

Effect of Operating Conditions on the Degradation Mechanism of Pt₃Co Nanocatalysts in PEM Fuel Cells- a Transmission Electron Microscopy Study

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Proton exchange membrane fuel cells (PEMFCs) are promising power sources for transport and stationary applications. Pt nanoparticles are currently used as the catalyst to promote the kinetics of the hydrogen oxidation and oxygen reduction reactions in the anode and cathode of the fuel cell, respectively. However, alloys of Pt with base metals are being investigated to replace Pt on the cathode as a way to improve the efficiency of the fuel cell, and reduce cost.

In this work, 4.9 nm size Pt₃Co catalyst nanoparticles present on the cathode side of a PEMFC membrane-electrode assembly (MEA) were analyzed by transmission electron microscopy after 10,000 voltage cycles under different operating conditions. The operating conditions include baseline condition (0.4-0.95 V, 80°C, 100% RH), high potential (0.4-1.05 V, other conditions the same as baseline), high temperature (90°C, other conditions the same as baseline), and low humidity (30% RH, other conditions the same as baseline). The results show that the cathode samples operated under baseline, high temperature, and high potential conditions exhibit an increase in the mean particle size, while the 30% RH samples exhibit no significant growth after 10,000 cycles.

TEM images of the cathode-membrane interface of the MEAs exposed to different operating conditions are shown in Figure. 1. Particle growth and particle loss to the membrane is more severe in the high potential sample than in the high temperature and baseline MEAs, while no significant particle growth and particle precipitation in the membrane can be observed in the low humidity sample. Indeed, large particles in the membrane are indicative of Pt dissolution and re-precipitation in the membrane by chemical reduction of dissolvable Pt²⁺ by hydrogen crossover which results in Pt loss from the cathode area [1]. Pt dissolution is accelerated at potentials higher than 0.95 V [2]. On the other hand, low humidity condition limits Pt and Co dissolution, as well as diffusion, which restricts Ostwald ripening in the cathode area and re-precipitation of Pt crystals in the membrane. Accordingly, we can conclude that to restrict the degradation of catalysts on the cathode of MEAs, it is critical to control the Pt dissolution and restrict Ostwald ripening of particles.

To better understand the precipitation of particles in the membrane, a careful TEM observation was conducted (Figure. 2a-d). Clearly, the larger particles located in the areas close to the cathode-membrane interface are polycrystalline in nature, while the small ones formed far from the interface are single crystals. Figure 2 shows the growth sequence from a single crystal to a polycrystalline particle. At the initial stages, a Pt single crystal is nucleated in the membrane by chemical reduction of soluble Pt with hydrogen molecules. Subsequently, the crystal grows, develops arms and finally forms a polycrystalline particle. EDS analysis of these particles show that they are pure Pt, and no Co peak is observed in the EDS spectrum (Figure 2e).

References

- [1] Y. Shao-Horn et al., *Top. Catal.* **46** (2007) 285.
 [2] P.J. Ferreira et al., *J. Electrochem. Soc.* **152** (2005) A2256.

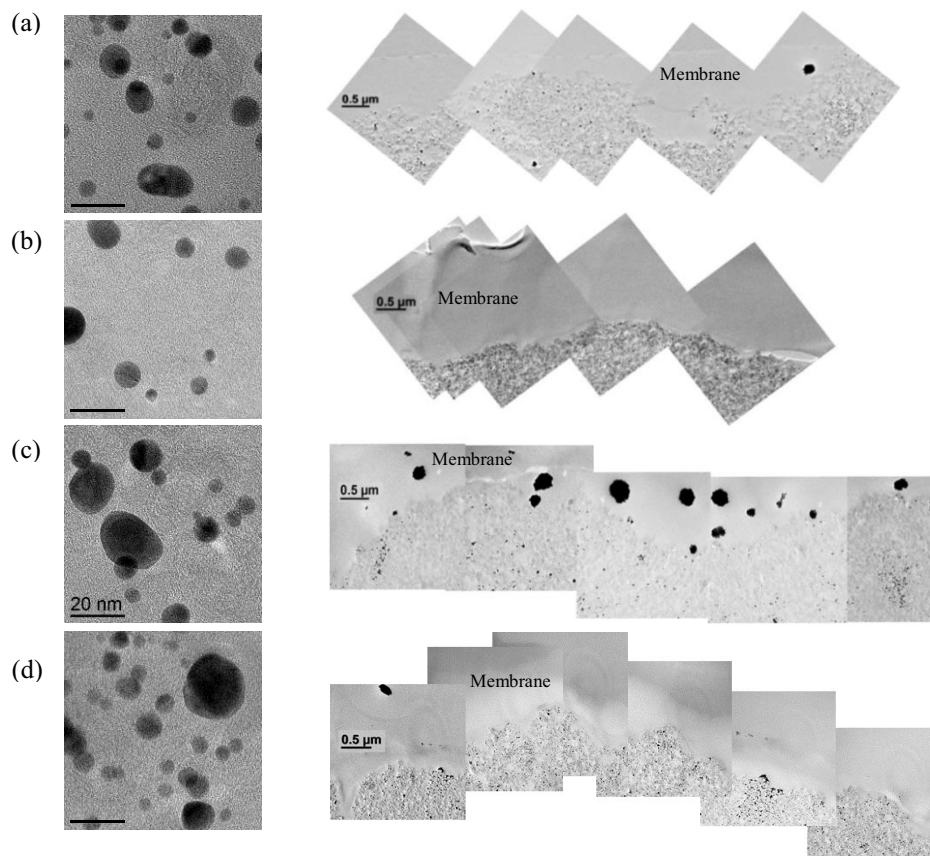


Figure. 1. TEM bright-field images of the nanoparticles in the cathode, and the cathode-membrane interface after 10K cycling under a) baseline; b) 30% RH; c) 1.05 V d) 90 °C.

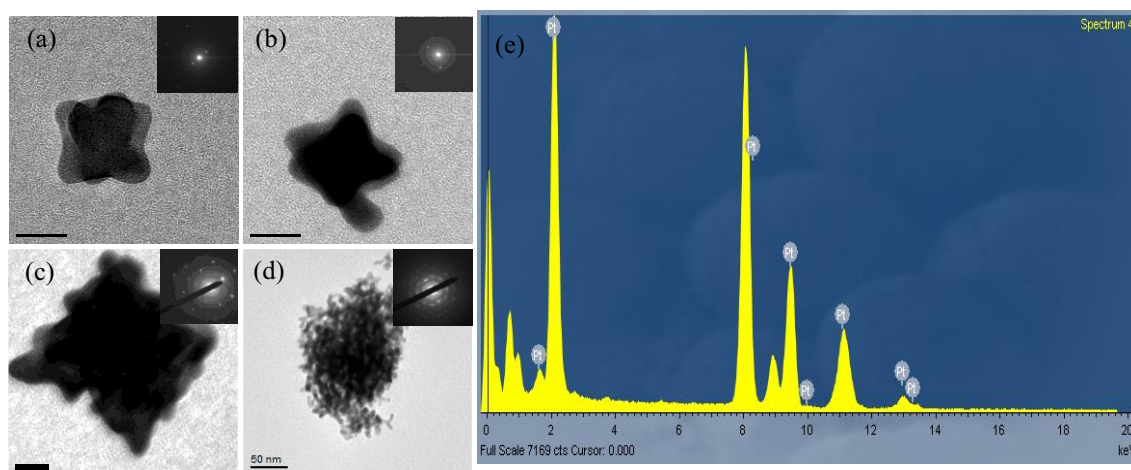


Figure. 2. TEM bright field images (a-d), corresponding diffraction patterns (insets) and EDS analysis (e) of the particles precipitated in the membrane.