Digging Behavior of Catalyst Metal Particles on HOPG under Hydrogen Atmosphere

S. Konishi, K. Nukii, R. Miyoshi, T. Matsuse
W. Sugimoto, Y. Murakami and Y. Takasu

Department of Fine Materials Engineering,
Faculty of Textile Science and Technology,
Shinshu University
3-15-1 Tokida, Ueda 386-8567, JAPAN

Introduction

An important subject for the development of direct methanol fuel cells (DMFCs) is to avoid the poisoning with oxidation intermediates of methanol. PtRu electrocatalysts are known to provide high activity for the electro-oxidation of methanol due to their excellent property to avoid the formation of strongly adsorbed poisoning species such as CO_{ad} on the platinum sites. For the preparation of highly active PtRu/C anode catalysts by an impregnation method, the condition of heat-treatment is an activity-controlling factor [1]. Although the catalysts are usually prepared at a moderate temperature typically between 200 to 500°C, they are occasionally prepared above 500°C in order to promote alloying of the metal elements. The preparation of carbon-supported metal catalysts at high temperature may not only bring about coagulation of catalyst metal particles, but also cause a consumption of carbon support forming hydrocarbons at the metal/carbon interface. In this investigation, the dynamic behavior of Pt, Ru and PtRu nano-particles supported on carbon at relatively high temperatures under hydrogen atmosphere was clarified utilizing electron microscopy by a model catalyst method.

Experimental

Highly oriented pyrolytic graphite (HOPG) was used as the support for catalyst metal particles. Ethanolic solutions of $Pt(NH_3)_2(NO_2)_2$ and $(RuNO(NO_3)_x$ were used as Pt and Ru sources, respectively. The precursor solutions were dropped onto the cleavage plane of HOPG. The precursor/HOPG specimen was placed on a Pt boat, set in a furnace tube, dried at 60°C under N_2 flow, and then heated at desired temperatures for 2 h under a flowing of a mixture gas of H_2 (10%) + N_2 (90%). The surface morphology of the Pt/HOPG, Ru/HOPG, $Pt_{50}Ru_{50}$/HOPG model cayalysts were observed by high-resolution scanning electron microscopy (HR-SEM, Hitachi S-5000) and atomic force microscopy (AFM, SII SPA-400).

Results and discussion

The dynamic behavior of the pyrolysis of the Pt and Ru complexes on the HOPG substrate could be clarified by electron microscopy. Figures 1 and 2 show HR-SEMs of a PtRu/HOPG model catalyst prepared at 900°C. As clearly shown in these images, the surface layer of the cleavage plane of HOPG was dug by the metal particles from edge or grain boundary of HOPG. Below 800°C, such a "digging phenomenon" of PtRu particles was not observed. The first noteworthy finding is that the "digging" of HOPG by PtRu particles resulted in linear grooves, and the second one is that the grooves were formed with specifically oriented direction of 60°, 30° or 120°. This "oriented digging" phenomenon suggests that the carbon atoms in a specified direction of the graphite structure are more reactive with hydrogen than those in

other directions. By an AFM observation of the surface, the direction and the depth of the grooves was characterized. The third notable result is that the extent of "digging" of HOPG by metal particles was in the order of Ru, PtRu and Pt. This difference must be attributed to the strength of metal-hydrogen interaction.

[1] Y. Takasu, T. Fujiwara, Y. Murakami, K. Sasaki, M. Oguri, T. Asaki, and W. Sugimoto, *J. Electrochem. Soc.* **147**, 4421(2000).
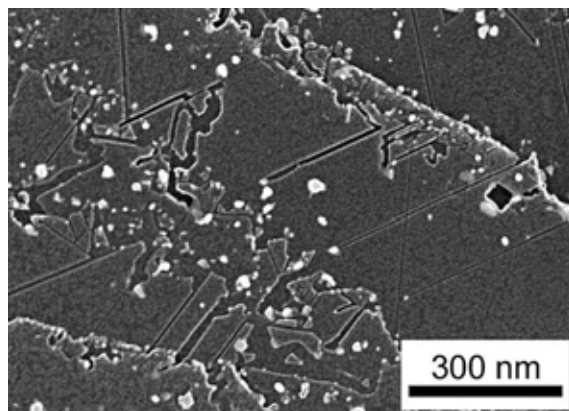
Figure 1 . A high-resolution scanning electron micrograph of a PtRu/HOPG model catalyst prepared at 900°C (An edge with terrace part).
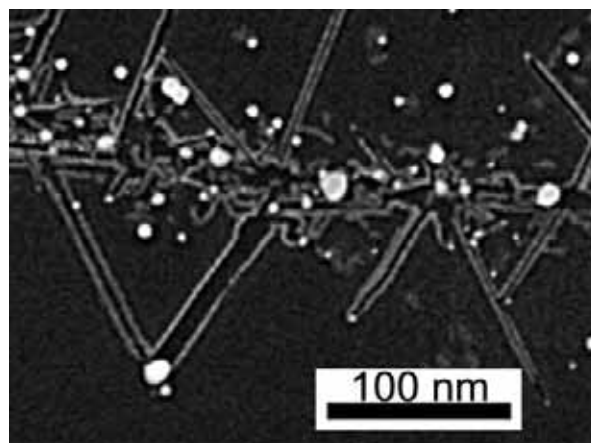

Figure 2 . A high-resolution scanning electron micrograph of a PtRu/HOPG model catalyst prepared at 900°C (A grain boundary part).