

In-Situ Liquid TEM Study on the Degradation Mechanism of Fuel Cell Catalysts

Hisao Kato
Toyota Motor Corporation

ABSTRACT

Electrode catalyst (platinum) degradation represents a major challenge to the performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) in Fuel Cell Vehicles (FCVs). While various mechanisms have been proposed and investigated previously, there is still a need to develop *in situ* imaging techniques that can characterize and provide direct evidence to confirm the degradation process. In the present study, we report an *in situ* transmission electron microscopy (TEM) method that enables real time, high-resolution observation of carbon-supported platinum nanoparticles in liquid electrolyte under working conditions. By improving the design of the Micro Electro Mechanical Systems (MEMS) sample holder, the migration and aggregation of neighboring platinum nanoparticles could be visualized consistently and correlated to applied electrode potentials during aging process (i.e., cyclic voltammetry cycles). It can be expected that information acquired through this novel approach would provide valuable insight that may lead to the optimal design of new electrode catalysts to resolve the catalyst degradation issue.

CITATION: Kato, H., "In-Situ Liquid TEM Study on the Degradation Mechanism of Fuel Cell Catalysts," *SAE Int. J. Alt. Power*, 5(1):2016, doi:10.4271/2016-01-1192.

INTRODUCTION

In December 2014, Toyota launched the Mirai, the world's first mass production fuel-cell vehicle (Figure 1). While there is a high level of expectation for fuel-cell vehicles to become the ultimate eco-cars, the cost and service life of fuel cells must be improved before fuel-cell vehicles can be widely accepted.

On the cathode of a fuel cell, protons and oxygen molecules receive electrons, resulting in a chemical reaction that forms water molecules. To promote this chemical reaction, platinum particles of several nanometers are used as a catalyst (Figure 2).



Figure 1. Toyota fuel cell vehicle "MIRAI"

Because platinum is a rare element and expensive, it is necessary to reduce its use. One of the factors behind the large usage of platinum is its degradation. It is known that platinum nanoparticles degrade while the fuel cell is generating electricity, thus reducing its output. Therefore, it is necessary to elucidate this degradation mechanism and implement a countermeasure. It would not be an overstatement to say that the very quality of automobiles depends on nanoscale analysis technologies. However, the mechanism behind the

degradation phenomenon of platinum nanoparticles has not been fully understood. This is largely due to the technical difficulty in directly observing the nanometer-sized platinum particles in liquid electrolyte under applied electrochemical potentials.

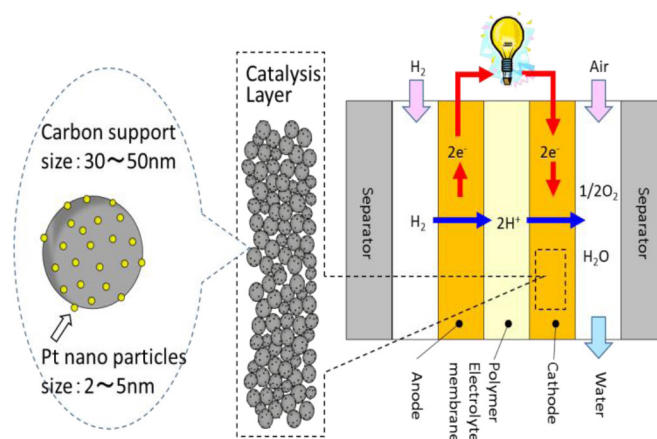


Figure 2. Schematic illustration of major fuel cell components and platinum nanoparticles as electrode catalyst

A transmission electron microscope (TEM) is a device that makes it possible to observe materials at the atomic level in size (0.1-0.2 nanometers). In observations of platinum nanoparticles made in the past(1, 2, 3), the platinum nanoparticle size in a pristine state was compared with the particle size after degradation based on TEM images (Figure 3).

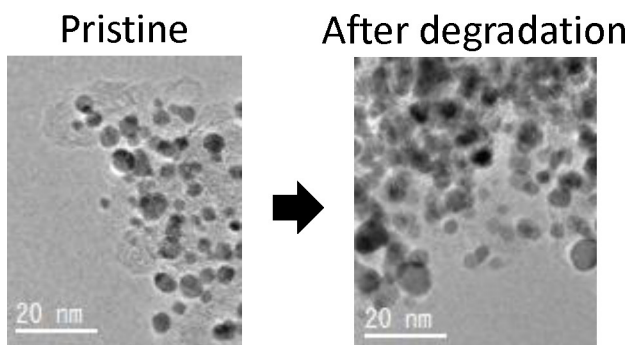
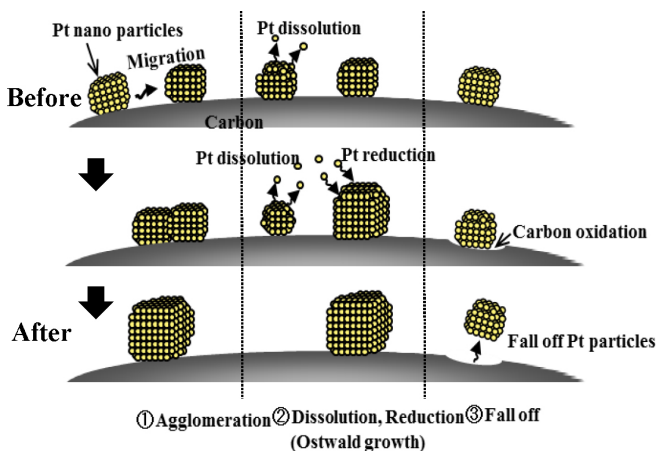


Figure 3. Comparison of platinum nanoparticles in a pristine state and after degradation observed by transmission electron microscope (it is possible to define condition of the durability tests, such as 10000 cycles, from 0.05 to 1.2V).

With this method, however, it was impossible to accurately understand the cause of degradation or its mechanism because the observed locations were different before and after degradation and the degradation mode could not be identified (Figure 4)(1,4).



- ① Agglomeration: Multiple platinum particles migrate and grow into one huge particle.
- ② Dissolution, reduction: Platinum oxidized and dissolved to become ionized in the electrolyte in an oxidative atmosphere. The Platinum ion is then reduced onto other platinum particles in a reducing atmosphere. The platinum particle recession and growth take place simultaneously.
- ③ Fall off: The carbon is oxidized with high electrolytic potential, and platinum particles fall off.

Figure 4. Hypothesis of platinum nanoparticle degradation mechanism (1,4)

As a means of observing changes in materials during a chemical reaction, environmental transmission electron microscope (ETEM) (5,6) has been developed, by which observations are made while a gas or heat is being applied to various types of materials. Structural changes have also been clarified (6, 7, 8, 9) in the catalyst for fuel cells when the gas type, such as oxygen or water vapor, and temperature are varied. However, in an actual fuel cell, liquid water is present and an electrochemical reaction that changes the potential of the catalyst is occurring, and the catalyst degradation mechanism inside this reaction has not yet been fully understood.

To understand cell voltage degradation, it is necessary to understand the degradation mechanism of the electrode catalyst. In order to see degradation directly, a new analysis method is developed. A high

resolution observation of platinum nanoparticles is carried out by controlling its voltage to provide reaction conditions similar to those in a fuel cell electrode. In order to carry out both, TEM observation and electrochemical control simultaneously, the in-situ TEM analysis technology is developed. In the past, several studies have been done, but they have not achieved high resolution observation which can provide the ability to distinguish platinum nanoparticle change step by step.

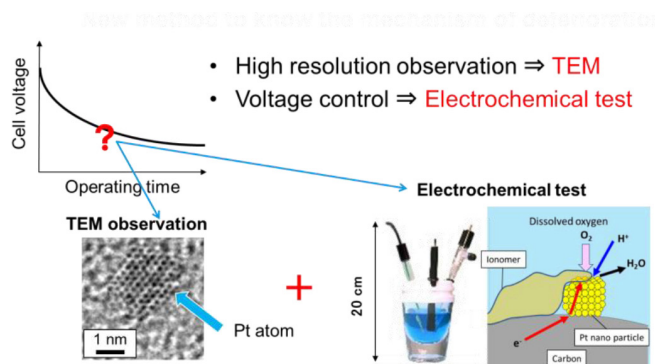


Figure 5. New method to know the mechanism of degradation

Therefore, a liquid in which the reaction occurring inside a fuel cell is simulated and an environment in which potential is applied were created, and efforts were made to develop a method of directly observing the degradation of platinum nanoparticles on a real-time basis in these environments using a TEM. This approach can be expected to clarify the types of degradation that occur and the potential at which they occur, making it possible to suggest the development of materials that would suppress degradation, designs, and ways to use catalysts so that they will not degrade.

EXPERIMENT METHOD

A system was developed that applies potential to platinum nanoparticles and circulates an electrolyte inside a TEM (Figure 6). As a result, an environment was created inside the TEM similar to that inside a fuel cell when it is generating electricity, making it possible to directly observe how platinum nanoparticles degrade.

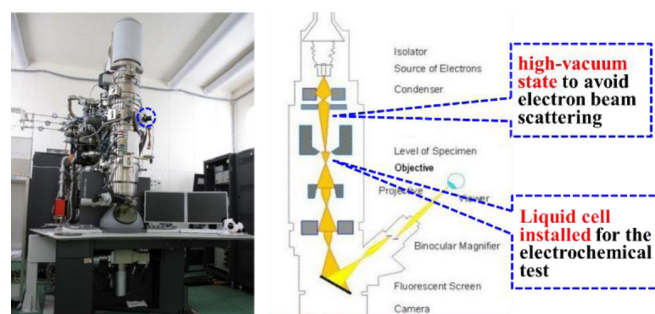


Figure 6. Transmission electron microscope (TEM)

A sealed space was created at the tip of the TEM specimen holder using Micro Electro Mechanical Systems (MEMS) chips, in which electrolyte was allowed to circulate. The three electrodes necessary for an electrochemical test were placed inside the MEMS chips, thus forming a reaction cell capable of accommodating an electrochemical test inside the TEM specimen holder. This system was created by modifying the Poseidon™ made by Proto-chips Incorporated of the U.S. (Figure 7)