Oxygen evolution activity and stability of iridium in acidic media. Part 1. – Metallic iridium

Serhiy Cherevko [a,b], Simon Geiger [a], Olga Kasian [a,c], Andrea Mingers [a], Karl J.J. Mayrhofer [a,b,d]

[a] Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany
[b] Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), Egerlandstraße 3, 91058 Erlangen, Germany
[c] Ukrainian State University of Chemical Technology, Gagarin ave. 8, 49005 Dnipropetrovsk, Ukraine
[d] Department of Chemical and Biological Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

ARTICLE INFO

ABSTRACT

A better understanding of iridium dissolution is important in the elucidation of the general mechanism of noble metals corrosion and in the design of more durable iridium based applied materials. In the current work iridium dissolution has been addressed by a complementary electrochemical and mass spectrometric technique based on a scanning flow cell (SFC) and inductively coupled plasma mass spectrometry (ICP-MS). Time- and potential-resolved iridium dissolution profiles are recorded and analyzed. It is found that during the anodic treatment dissolution is increasing constantly with potential. Anodic dissolution decreases with time, which is attributed to the buildup of a passivating oxide layer. In case a significantly low reductive potential is applied to the oxidized electrode, an additional dissolution process is observed. It is concluded that like other members of the noble metals group, e.g. gold and platinum, thoroughly studied before, dissolution of iridium is initiated by a change in the iridium oxidation state during the initial formation or reduction of a *thin compact anhydrous oxide layer*. Both transitions metal/oxide and oxide/metal during oxidation and reduction, respectively, result in dissolution. Thus, dissolution is a transient process. The Ir(III)/Ir(IV) transition in the *thick hydrous oxide layer*, responsible for iridium oxide electrochromism, do not lead, however, to any significant change in dissolution signal. At even higher anodic potentials, further destabilization is caused by a change in the oxidation number (increase and decrease) of iridium cations during oxygen evolution reaction (OER). At studied potentials OER on the metallic electrodes, covered by a *thin compact anhydrous oxide layer*, has Tafel slope of ca. 66 mV dec^{-1}, which is comparable to literature data on bulk IrO_2 electrodes and, probably, implies on similarities in the OER mechanism on these materials.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Like other members of the platinum metals group, iridium is considered to be very noble. Indeed, this metal is even sometimes called to be "the most resistant of all metals to corrosion" [1,2], e.g. it does not dissolve in the *aqua regia* even at elevated temperatures [3,4]. According to the Pourbaix diagram, iridium is stable towards dissolution at pH = 0 in aqueous solutions, which do not contain complexing agents, up to potential of E° = 0.926 V [3]. Thermodynamically, the most stable phase of iridium up to E° = 0.926 V, at which oxidation to Ir_2O_3 and/or IrO_2 oxides (the former is not stable in presence of oxygen [5]) should take place, is metallic iridium [3]. Despite these facts, even the relatively early reports on electrochemistry of iridium noted its oxidation at significantly lower potentials [6]. It has been shown that in an acidic electrolyte adsorption of oxygen (or hydroxyl) on iridium electrode starts at potentials as low as 0.4–0.5 V [7–12]. Depending on the timescale of experiment, already

at 0.6–0.65 V a monolayer coverage of O/OH has been reported [7]. Although, at typically employed scanrates in the potentiodynamic tests a monolayer coverage is completed at higher potentials of 1.1–1.2 V [8]. According to literature, formation of a "surface bulk phase" oxide through the so-called "place-exchange" process in the potentiodynamic treatment initiates at iridium at ca. 1 V against reversible hydrogen electrode (RHE) [8,13,14]. In all these aspects, iridium behaves similarly to platinum or gold, typically considered as model systems in electrochemical studies.

In comparison to these model systems, however, literature on the initial stages of iridium oxidation is scarce and contradictory. It is known, that electrochemistry of iridium in alkaline and acidic electrolytes is quite different, which means that transfer of knowledge collected in studies on different electrolytes is difficult. Based on the untypical shift of the main iridium oxidation peak with pH, the so-called "super-Nernstian" behavior of iridium was proposed by Burke et al. [15,16]. This was, however, questioned by Juodkazyte et al. [9]. Instead, explaining the pH dependence of the peaks, these authors concluded formation of different main compounds (having different redox potentials) in acidic and alkaline electrolytes. Another suggestion made by these authors is

contrary to the usually proposed underpotentially deposited OH⁻ ions, "bulk" Ir hydroxides form on iridium [9,10]. Standard potentials of "bulk" $Ir(OH)_3$ and $Ir(OH)_4$ formation were found to be ca. 0.8 and 0.9 V [10]. To assist in the resolving of the complex electrochemistry of iridium, ellipsometry, electron diffraction, electron microscopy, X-ray or ultraviolet photoemission spectroscopy (XPS and UPS), and probe beam deflection (photothermal deflection spectroscopy) have been traditionally employed [11,12,17–22]. More advanced *ambient* or in-situ X-ray spectroscopy and X-ray diffraction methods are typically used nowadays [23,24]. In most of these studies, however, behavior of the iridium oxide but not iridium metal, as a starting material, in the potential region of OER was addressed [25–31]. Oxidation and reduction of metallic iridium was only studied in a few works, e.g. by electrochemical quartz crystal microgravimetry (EQCM) [9] or UPS [11]. The outcome of these studies is that electrochemistry of Ir/Ir (hydro)-oxide(s) system is complex. It is, probably, much more complicated than that reflected in the Pourbaix diagram.

The question arises, if metallic iridium is indeed stable to corrosion as it is traditionally believed. While dissolution of iridium at potentials exceeding 1.65–1.8 V_{RHE} [32,33] and dependence on the structure of oxide is well studied [34–36], little to nothing is known about corrosion of this metal at lower potentials. Dissolution of iridium has been mentioned (but not confirmed) in some studies on the oxidation or reduction of iridium [9,10,37–40]. Besides these studies, as discussed above, it is typically reported that this metal is very stable [41,42]. Stability is usually assumed based on the thermodynamic properties of iridium up to ca. 1 V and/or on the some preliminary data on the stability of the electrochemical current or potential profiles over, usually, limited time intervals. This general belief is probably one of the reasons why literature on the stability of iridium dissolution is so deficient. The other reason is a consequence of iridium low abundance and high price, making its use in practical applications undesirable. Nevertheless, potential utilization of iridium in electrocatalysis or photo-(electro)catalysis of OER is a heavily discussed topic nowadays [42–44]. As in these applications iridium exists in the form of oxide, its stability is out of the discussion of this part of the work (see Part II). In some other cases, however, metallic iridium is used. The use of small amounts of metallic iridium (usually in form of finely divided particles, other nanostructures, or in form of alloys) can be justified in view of its high activity, tolerance to methanol, reported stability, or other properties [45–53].

According to radio-chemical methods extensively used by Kolotyrkin and Chemodanov et al., iridium dissolution in acidic electrolytes containing no oxidizing agents initiates at ca. 0.6 V_{RHE} and accelerates with potential [12]. In line with their previous works on dissolution of platinum, gold, rhodium, and palladium [54,55], Rand and Woods reported that also iridium dissolves when the potential is cycled between 0.06 and 1.54 V_{RHE} [56]. Even though the authors suggested an existence of anodic or cathodic mode of dissolution, it was impossible to identify the dissolution process more precisely using the available technique. No time or potential resolved results were presented. The authors even wrote that "ring-disc studies would be required to identify positively the processes involved" [56]. Surprisingly, it took 40 years until such work has been partially completed. In a very recent paper, Danilovic et al. presented rotating ring-disk electrode (RRDE) results on iridium dissolution [27]. Unfortunately, only data on dissolution from electrochemically and thermally formed oxides in the region of OER was shown. Thus, no information related to the main topic of the current work, on the stability of metal itself was provided. In our previous work in which we summarized the results on the stability of a group of noble metals in the region of oxide formation/reduction and during the OER, we already presented that iridium behaves very similarly to platinum in the sense that predominant dissolution takes place in the cathodic branch of CV [55]. It was also reported that metallic iridium in the potential region of OER is less stable than chemically prepared iridium oxides [57,58].

In the current work we aim to extend the previously reported scarce studies showing dissolution of metallic iridium during initial stages of the surface oxidation and reduction of the formed oxide. Electrochemical growth of bulk hydrous oxide and iridium dissolution during the growth as well as during application of the oxide towards OER are presented in Part II.

2. Experimental details

All experiments were conducted using a scanning flow cell (SFC) inductively coupled plasma mass spectrometer (ICP-MS) based setup [59]. The SFC with V-shaped inlet-outlet channels was made in-house out of a polycarbonate block using a CNC-milling machine (CAM 4-02 Impression Gold, vhf camfacture AG, Germany). The small opening at the intersection of the channels, which defines the area of the working electrode, was ca. 0.01 cm^2. All data are normalized to this exposed geometric area of the working electrode. A commercial saturated Ag/AgCl electrode (Metrohm, Germany) and a graphitic rod were used as reference and counter electrodes, respectively. All potentials in this work are presented with respect to the reversible hydrogen electrode (RHE) potential, which was acquired against the Ag/AgCl electrode using a Pt disk working electrode (5 mm diameter disk sealed in Teflon®, MaTeck, Germany) after hydrogen saturation. During investigation of iridium dissolution, the electrolyte was pumped to/from the cell by a standard ICP-MS (NexION 300×, Perkin Elmer) pump with a constant flow rate of ca. 200 μL min⁻¹ through Tygon® tubes (380 μm inner diameter) from a reservoir of argon-saturated electrolyte to the V-shaped channels of the polycarbonate cell and further downstream to the ICP-MS. The 0.1 M H_2SO_4 electrolyte was always freshly made by dilution of Suprapur® concentrated sulfuric acid (Merck, Germany) in ultrapure water (PureLab Plus system, Elga, 18 MΩ, TOC < 3 ppb). The on-line detection of concentration of dissolved iridium from the working electrode was performed by an ICP-MS, which was calibrated on each experiment day. 10 mg L⁻¹ ¹⁸⁷Re was used as an internal standard (mixing ratio 1: 1). The lag time between SFC and ICP-MS was ca. 15 s and was always taken into account during construction of the potential/dissolution vs. time graphs presented in the paper. The potentiostat (Gamry Reference 600, USA), electrolyte, gas flow, and SFC positioning were automatically controlled using an in-house built LabVIEW software [60]. The working electrode was an iridium disk of 5 mm in diameter (MaTeck, Germany) embedded in a Teflon® cylinder for ease of handling. Before each experiment, the electrode was successively polished with 1 and 0.3 μm alumina suspensions on a polishing cloth (Struers, MD Mol) followed by a short sonication in water, extensive washing in the ultrapure water and drying in a flow of argon. Shortly afterwards the electrode was placed on an *xyz*-positioning table and a tungsten needle was connected to the conducting working electrode holder to make an electrical contact. No additional electrochemical pretreatment was done. More details on the cell design, the setup, and on the ICP-MS measurements can be found in the experimental parts of the previous reports [61–63].

3. Results

3.1. Oxidation and reduction of iridium studied by cyclic voltammetry

In our previous reports on the dissolution of gold and platinum we have shown that dissolution of these metals correlates well with oxidative and reductive processes taking place at the electrodes when potential is changed, e.g. in a simple cyclic voltammogram (CV) [61,62, 64–68]. Therefore we start the study on iridium dissolution with investigation of iridium oxidation and reduction processes using the same technique. Typical CVs of a freshly polished polycrystalline iridium electrode acquired at a scan rate of $\upsilon = 50$ mV s⁻¹ recorded right after 100 cycles at $\upsilon = 500$ mV s⁻¹ up to upper potential limits (UPL) $1.1 \leq E_{UPL} \leq 1.6$ V_{RHE} with the constant lower potential limit (LPL) of $E_{LPL} = 0.04$ V_{RHE} are presented in Fig. 1 (results on the dissolution of iridium during the fast potential cycling to different UPLs are presented