Ir/TiON\(_x\)/C high-performance oxygen evolution reaction nanocomposite electrocatalysts in acidic media: synthesis, characterization and electrochemical benchmarking protocol

Anja Loncar\(^{1}\), Leonard Moriau\(^{1}\), Kevin Stojanovski\(^{1}\), Francisco Ruiz-Zepeda\(^{2}\), Primoz Jovanovic\(^{1}\), Marjan Bele\(^{1}\), Miran Gaberscek\(^{1}\) and Nejc Hodnik\(^{1,3}\)

\(^{1}\) Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, SI-1000 Ljubljana, Slovenia
\(^{2}\) Department of Materials Chemistry, National Institute of Chemistry, SI-1000 Ljubljana, Slovenia
\(^{3}\) These authors contributed equally to this work.

E-mail: nejc.hodnik@ki.si

Keywords: electrocatalysis, electrolyzer, oxygen evolution reaction, iridium, benchmark, TiON\(_x\)

Abstract

More efficient utilization of iridium is of immense importance for the future development of proton exchange membrane electrolysers. In this study, we introduce a new facile and scalable synthesis of an Ir-based high-performance oxygen evolution reaction (OER) electrocatalytic nanocomposite. The composite consists of Ir nanoparticles with an average size of 3–4 nm, which are effectively anchored on a titanium oxynitride support (TiON\(_x\)), which is distributed across high-surface-area Ketjen Black carbon (Ir/TiON\(_x\)/C). We provide complete structural, morphological and compositional characterization (x-ray diffraction, scanning transmission electron microscopy and energy-dispersive x-ray spectroscopy) and propose a proper benchmark protocol to measure true electrochemical performance. Compared to the state-of-the-art Ir Black electrocatalyst, Ir/TiON\(_x\)/C exhibits approximately three times higher OER performance.

1. Introduction

In the future, fossil-fuel energy will need to be replaced by clean and abundant sources. Indeed, the production of chemicals and fuels through electrolysis coupled with intermittent renewable energy such as solar and wind is a promising way to store chemical energy, which can later be converted back to electricity with for instance, in fuel cells [1–3]. The hydrogen and CO\(_2\) electrochemical cycles (utilizing an acidic membrane) present some of the most promising options. However, both electrolyzer technologies have a major common issue: high overpotential losses due to sluggish kinetics on the anode side, namely the oxygen evolution reaction (OER) [4, 5]. Nowadays, the most state-of-the-art catalysts are Ir or its oxide analogues as they display the best activity/stability balance [6–8]. However, this precious metal is extremely rare (produced at a rate of less than 10 T per year [9]) and expensive. Thus, decreasing the usage of iridium at the proton-exchange membrane water electrolyzer (PEMWE) anode by a factor of about 50 is a critical requirement for the technology to make an impact on a global scale [10, 11]. Indeed, alkaline electrolysers could present a simpler solution since cheaper catalysts can be used; however, they lack sufficient conductivity and stability of the anion membrane [11, 12].

Therefore, a lot of effort is invested into either finding intrinsically more active electrocatalysts with at least the same stability as Ir, or increasing the utilization of Ir. Achieving the latter is directly related to the development of sufficiently stable and conductive supports. To increase the utilization, Ir has been supported with stable and conductive oxides such as antimony tin oxide (ATO), indium tin oxide (ITO), titanium oxynitride (TiON\(_x\)), etc [13–17]. In addition to the better distribution of Ir on the support’s surface, the overall
activity can sometimes also be affected by the strong metal-support interaction (SMSI) [18, 19]. One of the strategies for OER activity enhancement is through alloying with transition metals [20–23]. However, in a real device, dealloying of the less noble metal could cause membrane stability issues with time of operation, as is already the case in the proton-exchange membrane (PEM) fuel cell [24].

Another equally important but rarely addressed problem in the OER community is how to adequately and reliably measure the catalyst’s OER performance, and also how to compare it between different laboratories and with the literature data [10, 25, 26]. As a consequence, many reports cannot be trusted or, alternatively, some prospective catalysts might have been overlooked due to poor measurement protocol. For instance, due to the lack of unified benchmark protocols in the OER community, many different activity parameters are used (the value of current at 1.55 V, 1.6 V or the value of voltage at 10 mA cm⁻², etc [27, 28]), which then results in an inability to compare the outcomes between different groups. Moreover, parameters like an activation protocol or the loading of the catalyst, which would assure reproducibility of measurements, are lacking in systematic study and standardized protocols, besides a few recent studies [12, 29–31]. Even though some important parameters have already been assessed (impact of the electrolyte [29], the backing electrode [32], the gas saturation [33] or rotation speed [34]), they are rarely taken into account when presenting results.

In light of the issues stated above, the present study systematically evaluates the impact of parameters such as loading, an activation protocol, the backing electrode and catalyst ink composition on the OER activity for a state-of-the-art industrial Ir Black (Alfa Aesar) catalyst. The findings are to present guidelines on how to achieve a reproducible intrinsic OER activity. By appropriate benchmarking OER activity via reproducible measurements and with meaningful normalization, we can now accurately compare Ir Black to our new Ir/TiONₓ/C electrocatalytic composite and justly proclaim its superior activity. It is based on a new, facile and scalable synthesis procedure. We note that a small and exceptionally narrow particle size distribution of Ir is obtained, which, along with the SMSI, is the main driving force for high OER performance.

2. Experimental

2.1. Synthesis

In the first step of the synthesis, Ti-isopropoxide (Aldrich, 97%) was physically mixed with Ketjen Black EC600 in a H₂O–propanol solvent (75/25) (Honeywell, 99.8%—Milli-Q water 18.2 MΩ cm). The weight percentages of Ti and C were 52% and 48%, respectively. The mixture was then dried at 80 °C for 1 h before high-temperature treatment to obtain an amorphous TiO₂/C composite. The obtained powder was then annealed at 730 °C for 10 h (5 °C min⁻¹) in a NH₃ atmosphere before being cooled down to 50 °C (5 °C min⁻¹) to obtain the TiONₓ composite. Once the support was ready, it was mixed with IrBr₃ × H₂O (Alfa Aesar) (40 wt%) in water. The catalyst was then dried at 120 °C in Ar/H₂ atmosphere for 1 h (7 °C min⁻¹), after which the temperature was slowly (2 °C min⁻¹) increased to 450 °C, where the annealing continued for 1 h more in the same Ar/H₂ atmosphere to form Ir nanoparticles. Finally, the catalyst was cooled down to room temperature (3 °C min⁻¹) to obtain the Ir/TiONₓ/C nanocomposite.

2.2. Electrochemistry

Catalyst ink was prepared by mixing 1 mg of catalyst in different volume ratios of Milli-Q water (18.2 MΩ cm) and isopropanol (Isop) (Merck). In the case of Ir Black, different concentrations were prepared: 1 mg in 4 ml, 1 mg in 5 ml and 1 mg in 8 ml. Two inks containing isopropanol were tested (volume ratio 7/1 and 5/3 Milli-Q/Isop). For all experiments, 10 μl drops were deposited on the working electrode resulting in the loading of 6.4 μg cm⁻², unless noted differently. Before the activity measurements, a pre-treatment protocol was performed in order to activate (oxidize) the Ir nanoparticles. Two different activation protocols were tested. The first activation consisted of fast cycling (300 mV s⁻¹) between 0.45 and 1.45 V versus reversible hydrogen electrode (RHE). The lower potential limit (LPL) was chosen so as to avoid a complete reduction of Ir-oxide, which is known to trigger Ir dissolution [35–37]. The upper potential limit (UPL) limit was ca. 20 mV lower than the onset potential. The second activation consisted of cycling between 0.05 and 1.45 V versus RHE. This second protocol is similar or closer to the potential range usually chosen in the literature [20, 29, 36, 38, 39]. The OER activity was recorded by performing a minimum of eight cycles between 1.2 and 1.6 V versus RHE, 1600 rpm, 20 mV s⁻¹, under Ar atmosphere in a 0.1 M HClO₄ (Merck, Suprapur, 70%) electrolyte. All the experiments were iR drop compensated. A Parstat 2273 (Princeton Applied Research) controlled by PowerSuite software was used to conduct the experiments. The homemade Au and glassy carbon (GC) electrodes were mounted on an OrigaTrod rotator or Pine rotator (for Pt Pine electrodes).
2.3. Structural characterization

X-ray diffraction (XRD) studies were carried out with a Siemens D5000 instrument with Cu K-alpha-1 radiation ($\lambda = 1.5406$ Å) in the $2\theta$ range from 10° to 60°. X'pert Highscore Plus software was used to analyze the spectrum. The samples were prepared on a Si holder.

Scanning transmission electron microscope (STEM) imaging and energy-dispersive x-ray spectroscopy (EDX) were performed using a Cs-corrected microscope CF-ARM Jeol 200 equipped with an SSD Jeol EDX spectrometer.

3. Results and discussion

The prepared catalysts were first characterized by XRD. Both the benchmark, Ir Black, and our homemade Ir/TiON$_x$/C show typical metallic Ir diffraction peaks at around 41° and 48° (04-016-112) as seen in figure 1(a). In the case of our catalyst, the Ir peaks are broad, indicating small particles as confirmed by the TEM images (figures 1(b) and (c)). In contrast, a careful examination of the Ir Black spectrum reveals that each of the peaks consists of two superimposed peaks, namely a broad and a sharp one, which is indicative of two different particle sizes: particles below the range of 15 nm and above ca. 100 nm, respectively (estimated with the Scherrer equation). TiON$_x$/C, by contrast, exhibits two peaks at 37° (220 planes) and 43° (311 planes) that are typical of TiON (00-049-1325) as indicated in the supporting information (figure S1 is available online at stacks.iop.org/JPENERGY/2/02LT01/mmedia). No presence of the TiO$_2$ (01-073-8760) initially deposited on the carbon was found, proving an efficient formation of TiON$_x$ in our sample (figure S1). The coverage of O and N was proven by EDX (figure S2).

The TEM micrographs of Ir Black AA confirm the presence of big agglomerates due to agglomeration of unsupported, small (2–5 nm) Ir particles in the sample, as seen in figure S3, which is in accordance with the
approximation of less than 15 nm. In contrast, the Ir/TiONx/C catalyst is composed mainly of very small Ir particles with an average size of 3–4 nm (see particle size distribution graph in figure S4). The increased dispersion and small overall sizes are a result of their physical separation due to the high-surface-area support used.

High-surface-area carbon was used in the nanocomposite as it was shown to be beneficial for two reasons. Firstly, it effectively induces a high dispersion and thus a high-surface area of TiONx. Secondly, it enables a more efficient transformation of TiO2 to TiONx in the ammonia atmosphere as it acts as a reducing agent and/or a catalyst. Without the presence of carbon, the formation of TiONx was never effective in our experiments. More specifically, some TiO2 was always left unreacted. Thus, much longer exposures and higher temperatures would be necessary, both of which negatively affect the efficiency and usefulness of the synthetic route. By using the beneficial properties of TiO2, which is known to be an inherently stable material even under the harsh OER conditions, and TiN, which exhibits a metallic electrical conductivity, stable and conductive support could be achieved [17].

Importantly, the EDX mapping in figure 1(f) shows that Ir is almost exclusively present on TiONx and not on the carbon. For better clarity, the Ir/TiONx/C nanocomposite is schematically presented in figure 2. This is crucial for the occurrence of the SMSI effect on Ir. However, the lack of a direct physical contact between the noble metal and carbon is of vital importance for the long-term performance of OER electrocatalysts as the carbon is not electrochemically stable at the OER conditions in the presence of catalyst particles, i.e., it oxidizes to CO2 [40, 41]. Therefore, a long-term performance can hardly be expected if Ir and C are in contact. We note here that the stability of the TiONx support is currently under investigation and is out of the scope of the present work.

In order to test the electrochemical performances of OER catalysts, the effects of different measurement parameters need to be understood first. Thus, we investigated the influence of the ink preparation method, the activation pre-treatment, the loading for Ir Black and the effect of the material of the backing electrode. The effect of the loading was investigated by preparing a different suspension of Ir Black in Milli-Q water. In contrast to the CO-stripping method for supported Pt catalysts, there is no generally accepted benchmark method to measure ECSA of supported Ir catalysts in the community. Recent studies propose a couple of new methods to measure ECSA for Ir-based catalysts [42–45]; however, they are not always suitable for different samples (e.g. supported or unsupported Ir). Thus, the performances are often normalized by geometric surface area or, in our opinion more appropriately, by the mass of iridium. This is industrially the most important parameter. To our knowledge, no systematic study of the impact of loading on the activity of a benchmark in RDE has been performed. Interestingly, similar studies have been done in PEMWE [12, 46, 47]. Thus, three suspensions with different concentrations were prepared and 10 μl of each were deposited on a Pt backing electrode. The mass-normalized activities for each suspension were compared at 1.55 V and 1.6 V as seen in table 1. We can see that at these loadings there is no effect on the OER performance.

### Table 1. Mass-normalized OER activities for each Ir Black loading on the Pt working electrode.

| Suspension   | Loading (μg cm⁻²) | Average (A mg⁻¹ at 1.55 V) | Average (A mg⁻¹ at 1.6 V) | RSD |
|--------------|-------------------|-----------------------------|-----------------------------|-----|
| 1 mg Ir Black AA/4 ml Milli-Q | 12.7              | 0.54                        | 1.9                         | 0.3 |
| 1 mg Ir Black AA/5 ml Milli-Q | 10.2              | 0.55                        | 1.9                         | 0.2 |
| 1 mg Ir Black AA/8 ml Milli-Q | 6.4               | 0.52                        | 2.0                         | 0.1 |
Afterwards, the activity of Ir Black was tested on three different backing electrodes: Au, Pt and GC (figure 3). Activity of 950 mA/mgIr at 1.6 V versus RHE (273 mA/mgIr at 1.55 V versus RHE) was measured on GC, which is similar to the best activity recorded for the Ir benchmark (from AA) in the literature [30, 48]. Nevertheless, about twice as much activity was measured on the Pt and Au working electrodes (1877 and 1911 mA/mgIr, respectively). This was surprising as the backing electrode material should not have had any influence on the intrinsic activity of the catalyst. One possible explanation is the quality of the film, which can depend on the nature of the backing electrode material. Indeed, by using another suspension with a mix of water and isopropanol (volume ratio 7/1), the activity of Ir Black on GC reached 1463 mA/mgIr, as seen in figure S5. This result emphasizes the importance of ink preparation, which should be optimized for each different catalyst and backing electrode. Even better activity (2554 mA/mgIr) was measured on the Au electrode, but with a different volume ratio of solvents (MQ/Isop: 5/3) as seen in figure S6. The other explanation for the lower activity recorded on GC is the difference in the charge transfer resistance, which could depend on the backing electrode material. The selection of the backing electrode material has rarely been justified in state-of-the-art research dealing with laboratory-level screening of an OER catalyst. Almost exclusively, GC backing electrodes are chosen for performance testing in spite of the fact that GC demonstrably passivates already at very short time intervals under OER operation conditions [32, 49–52]. This increase of the contact resistance as a result of GC corrosion can ultimately lead to misleading conclusions on OER trends regarding the activity as well as the stability. In this respect, more stable backing electrode materials such as gold and boron-doped diamond were recently demonstrated to be suitable for OER studies [32]. Here we note that the quality and ratio of sp2 and sp3 hybridization of carbon groups of boron-doped diamond electrodes influence its stability and conductivity. Thus, the choice of working electrode material and further studies into the effect of the backing electrode are of primordial importance.

Additionally, the effect of electrochemical pre-treatment was investigated by studying two different ‘activation’ protocols. Indeed, the history of the Ir-based catalyst can influence the activity for OER. An activation protocol is commonly used to clean the surface or to ensure a stable and reproducible state of catalyst surface is reached. There is no agreement on an OER activation protocol, but in general, two different methods can be used. Sometimes, the electrode is cycled under OER potential range until a stable CV is reached [30, 53], but most frequently fast cycling between a low potential (like 0.05 V or 0.025 V versus RHE) and a potential close to the onset of OER (between 1.3 V and 1.45 V versus RHE) is employed until stable CVs are reached [20, 29, 36, 38, 39]. In the present study, two different potential windows were compared. In the first case, the activation was performed by fast cycling between 0.45 V and 1.45 V versus RHE. In the second case, the potential window was broadened to 0.05 to 1.45 V versus RHE. Further explanation is available in the experimental section (part 2.2). The experiments were performed on an Au electrode. The ink used was 1 mg of catalyst in 5 ml of Milli-Q water + 3 ml of isopropanol. As seen in figure 4, the activity after the activation in the broader potential range is lower (in red). This could be due to the dissolution of Ir. It is known that Ir dissolves via transient dissolution when oxides are formed, however notably more when reduced [35–37]. Thus, going to a lower potential limit involves the potential degradation of the catalyst before the activity evaluation.

With this knowledge on important experimental parameters, a more adequate comparison of homemade supported Ir/TiONx/C and the benchmark Ir Black could be performed. The performance comparison was done on an Au working electrode substrate, which enables the preparation of homogeneous catalyst films compared to Pt, where the quality of the films was generally the worst. In the same way as for Ir Black, suspensions with only Milli-Q water and Isop were compared. Similarly to the case of the GC backing electrode,
better activity was measured with the solution containing Isop (see figure S8). In the same way as for Ir Black on Pt, the loading did not have any influence on the activity, as seen in figure S9.

A comparison between the mass activities of Ir/TiONx/C catalyst and the Ir Black benchmark can be seen in figure 5. In addition, the support without Ir is shown. Interestingly no activity was recorded, which is in contradiction to some reports showing OER activity of TiONx [54]. The 2.6 times higher activity at 1.6 V (6.61 mA/μgIr and 2.54 mA/μgIr for our material and the benchmark, respectively) is associated with the better dispersion and thus better utilization of Ir on the high-surface-area support. Moreover, the use of TiONx support with metallic nanoparticles leads to the SMSI effect, which was shown to affect the intrinsic activity of Ir [17].

Finally, the two different activation protocols were also performed on our supported catalyst (figure 6(a)). Surprisingly, the opposite trend to that seen in Ir Black was found. The activity was higher after the broader potential activation (figure 6(b)). This trend indicates that the activation protocol with the broader potential range induced more, instead of fewer, OER active sites in the Ir/TiONx/C analogue. It is hypothesized that the composition of the oxide layer is different in the two analogues after the activation protocol. This strongly indicates that in the case of Ir/TiONx/C the active Ir sites are regenerated via electrochemical reduction (presumably Ir(III) [55–60]), whereas in the case of Ir Black the oxide layer grows too thick (is irreversibly oxidized) to be electrochemically reduced during the activation protocol. These results indicate that the SMSI between the TiONx support and Ir nanoparticles most likely inhibits the growth of oxide, which can be electrochemically reduced to more OER-active [55–60], lower-valency Ir species. This inhibition of Ir oxide formation was shown in our previous study where Ir on TiONx exhibited the HUPD peaks, specific of metallic iridium, even after cycling until oxidative potential [17]. Thus, the activation protocol should also be optimized for each catalyst, especially for supported ones.

In conclusion, several parameters related to the measurement of intrinsic activity for OER have been investigated using an Ir Black benchmark catalyst. The loading was shown to have no effect on mass activity. However, ink preparation, backing electrode material and activation protocol were shown to be of fundamental importance. Moreover, a homemade Ir/TiONx/C electrocatalytic nanocomposite with small nanoparticles displays almost three times higher activity than the Ir Black benchmark. However, the impact of the choice of
activation protocol reveals the opposite trend in the activity increase after different activation procedures. This highlights the importance of optimization of conditions for different supported or unsupported Ir-based catalysts.

Acknowledgments

This study was supported by the Slovenian Research Agency for the research programme P2-0152, P1-0034, and P2-0393 and project N2-0106. Primoz Jovanovič (P J) acknowledges the financial support provided by the Slovenian Research Agency within the project Z1-9165.

ORCID iDs

Francisco Ruiz-Zepeda https://orcid.org/0000-0002-2637-3433
Miran Gaberscek https://orcid.org/0000-0002-8104-1693
Nejc Hodnik https://orcid.org/0000-0002-7113-9769

References

[1] Schlogl R 2010 ChemSusChem 3 209
[2] Montoya JH, Seitz I, Chakraborty P, Vojvodic A, Jaramillo TF and Nørskov JK 2017 Nat. Mater. 16 70
[3] Barreto I, Makihiro A and Riahi K 2003 Int. J. Hydrogen Energy 28 267
[4] Babic U, Suermann M, Buchi FN, Gubler L and Schmidt T J 2017 J. Electrochem. Soc. 164 F387
[5] Lu Q and Jiao F 2016 Nano Energy 29 149
[6] Pourbaix MN, Van Muylder J and de Zoubov N 1959 Platinum Met. Rev. 3 100
[7] Geiger S, Kiasian O, Shrestha BR, Mingers AM, Mayrhofer K J and Cherevko S 2016 J. Electrochem. Soc. 163 F3132
[8] Reiter T, Oezaslan M and Strasser P 2012 ACS Catal. 2 1765
[9] Johnson Matthey 2018 PGM Market Report May 2018 http://platinum.matthey.com/documents/new-item/pgm%20market%20reports/pgm_market_report_may_2018.pdf
[10] Kibsgaard J and Ib Chorkendorff I 2019 Nat. Energy 4 430
[11] Nørskov JK 2018 Research needs towards sustainable production of fuels and chemicals EnergyX https://www.energy-x.eu/wp-content/uploads/2019/09/energy-X_Research-needs-report.pdf
[12] Carmo M, Fritz DL, Mergel J and Stolten D 2013 Int. J. Hydrogen Energy 38 4901
[13] Oh HS, Nong HN, Reiter T, Bergmann A, Gleich M, Ferreira de Araújo J, Willinger E, Schlogl R, Teschner D and Strasser P 2016 J. Am. Chem. Soc. 138 12552
[14] Puthiyapura V K, Mamlok M, Pasupathi S, Pellet BG and Scott K 2014 J. Power Sources 269 651
[15] Nhan Nong H, Oh H S, Reier T, Willinger M G, Petkov V, Teschner D and Strasser P 2015 Angew. Chem. Int. Ed. 54 2975
[16] Puthiyapura V K, Pasupathi S, Su H, Liu X, Pellet B and Scotta K 2014 Int. J. Hydrogen Energy 39 1905
[17] Bele M et al 2019 ChemCatChem 20 5038
[18] Campbell CT 2012 Nat. Chem. 4 597
[19] Huang S H, Ganesan P, Park S and Popov BN 2009 J. Am. Chem. Soc. 131 13898
[20] Kim Y T et al 2017 Nat. Commun. 8 1449
[21] Nong H N, Oh H S, Reiter T, Willinger E, Willinger M G, Petkov V, Teschner D and Strasser P 2015 Angew. Chem., Int. Ed. 54 2975
[22] Alia SM, Shulda S, Ngo C, Pylypenko S and Pivovar BS 2018 ACS Catal. 8 2111–20
[23] Nong H N et al 2018 Nat. Catalysis 1 841
[24] Yu Z, Zhang L, Liu Z, Ziegelbauer JM, Xin H, Dutta L, Muller DA and Wagner FT 2012 J. Phys. Chem. C 116 19877
[25] Wei C, Rao RR, Peng J, Huang B, Stephens IE L, Risch M, Xu Z J and Shao–Horn Y 2019 Adv. Mater. 31 1806296
[26] Spori C, Briois P, Nong HN, Reiter T, Billard A, Kühle S, Teschner D and Strasser P 2019 ACS Catal. 9 6653
[27] Gorlin Y and Jaramillo TF 2010 J. Am. Chem. Soc. 132 13612
[28] Frydendal R, Paoli E, Knudsen BP, Wickman B, Malacrida P, Stephens IE L and Chorkendorff I 2014 ChemElectroChem 1 2075

Figure 6. Comparison between two different activation protocols for Ir/TiON/C. CVs of (a) activation protocol and (b) OER activity.
