# Observation of Ultra-fine Palladium Particles on a Flat Glassy Carbon Electrode with a High Resolution Scanning Electron Microscope

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Ultra-fine palladium particles (>2 nm diam.) which were well aged by electrochemical oxidation–reduction in an aqueous solution of $HClO_4$ after being vacuum-evaporated on a flat plane of a glassy carbon electrode, have been observed by high resolution scanning electron microscopy (SEM).

Electrocatalysts, consisting of ultra-fine noble metal particles and porous active carbon or carbon black as supporting materials, have been used as the electrodes of fuel cells; however, the effects of size of the metal particles on their catalytic properties have not yet been established.[1,2] In order to clarify these effects, we have adopted the 'model catalyst method' in this study.[3—5] The model catalyst electrode prepared by vacuum evaporation of the catalyst metal onto a flat and electrically conducting material has the following advantages. Firstly, both the real shapes of metal particles and the surface of the supporting materials can be observed by electron microscopy. Secondly, any effect of pore structure can be neglected and thirdly, use of electron spectroscopy is easy[3] because the surface is flat and clean. Although transmission electron microscopy (TEM) has frequently been adopted for the observation of the metal particles on catalyst electrodes, it can give only the transmitted shapes of the metal particles and the supporting material of a fractured plane of catalyst electrodes[6] other than model catalyst electrodes.[7]

In this communication, the real shapes of ultra-fine palladium particles and the flat plane of a glassy carbon support have been successfully observed by high resolution scanning electron microscopy (SEM).

A high purity glassy carbon rod (Tokai Carbon Ltd., GC-30S, 6 mm diam., 2 mm length; 100 p.p.m. total ash) was used as the support; the base of the rod was polished with an alumina suspension (particles *ca.* 0.06 μm diam.) and the specimen was sonicated in acetone and distilled water. The test electrode Pd/GC (GC = glassy carbon) was prepared by vacuum evaporation of palladium onto the base of the glassy carbon rod support. The amount of palladium deposited was measured with a quartz thickness monitor (Anelva, EVM-32B). The electrochemical measurements were carried out using a glass beaker cell, filled with a $HClO_4$ solution (0.2 $dm^3$,

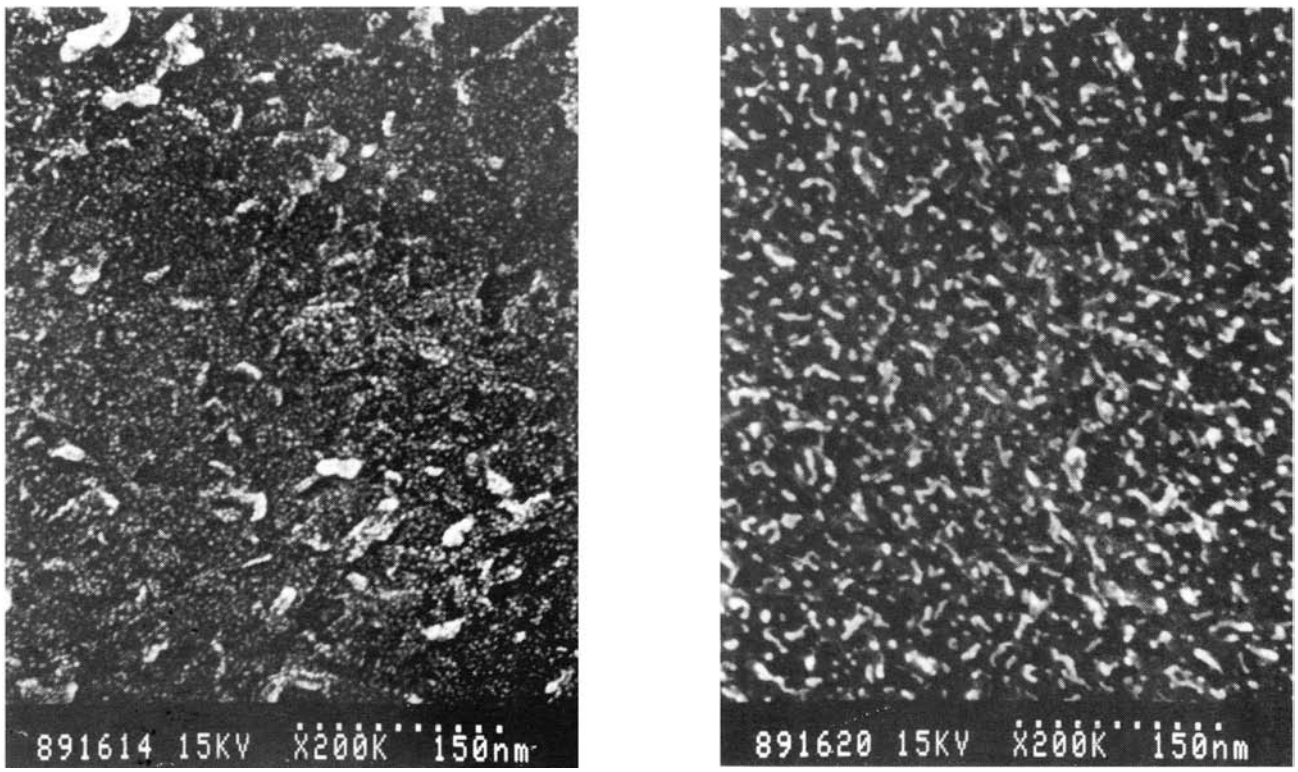


**Figure 1.** SEM micrographs of Pd/GC model catalyst electrodes before and after the electrochemical aging treatment. The amount of palladium evaporated was $6.9 \times 10^{15}$ Pd atom $cm^{-2}$. Treatment: (a) as evaporated, (b) electrochemical aging (see text).

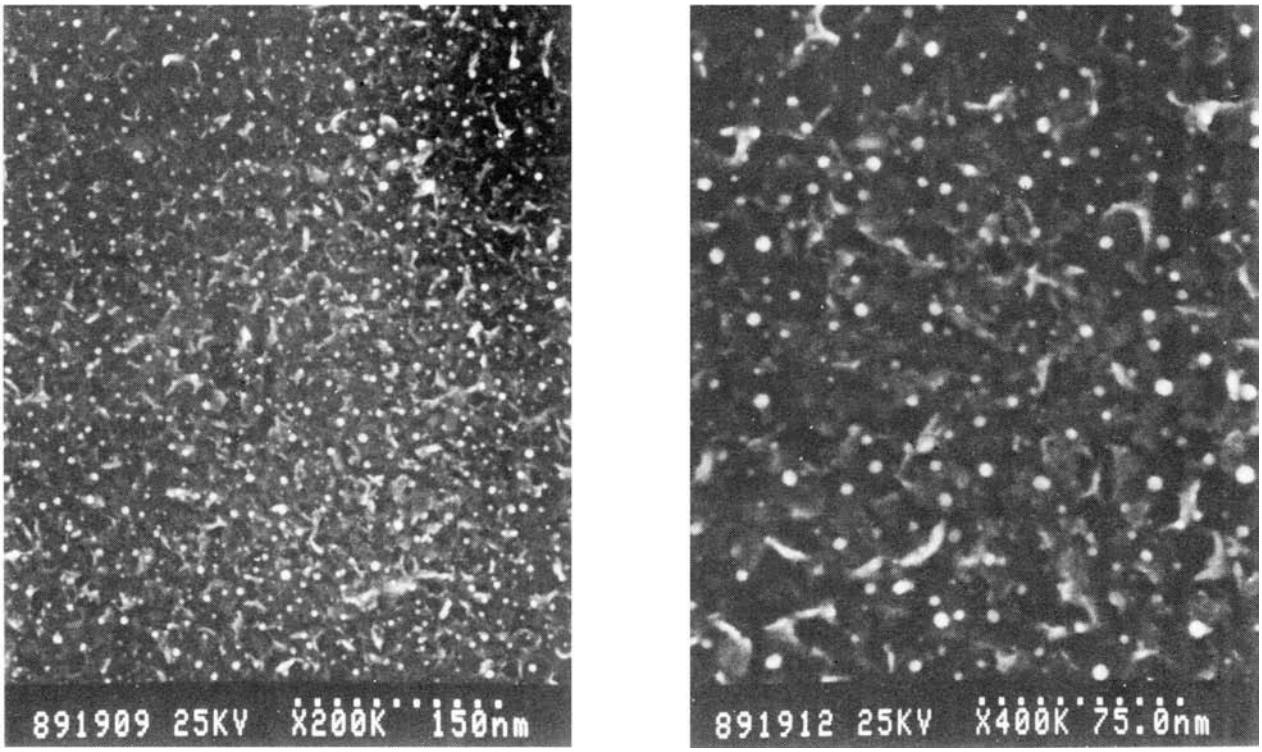


**Figure 2.** SEM micrographs, at two different magnifications, of a Pd/GC model catalyst electrode after the electrochemical aging treatment. The amount of palladium evaporated was $2.8 \times 10^{15}$ Pd atom $cm^{-2}$. Treatment: see text.

0.005 M), and a platinum plate counter electrode at room temperature. The aging treatment for the evaporated palladium was done by sweeping the electrode potential repeatedly between the potential at which hydrogen evolved rapidly and 1.00 V [*vs.* hydrogen electrode (RHE)] at a sweep rate of 500 mV $s^{-1}$ for 10 min. The surface of the glassy carbon on which the palladium particles were embedded was observed by high resolution SEM (Hitachi, Model S-900). Before the aging treatment, round-shaped palladium particles were almost homogeneously dispersed over the glassy carbon (see Figure 1a). On aging, the shapes of the particles changed greatly; *i.e.* worm-like or large round-shaped particles were formed as a result of a rearrangement of the palladium atoms. When the amount of palladium evaporated was reduced to $2.8 \times 10^{15}$ Pd atom $cm^{-2}$, all the palladium particles after aging had a round shape as shown in Figure 2. It is also noteworthy that very small palladium particles with a diameter of about 2 nm, as well as the detailed surface structure of the glassy carbon support, could clearly be seen in the photograph [Figure 2(b)]. The white crescent-shaped features are edges of the glassy carbon. As described in the introduction, this model system for supported metal catalyst electrodes offers visualization of the real surface structure of the electrode surface.

We thank Miss Mine Nakagawa, Mr. Kanoh Suzuki, and Dr. Takashi Nagatani of the Hitachi Techno Research Laboratory, Hitachi Instrument Engineering Co., Ltd., Japan, for observation of these model catalysts by SEM, and Mr. Ikuya Nakanishiki of the Nissei Sangyo Co. Ltd. for help in arranging for the SEM. This work was partly supported by the Grant of the Asahi Glass Foundation for Industrial Technology.

*Received, 22nd September 1989; Com. 9/04041B*

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