Evidence of Strong Metal-Support Interaction between Pt and Crystalline RuO$_2$ Nanosheets by In-Situ AFM

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The enhancement in durability of Pt nanoparticles modified by nanostructured RuO$_2$ was studied using a model electrode consisting of vacuum deposited Pt on single crystalline RuO$_2$ nanosheets coated on highly oriented pyrolytic graphite (HOPG) surface with sub-monolayer coverage. Atomic force microscopy images showed that Pt on HOPG aggregated and tended to form 3-dimensional islands. On the other hand, Pt formed a well-defined, 2-dimensional over-layer on the RuO$_2$ nanosheet surface. In-situ atomic force microscopy images showed that deposited Pt on the HOPG surface readily dissolved and easily migrated with potential cycling in sulfuric acid, while no such phenomena could be observed on the RuO$_2$ nanosheets. The results indicate that RuO$_2$ nanosheet has a strong affinity toward Pt, namely strong metal-support interaction for Pt, which can be considered as one of the reasons for the enhanced durability of Pt/C modified by RuO$_2$ nanosheets.

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Carbon supported Pt (Pt/C) is widely used as the cathode catalyst in polymer electrolyte fuel cells (PEFCs). The loss of the electrochemically active surface area due to the dissolution and coalescence of Pt nanoparticles during longtime operation is one of the major obstacles for wide-spread commercialization of PEFCs. Modifying Pt/C catalyst with oxides such as TiO$_2$, $^{1,2}$ SiO$_2$, $^{3}$ TiO$_2$, $^{6,7}$ WO$_3$, $^{8}$ SnO$_2$, $^9$ RuO$_2$ $^{10-12}$ as corrosion-resistant support for Pt nanoparticles have been proposed to minimize the loss of activity. As an additive or support, it is desirable that the oxide phase is electrically conductive and stable in acidic environment. RuO$_2$ with electronic conductivity comparable to or higher than most carbonaceous materials, and with high resistance to corrosion seems to be an ideal material. Since RuO$_2$ is a precious metal oxide, it is essential to consider the difference in the adsorption strength of metallic Pt on RuO$_2$ nanosheet.17,18 Model electrode studies have elucidated that there is a strong affinity toward Pt, namely strong metal-support interaction for Pt, which can be considered as one of the reasons for the enhanced durability of Pt/C modified by RuO$_2$ nanosheets.

RuO$_2$ nanosheets were synthesized by elemental exfoliation of an ion-exchangeable layered potassium ruthenate (K$_{0.2}$RuO$_{2.1}$·nH$_2$O) following our previous report.20 Proton-exchange of the interlayer potassium was conducted with 1 mol dm$^{-3}$ HCl for 3 days at 60 °C, resulting in the layered rutheranic acid (H$_2$RuO$_2$·0.9H$_2$O). The layered rutheranic acid was added to an aqueous solution of tetrabutylammonium hydroxide (TBAOH) with the molar ratio of TBA ions to the exchangeable protons in H$_2$RuO$_2$·0.9H$_2$O adjusted to TBA°/H$^+$ = 1.5. The dispersion was vigorously shaken for 10 days to exfoliate H$_2$RuO$_2$·0.9H$_2$O into elementary RuO$_2$ nanosheets. Non-exfoliated impurity was removed by centrifugation at 2000 rpm for 30 min. The as-exfoliated nanosheet colloidal was finally diluted to 0.1 (g·RuO$_2$)·L$^{-1}$ with ultrapure water (Milli-Q, >18 M2 cm). HOPG (Bruker, 2YH-grade, 12 × 12 mm$^2$) was freshly cleaved using adhesive tape and then immersed into this diluted nanosheet colloid for 2 minutes to coat RuO$_2$ nanosheet (RuO$_2$ nanosheet/HOPG). Pt was evaporated onto the surface of RuO$_2$ nanosheet/HOPG using a vacuum evaporation equipment (Shimadzu, E-250A). A Pt wire (Nilaco, 0.5 mm in diameter, 10 mm in length, 99.95%) acted as the evaporation source. The amount of Pt deposited ($M_a = 0.22 \times 10^{15}$ or 1.33 $\times 10^{15}$ atoms cm$^{-2}$) was monitored by a quartz thickness monitor (Anelva, INFICON SQM-I60).

The surface of the model electrodes was characterized using an electrochemical-atomic force microscope (EC-AFM, Bruker, Digital Instruments Nanoscope III D ADC 5) equipped with a bi-potentiostat. Images were recorded using a SiN probe (Bruker, SNL-10). Cyclic voltammetry was performed from 0 to 1.2 V vs. RHE at a scan rate of 50 mV s$^{-1}$ in a three-electrode electrochemical cell (Bruker, Multi-Mode) with 0.5 M H$_2$SO$_4$ as the electrolyte at room temperature in air (without de-aeration due to the small size of the EC-AFM cell). The model electrode acted as the working electrode and two high purity Pt wires with diameter of 0.5 mm and 0.1 mm acted as the reference and the counter electrodes, respectively. All the potentials in the paper have been converted to reversible hydrogen electrode (RHE) scale by adding 0.90 V to the values measured with the Pt quasi-reference electrode which was calibrated against a reversible hydrogen electrode. The geometric area of the working electrode in contact with the electrolyte was 0.5 cm$^2$. The time for acquiring an AFM image was approximately 5 minutes. All the AFM images were processed using Nanoscope V531r1 software.

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Results and Discussion

Figure 1 shows typical AFM images and height profiles of RuO2 nanosheet/HOPG model electrodes with different amounts of deposited Pt (Pt-RuO2 nanosheet/HOPG), $M_a = 0.22 \times 10^{15}$ and $1.33 \times 10^{15}$ atoms cm$^{-2}$. On bare HOPG, the deposited Pt aggregates to form islands. On the contrary, Pt forms a well-defined over-layer on the nanosheets. For the model electrode with lower amount of Pt ($M_a = 0.22 \times 10^{15}$ atoms cm$^{-2}$), the Pt islands on HOPG have a height of $1.1 \pm 0.7$ nm and the height of RuO2 nanosheet covered with Pt is $1.2 \pm 0.4$ nm (Figure 1a). Since the thickness of RuO2 nanosheet is $1.0 \pm 0.1$ nm, the Pt over-layer should be $\sim 0.2$ nm thick. Taking into account of the diameter of Pt atom as 0.28 nm, the Pt over-layer deposited on RuO2 nanosheet is close to a thin continuous monolayer (ML) film. For the model electrode with more Pt ($M_a = 1.33 \times 10^{15}$ atoms cm$^{-2}$), the height of Pt deposits on HOPG was $1.5 \pm 0.8$ nm (Figure 1b). The height of RuO2 nanosheet with Pt over-layer was $1.6 \pm 0.7$ nm, thus the thickness of Pt over-layer should be $\sim 0.6$ nm. This thickness is about twice the atomic diameter of Pt (0.28 nm), thus the Pt over-layer is considered as a 2 ML film. The 3-dimensional growth of Pt deposits on HOPG and 2-dimensional growth on RuO2 nanosheet indicate two different film growth modes, namely Volmer-Weber growth (3-dimensional growth) and Frank-van der Merwe growth (2-dimensional growth). The two different growth modes reveal that RuO2 nanosheet has a stronger adsorption strength or affinity to Pt compared to HOPG. This is in good agreement with density functional theory calculations that predicted strong adsorption of Pt on RuO2(100) leading to energetically favorable 2-dimensional growth of up to 1.25 ML. RuO2 nanosheet evidently has similar properties with bulk RuO2.

Next, the electrochemical stability of Pt aggregated on HOPG (Pt/HOPG) compared to Pt on RuO2 nanosheet (Pt/RuO2 nanosheet) was studied by in-situ EC-AFM. Figure 2 shows a sequence of in-situ EC-AFM images and the respective height profiles of the Pt-RuO2 nanosheet/HOPG model electrode ($M_a = 1.33 \times 10^{15}$ atoms cm$^{-2}$) with potential cycling (0–1.2 V vs. RHE, 50 mV s$^{-1}$) in 0.5 M H2SO4 at room temperature. The topographic images clearly show that the amount of Pt on bare HOPG gradually decreases and more HOPG surface is exposed with increasing number of potential cycling. On the other hand, the maximum thickness of the Pt over-layers on nanosheets increases with potential cycling from $\sim 0.9$ nm for the 10th cycle to $\sim 1.4$ nm after 40 cycles as shown in the height profiles in Figure 2. This result can also be identified clearly from the comparison of the height profiles shown in Figure 3. This strong affinity of RuO2 nanosheet with metallic Pt is an indication of the so-called strong metal-support interaction (SMSI) as found in oxides such as CeO2 and TiO2. It is noted that the Pt deposit on HOPG shown in Figure 3 is moving to the right with potential cycling, which indicates that the deposited Pt on HOPG migrates easily; i.e. Pt nanoparticles have weak affinity to HOPG.

Figure 4 shows the cyclic voltammograms (CVs) of the Pt-RuO2 nanosheet/HOPG model electrode in 0.5 M H2SO4 corresponding to Figure 2a–2d. The negative shift in currents observed below 0.8 V vs. RHE is due to oxygen reduction reaction, since measurements were conducted in atmospheric conditions. De-aeration of the electrolyte was difficult to conduct due to the small size of the EC-AFM cell. Distinctive peaks
attributed to surface redox process on RuO$_2$ nanosheet are observed at half wave potential of $E_{1/2} = 0.11$ and 0.62 V vs. RHE in the CVs. The redox pair at $E_{1/2} = 0.62$ V vs. RHE does not change, indicating the stability of the RuO$_2$ nanosheets with potential cycling. On the other hand, the current below 0.2 V decreases with potential cycling. The current observed in this region is due to double-layer charging, hydrogen adsorption/desorption on Pt, and pseudocapacitance of RuO$_2$ nanosheets. Since the RuO$_2$ nanosheets do not degrade, the decrease in current can be attributed to loss in electrochemical active surface area of Pt due to Pt dissolution or aggregation. This phenomenon can also be seen from the decrease in anodic current > 1.0 V vs. RHE, which is related to the oxidation of Pt. It is assumed

![Figure 2](image-url)
AFM images show that on HOPG, Pt aggregates and forms mitigation of Pt loss with RuO$_2$ nanosheets, and is presently under average should allow a more quantitative discussion on the degree of difference in the interaction between Pt with RuO$_2$ nanosheet or partially covered with crystalline RuO$_2$ nanosheets to investigate the consideration.

that both Pt on HOPG and Pt on RuO$_2$ nanosheet/HOPG are active. Further model electrode studies with different RuO$_2$ nanosheet coverage should allow a more quantitative discussion on the degree of mitigation of Pt loss with RuO$_2$ nanosheets, and is presently under consideration.

Conclusions
Pt was vacuum deposited on model electrodes composed of HOPG partially covered with crystalline RuO$_2$ nanosheets to investigate the difference in the interaction between Pt with RuO$_2$ nanosheet or HOPG. AFM images show that on HOPG, Pt aggregates and forms 3-dimensional islands via Volmer-Weber growth, whereas Pt is de- posited as a thin over-layer on the RuO$_2$ nanosheet surface via Frank-van der Merwe growth (2-dimensional growth). The two different growth modes reveal that Pt has a stronger adsorption strength or affinity to RuO$_2$ nanosheet compared to HOPG, i.e. strong metal-support interaction. In-situ EC-AFM experiments reveal that Pt nanoparticles on HOPG are more susceptible to electrochemical active surface area loss than the Pt over-layer on RuO$_2$ nanosheet. The results suggest that RuO$_2$ nanosheet supported Pt is likely to be a more stable catalyst than carbon supported Pt. RuO$_2$ nanosheet can be anticipated to play multiple roles in enhancing the durability of practical carbon supported Pt catalysts for polymer electrolyte fuel cells, including strong metal-support interaction, electrostatic interaction with dissolved Pt cations, and also as a stable oxide support.

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