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Published in:
Chemical Science

Link to article, DOI:
10.1039/c4sc02685c

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

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Oxygen evolution on well-characterized mass-selected Ru and RuO$_2$ nanoparticles†

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Oxygen evolution was investigated on model, mass-selected RuO$_2$ nanoparticles in acid, prepared by magnetron sputtering. Our investigations include electrochemical measurements, electron microscopy, scanning tunneling microscopy and X-ray photoelectron spectroscopy. We show that the stability and activity of nanoparticulate RuO$_2$ is highly sensitive to its surface pretreatment. At 0.25 V overpotential, the catalysts show a mass activity of up to 0.6 A mg$^{-1}$ and a turnover frequency of 0.65 s$^{-1}$, one order of magnitude higher than the current state-of-the-art.

Introduction

Renewable sources of energy, such as wind or solar, are inherently intermittent. As they contribute an increasing amount to overall energy usage, more effective and sustainable methods are required to store the energy harvested. For instance, renewable energy could be used to split water electrochemically or photoelectrochemically to form hydrogen, as an energy carrier.1–5 Nonetheless, the efficiency of water splitting devices is largely defined by the sluggish kinetics of the oxygen evolution reaction (OER). As such, a judicious choice of the electrocatalyst material is imperative. The catalyst needs to be active, stable, and minimize the use of any scarce elements, so that it is scalable. Indeed, no water splitting device will make an impact to the global energy landscape, unless it can be scaled to the Terawatt (TW) level.6,7 This is a set of stringent requirements for the catalyst material. Indeed, there is a general call for more scalable.6,11,20 One solution to this problem could be to replace the precious metals with more abundant elements. However, the harsh acidic and oxidizing conditions at the anode render most catalysts inactive or unstable, except for oxides of Ir or Ru,8 the latter also being subject to severe supply limitations.8

Consequently, a prerequisite for TW-scale PEM electrolyser technology is the development of a catalyst that has an appreciably higher mass activity (in A g$^{-1}$ precious metal) than the current state-of-the-art. It turns out that RuO$_2$ is more active than IrO$_2$,11,20–22 but it is somewhat unstable towards dissolution towards RuO$_4$.23–26 According to the theoretical “volcano” model developed by Rossmeisl, Nørskov and coworkers, RuO$_2$ is the most active pure metal oxide catalyst for OER, because it exhibits the closest to optimal binding to the reaction intermediates.11 Further improvements can be achieved by combining ruthenium with nickel and cobalt;27–31 however, these bimetallic materials are highly unstable under acidic conditions.

Most studies of the OER on RuO$_2$, simply report the catalytic activity, but neglect corrosion; when the corrosion rate has been monitored, it has been significant, at around 10–40% of the total anodic current.13,24,26,32–35 Nonetheless, it turns out that RuO$_2$ can be stabilized, both by mixing with other oxides such as Ir or Ti,23,36–39 or by providing it with appropriate oxidation...
Oxides grown anodically under ambient conditions from metallic precursors tend to be highly active, but also unstable. Moreover, according to a recent report by Strasser and coworkers, nanoparticles of 4–6 nm in diameter, with anodically-grown surface oxides, will show much lower stability than extended surfaces with the same pre-treatment. On the other hand, should extended surfaces of RuO₂ be formed under thermal oxidation conditions, by pre-treating in O₂ at temperatures above 350 °C, they will show much higher stability than the anodic oxides, but somewhat lower activity. Thus far, no studies have provided a comprehensive examination of the activity and stability of nanoparticulate RuO₂ under well-defined conditions. As highlighted by Mayrhofer and coworkers in a recent review, systematic studies on the effect of particle size for the oxygen evolution reaction are missing, unlike the oxygen reduction reaction. Although size effects are reported on chemically synthesized RuO₂ particles greater than 15 nm in diameter, it is of greater technological relevance to examine smaller particles, where the surface area is maximised. Moreover, size effects are typically likely to be more pronounced for particles smaller than 10 nm in diameter.

Herein, we focus on the evaluation of oxygen evolution activity and corrosion of well-defined, mass-selected Ru nanoparticles, as a function of size. In particular, we aim to establish the extent to which the mass activity of nanoparticulate RuO₂ can be maximized and at the same time monitor the catalyst stability. We adapt a methodology previously used in our laboratory to investigate the oxygen reduction reaction. The mass selected electrocatalysts are prepared in a magnetron sputter source, using an ultra-high-vacuum (UHV) compatible technique. This allows a high degree of control over critical parameters such as particle size, electrode coverage and density, and it avoids the inherent artefacts introduced by chemical synthesis from precursors and surfactants.

Results and discussions

The catalysts were formed by vacuum deposition of mass-selected nanoparticles from a ruthenium target, deposited directly onto glassy carbon or Au electrodes. The mass ranged from 0.035 × 10⁶ u to 2.9 × 10⁶ u, which would correspond to a range in size of 2–9 nm, assuming perfectly spherical particles. We tested both (a) as-deposited particles (Ru NPs) which were not subjected to any further treatment before exposure to the electrochemical environment and (b) thermally oxidized particles (RuO₂ NPs), which, prior to electrochemical measurements, were treated in a tube furnace at 400 °C under 1 bar oxygen for 1 minute. The loading was determined directly from the deposition current. The structure and composition were tested using X-ray Photoelectron Spectroscopy (XPS), Glancing Angle X-Ray Diffraction (GA-XRD), High Angle Annular Dark Field – Scanning Transmission Electron Microscopy (HAADF-STEM) and Scanning Electron Microscopy (SEM). The electrocatalysts were tested in a Rotating Ring Disk Electrode set-up. Furthermore, Electrochemical Scanning Tunneling Microscopy (EC-STM) was used to directly observe the catalyst dissolution under reaction conditions. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was used to analyze the electrolyte post-OER.

The catalyst composition and crystallographic structure were probed using XPS and GA-XRD. The as-deposited particles (Fig. 1a) exhibit two pairs of doublets for the Ru 3d core level, with a separation of ~1 eV; this indicates the presence of both metallic and oxidized Ru in the near-surface region. On the other hand, the thermally oxidized particles (Fig. 1b) could only be fitted to a single doublet, confirming that a RuO₂ layer of at least 1.5 nm has formed.

GA-XRD measurements confirm the full oxidation of the particles (Fig. 2). The most intense peak from the reference pattern for metallic ruthenium can be identified in the as-deposited ruthenium catalyst. However, the peaks of the thermally oxidized ruthenium correspond closely to the RuO₂ rutile phase. The remaining peaks correspond to the Au(111) substrate.

The projected particle area distribution for four different thermally oxidized samples, together with the corresponding HAADF-STEM images, are shown in Fig. 3a–d. Smaller particles show a more regular, spherical shape, whereas the larger particles are rough and form tetrahedrons. These observations correspond well with earlier studies from our laboratory on metallic Ru.

The OER activity of glassy carbon supported thermally oxidized RuO₂ nanoparticles was measured voltammetrically in N₂-saturated 0.05 M H₂SO₄. The OER mass activity of the thermally oxidized RuO₂ particles is plotted in Fig. 4a as a function of particle mass. There is some scatter in the data, which we attribute to uncertainties in the total mass deposited. This is despite significant endeavours to minimize the error in the measurement, by carefully choosing deposition parameters and monitoring the coverage of particles using XPS, as described in the ESI†. Incidentally, we obtained a similar catalytic activity on a polycrystalline gold electrode, indicating no influence from the substrate. We can tentatively identify a maximum in activity for the particles with a diameter of ~5 nm. This could suggest the terrace is the active site for oxygen evolution, analogous to similar reports for the oxygen reduction reaction. Smaller particles will have a decreased number of terraces sites, and hence will exhibit a lower specific activity.

It is challenging to assess the specific activity of the catalyst as a function of particle size, as we do not have an accurate measure of the surface area for all particle sizes, in particular the larger nanoparticles, which have a non-spherical morphology. Nevertheless, since the smaller particles do in fact exhibit a spherical morphology, we can estimate the surface area and hence the specific activity. It turns out that the specific activity of the 0.1 × 10⁶ u RuO₂ nanoparticles at 1.48 V (vs. RHE) is 0.32 mA cm⁻² which is over an order of magnitude more active than both films and nanoparticles reported in the literature. For further details see the ESI†. Moreover, based on the specific activity and mass activity, we can also estimate the turnover frequency (TOF), a fundamental parameter which represents the number of oxygen molecules produced per second. We can estimate the lower bound, i.e.
TOF_{\text{min}}, by assuming that each Ru atom is active for the OER. On the other hand, we can estimate the upper bound, TOF_{\text{max}}, by assuming only the surface atoms are active (in reality, we view this TOF_{\text{max}} as a conservative estimate; the surface will be covered with a range of different catalytic sites, whereas the activity will be dominated by the most active). In Fig. 4b we show the estimated TOF of the 0.1 \times 10^6 \ u RuO_2 nanoparticles from this work, in comparison with the most active catalysts in the literature (we have only included catalysts with a well-defined mass or surface area). For further details on how the TOF was estimated, see the ESI.†

Although it is a prerequisite for efficient catalysts to have high activity, it is also essential that the catalyst stability is tested, particularly due to the corrosive conditions under which OER catalysts operate. The cyclic voltammogram of the largest nanoparticles, 2.9 \times 10^6 \ u, is plotted in Fig. 5a. The as-deposited Ru particles possess a higher activity than the thermally oxidized RuO_2 particles, in agreement with earlier reports on extended surfaces. Even so, the as-deposited nanoparticles corrode immediately to form RuO_4. According to ring current measurements, the anodic dissolution on our Ru nanoparticles constituted 15% of the total current, a similar degree of stability to commercial Ru/C catalysts or polycrystalline Ru. On the other hand, the thermally oxidized RuO_2 nanoparticles showed a negligible ring current, suggesting that the activity should be solely due to the OER. This notion was confirmed by both ICP-MS and the direct measurement of oxygen using gas chromatography, as described in the ESI.†

Most strikingly, the particles tested here show a mass activity of at least one order of magnitude higher than the state-of-the-art for precious metal based OER catalysts in acid, as shown in Fig. 6. The thermally oxidized 0.5 and 0.1 \times 10^6 \ u RuO_2 particles exhibit a 43-fold increase, relative to RuO_2.
nanoparticles prepared by a chemical route, a 30-fold improvement compared to the PtIrO$_x$ in an electrolyser at 80 °C, and a 9-fold enhancement relative to IrNi$_{3.3}$ core–shell nanoparticles. Assuming that the activity enhancement persists to higher overpotentials, we demonstrate that the precious metal oxide loading in a PEM electrolyser and in other technologies using oxygen evolution could be decreased by an order of magnitude. Our data provides an impetus for synthetic chemists to produce such active catalysts, using a more scalable method.

![Fig. 3 Nanoparticle area distributions and HAADF-Scanning Transmission Electron Microscopy images of thermally annealed RuO$_2$/Si$_3$N$_4$ samples for particle mass of (a) $0.1 \times 10^6$, (b) $0.5 \times 10^6$, (c) $1.4 \times 10^6$ and (d) $2.9 \times 10^6$ u.](image)

![Fig. 4 (a) OER mass activities at 1.48 V (vs. RHE) of different thermal oxidized RuO$_2$ particle masses ($0.035 \times 10^6$ u, $0.1 \times 10^6$ u, $0.5 \times 10^6$ u, $1.4 \times 10^6$ u and $2.9 \times 10^6$ u) on a Glassy Carbon (GC) disk, from the first ohmic and capacitance corrected CV. The Ru mass was evaluated from the deposition current. The error bars are based on four independent measurements. The activity for $2.9 \times 10^6$ u nanoparticles on a Au polycrystalline disk is also shown. The particle size is shown as both the (particle mass)$^{1/3}$ and the equivalent diameter that the particles would be, should they be perfectly spherical. (b) Turnover frequency comparison of different catalysts in acid. When possible, both minimum and maximum TOF were estimated. Data adapted from this work for thermally oxidized $0.1 \times 10^6$ u NPs; adapted from ref. 57 for RuO$_2$ and IrO$_2$ NPs; from ref. 22 for RuO$_2$ (100); and from ref. 59 for Ir NPs and IrNi$_{3.3}$ NPs.](image)
investigation of the OER on RuO$_2$ and the effect of particle size. The particles reported here exhibit a one order of magnitude improvement in activity relative to the state-of-the-art and a tentative maximum at around 3–5 nm. An appropriate oxidation treatment can provide moderate stability to RuO$_2$, and only slightly compromise on its high activity. Moreover, the well-defined shape and small size of the nanoparticles reported herein allow us to make an accurate estimate of the turnover frequency; it turns out it is appreciably higher than previous reports from the literature for oxygen evolution on any catalyst in acid. Should further improvements be made to the stability of RuO$_2$ nanoparticles (for instance through the addition of Ir or Ti$^{23,36–39}$), PEM electrolysis, as well as other technologies which are limited by oxygen evolution, could eventually become scalable to the TW level.

**Author contributions**

E.A.P. performed the measurements of the electrocatalytic activity and stability, the GA-XRD experiments, and wrote the first draft and designed the figures; R.F. co-performed the electrochemical measurements and GA-XRD; F.M. prepared the nanoparticles, performed XPS and SEM; D.D performed STEM; C.S. performed EC-STM; M.M performed the gas chromatography experiments; T.W.H. supervised the STEM; S.H. supervised the EC-STM experiments; I.E.L.S supervised the electrochemical measurements and co-wrote the first draft; I.C. supervised the vacuum experiments and conceived the idea. All authors discussed and analysed the data and commented on the manuscript.

**Acknowledgements**

The authors gratefully acknowledge financial support from the Danish Ministry of Science’s UNIK initiative, Catalysis for Sustainable Energy and the Danish Council for Strategic Research’s project MEDLYS (10-09306). The Center for Individual Nanoparticle Functionality is supported by the Danish National Research Foundation (DNRF54).

**References**


**Conclusion**

In summary, we have investigated the activity and stability of as-deposited and thermally oxidized Ru nanoparticles. By using mass selected nanoparticles, our work provides a model...

