

## In-Situ SEM/TEM Observation of Platinum Catalysts on Carbon Support in a Gaseous Atmosphere Using a 300 kV CFE TEM/SEM

H. Matsumoto<sup>1</sup>, T. Sato<sup>1</sup>, K. Nakano<sup>1</sup>, T. Yaguchi<sup>2</sup>, I. Nagaoki<sup>2</sup> and Y. Nagakubo<sup>2</sup>

1. Hitachi High-Technologies Corp., 11-1 Ishikawa-cho, Hitachinaka, Ibaraki, 312-0057 Japan
2. Hitachi High-Technologies Corp., 882 Ichige, Hitachinaka, Ibaraki, 312-8504 Japan

In the development of catalysts and fuel cell materials, there is an increasing demand for fine structural characterization using transmission electron microscopes (TEMs) which can provide catalytically-essential temperatures and gas environments. We have developed a gas environmental TEM (Hitachi-H-9500) with a humid air supply system to study the deterioration mechanism of fuel cell electrocatalyst [1]. In addition, the behavior of Au nanocatalysts on a Fe<sub>2</sub>O<sub>3</sub> support at high temperature has been characterized using the Hitachi 300 kV cold field emission (CFE) HF-3300 TEM equipped with an SEM imaging capability [2]. In this study, we combined the gas accommodation capability with the HF-3300 to develop a 300 kV CFE in-situ SEM/TEM instrument with a high efficiency secondary electron detector to investigate the behavior of catalyst particles under heating and air gas surrounding.

Figure 1 shows (a) a picture, and (b) a schematic diagram of the specially designed Hitachi HF-3300 gas environmental TEM/SEM with an additional evacuation system for accommodating gas in the specimen chamber. The additional IP3 pump and an orifice between the gun valve and specimen chamber made totally three stages in the differential pumping system along the column. Hitachi unique gas injection-heating specimen holder was used which allowed an in-situ TEM observation under a gas pressure up to 10Pa near the specimen and at elevated temperature up to 1500°C (Figure 2) [3].

Figure 3 shows a sequence of TEM images to show Pt particle behavior under a heating temperature of 673K. The time (in seconds) marked in each image frame corresponds to the duration after gas injection. The injected gas was air and the pressure was  $4.3 \times 10^{-2}$  Pa. Most of the Pt particles were coalesced and migrated actively; some Pt particles coalesced to form larger sized particles with increased air injection time.

Figure 4 shows a sequence of in-situ SEM images recorded at 300 kV to reveal behavior of Pt particles on the surface of the carbon support at a heating temperature of 673K. The time (in seconds) marked in each image corresponds to the duration after gas injection. The injected gas was air and the pressure was  $5.4 \times 10^{-1}$  Pa. Before air injection (0s, Fig. 4a), uniformly dispersed Pt particles on the surface are clearly shown. After air was injected, some Pt particles were seen coarsening and penetrating into the carbon support. After 610 seconds of gas injection, most Pt particles were buried in the carbon support which itself was turned into a porous structure. Pt particle erosion is speculated to be related to the degradation mechanism of the catalyst function.

### References

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- [2] Jane Y. Howe et al., *Microscopy and Microanalysis proceedings*. **210** (2010).
- [3] T. Kamino et al., *Journal of Electron Microscopy*. **54**: 497-503(2005).

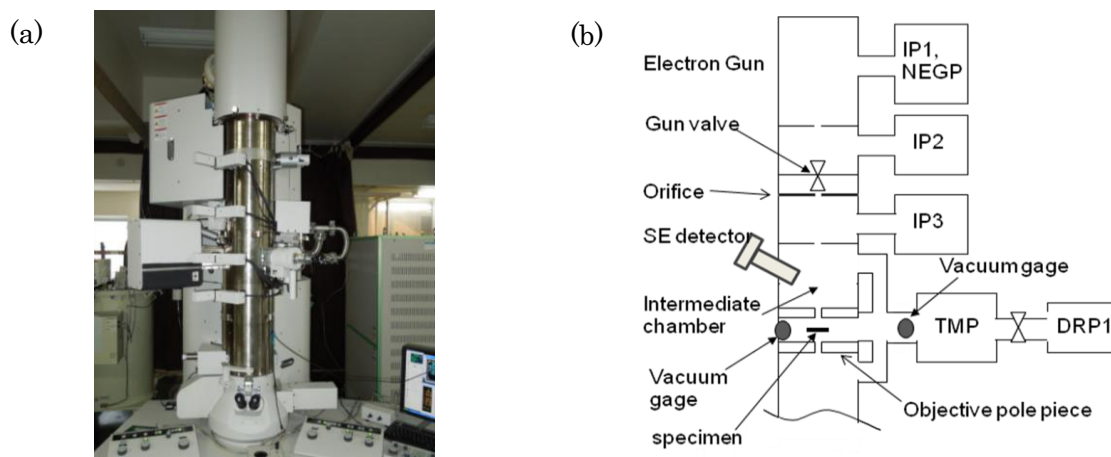


FIG.1. (a) a picture, and (b) a schematic diagram of the modified 300 kV CFE in-situ TEM/SEM (Hitachi HF-3300) with an additional evacuation system

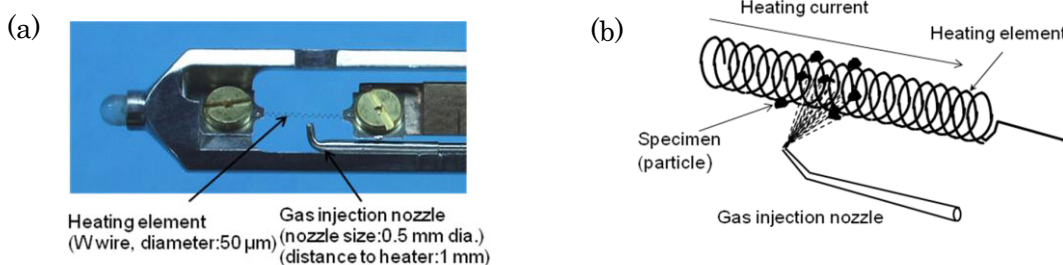


FIG.2. External view (a) and schematic diagram (b) of the gas injection heating TEM holder

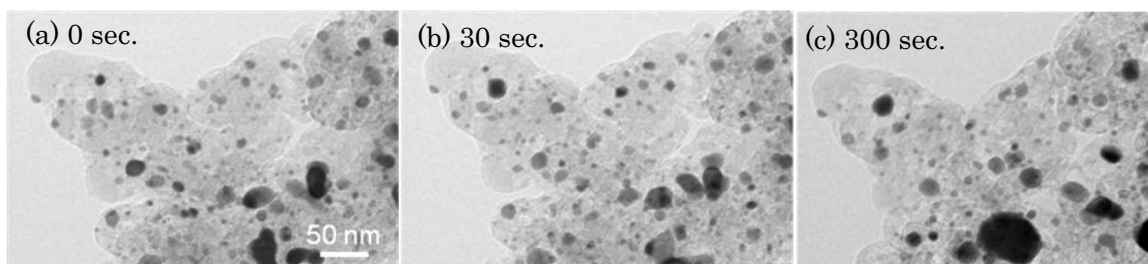


FIG.3. Sequence of TEM images showing coalescence, migration, and grain growth of Pt particles on the carbon support at 673K under  $4.3 \times 10^{-2}$  Pa of air. The progress time after air injection is marked in each image.

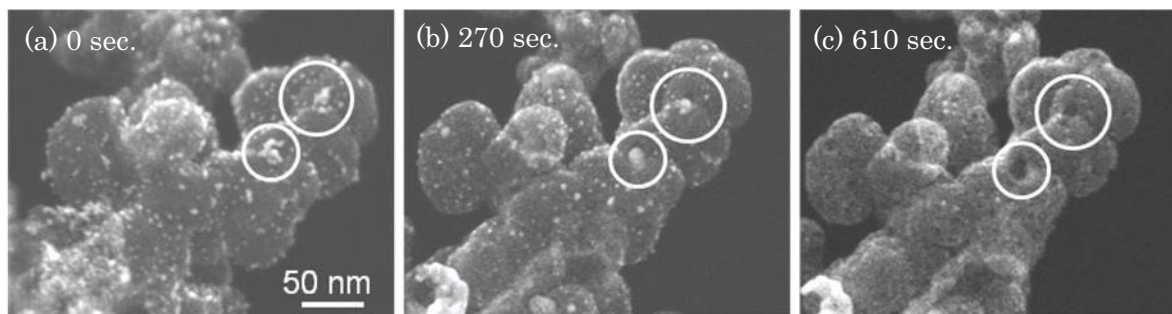


FIG.4. Sequence of SEM images showing a movement of Pt particles on the carbon surface at 673K under  $5.4 \times 10^{-1}$  Pa of air. Before injecting air to the specimen area (0s. Fig.4(a)), particles are seen on the carbon surface. 270 sec. after the air injection shows coalescence of some particles (Fig.4 (b)). 610sec. after the air injection shows movement of some Pt particles into the carbon support.