

Special Contributions

Studies on Degradation Mechanism of Electrocatalysts for Fuel Cells through In-situ SEM/STEM Observation

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OVERVIEW: Electrode catalysts play a crucial role as the key determinant of the performance of fuel cells, a technology recognized as being central to the wider adoption of hydrogen-based energy. Electrode catalysts are composed of platinum nanoparticles distributed on a carbon support, and this carbon is known to degrade at high voltage due to oxidation. This article describes a technique for assessing catalyst durability through in-situ observation under an SEM/STEM in a controlled atmosphere. The technique introduces air to create an oxidizing atmosphere and performs in-situ observation of the degradation process. Simultaneous SEM/STEM observation identified the sinking of platinum particles due to carbon oxidization as one of the degradation mechanisms. This direct observation of this degradation process will provide a valuable analytical technique for the future design of materials with high durability.

INTRODUCTION

POLYMER electrolyte fuel cells (PEFC) are recognized for their potential as a core technology for the wider adoption of hydrogen-based energy. Having first come onto the market in 2009 for stationary applications, PEFCs have also been commercially available for use in fuel cell vehicles since December 2014. However, mainstream adoption of fuel cells will also require rapid improvements in performance, durability, and cost. Among the constituent materials in fuel cells, electrode catalysts are a crucial element with the greatest influence on cell performance, and typically, these electrode materials in which platinum nanoparticles are supported on a carbon support. The platinum catalyst degradation that occurs during starting, stopping, and idling is a known major factor in cell deterioration. Particularly during starting, cathodic potential rises to a peak value of approximately 1.5 V, which corrodes (oxidizes) the carbon support⁽¹⁾. In conjunction, platinum-carbon support interactions decrease, causing phenomena such as particle growth in the platinum catalyst and loss or dissolution from the support, and degrading the electrode catalyst. In this context, recent research has re-examined catalysts, supports, and catalyst-support interactions to offer new, corrosion-resistant materials which improve fuel

cell durability. Our research group has succeeded in improving electrode catalyst durability by applying a heat treatment to a carbon support to form a graphite surface and controlling its degree of graphitization⁽²⁾.

Techniques for evaluating electrode catalyst performance include “half-cell” techniques evaluating only the cathodic side of a cell, and fabrication of membrane electrode assemblies (MEAs) to evaluate fuel cells in cell units. In either case, durability is generally evaluated according to electric potential cycle protocols proposed by the Fuel Cell Commercialization Conference of Japan^{(1), (3)}. For example, in an electric potential cycle protocol simulating automobile starting and stopping, cycling between 1.0 and 1.5 V is repeated at the rate of 1 cycle every 2 seconds. Repetition of 60,000 cycles allows evaluation of durability over approximately 20 years. This is a useful evaluation protocol which can also be implemented in ordinary university research laboratories. However, while the protocol allows detailed evaluation of, for example, degradation every 10,000 cycles, 2 to 3 days per sample elapse before 60,000 cycles are completed; and moreover, it is difficult to study issues bearing on an understanding of degradation mechanisms, such as nanoscale structural change during cycling.

Consequently, in cooperation with the Matsumoto group at Hitachi High-Technologies Corporation, we

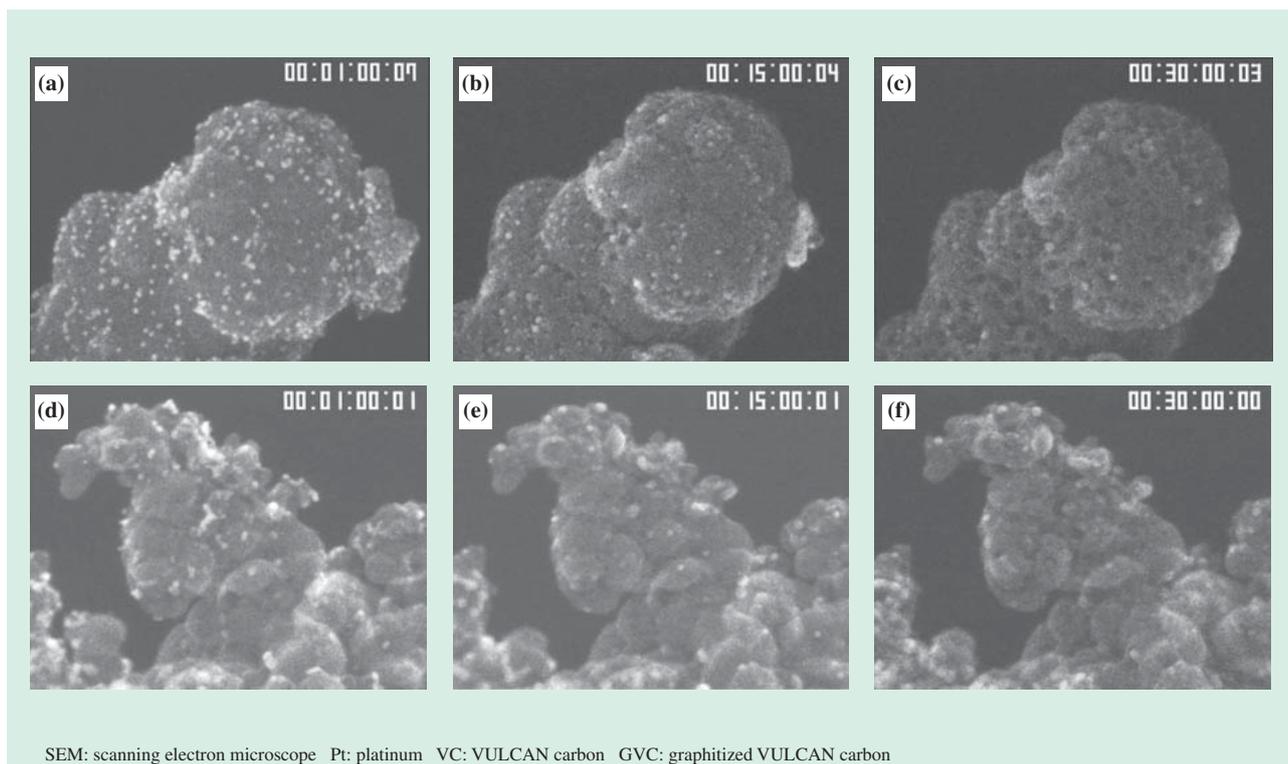


Fig. 1—In-situ SEM Observation.

The photographs show Pt/VC (a) 1 min., (b) 15 min., and (c) 30 min. after air introduction, and Pt/GVC1600 (d) 1 min., (e) 15 min., and (f) 30 min. after air introduction.

experimented with a new technique⁽⁴⁾ for evaluating electrode catalyst durability a short time frame of 30 minutes through use of an accelerated degradation testing protocol entailing heating of electrode catalyst specimens in an atmospheric air environment, and simultaneous, in-situ scanning electron microscope/scanning transmission electron microscope (SEM/STEM) observation.

EXPERIMENTAL PARAMETERS

Our research used TEM/STEM equipped with SEM functionality and an air supply system developed for in-situ TEM use to perform in-situ observation of the behavior of platinum nanoparticles on carbon in an atmospheric environment. Simultaneous in-situ SEM/STEM observation was carried out for 30 minutes with air introduced near the observed specimen and a specimen heating temperature of 200°C. The specimens used for observation were platinum/VULCAN*¹ carbon (VC) produced by a method⁽⁵⁾ using commercial VULCAN XC72 and a platinum acetylacetonate precursor. For comparison, platinum/

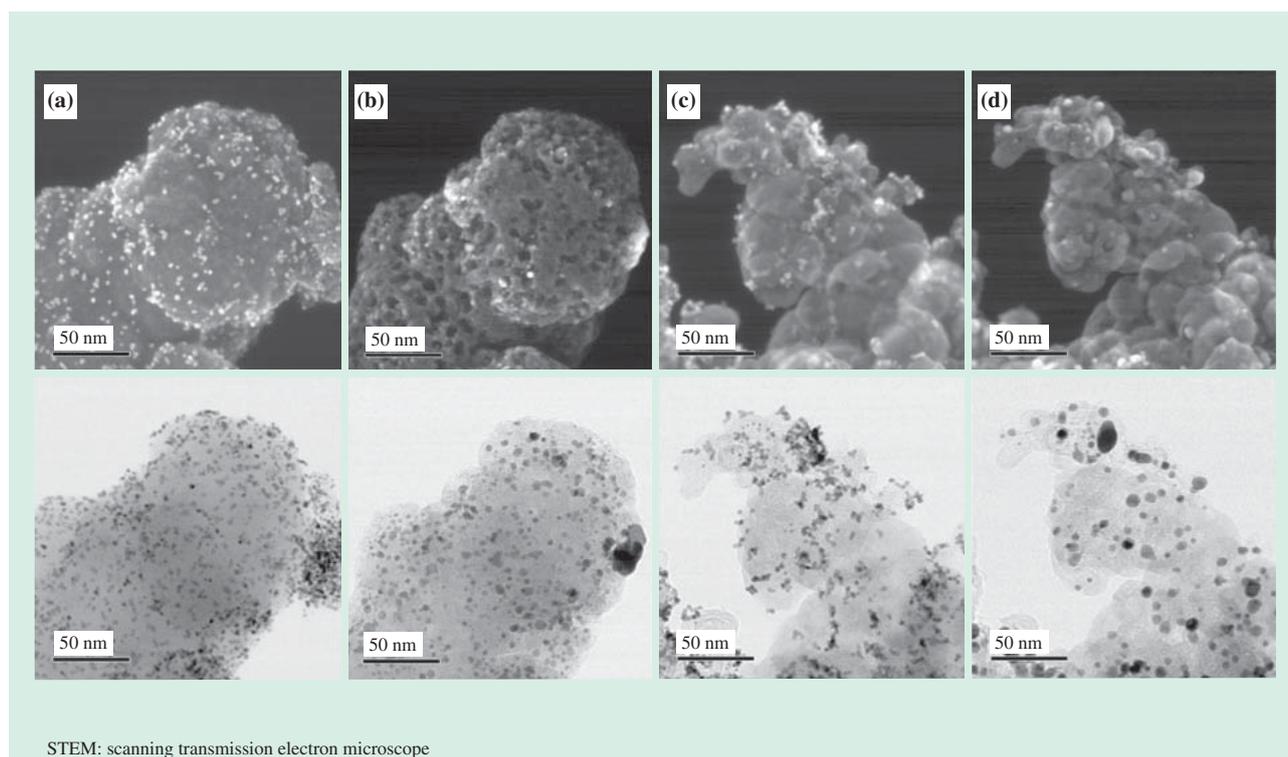
graphitized VULCAN carbon 1600 (GVC1600) carrying platinum was used in an analogous method following heat treatment of VULCAN XC72 at 1,600°C to graphitize the surface. The amount of platinum carried was approximately 20% in each samples. A previous report⁽²⁾ states that, among both samples, durability was improved in platinum/GVC1600 with a graphitized surface after evaluation by the electric potential cycle protocol described above. In addition to these two samples, a platinum/Ketjen Black (KB: commercial Ketjenblack*² EC-600JD) catalyst carrying platinum in similar fashion was used in ex-situ SEM/STEM observation. Platinum/KB, a sample demonstrating very low durability in electric potential cycle testing, was evaluated for comparison to platinum/VC and platinum/GVC1600.

IN-SITU SEM/STEM OBSERVATION

Fig. 1 shows SEM images at 1, 15, and 30 minutes after introduction of air to platinum/VC and platinum/GVC1600 specimens. As shown in Fig. 1 (a), approximately 2 nm of platinum particles was found

*1 VULCAN is a registered trademark of Cabot Corporation.

*2 Ketjenblack is a registered trademark of Akzo Nobel Chemicals B.V.



STEM: scanning transmission electron microscope

Fig. 2—Simultaneous In-situ SEM/STEM Observation.

The photographs show Pt/VC after (a) 1 min. and (b) 30 min., and Pt/GVC1600 after (c) 1 min. and (d) 30 min.

to be distributed uniformly on the carbon support surface in the initial platinum/VC. After introduction of air, virtually no movement of platinum particles on the carbon support was observed, and likewise, virtually no associated aggregation or coarsening. As seen from the SEM image after 15 minutes shown in Fig. 1 (b), the process of platinum particle penetration to the interior of the carbon support was observed actively. Thereafter, the shape of the carbon support was maintained, but as reaction time proceeded, the surface structure changed into a porous form, and after 30 minutes, as shown in Fig. 1 (c), nearly all of the platinum particles were found to have sunk into the support interior. As seen from the simultaneous SEM/STEM observation images shown in Fig. 2 (a), in early stages, both images show nearly identical platinum particles, indicating that platinum particles were present only on the surface of the carbon support. However, major differences in the SEM and STEM images are seen in Fig. 2 (b) 30 minutes after observation, and simultaneous observation with SEM showed that degradation of the catalyst not apparent from the STEM image alone was caused by a decrease in active sites, the major reason for which was the phenomenon of particle sinking, rather than particle growth.

In the GVC1600 specimen, similarly, dispersion soon after air introduction in Fig. 1 (d) was somewhat worse than in the platinum/VC specimen, with particles of approximately 2–3 nm supported on the carbon support. However, as air was introduced, as shown in Fig. 1 (e), the platinum/GVC1600 specimen demonstrated aggregation and coarsening of platinum particles in conjunction with their movement on the carbon support surface, a phenomenon virtually unobserved in the platinum/VC specimen. At such time, no apparent sinking of platinum particles into the support was observed. Thereafter, as reaction time proceeded, some sinking of platinum particles into the support was observed, but as shown in the SEM image in Fig. 1 (f) after 30 minutes, the sinking of platinum was largely suppressed. Then, as shown in the simultaneous SEM and STEM observation images in Fig. 2 (c) and (d), initially and after 30 minutes, respectively, no major difference was seen in the state of platinum dispersion, another indication that sinking of platinum particles into the support was largely suppressed.

Our research discovered that aggregation, dissolution, and loss, the previously conceived mechanisms of platinum degradation, are also augmented by a new mechanism of platinum

degradation⁽⁴⁾, specifically, corrosion of the carbon support surface by platinum particles, with sinking of particles into the support, and substantial reduction in the platinum-active surface. While it has become apparent that graphitization of a carbon surface suppresses carbon corrosion and improves durability by previous evaluations based on electric potential cycle protocols, improved durability was also confirmed by our new technique.

EX-SITU SEM/STEM OBSERVATION⁽⁶⁾

The new degradation mechanism of platinum particle sinking is important to PEFC research for its consistency with actual degradation mechanisms occurring in PEFC. For this reason, we carried out simultaneous ex-situ SEM/STEM observation of degraded Pt/VC and Pt/GVC1600 through electric potential cycling protocols. Fig. 3 (a) and (b) present the results for Pt/VC, and Fig. 3 (c) and (d) present the results for Pt/GVC1600. In all samples, there was no observed discrepancy in Pt dispersion in SEM versus STEM images, and the phenomenon of platinum sinking was not confirmed.

We therefore performed simultaneous ex-situ SEM/STEM observation of platinum/KB specimens, which have very low durability in electric potential cycle testing, after such testing. As shown in Fig. 4 (a) and (b), platinum particles seen in STEM images were not seen in SEM images, and SEM images confirmed

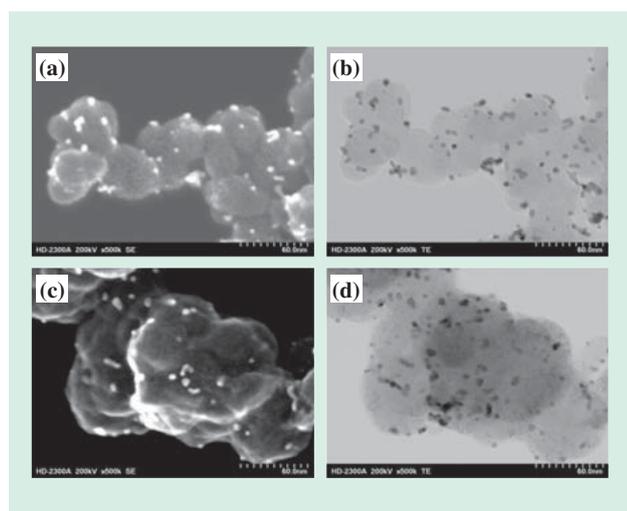


Fig. 3—Simultaneous Ex-situ SEM/STEM Observation of Pt/VC and Pt/GVC1600.

The photographs show (a) SEM and (b) STEM images of Pt/VC, and (c) SEM and (d) STEM images of Pt/GVC1600 after electric potential cycle degradation testing (60,000 cycles).

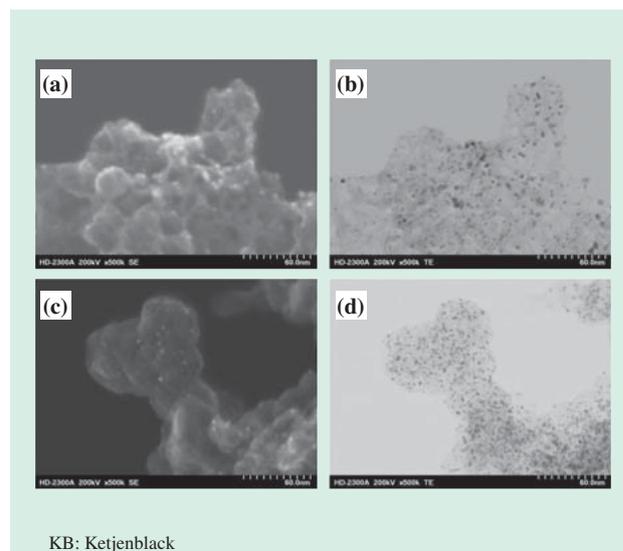


Fig. 4—Simultaneous Ex-situ SEM/STEM Observation of Pt/KB. The photographs show (a) SEM and (b) STEM images after, and (c) SEM and (d) STEM images before electric potential cycle degradation testing (60,000 cycles).

the presence of holes opened on the surface of the support, suggesting, in other words, that carbon surface corrosion opened holes, and platinum particles sank. Here we note that comparison of platinum/KB SEM/STEM images before electric potential cycle testing did not show as many platinum particles in SEM images as were seen in STEM images, due to the hollow structure of KB, and this comparison did not confirm the presence of holes opened in the carbon surface. From this fact, we understand that one degradation mechanism entails degradation of carbon by application of electric potential cycling, formation of holes, and sinking of platinum particles into the carbon.

In sum, we have concluded that an accelerated degradation testing protocol involving heating of an electrode catalyst material in an environment of atmospheric air presents accelerated degradation conditions more severe than those in electric potential cycle testing, but similar mechanisms cause degradation.

CLOSING REMARKS

Through an in-situ SEM/STEM simultaneous observation protocol, we confirmed that the accelerated degradation testing protocol used in our research, wherein an electrode catalyst material is heated in an atmospheric air environment, allowed evaluation of electrode catalyst durability in a short time frame. The evaluation results were also consistent with patterns in

results to date for electric potential cycle testing. We believe that this protocol will prove to be an extremely important analytical technique in fuel cell research, and we hope that its adoption will extend beyond observation of electrode catalysts to observation of catalyst layers including ionomers, thereby furthering fuel cell research.

REFERENCES

- (1) A. Ohma et al., "Membrane and Catalyst Performance Targets for Automotive Fuel Cells by FCCJ Membrane," *Catalyst, MEA WG, ECS Transactions* **41**, Issue 1, pp. 775–784 (2011).
- (2) X. Zhao et al., "Evaluation of Change in Nanostructure through the Heat Treatment of Carbon Materials and Their Durability for the Start/Stop Operation of Polymer Electrolyte Fuel Cells," *Electrochimica Acta* **97**, pp. 33–41 (2013).
- (3) Fuel Cell Commercialization Conference of Japan, "Proposals of the Development Targets, Research and Development Challenges and Evaluation Methods Concerning PEFCs," (2011) in Japanese.
- (4) H. Matsumoto et al., "Simultaneous In Situ SEM and STEM Analysis of Gas/Catalyst Reaction in a Cold Field-emission Environmental TEM," *Microscopy and Analysis* **27** (2013).
- (5) A. Hayashi et al., "Preparation of Pt/Mesoporous Carbon (MC) Electrode Catalyst and Its Reactivity toward Oxygen Reduction," *Electrochimica Acta* **53**, Issue 21, pp. 6117–6125 (2008).
- (6) X. Zhao et al., "Development of Durable Electrocatalysts for PEFC through Graphitization of Carbon Support Surface," *ECS Transactions* **53**, Issue 12, pp. 23–29 (2013).

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