

## Activity Enhancement of Platinum Nanoparticle Catalysts on Ion-Beam-Irradiated Carbon Support

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Platinum (Pt) nanoparticle catalysts were prepared on the glassy carbon substrate pre-irradiated with energetic argon ions. The X-ray photoelectron spectra in the Pt4f and C1s regions demonstrated that Pt-C bonding was formed between Pt nanoparticles and the irradiated substrate. From the electrochemical measurements, the ion-irradiation of the carbon support was found to enhance the catalytic activity of the Pt nanoparticles for the oxygen reduction reaction. X-ray absorption studies at the Pt M<sub>3</sub> edge indicated that the Pt oxidation was suppressed on the ion-irradiated carbon support; this chemical-state change would result in the observed high catalytic activity.

### 1 Introduction

Polymer electrolyte fuel cell (PEFC) is one of the important candidates of the clean power sources for automotive and residential applications. In PEFC, carbon-supported platinum nanoparticles (Pt NPs) are commonly employed as cathode catalysts for the oxygen reduction reaction (ORR). However, insufficient ORR activity of the Pt NPs is the serious challenge to overcome before wide commercialization of PEFCs, and many studies have been carried out to achieve activity enhancement of the Pt catalysts.

One promising strategy for improving the activity is to utilize the Pt-carbon support interaction. Recent theoretical investigations by first-principle calculations have suggested that the lattice vacancy in the graphitic structure of the carbon support could enhance the ORR activity of the supported Pt NPs [1], but no experimental evidence has been reported. This could be because the conventional methods of support-surface modification using chemical treatments [2] cannot introduce lattice vacancy.

Ion-beam irradiation is an excellent technology for creating lattice vacancies in a material; their density can be well controlled. In this study, therefore, we used the ion beam to induce vacancy formation in the carbon support, expecting that a high ORR activity would be realized by the Pt-carbon interfacial electronic interaction.

### 2 Experiment

Unpolished 1-mm-thick glassy carbon (GC) substrates were irradiated with 380 keV Ar<sup>+</sup> at the fluence of  $1.0 \times 10^{16}$  ions/cm<sup>2</sup> using the ion implanter at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) facility of Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and

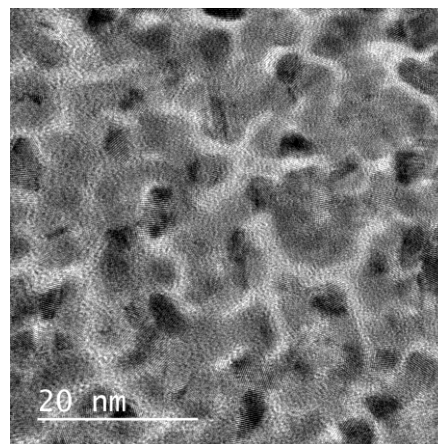


Fig. 1: TEM image of the deposited Pt NPs on a grid mesh for electron microscopy.

Radiological Science and Technology. The irradiated GC substrate was then heated at 400°C in an N<sub>2</sub> atmosphere for 1 h. Pt NPs were prepared on the substrate by RF magnetron sputtering. The sputtering time and the plasma output were 60 s and 20 W, respectively. As the comparative sample, the Pt NPs were also sputtered on the non-irradiated GC substrate. These prepared samples were called “irradiated sample” and “non-irradiated sample” respectively later in this report. Figure 1 shows a transmission electron microscope (TEM) image of the Pt NPs deposited directly on a TEM grid under the same conditions. The Pt NPs observed as black circles had an average diameter of about 5 nm.

The X-ray photoelectron spectroscopy (XPS) measurements were performed using PHI 5000 Versa Probe (ULVAC-PHI, Inc., Japan) with an Al K $\alpha$  (1486.6 eV) X-ray as the light source. The Pt 4f and C 1s spectra

were taken with a pass energy of 23.5 eV with a 0.1 eV step and averaged for 20 and 40 scans, respectively. A 2 keV Ar<sup>+</sup> sputtering gun was used for surface cleaning. The duration of the sputtering was set to 5 s, which corresponded to a sputter depth of less than 1 nm.

The ORR activity of the irradiated and non-irradiated samples was analyzed by electrochemical measurements using HZ-5000 Potentiostat (HOKUTO Denko Corp., Japan). All measurements were carried out in a three-electrode cell with an Ag/AgCl reference electrode and a Pt wire counter electrode. All the potentials in this report are given with respect to the reversible hydrogen electrode (RHE). Cyclic voltammogram (CV) was recorded at 25°C in an N<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution. The potential was swept between 0.05 and 1.25 V at a scan rate of 50 mV/s. The electrochemical surface area (ECSA) was evaluated from the hydrogen adsorption region of the CV [3]. After the CV measurements, the rotating disk electrode (RDE) measurements were conducted in the same potential range in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> solution at a scan rate of 20 mV/s. The speeds of the rotation were set to 400, 900, 1600, and 2500 rpm.

The X-ray absorption data at the Pt M<sub>3</sub> edge were measured in the total electron yield mode by recording the sample current. The measurements were performed using the synchrotron radiation on the BL-27A at Photon Factory in the high energy accelerator research organization. The synchrotron radiation beam was generated from the bending magnet and it was linearly polarized in the horizontal direction. In the BL-27A, double-crystals of InSb (111) were used as a monochromator. The details of the BL-27A were reported elsewhere [4].

### 3 Results and Discussion

Figure 2 shows the Pt 4f XPS spectra of (a) the irradiated sample and (b) the standard Pt plate. The Pt 4f<sub>7/2</sub> peak was broader on the high energy side in (a) than in (b), suggesting the presence of Pt-C bonding between the GC substrate and the deposited Pt NPs. Figure 3 compares the C 1s XPS spectra between (a) the irradiated sample and (b) a pristine GC substrate. Spectrum (a) in Figure 3 exhibited a slightly wider peak; interestingly, it had a small bump on the low energy side in addition to a tail on the high energy side. This result can be attributed to carbide formation, making it possible to confirm the existence of Pt-C bonding at the interface. In other words, the usage of the ion-irradiated GC as a support of Pt catalysts induced the interfacial Pt-C bonding [5].

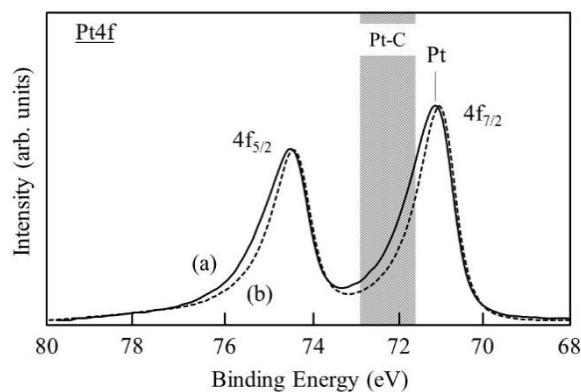


Fig. 2: Pt 4f XPS spectra of (a) the Pt NPs on the Ar<sup>+</sup>-irradiated GC substrate and (b) standard Pt plate.

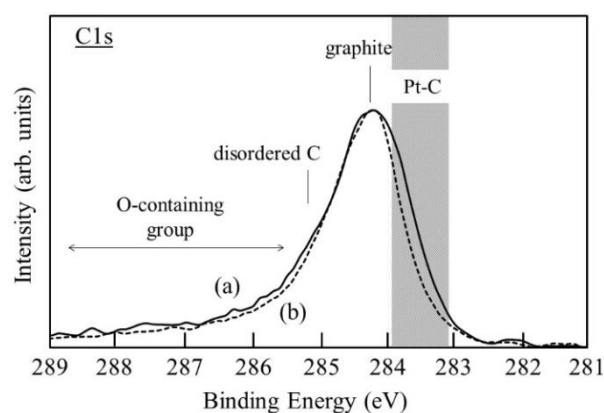


Fig. 3: C 1s XPS spectra of the Pt NPs on the (a) pre-irradiated and (b) pristine GC substrates.

The mass-transport-corrected kinetic current,  $I_k$  was calculated by applying the measured current,  $I$  and the measured diffusion limited current,  $I_\infty$  to the following equation [6].

$$I_k = \frac{I \cdot I_\infty}{I_\infty - I}$$

Then, the specific activity,  $i_k$  was derived by standardizing  $I_k$  by the ECSA. Figure 4 shows the Tafel slopes for the irradiated and non-irradiated samples. The specific activity was higher for the irradiated sample than for the non-irradiated one at any voltage. Strikingly, only by the ion-irradiation of the carbon support, the specific activity at 0.85 V was increased by about 2.5 times [7].

In order to clarify the mechanism of the observed high activity, X-ray absorption data were acquired. Figure 5 shows the X-ray absorption near edge structure (XANES) spectra of the irradiated and non-irradiated samples after normalization and background subtraction. The intensity of the peak in the vicinity of the threshold in the XANES (also called white-line) was lower for the irradiated sample. The white-line intensity generally gets lower as the Pt 5d orbital is more filled. Thus the result indicates that more electrons were populated in the Pt 5d orbital in

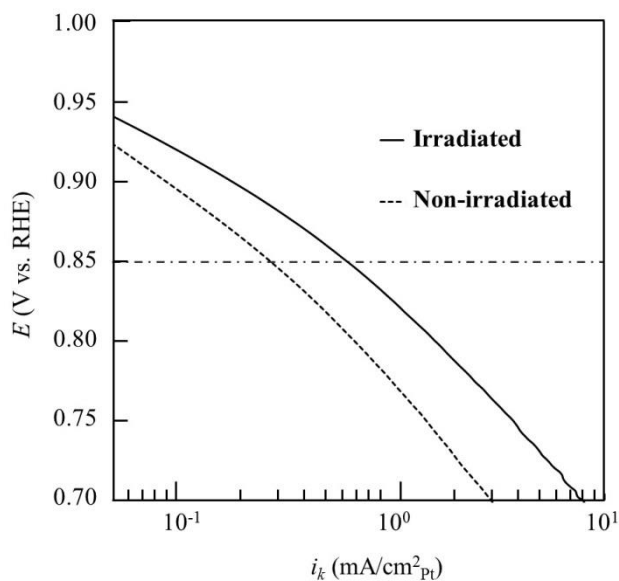


Fig. 4: Tafel plots for the ORR of the irradiated and non-irradiated samples.

the irradiated sample than in the non-irradiated one. We consider here that the Pt NPs on the irradiated substrate could be less oxidized [8]; in other words, the Pt-carbon support interaction formed by the pre-irradiated GC substrate possibly suppresses the formation of Pt oxide. Stamenkovic et al. [9] reported that this chemical-state change of the Pt NPs increased the kinetics of the rate-limiting step of the ORR (the removal of adsorbed O and OH species from the Pt NPs). Therefore, the suppression of the Pt oxidation resulting from the Ar<sup>+</sup>-irradiation of the carbon support would account for the observed high ORR activity of the Pt NPs.

In conclusion, the Pt-C bonding formed between the ion-beam-irradiated carbon support and the Pt NPs suppressed the Pt oxidation, thereby improving the catalytic activity of the Pt NPs for the ORR. Theoretical computations based on the density functional theory are now in progress to study how the ion-beam-induced vacancies in the carbon support resulted in the suppression of the Pt oxidation [10].

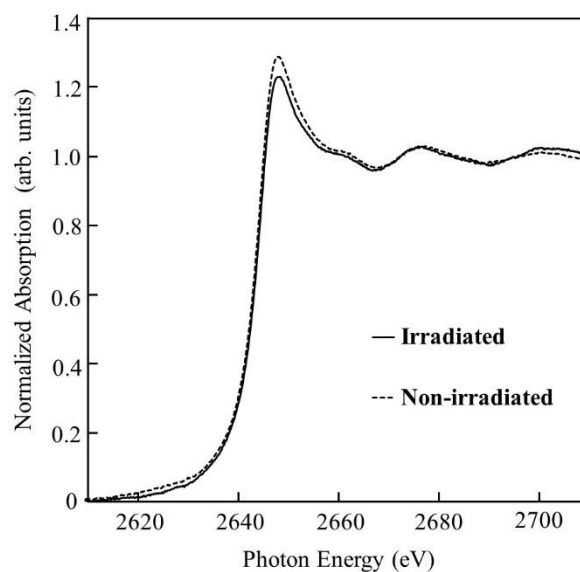


Fig. 5: Pt M<sub>3</sub> edge XANES spectra of the irradiated and non-irradiated samples.

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