

# Highly stable silica-doped ceramic supports for Iridium-based OER catalysts for PEM electrolysis (O-9H)

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## 1. Introduction

The development of technologies that can efficiently use energy from renewable sources is a top-priority challenge that society faces today [1,2]. In this context, green hydrogen, produced by water electrolysis using surplus renewable electricity, arises as a sustainable and clean energy vector. Among the different types of electrolyzers, the Proton Exchange Membrane (PEM) technology stands out due to its compact design, high power density and dynamic operation [3]. However, among the main technological barriers to its widespread commercialisation are the prohibitively high costs of precious group metal (PGM) catalysts (Iridium - Ir at the anode and Platinum - Pt at the cathode) and their lack of stability for long-term utilisation [4]. The latter is especially problematic on the anode side since the oxygen evolution reaction (OER) is known to generate a very corrosive environment [5]. Therefore, it is critical to drastically reduce the overall system cost (1900-2300 €·kW<sup>-1</sup>) [6,7] by lowering the state-of-the-art loading of PGMs (ca. 2-4 mg·cm<sup>-2</sup>) [8]. It is important to redesign the catalyst structure towards decreasing Ir loadings while not limiting the electrochemical performance. This can be achieved by maximising Ir utilisation via its dispersion onto high surface-area supports rather than using conventional unsupported, typically unstable electrocatalysts. Simultaneously, the support must display corrosion resistance and good electrical conductivity. This strategy will allow to obtain a smaller average Ir particle size that may exhibit a higher OER mass-activity.

Ceramic oxides, such as zirconium (IV) dioxide (ZrO<sub>2</sub>) and cerium (IV) oxide (CeO<sub>2</sub>), are well known for their long-term stability in harsh environments, which is a key factor to develop durable OER supported catalysts [9]. Still, ZrO<sub>2</sub> and CeO<sub>2</sub> are semiconductor materials and present low electrical conductivity and surface area, which deeply affect the anode performance. Thus, surface engineering is crucial to enhance the catalytic activity without harming the support durability [10]. In this regard, a promising approach is to incorporate silicon dioxide (SiO<sub>2</sub>) in the metal oxide supports. Silica contains a porous structure and silanol groups (Si-OH), which are responsible for its hydrophilic properties. As so, water molecules can easily reach Ir particles for OER to occur, leading to a decrease in both

mass transport resistances and an increase in OER activity. Moreover, silica will act as a binder between Ir particles and the support, which might help prevent the main signs of early catalytic degradation, such as Ir migration and/or agglomeration and diffusion of dissolved Ir particles throughout the support [11,12].

In this work, silica-doped ceramic oxides were used as supports for Ir-based catalysts with ca. 30 wt.% of electrochemical active metal. The electrocatalysts referred to as Ir/SiO<sub>2</sub>-ZrO<sub>2</sub> and Ir/SiO<sub>2</sub>-CeO<sub>2</sub>, were prepared using a modified polyol synthesis method. The synthesised catalysts were then extensively characterised electrochemically to measure their catalytic activity and stability. Physicochemical characterisations were also carried out, namely TEM, TGA, XPS and B.E.T (not shown) to complement and corroborate the electrochemical measurements. To the best of the authors' knowledge, this study reports the utilisation of such materials for conducting OER in the mentioned conditions for the first time. The results obtained with the as-prepared catalysts were compared with the commercially available IrO<sub>2</sub> from Premetek and with Ir/CeO<sub>2</sub> and Ir/ZrO<sub>2</sub> prepared without SiO<sub>2</sub> via the same synthesis procedure.

## 2. Experimental

### 2.1 Synthesis procedure

The catalysts were prepared via the polyol method in alkaline media and the synthesis setup consisted of a three-neck round bottom flask placed in a heating plate and connected to a reflux condenser and a thermometer. The synthesis procedure is as follows: NaOH pellets (Sigma Aldrich) were dissolved in ethylene glycol (VWR) to form the reducing medium; after complete dissolution, silica (SiO<sub>2</sub> – Sigma Aldrich) and ceramic oxides (CeO<sub>2</sub> or ZrO<sub>2</sub> - Sigma Aldrich) were added to the solution under moderate stirring; then, iridium salt precursor – IrCl<sub>3</sub>·xH<sub>2</sub>O (Sigma Aldrich) was added to the mixture. The obtained slurry was heated under reflux and kept at ca. 180 °C for 3 h. After the synthesis, 1 M HNO<sub>3</sub> solution was added drop-wise to adjust the pH. A filtration step was used to recover the catalyst nanoparticles, which were then washed with ultrapure water (18.2 MΩ cm, Millipore) and dried at 80 °C for 5 h.

### 2.2 Electrochemical characterisation: activity and stability

Electrochemical measurements were carried out in a rotating disk electrode setup and the catalytic suspension was

prepared as follows: 5 mg of catalyst were dispersed in a 1:4 mixture of isopropanol (Merck) and ultrapure water with Nafion ionomer suspension (5 wt.%, QuinTech). Then, the working electrode (WE) tip (gold - Au, 0.196 cm<sup>2</sup>) was coated with 20  $\mu$ L of the suspension, dried under rotation until producing a catalytic layer with *ca.* 0.015 mg<sub>Ir</sub>-cm<sup>-2</sup>.

The electrochemical characterisation, including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS), was performed in a setup composed of an electrochemical station (Zahner IM6-ex), a rotator (RDE710, Gamry Instruments) and a three-electrode jacketed cell (Gamry Instruments). A saturated Ag/AgCl and a graphite rod were used as reference and counter electrodes, respectively.

Prior to any electrochemical measurement, the electrolyte (0.1 M HClO<sub>4</sub>) was purged and kept under Ar flow. The activity test protocol starts with an activation phase (100 CVs between 0 V and 1.4 V vs RHE at 100 mV·s<sup>-1</sup>), and after that, a complete characterization is performed, including: 1) three CVs recorded in the same potential range at 20 mV·s<sup>-1</sup>; 2) three LSVs recorded from 1.1 V to 1.7 V vs RHE at 10 mV·s<sup>-1</sup> while rotating the WE at 1600 rpm; 3) finally, EIS at 1 kHz and with 5 mV of amplitude was retrieved and served to estimate the ohmic resistance assigned to the electrolyte.

The electrochemical active area was obtained through the Cu<sub>upd</sub> technique. The WE was kept at 0.05 V vs RHE in N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> to reduce all the Ir species. Then, a first background was retrieved by cycling the potential between 0.2 V and 0.72 V vs RHE at 20 mV·s<sup>-1</sup>. The procedure was repeated by changing the electrolyte to 0.5 M H<sub>2</sub>SO<sub>4</sub> with 5 mM CuSO<sub>4</sub> to obtain the CV where Cu species adsorb in the catalyst active sites.

To evaluate the OER stability of the electrocatalysts, an accelerated stress test (AST) was performed. It consisted of 10 000 potential cycles between 0.8 V and 1 V vs RHE at 100 mV·s<sup>-1</sup>, while rotating the WE at 200 rpm [13].

### 3. Results and Discussion

#### 3.1 Electrochemical characterisation of the synthesised catalysts

Fig. 1 shows the CV curves obtained for the synthesised catalysts. Both supported catalysts exhibit typical Ir redox peaks between 0.8 and 1.2 V vs RHE, which correspond to the transition from Ir(III) to Ir(IV) and from Ir(IV) to Ir(V) [14]. Moreover, forward and backward scans are separated by a considerable gap in current density and both show pronounced, well-shaped and symmetric pair of redox peaks. This indicates that the supported catalysts are stable when subjected to subsequent reduction and oxidation events and that SiO<sub>2</sub> particles did not affect the catalytic surface area available for conducting OER. Concerning the commercial IrO<sub>2</sub> catalyst, Ir redox peaks are less pronounced than the supported samples, which in turn display higher charge density, suggesting the existence of more electrochemically active sites.

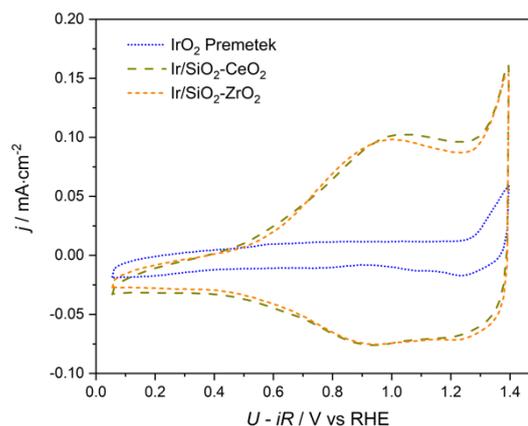


Fig. 1. CVs of the prepared catalysts (electrolyte: Ar-purged 0.1 M HClO<sub>4</sub>; scan rate: 20 mV·s<sup>-1</sup>).

According to the LSV measurements (Fig. 2.), supported catalysts with SiO<sub>2</sub> display an earlier onset at *ca.* 1.46 V vs RHE, whereas supported catalysts without SiO<sub>2</sub> show an onset at *ca.* 1.50 V vs RHE and a significant mass transport resistance, since the latter require a considerable overpotential to reach higher current densities. Regarding the commercial IrO<sub>2</sub> sample, OER on-set potential is *ca.* 1.60 V vs RHE. This means that OER kinetics are clearly favoured in the prepared catalysts (especially those with SiO<sub>2</sub>), since a much lower overpotential is required to overcome the reaction activation energy barrier. These results suggest that the presence of silica particles not only decreases the ohmic resistance but also facilitates the kinetic mechanisms for OER to occur.

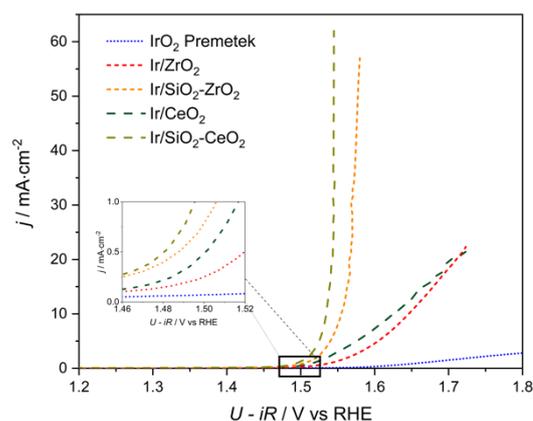


Fig. 2. Polarisation curves for the prepared catalysts (electrolyte: Ar-purged 0.1 M HClO<sub>4</sub>; RDE rotation: 1600 rpm; scan rate: 10 mV·s<sup>-1</sup>).

In Figure 3, the OER mass activity and the electrochemical active area values are presented. The OER mass activity (mA·mg<sub>Ir</sub><sup>-1</sup>) was retrieved from the current density recorded at 1.51 V vs RHE normalised by the mass of Ir in the Au tip, whereas the active area was calculated by the charge variation between the background CV and the Cu<sub>upd</sub> CV. The dispersion of Ir particles in support materials such as ZrO<sub>2</sub> and CeO<sub>2</sub> allows obtaining higher Ir utilization, reducing the Ir particle size, which also improves the OER activity. Moreover, the addition of SiO<sub>2</sub> leads to a further increase in both parameters.

The latter indicates that a structure of extended surface area and number of active sites is formed with the addition of SiO<sub>2</sub> to the ceramic oxides. Ir/SiO<sub>2</sub>-CeO<sub>2</sub> displays the highest OER activity (193.97 mA·mg<sub>Ir</sub><sup>-1</sup>) and active area (4.18 × 10<sup>11</sup> m<sup>2</sup>), which represents an improvement of ca. 97 % and 63 %, respectively, compared to the values obtained for the benchmark IrO<sub>2</sub> catalyst.

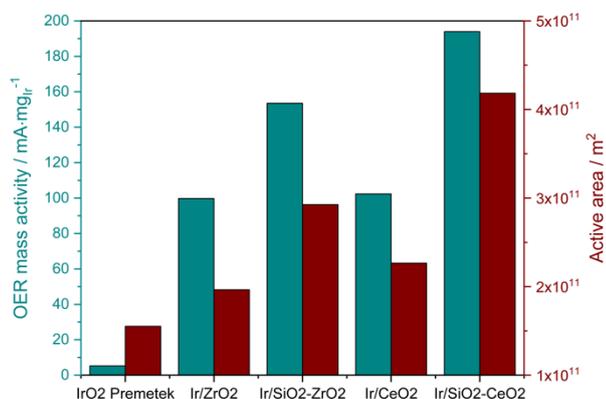


Fig. 3. OER mass activity and electrochemical active area values obtained for the prepared catalysts.

### 3.2 Stability assessment

After performing the degradation test, CV, LSV and EIS were again recorded to quantify the overall loss of performance. This is typically assessed by comparing the OER mass activity values from the beginning of life (BoL) with those at the end of life (EoL - after 10000 cycles) (Table 1).

Table 1. OER mass activity values at BoL and EoL.

AST	IrO <sub>2</sub> Premetek	Ir/ ZrO <sub>2</sub>	Ir/ SiO <sub>2</sub> -ZrO <sub>2</sub>	Ir/ CeO <sub>2</sub>	Ir/ SiO <sub>2</sub> -CeO <sub>2</sub>
OER mass activity at BoL (mA·mg <sub>Ir</sub> <sup>-1</sup> )	5.27	99.72	153.51	102.33	193.97
OER mass activity at EoL (mA·mg <sub>Ir</sub> <sup>-1</sup> )	2.87 (- 46 %)	72.75 (- 27 %)	154.61 (+ 0.7 %)	82.18 (- 19 %)	200.24 (+ 3.1 %)

Once again, commercial IrO<sub>2</sub> catalyst presents the worst performance, losing ca. 46 % of OER mass activity upon 10000 cycles. On the other hand, supported catalysts without SiO<sub>2</sub> show a decrease in OER mass activity of ca. 20 %, which can be assigned to Ir dissolution or particle agglomeration. Interestingly, supported catalysts with SiO<sub>2</sub> maintain a remarkable performance after the AST, demonstrating no loss in OER activity. This suggests that silica particles act as a shield of the catalyst structure, preventing Ir migration from the support and thus improving its stability.

## 4. Conclusions

Catalysts consisting of ca. 30 % of Ir dispersed in silica-doped ceramic oxides were effectively prepared through a polyol synthesis. The as-prepared catalysts not only displayed higher OER activities (153.51 mA·mg<sub>Ir</sub><sup>-1</sup> for Ir/SiO<sub>2</sub>-ZrO<sub>2</sub> and 193.97 mA·mg<sub>Ir</sub><sup>-1</sup> for Ir/SiO<sub>2</sub>-CeO<sub>2</sub>, respectively) but

also an improved durability after intensive potential cycling, compared with the benchmark IrO<sub>2</sub> catalyst.

To the best of the authors knowledge, this is the first work concerning the enhancement of Ir-based catalysts with incorporation of SiO<sub>2</sub> particles in the catalyst composition for OER. According to the obtained results, the addition of silica allows the improvement of OER mass activity due to its hydrophilic and porous nature and an increase in catalytic stability when subjected to an accelerated stress test. Its presence in the composite support prevents Ir degradation mechanisms, such as Ir particle growth and Ir detachment from the support. The prepared catalysts emerge as very promising solutions for use as anodes of PEM electrolyzers, given their excellent performance during long-term utilisation.

To validate the new catalyst's performance under real conditions, those will be used to produce membrane electrode assemblies (MEAs) and then, tested in a single-cell configuration to perform PEM water electrolysis. Additionally, to further optimise the PGM loading, some studies should be carried out in order to boost electrical conductivity with even decreased Ir contents.

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