

Improving ORR activity and durability of 1.5 nm Pt by addition of ruthenium oxide nanosheets

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Abstract

The durability of commercial carbon supported Pt nanoparticles with average particle size of 1.5 nm (20 mass% Pt/C) has been improved by the addition of ruthenium oxide nanosheets (RuO₂ns) without sacrificing the initial activity towards oxygen reduction reaction. The initial oxygen reduction reaction activity of the composite catalyst was slightly higher than as-received Pt/C. The electrocatalytic activity after consecutive potential cycling tests of the composite catalyst was c.a. 1.3 times higher than non-modified Pt/C. The increased durability of the composite catalyst is attributed to the improved preservation of the electrochemically active Pt surface area with the addition of ruthenium oxide.

Keywords: Polymer electrolyte fuel cell; Oxygen reduction reaction; Durability; Ruthenium oxide; Nanosheets

1. Introduction

A large amount of Pt is currently used at the cathode catalyst layer in polymer electrolyte fuel cells due to the slow kinetics of the oxygen reduction reaction (ORR) [1]. In addition to the unsatisfactory ORR activity, there are also problems associated with performance loss with long term operation due to aggregation and dissolution of Pt particles and carbon corrosion [2–7]. Consequently, the activity and durability of Pt/C catalysts must both be improved for wide-spread commercialization of polymer electrolyte fuel cells [1,8]. Catalysts composed of Pt nanoparticles with average diameter of 2-3 nm supported on carbon are commonly used as cathode catalysts, offering the best combination of mass activity and long-term performance. The Pt loading depends on the surface area of the carbon support; for example 50 mass% Pt can be loaded onto Ketjen Black with specific surface area of $800 \text{ m}^2 \text{ g}^{-1}$ and 30 mass% Pt for Vulcan Carbon with $250 \text{ m}^2 \text{ g}^{-1}$. Smaller particle size, which in turn leads to higher electrochemically active Pt surface area, can be achieved at lower Pt loadings; for example 20 mass% Pt on Ketjen Black have Pt nanoparticles with 1.5 nm in diameter. However, such smaller nanoparticles generally have a higher rate of dissolution [9–13] and thus have so far been considered not beneficial for practical fuel cells.

The addition of oxides to Pt/C has recently been pursued as an approach to improve the performance of ORR catalysts. For example, addition of various metal oxide such as CeO_x , WO_3 , and TiO_2 was reported to improve the ORR activity [14,15]. Unfortunately, the

durability of these composite catalysts was not described. Improved durability was reported for Pt/C with titanium oxide, albeit with lower initial ORR activity than Pt/C [16,17]. Similarly, a carefully-controlled thin layer of SiO₂ on Pt/carbon nanotube was reported to show increased catalysts durability, but also lower initial performance [18,19]. Thus, in most cases, the addition of oxides increases either the initial activity or the durability, in other words, there seems to be a trade-off between ORR activity and durability. In this communication, we report that activity and durability of commercially available 1.5 nm Pt nanoparticles with initially high activity but insufficient long term durability can be easily improved by modification with RuO₂ nanosheets.

2. Experimental section

RuO₂ nanosheet was derived via exfoliation of layered H_{0.2}RuO_{2.1}·*n*H₂O following a process reported previously [20]. Briefly, 0.1 g of layered H_{0.2}RuO_{2.1}·*n*H₂O was added to 24.42 mL of ultrapure water, to which 0.577 mL of a 3.3 M tetrabutylammonium hydroxide aqueous solution was added and shaken for 10 days. The dispersion was centrifuged at 2000 rpm to remove any non-exfoliated material. Composite catalyst was prepared by adding the RuO₂ns colloid to an aqueous dispersion of a commercial Pt/C catalyst (20 mass% Pt, TEC10E20A, Tanaka Kikinzoku Kogyo) with a molar ratio of RuO₂:Pt=0.3:1. The dispersion was magnetically stirred and ultrasonicated to ensure homogenous reaction. After sedimentation,

the composite powder was washed and dried to yield the composite catalyst RuO₂ns-Pt/C. Catalyst morphology was characterized by transmission electron microscopy (TEM, JEOL 2010) operated at an accelerating voltage of 200 kV. Oxygen reduction reaction activity was analyzed using a rotating disk electrode (Nikko Keisoku). The catalyst suspension was prepared by dispersing 18.5 mg of catalyst in 15 mL of 2-propanol/water solution. A 5 wt % Nafion solution (0.352 mL) was added to the dispersion as a binder. The working electrode was prepared by depositing 17.3 μg-Pt cm⁻² on a mirror-polished glassy carbon rod (6 mm in diameter). Carbon fiber was used as the counter electrode and a reversible hydrogen electrode (RHE) served as the reference electrode. All electrochemical measurements were performed in 0.5 M H₂SO₄ at 25°C.

3. Results and discussion

Cyclic voltammograms of as-received Pt/C and the composite catalyst RuO₂ns-Pt/C de-aerated with N₂ gas in 0.5 M H₂SO₄ (25°C) are shown in [Fig. 1](#). Distinctive peaks attributed to surface redox process on RuO₂ns are observed at $E_{1/2}=0.13$ and 0.65 V vs. RHE in the cyclic voltammograms of RuO₂ns-Pt/C. The redox pair at 0.13 V vs. RHE is unique to RuO₂ns supported on carbon. As this peak overlaps with the hydrogen adsorption/desorption region, the electrochemical active Pt surface area (ECSA) of RuO₂ns-Pt/C was calculated by excluding the contribution from RuO₂ns. It is noted that the ECSA value obtained from CO stripping

measurements [21] gives the same ECSA value after this background subtraction. The ECSA determined from the hydrogen desorption region for RuO₂ns-Pt/C was 78 m² g⁻¹, which is comparable with that of Pt/C. Thus, RuO₂ns does not obstruct electrolyte diffusion to the Pt surface. Accelerated durability test (ADT) was performed by cycling between 0.6–1.2 V vs. RHE at 100 mV s⁻¹ in saturated at O₂ at 1600 rpm for 300 cycles. The ECSA of Pt/C after ADT decreased to 36 m² g⁻¹, which corresponds to a loss of 54%. Under the same experimental conditions, the ECSA of RuO₂ns-Pt/C after ADT was 48 m² g⁻¹, showing a loss of only 38%. The degradation rate of ECSA is relaxed by the RuO₂ns addition and the ECSA after ADT of RuO₂ns-Pt/C was 1.33 times higher than that of the non-modified Pt/C (Table 1). RuO₂ns is very stable under electrochemical conditions similar to what has been applied in this study [21,22]. This is also clear from the almost constant redox peaks attributed to RuO₂ns ($E_{1/2}$ = 0.13 and 0.65 V vs. RHE) before and after ADT.

Fig. 2 shows TEM images and the corresponding particle size distribution histograms of the fresh catalyst and catalyst after ADT. The average particle size for Pt/C and RuO₂ns-Pt/C were initially 1.5 nm and 1.6 nm, respectively. The Pt particle size after ADT for Pt/C and RuO₂ns-Pt/C were 3.6 and 2.6 nm, respectively. It is clear from TEM analysis that the addition of RuO₂ns inhibited particle growth. Also, more Pt particles were found supported on the carbon for RuO₂ns-Pt/C compared to Pt/C.

Linear sweep voltammograms (background subtracted, anodic scan) of the catalysts

before and after ADT measured in O₂ saturated 0.5 M H₂SO₄(25°C) are given in Fig. 3 and the Koutecky-Levich plots are shown in Fig. 4. Background subtraction was conducted by subtracting the linear sweep voltammograms collected under de-aerated conditions (N₂) at the respective rotation rates from the voltammograms taken in O₂-saturated electrolyte. The initial ORR activity increased from 192 to 221 A (g-Pt)⁻¹ by the addition of RuO₂ns (Table 1). As the ECSA of both electrocatalysts were equal, the addition of RuO₂ns seems to have a positive effect on the increase in the utilization of Pt for the ORR. The ORR activity after ADT for Pt/C decreased 55% to 87 A (g-Pt)⁻¹. The decrease was restrained to 50% for RuO₂ns-Pt/C, leading to an overall 1.26 times higher ORR activity after ADT for RuO₂ns-Pt/C (110 A (g-Pt)⁻¹) compared to Pt/C (87 A (g-Pt)⁻¹).

In summary, we attempted to increase the durability of high-surface area, 1.5-nm Pt nanoparticles (20 mass% Pt supported on carbon) which are known to have high initial ORR activity but poor durability by the addition of RuO₂ nanosheets. The RuO₂ns-Pt/C composite catalyst exhibited 15% higher initial activity and 26% higher activity after consecutive potential cycling tests. Based on TEM analysis, the enhanced ORR activity after the durability test is attributed to the suppression of particle growth and possible Pt loss with the addition of RuO₂ nanosheets.

Acknowledgments

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Figure caption

Figure 1 Cyclic voltammograms of Pt/C and RuO₂ns-Pt/C catalysts (a) before and (b) after ADT in 0.5 M H₂SO₄ (25°C) at $\nu = 50 \text{ mV s}^{-1}$.

Figure 2 Typical TEM images and the corresponding particle size distribution histograms of (a) initial Pt/C, (b) initial RuO₂ns-Pt/C, (c) Pt/C after ADT, and (d) RuO₂ns-Pt/C after ADT.

Figure 3 Linear sweep voltammograms of (a) Pt/C and (b) RuO₂ns-Pt/C before (red solid line) and after (black dotted line) ADT in 0.5 M H₂SO₄ (25°C) at $\nu = 10 \text{ mV s}^{-1}$.

Figure 4 Koutecky-Levich plots of Pt/C (circles) and RuO₂ns-Pt/C (squares) catalysts before (open markers) and after (closed markers) ADT at 0.85 V vs. RHE in 0.5 M H₂SO₄ (25°C).

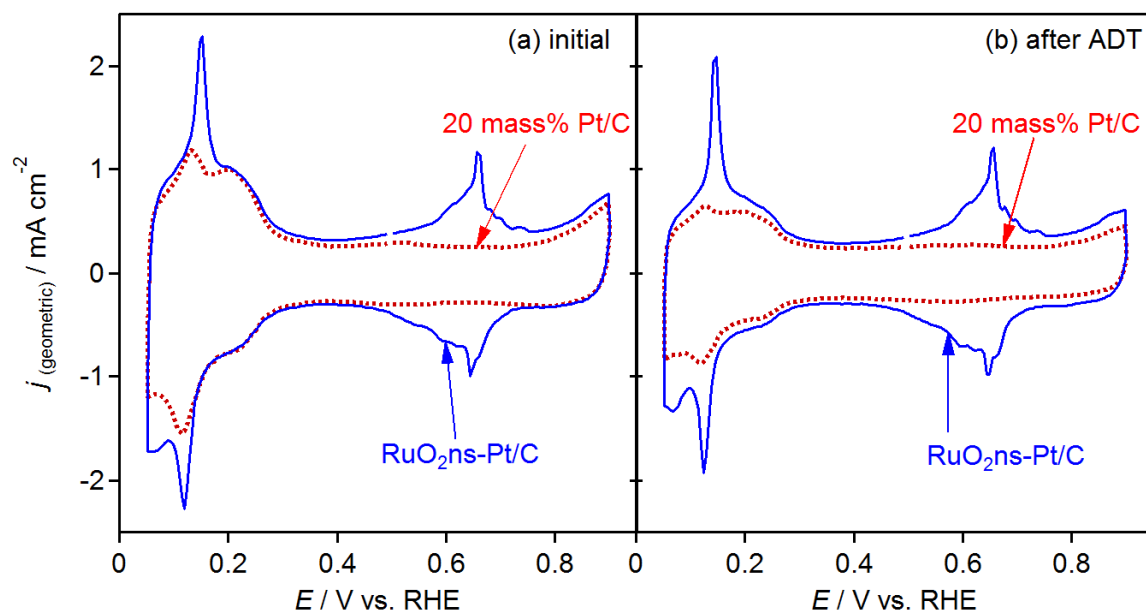


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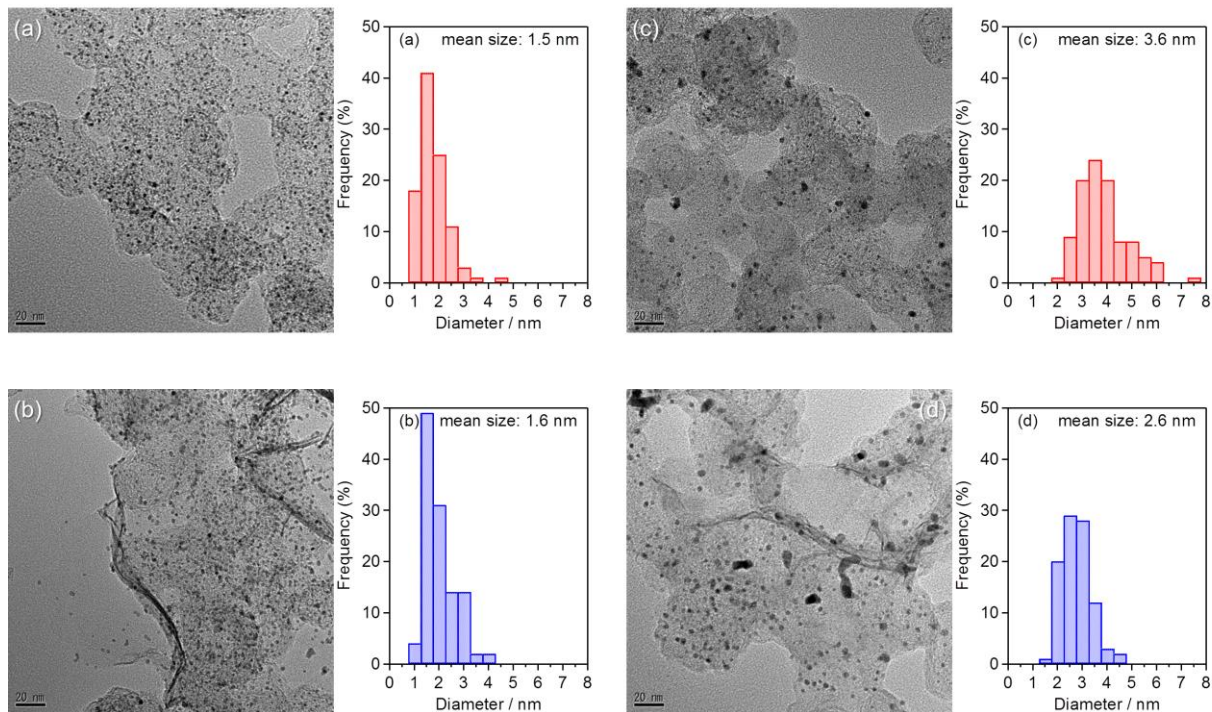


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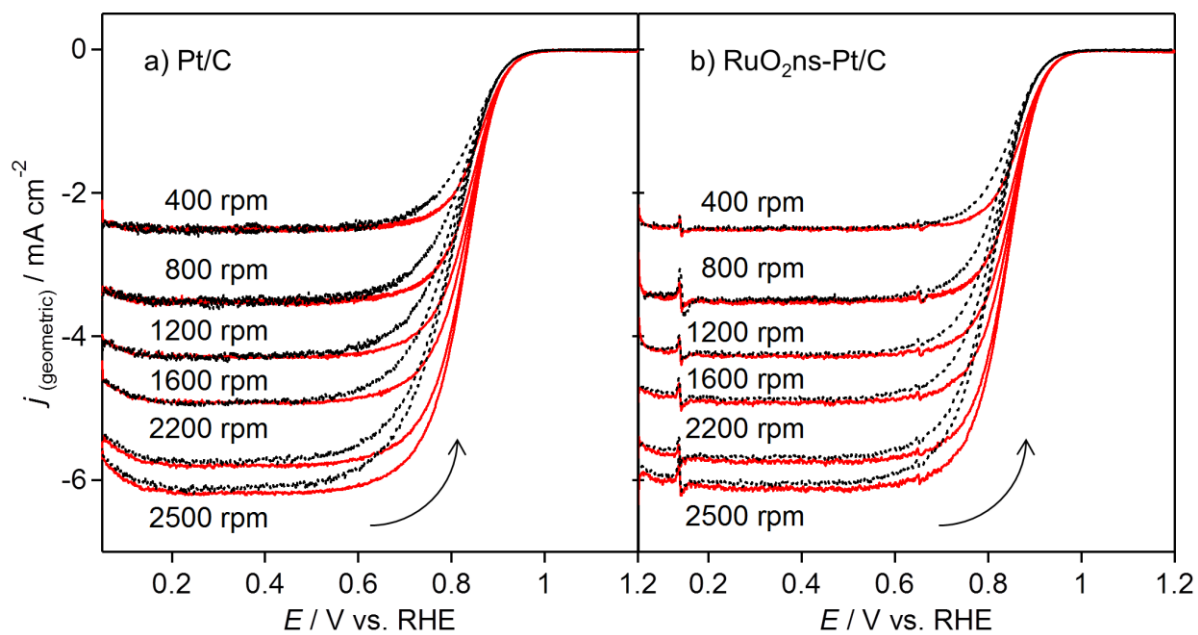


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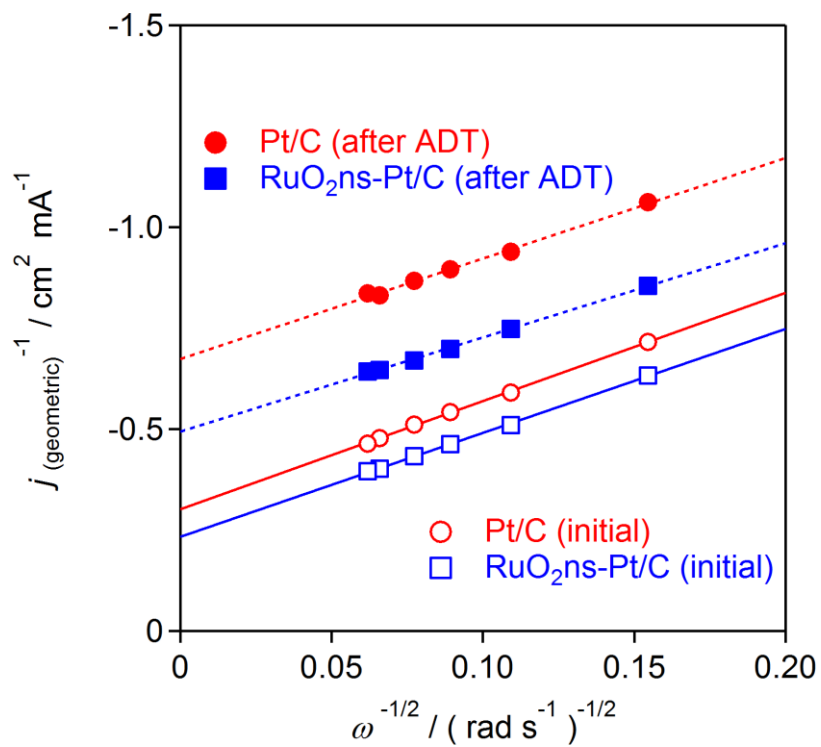


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Table 1 Electrochemically active Pt surface area estimated by hydrogen desorption charge and ORR activity from Koutecky-Levich plots at 0.85 V vs. RHE.

Catalyst	ECSA / m ² g ⁻¹		j_k / A (g-Pt) ⁻¹	
	initial	after ADT	initial	after ADT
Pt/C	78	36(54%)	192	87(55%)
RuO ₂ ns-Pt/C	78	48(38%)	221	110(50%)

degradation rate: $(j_{k(\text{initial})} - j_{k(\text{after ADT})}) / j_{k(\text{initial})}$