suggest we should induce much stronger trapping sites on the carbon supports for use on the PEMFC cathode.

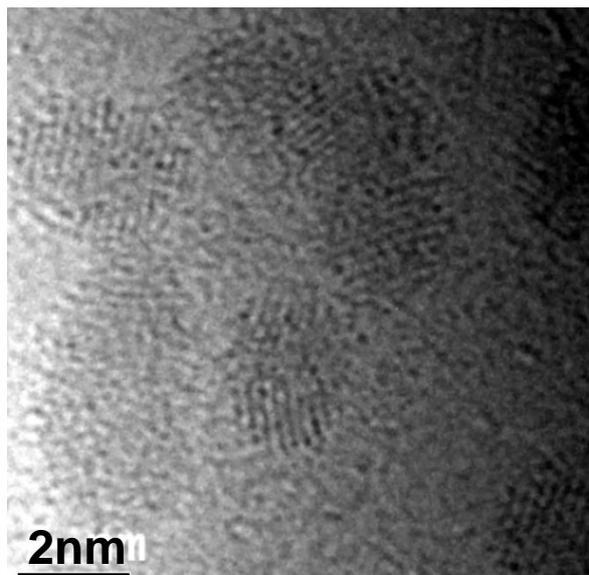


Figure 3. SAC image from a dynamic movie obtained with magnification of 1M times and time resolution of 0.05 s. Image size is 512 × 512 pixel.

Finally, we present the highest magnification SAC image for discussion of future experiments. The SAC image demonstrates the potential of our system for visualising single atoms in ETEM. Such dynamic visualization of single atom behaviour would help a deeper understanding of the mechanisms of deactivation processes for Pt/Carbon catalysts and contribute to development of more robust catalyst electrodes.

4. Conclusion

In this paper we introduce the modified gas injection system, which was newly developed in order to study the deactivation process due to moisture (hydroxylation) of carbon supports. The movements of platinum nanoparticles were successfully visualised on the atomic scale in moisturized nitrogen and pure nitrogen atmospheres.

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6. References

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