Lateral Size Effects of Two-dimensional IrO₂ Nanosheets towards the Oxygen Evolution Reaction Activity

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ABSTRACT

The oxygen evolution reaction of anode catalyst is an important reaction in polymer electrolyte membrane water electrolysis. Recent research has focused on understanding the factors governing the catalytic properties of nanostructured IrO₂ in order to decrease the use of expensive and precious IrO₂. We demonstrate here the equivalent diameter (D_e) effect (lateral size effect) of IrO₂ nanosheets for the oxygen evolution reaction. IrO₂ nanosheets with four different D_e from 110 to 260 nm and same thickness (~ 1.5 nm) were prepared. The electrical double layer capacitance, which should be proportional to the electrochemically active surface area, of IrO₂ nanosheets was independent of D_e . On the other hand, the pseudo-capacitance, which is related to surface redox processes, and the oxygen evolution reaction activity increased with decreasing D_e . The enhanced oxygen evolution reaction activity is discussed based on the electrochemically active surface area and edge effect.

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Keywords : Oxygen Evolution Reaction, Iridium Oxide, Nanosheet, Lateral Size Effect

1. Introduction

Polymer electrolyte membrane water electrolyzer is an attractive system for hydrogen and oxygen production.^{1–3} One of the major problems is the large overpotential for the oxygen evolution reaction (OER) of anode catalysts. Platinum group metal oxides such as IrO₂ and RuO₂ are typically used as the electrocatalyst for OER in acidic media.^{4–6} RuO₂ shows the smallest overpotential for OER, and IrO₂ exhibits the second smallest overpotential.⁷ However, RuO₂ is less stable than IrO₂, which is due to the formation of soluble RuO₄ above 1.45 V vs. RHE.^{8,9} Thus, IrO₂ is preferred over RuO₂ for practical anode catalysts.

Recent studies have focused on the enhancement of the OER activity by using IrO₂ nanomaterials to obtain high activity. The OER mass activity of IrO₂ nanomaterials is affected by many factors including surface area,^{10–12} edge sites,¹³ and exposed crystal plane.¹⁴ For example, the OER mass activity of IrO₂ nanoparticles increased with increasing surface area.¹² It was also reported that the edge sites act as active sites for OER.¹³ Higher OER activity for IrO₂(100) compared with IrO₂(111) has been reported and attributed to the higher density of the active site compared to IrO₂(110).¹⁴ Based on these studies, the morphological control of nanostructured IrO₂ should help to identify the active sites for OER and improve catalytic performance.

We recently reported the synthesis of IrO₂ nanosheets with thickness of less than 1.5 ± 0.3 nm via exfoliation of layered IrO₂.¹⁵ The OER activity of IrO₂ nanosheets was 6 times higher than that of IrO₂ nanoparticles with 3 nm diameter. Here we report the OER activity of IrO₂ nanosheets with different lateral size in order to elucidate the edge site effects of IrO₂ nanosheets for OER and to enhance the activity. It will be shown that the IrO₂ nanosheets with large edge/plane ratio improves the OER activity, suggesting that the edge sites are more active than the plane sites.

2. Experimental

IrO₂ nanosheets were derived via exfoliation of layered iridium oxide following a process reported previously.¹⁵ IrO₂ nanoparticles with 3 nm diameter were prepared as a control sample by the Adam's fusion method.¹⁶ A 1:1 mixture (molar ratio) of K₂CO₃ and IrO₂ was pelletized and calcined first at 750°C (rate of temperature increase: 5°C/min) for 1 h under Ar flow (flow rate: 150 mL/min). The pellet was ground into a fine powder under inert atmosphere, pelletized again, and calcined at 780°C for 1 h under Ar flow (flow rate: 150 mL/min). The heat treatment at 780°C was repeated three times. The final product was washed with Milli-Q deionized water (> 18 MΩ cm, Millipore) to remove water-soluble impurities. The product was then treated with 1.0 M HCl for three days at 60°C to obtain the protonated layered IrO₂. The acid solution was replaced every day. The acid-treated sample was shaken in an aqueous solution of tetrabutylammonium hydroxide (10 vol% TBAOH, Wako Pure Chemical Industries) for 1 week to trigger exfoliation. The suspension was centrifuged at 2,000 rpm for 30 minutes to remove non-exfoliated material. The IrO₂ nanosheet suspension was ultrasonicated (Sonic & Materials, Inc., VCX-750, power of 750 W, 20 kHz) for 5 to 30 min to decrease the average equivalent diameter (D_e). A tapping mode atomic force microscope (AFM, Bruker, Digital Instruments Nanoscope IIIa) was used to characterize the thickness (t) and morphology of IrO₂ nanosheets deposited on Si wafers. A cleaned Si wafer was immersed in the colloidal suspension of IrO₂ nanosheets for 2 min, which was followed by rinsing with copious amounts of water and drying. AFM images were acquired in tapping mode using a Si tip cantilever with a force constant of 40 N m⁻¹ and resonance frequency of 320 kHz (Bruker, NCHV-A). The area (A) and perimeter (P) of individual IrO₂ nanosheet in the AFM images were measured, and D_e was calculated by the following equation.

Scheme 1. (Color online) Schematic representation of nanosheet dimensions and downsizing effect.

Figure 1. (Color online) Typical TEM and AFM images of (a, a') IrO₂ns(260 nm), (b, b') IrO₂ns(210 nm), (c, c') IrO₂ns(170 nm) and (d, d') IrO₂ns(110 nm).

$$D_e = \frac{4 \times A}{P} \quad (1)$$

The edge/plane ratio is defined as the surface area at edge and plane according to

$$\frac{\text{edge}}{\text{plane}} = \frac{t \times P}{2A} \quad (2)$$

The dimensions of the nanosheet are schematically shown in Scheme 1.

Electrochemical measurements were conducted with a rotating disk electrode (Nikko Keisoku, SC-5) connected to a potentiostat (Hokuto Denko, HZ-110). The working electrode was prepared by dropping 20 μL of IrO₂ nanosheet colloid (100 mg mL⁻¹) on a mirror-polished glassy carbon (GC) electrode (6 mm in diameter). A Nafion[®] alcohol/water solution (Nafion mass fraction 5%, Sigma-Aldrich) was diluted with methanol (>99.5%, Wako Pure Chemical Industries) to 1/150 of the original concentration, and 10 μL of the diluted solution was coated on the IrO₂ nanosheet/GC electrode as a binder. Before the electrochemical characterization of IrO₂ nanosheet, the potential was cycled between 0.05 and 1.2 V vs. RHE to clean the catalyst surface. The overall specific capacitance (C_{all}) was calculated by averaging the anodic and cathodic charges measured by cyclic voltammetry at 50 mV s⁻¹ between 0.4 and 1.4 V vs. RHE.

The electric double layer capacitance (C_{dl}) was estimated from the scan rate independent region. The redox-related capacitance (C_{redox}) was calculated by subtracting C_{dl} from C_{all} ($C_{\text{redox}} = C_{\text{all}} - C_{\text{dl}}$). The formal potential ($E_{\text{p}/2}$) is defined as $(E_{\text{p,a}} + E_{\text{p,c}})/2$, where $E_{\text{p,a}}$ is the anodic peak potential and $E_{\text{p,c}}$ is the cathodic peak potential. The onset potential of the OER was estimated from the anodic branch of cyclic voltammograms measured between 1.0 and 1.7 V vs. RHE at a scan rate of 10 mV s⁻¹. The OER activity was measured by chronoamperometry at 1.55 V vs. RHE at a rotation rate of 1600 rpm. A carbon fiber was used as the counter electrode and a reversible hydrogen electrode (RHE) was used as the reference electrode. All electrochemical measurements were conducted in 0.5 M H₂SO₄ (25°C).

3. Results and Discussion

Figure 1 shows typical TEM and AFM images of IrO₂ nanosheets with different ultrasonification time. All samples retained the two-dimensional morphology of the as-prepared nanosheets after ultrasonification. The thickness of IrO₂ nanosheets were between 1.3 $\pm$ 0.5 nm to 1.7 $\pm$ 0.3 nm for all samples, determined from 200–250 individual nanosheets for each sample (Table 1). The D_e of IrO₂ nanosheets were 258 $\pm$ 79, 206 $\pm$ 46, 165 $\pm$ 21,

Table 1. Average thickness (t), equivalent diameter (D_e) and edge/plane ratio of IrO₂ nanosheet samples.

Samples	Thickness, t /nm	Equivalent diameter, D_e /nm	Edge/plane ratio*
IrO ₂ ns(260 nm)	1.6 ± 0.3	258 ± 79	0.025
IrO ₂ ns(210 nm)	1.3 ± 0.5	206 ± 46	0.029 (1.2)
IrO ₂ ns(170 nm)	1.7 ± 0.3	165 ± 21	0.041 (1.7)
IrO ₂ ns(110 nm)	1.5 ± 0.4	111 ± 15	0.054 (2.2)

*Relative increase in the edge/plane ratio is shown in parentheses.

111 ± 15 nm for ultrasonification of 0, 5, 15, 30 min, respectively (Fig. 2a and Table 1). Hence, four different IrO₂ nanosheet samples with different D_e but with the same thickness were successfully prepared. The samples will be denoted as IrO₂ns(260 nm), IrO₂ns(210 nm), IrO₂ns(170 nm) and IrO₂ns(110 nm). The edge/plane ratio of IrO₂ nanosheets increases with decreasing D_e (Fig. 2b and Table 1). The edge/plane ratio of IrO₂ns(110 nm) was 0.054, which is 2.2 times higher than that for IrO₂ns(260 nm).

Three redox pairs (A1/C1, A2/C2, and A3/C3) at $E_{p/2} = 0.82$, 0.95, and 1.2 V vs. RHE are observed in the cyclic voltammograms (Fig. 3a). The A1/C1 pair is attributed to the adsorption/desorption of anionic species onto the IrO₂.¹⁵ The A2/C2 and A3/C3 pairs are

Figure 2. (Color online) (a) Nanosheet equivalent diameter (D_e) distribution histogram for IrO₂ nanosheets prepared with different ultrasonification time between 0 and 30 min. (b) Edge/plane ratio for IrO₂ nanosheet as a function of D_e . **Figure 3.** (Color online) (a) Cyclic voltammograms in 0.5 M H₂SO₄ (25°C) at a scan rate of 50 mV s⁻¹ for IrO₂ nanoparticles (dashed line) and IrO₂ nanosheets with different D_e (solid lines). (b) The overall specific capacitance (C_{all} , left axis, circles) and the electrical double layer capacitance (C_{dl} , right axis, squares) for IrO₂ nanosheets as a function of D_e . (c) The C_{redox} of A1/C1 (circles), A2/C2 (squares), and A3/C3 (triangles) for IrO₂ nanosheets as a function of D_e . (d) Relative increase in C_{redox} at A1/C1 (circles), A2/C2 (squares) and A3/C3 (triangles) for IrO₂ nanosheets as a function of D_e .

Table 2. Electrochemical properties of IrO₂ nanosheets and IrO₂ nanoparticles.

Samples	C_{all} /F (g-IrO ₂) ⁻¹	C_{dl} /F (g-IrO ₂) ⁻¹	C_{redox} /F (g-IrO ₂) ⁻¹	OER activity /A (g-IrO ₂) ⁻¹	Onset potential /V vs. RHE	Tafel slope /mV dec ⁻¹
IrO ₂ ns(260 nm)	318	134	184	175	1.52	62
IrO ₂ ns(210 nm)	344 (1.1)	138 (1.0)	206 (1.1)	193 (1.1)	1.51	61
IrO ₂ ns(170 nm)	371 (1.2)	136 (1.0)	235 (1.3)	235 (1.3)	1.50	59
IrO ₂ ns(110 nm)	398 (1.3)	138 (1.0)	260 (1.4)	437 (2.5)	1.50	57
Nanoparticles	167	131	36	52	1.53	61

*Relative increase in C_{all} , C_{dl} , C_{redox} and OER mass activity are shown in parentheses.

Figure 4. (Color online) (a) Linear sweep voltammograms in 0.5 M H₂SO₄ (25°C) at a scan rate of 10 mV s⁻¹ for IrO₂ nanoparticles (dash line) and IrO₂ nanosheets (solid lines). (b) Chronoamperograms in 0.5 M H₂SO₄ (25°C) at 1.55 V vs. RHE at a rotation rate of 1600 rpm for IrO₂ nanoparticles (dash line) and IrO₂ nanosheets (solid lines). (c) Plots of OER mass activity at 1.55 V vs. RHE obtained from chronoamperometry for IrO₂ nanosheets as a function of D_e . (d) Tafel plots of IrO₂ nanoparticles (open markers) and IrO₂ nanosheets (solid lines).

attributed to the Ir(III)/Ir(IV) and Ir(IV)/Ir(V) surface redox process, respectively.^{17–19} The C_{dl} values obtained from the scan rate independent region (shown in the shaded region in Fig. 3a) of all IrO₂ nanosheet samples were similar (Fig. 3b (right axis) and Table 2). The C_{all} of IrO₂ nanosheets increased with decreasing D_e (Fig. 3b (left axis) and Table 2), and IrO₂ns(110 nm) showed 1.3 times higher C_{all} than IrO₂ns(260 nm). The higher C_{all} of smaller-sized nanosheets is attributed to the larger C_{redox} . The IrO₂ns(110 nm) exhibited the highest C_{redox} of 260 F (g-IrO₂)⁻¹, 1.4 times higher than IrO₂ns(260 nm) and 7.2 times larger than that of IrO₂ nanoparticles. The C_{redox} of each A1/C1, A2/C2 and A3/C3 pair are shown in Fig. 3c. The trend in the increase in C_{redox} with decreasing D_e for A2/C2 and A3/C3 were slightly higher than that of the C_{redox} at A1/C1. The C_{all} and C_{redox} of all IrO₂ nanosheet samples were higher than nanoparticles, and the C_{dl} of all IrO₂ nanosheet samples were similar to nanoparticles (Table 2).

Figure 4a shows typical cyclic voltammograms in the high potential region (1.0–1.5 V vs. RHE). The onset potential, defined as the electrode potential at $j_{\text{(geometric)}} = 1 \text{ mA cm}^{-2}$ on the anodic scan, is independent of D_e (Table 2) and similar to or slightly lower than IrO₂ nanoparticles (1.53 V vs. RHE). The OER mass activity was estimated from the quasi-steady state current obtained from chronoamperometry at 1.55 V vs. RHE (Fig. 4b). The OER mass activity of IrO₂ nanosheets increased with decreasing D_e (Fig. 4c and Table 2). IrO₂ns(110 nm) exhibited 2.5 times higher activity than IrO₂ns(260 nm) and 8.4 times higher OER mass activity than nanoparticles. The activity of IrO₂ns(110 nm) was 8.4 times higher than that of IrO₂ nanoparticles (52 A (g-IrO₂)⁻¹). The IR -corrected Tafel plots obtained from the quasi-steady state current at each potential are given in Fig. 4d. The Tafel slope for all of the IrO₂ nanosheet samples was in the range of 57–62 mV dec⁻¹, similar to nanoparticles (61 mV dec⁻¹) (Table 2). This suggests that the OER mechanism of nanosheets is comparable to that of nanoparticles.

Figure 5. (Color online) Normalized edge/plane ratio (left, circles) and normalized OER mass activity (right, squares) for IrO₂ nanosheets as a function of D_e .

It is generally accepted that the C_{dl} of an electrode material is proportional to the electrochemically active surface area. As expected, the C_{dl} was not affected by the D_e of IrO₂ nanosheet (Fig. 3b). In contrast, the OER mass activity of IrO₂ nanosheets increased with decreasing D_e . This implies an increase in the OER specific activity (OER activity at 1.55 V vs. RHE normalized by the electrochemically active surface area).

The increase in OER specific activity is discussed based on the increase in the edge/plane ratio. The edge sites of nanosheets such as graphene and sulfides have been reported to act as the active sites for electrocatalysis.^{20–23} As shown in Fig. 5, the trend in the improvement factor for the edge/plane ratio corresponded well to that for the OER mass activity. In addition, from the cyclic voltammograms (Figs. 3c and d), the improvement factor of C_{redox} for the A3/C3 pair also corresponds well with the decreasing D_e . The active site for water oxidation of IrO₂ has been suggested to be the Ir(V) site on the metal oxide surface.^{24,25} Operando XAS experiments has also suggested that Ir(V) on the near-surface layer of the IrO₂ nanoparticle triggers the OER.²⁶ From these results, we believe that the Ir(V) on the edge sites of IrO₂ nanosheet are the active sites for OER.

4. Conclusion

The OER mass activity of IrO₂ nanosheet can be enhanced by controlling the lateral size of the IrO₂ nanosheets. The higher C_{all} of smaller-sized nanosheets was attributed to the higher C_{redox} on the metal oxide surface, since C_{dl} does not change by decreasing D_e . The OER mass activity enhanced with decreasing D_e , and the

smaller-sized nanosheets exhibited 2.5 times higher activity than larger-sized nanosheets. The enhanced OER mass activity with decreasing D_e is attributed to the edge effects of nanosheets.

Acknowledgment

This research was supported in part by the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for JSPS Fellows, Grant Number 16J09715.

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