



Electrochemistry of Oxygen at Ir Single Crystalline Electrodes in Acid



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ARTICLE INFO

Article history:

Received 11 March 2017

Received in revised form 7 May 2017

Accepted 16 May 2017

Available online 3 June 2017

Keywords:

Iridium single crystalline electrodes
oxygen reduction reaction
hanging meniscus rotating disk electrode
configuration
reaction kinetics
volcano plot

ABSTRACT

The oxygen reduction reaction (ORR) at iridium single crystalline electrodes, Ir(111) and Ir(332), in 0.1 M HClO₄ and 0.5 M H₂SO₄ solution, was studied using cyclic voltammetry and potential step chronoamperometry under a hanging-meniscus rotating disk electrode configuration. The results are compared to the ORR behaviors observed on platinum single crystal electrodes with the same surface orientation. We found that i) The kinetics for ORR on Ir(111) are significantly slower than those on Pt(111), the onset potential and half-wave potential for ORR are ca. 100 mV and 370 mV more negative than those on Pt(111), respectively; ii) in 0.1 M HClO₄ only H₂O₂ is formed on Ir(111) at E > 0.55 V, and when E < 0.4 V the major product is H₂O, in 0.5 M H₂SO₄ a significant amount of H₂O₂ is produced even the potential is as low as 0.15 V; iii) Ir(332) exhibits lower ORR activity than Ir(111), with a half-wave potential that is ca. 30 mV more negative, and the diffusion-limited ORR current is not reached from 0.8 V down to 0.05 V, indicating that at Ir(332), incomplete reduction of O₂ to H₂O₂ occurs in a wide potential region; iv) significant decay of ORR current with potential scan rate and reaction time in the current transient measurements are observed on both Ir(111) and Ir(332), similar to those observed on Pt(111) and Pt(332) electrodes. The structure-activity relationship of Ir(hkl) toward ORR is discussed.

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1. Introduction

Fuel cells (FCs) are promising power sources for stationary and mobile applications, due to their high energy efficiency and low pollutant emission. The electrochemical oxygen reduction reaction (ORR) is the primary cathode reaction for the FCs. Even though platinum is the most effective monometallic electrocatalyst for ORR [1–3], the reaction sets in with a sizable overpotential (ca. 0.25 V). In addition, its reserves are limited, it is expensive, and the durability of Pt nanocatalysts are still not good enough. All of this makes ORR a limiting reaction for the performance of FCs [1]. Iridium (Ir), being a neighbor of platinum (Pt) in the periodic table of elements, is very similar to Pt when their physical and chemical properties are considered [4–8]. Furthermore, Ir is one of the more stable metals among Pt-group metals, and it resists corrosion in acidic solution [9]. IrO₂ has also been used as the anode for the oxygen evolution reaction (OER) in many industrial electrochemical processes [10]. The high stability, as well as its similarity to Pt, suggests that studies of the ORR on Ir electrodes will not only help

in the understanding of the structure-activity relationship in electrocatalysis, but they may also help in the rational design of practical cathode catalysts for FCs.

However, in contrast to the extensive studies on Pt and Pt based electrocatalysts for ORR [1–3], only a few studies on ORR at Ir based electrodes have been reported [11–14]. Gnanamuthu et al. found that the kinetics of ORR on polycrystalline Ir (pc-Ir) electrode is slow. An overpotential of 0.47 V is needed in order to flow 10 μA/cm² of ORR current [11]. Sepa et al. systematically examined the pH and temperature effects on ORR at pc-Ir [13]. They found that oxygen reduction at pc-Ir electrodes in both acid and alkaline solutions is characterized by two linear Tafel regions with Tafel slopes of –120 mV/decade and –60 mV/decade for the high and low current density regions, respectively. The reaction order is equal to 1 with respect to molecular oxygen in both current density regions. Furthermore, for the high current density region, there is an uncommon pH dependence, which leads to a fractional reaction order of 1/2 with respect to H₃O⁺ [12]. The only report of ORR on single crystalline Ir available so far is from Adzic's group [15]. They systematically compared ORR activity on M(111) (M = Ag, Au, Pd, Pt, Rh, Ir) and Ru(0001) in 0.1 M NaOH, and found that that ORR activity decreases in the order of Pt(111) > Pd(111) > Au(111) > Ag

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(111) > Rh(111) > Ir(111) > Ru(0001) [15]. The half-wave potentials for ORR at Ir(111), Ru(0001) and Rh(111) are ca. 600 mV, 550 mV and 250 mV more negative, respectively, than those on Pt(111). However, no similar comparison for ORR on M(111) in acid solution is reported. Two recent studies of ORR on supported Ir nanoparticles also confirmed that, in acid solution, there is a large onset overpotential for ORR on Ir surfaces (ca. 0.4 V) [16,17].

Calculations based on density functional theory (DFT) have been quite successful in guiding the rational design of electrocatalyst for fuels cells, and in particular for the ORR. The most cited work is that of Nørskov et al. [18,19], who argued that the binding energy of oxygen to the surface of the catalyst is a good descriptor of the catalytic activity in acid solutions, and derived a corresponding volcano plot. The slow kinetics of ORR on Ir can be roughly rationalized by larger binding energy of O to Ir comparing to that on Pt based on DFT calculations [20,21]. However, there are still some discrepancies between the theoretical predictions with experiments, e.g., the volcano curve predicts, that the ORR activity on Ir should be as bad as (or even worse than) that on Ag, which lies on the other branch of the volcano, but experimental results reveals that ORR activity on Ir is several orders of magnitude faster than that on Ag [22]. Another discrepancy is that the DFT calculation reveals that the binding of O/OH to Rh(111) is ca. 0.3–0.5 eV stronger than that on Ir(111) [21], however, in alkaline solution, ORR activity on Rh(111) is much higher than that on Ir(111) [15]. No corresponding experimental data on ORR at iridium single crystalline electrode in acid is available so far, so it is not possible to verify the validity of the conclusions derived based on the DFT calculation. Furthermore, theoretical calculations also predict that stepped platinum single crystalline electrode surfaces should have lower ORR activity than Pt(111), due to their stronger binding energies to ORR intermediates [23–25]. However, recent experiments on well-defined single crystalline electrodes show that ORR activity increases with increasing step density [26,27].

In order to provide solid experimental evidences for the structure-activity relationship for ORR and to understand the origins for the discrepancies between the experimental observations and the predictions by DFT calculations, our group has carried out systematic studies of ORR on well-defined, single crystalline electrodes M(hkl) (M = Pt and Ir) with different surface orientations. In this work, we report the electrochemical behavior of ORR at Ir(111) and Ir(332) electrodes in 0.1 M HClO₄ and 0.5 M H₂SO₄ studied by both cyclic voltammetry and potential step chronoamperometry under a hanging-meniscus, rotating-disk electrode configuration. The results are compared with those obtained at Pt(111) and Pt(332), and the kinetic implications for ORR and the structure-activity relationship will be discussed.

2. Experimental

The working electrodes used in the present study were Ir(111) and Ir(332) single crystalline surfaces. The Ir(332) electrode was composed of (111) terraces and (111) steps (denoted as Ir[n(111) × (111)] with n = 6). The single crystalline electrodes were homemade using Clavilier's method by melting and subsequent slow crystallization of Iridium wire (99.99%, 0.8 mm in diameter, Tanaka Noble Metal Corp.). The single crystal bead was oriented, cut, and polished [5–7,28–30]. Prior to each experiment, the Ir single crystal was annealed at 1800–2000 °C for 10 s in N₂ + H₂ atmosphere using induction heating equipment (Easyheat 244, Ambrell Companies), then cooled in a reducing atmosphere (N₂ + H₂), and finally quenched in ultra-pure water in equilibrium with the same atmosphere. The electrode surface was covered by a deoxygenated water droplet to prevent contact with impurities

during transfer to the electrochemical cell. It was immersed in the solution under potential control, typically at 0.2 V (vs. reversible hydrogen electrode, RHE). A meniscus configuration was maintained between the electrode surface and the electrolyte during all measurements [31].

A conventional three-electrode glass cell was used for all experiments. A Pt wire and a RHE were used as the counter electrode (CE) and the reference electrode (RE), respectively. All potentials in the paper are quoted against the RHE. 0.5 M H₂SO₄ or 0.1 M HClO₄ were used as the supporting electrolyte, which was prepared using concentrated H₂SO₄ (96%, Suprapure, Merck KGaA) or perchloric acid (70%, Suprapure, Sigma Aldrich) and ultra-pure water (18.2 MΩ cm, from Milli Q water system). The base CVs were recorded in N₂-saturated 0.5 M H₂SO₄ and 0.1 M HClO₄ to make sure that the CVs show the well-documented features for electrodes in the respective electrolytes. The polarization curves for the ORR were recorded by cyclic voltammetry in O₂-saturated 0.1 M HClO₄ or 0.5 M H₂SO₄ under a hanging-meniscus rotating-disk electrode (HMRDE) configuration at various electrode rotation speeds and potential scan rates [32]. The current transients were recorded by stepping the electrode potential from a potential in the H-UPD region to the half-wave potential for ORR in the respective solutions at 1600 rpm. All gases used in this study i.e., O₂, N₂ and H₂ were 99.999% pure and came from Nanjing Special Gas Corp.

The electrode rotation speed (ω) was controlled by a modulated rotator (Hokuto Denko Ltd. HR-202). During all the electrochemical measurements, the atmosphere in the cell above the electrolyte was purged continuously with the same gas that was used to purge the electrolyte. All experiments were carried out at room temperature (ca. 25 ± 2 °C). When recording current-potential (i-E) curves for ORR, IR compensation was carried out automatically by the CHI instrument based on the positive feed-back principle. The uncompensated Ohmic resistance was measured using the current interruption method. The current densities displayed in the figures are normalized to the geometric surface areas of the respective electrodes.

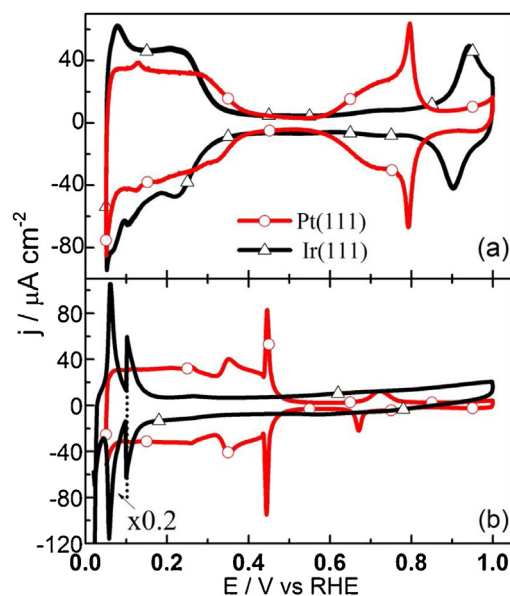


Fig. 1. Cyclic voltammograms of Ir(111) (triangle) and Pt(111) (circle) in 0.1 M HClO₄ (a) and 0.5 M H₂SO₄ (b), scan rate: 50 mV/s. For clarity, the part from 0.02 to 0.1 V of the CV on Ir(111) in 0.5 M H₂SO₄ in (b) is reduced to 1/5 of its original values.

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