

Synthesis of Iridium Nanocatalysts for Water Oxidation in Acid: Effect of the Surfactant

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Proton exchange membrane water electrolyzers are very promising renewable energy conversion devices to produce hydrogen from sustainable feedstocks. These devices are mainly limited by the sluggish kinetics of the oxygen evolution reaction (OER). Therefore, efficient catalysts in acidic media that allow operating at low overpotential are necessary. Ir-based nanoparticles are both active and stable for the OER. Surfactants are widely used in the preparation of nanoparticle colloids. A severe drawback for catalysis is the need to remove surfactants by typically costly, hazardous, time and/or energy consuming steps. Herein we present a modified approach of the polyol synthesis that consists of a simple surfactant-free and NaOH-free synthesis of Ir nanoparticles in ethylene glycol leading to colloidal nanoparticles of *ca.* 2.5 nm in diameter. The benefits and drawbacks of the surfactant-free synthesis are illustrated by comparison with commercial Ir black nanoparticles and Ir nanoparticles obtained using surfactant for the electrocatalytic OER in acidic media.

There is an urgent need to develop a sustainable energy economy. Water electrolysis, coupled with renewable energy sources, allows producing hydrogen from sustainable feedstocks, a very interesting approach to fulfil the future energy

demand.^[1,2] Proton exchange membrane (PEM) electrolyzers are promising water splitting devices. They can operate at high current densities,^[3] present lower ohmic losses and a more mature membrane technology than alkaline anion exchange membrane electrolyzers.^[4] However, developing catalysts that resist the harsh acidic and oxidising conditions in PEM electrolyzers remains a major challenge at the anode side, where the oxygen evolution reaction (OER) takes place.^[5] The OER causes significant energy losses in PEM electrolyzers.^[6,7] This challenge must be addressed by designing and developing efficient OER catalysts in acidic media.^[4]

Only iridium-based catalysts have shown both reasonable OER activity and stability in acidic media thus far.^[3] Given that Ir is both very scarce and expensive,^[8] it is critical to reduce the amount of Ir in PEM electrolyzers.^[9] To ensure a sustainable use of this precious metal, a careful design of the catalyst is needed.^[8] Much effort has been recently devoted to develop Ir-based nanoparticulate catalysts to maximise the electrochemical activity per amount of Ir.^[10–19]

Colloidal syntheses approaches offer promising routes to produce small-size nanoparticles (NPs). However, surfactants are in general required to achieve size control and avoid NP agglomeration.^[10,20,21] Unfortunately, surfactants are detrimental since they typically need to be removed as they block the active surface of NP catalysts. The removal requires energy and time consuming steps.^[22–25] In addition, those additives are typically derived from petroleum sources and so can be considered harmful to the environment and undesirable.^[26]

Polyvinylpyrrolidone (PVP) is one of the most common surfactants used in the popular polyol synthesis.^[20,27] Arguably, PVP is a non-toxic polymer,^[24,28] yet it is still derived from hydrocarbons. Developing 'green' synthesis methods of nanomaterials is a challenge to address in light of sustainability matters^[26] and an increase driving force for industry relevant technologies.^[29] Synthesis methods without surfactant therefore bear appealing features for the simple production of nanomaterials with enhanced catalytic properties.^[30–34] Alkaline ethylene glycol has been reported as a suitable solvent and reducing agent for colloidal synthesis of NPs, in particular platinum.^[35] Ethylene glycol stabilises the colloids due to its high viscosity^[36] without direct interaction with the NP surface.^[37] Thus, the surfactant-free NPs obtained by this method bear promising features for catalysis. We report here a surfactant-free production method of small (*ca.* 2.5 nm) Ir NPs obtained by simple thermal reduction of IrCl₃ in ethylene glycol. The benefits and drawbacks of the surfactant-free synthesis are illustrated by comparison with NPs obtained using different

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 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.201902190>. This publication is part of the Young Researchers Series. More information regarding these excellent researchers can be found on the ChemCatChem homepage.

amount of PVP as surfactant and commercially available Ir black NPs.

Transmission electron microscopy (TEM) micrographs of Ir NPs produced by the NaOH-free and surfactant-free synthesis (Ir-no-PVP) show individual NPs despite the absence of surfactant (see Figure 1a). Small angle X-ray scattering (SAXS) analysis (see Figure 1b) results in an average diameter estimation of 2.4 ± 0.2 nm, in agreement with TEM analysis (see Figure S4 and Table S1). Polyol methods may require to adjust the 'pH' (or OH/Ir molar ratio) or water content to modify the NPs size.^[30,35,38] Therefore, we also compare the size effect of adding NaOH, HCl or water in the synthesis of the Ir NP. It is found that adjusting the 'pH' (or OH/Ir molar ratio) in ethylene glycol is not needed to obtain small size NPs (see Table S2). This is in contrast with surfactant-free Pt NPs^[30] as well as some works in the literature stressing the need for surfactant in the polyol synthesis.^[27,35] Avoiding 'pH' control is a potential benefit to achieve better reproducibility in the synthesis of Ir NPs. The addition of PVP only slightly reduces the size of the NPs to ca. 2 nm. The use of PVP therefore does not lead to major benefits on size control.

After the synthesis, the colloidal NPs were washed and precipitated to be collected. Ir-no-PVP NPs were easily washed with 2 M HCl, while in the presence of PVP, the acid washed

colloid dispersion did not precipitate after centrifugation. The NPs prepared with PVP were therefore washed with acetone. Thus, for proper comparison, Ir-no-PVP NPs were also washed with acetone and their catalytic activity evaluated.

The electrochemically active surface area (ECSA) of metallic Ir NPs was estimated measuring the charge in the hydrogen adsorption region by cyclic voltammetry, as shown in Figure 2. Ir-no-PVP NPs washed with 2 M HCl exhibit an ECSA of 26 ± 1 m²g⁻¹_{Ir}. This value is comparable with the ECSA of commercial and synthesised NPs reported in the literature.^[39,40] Ir-no-PVP NPs washed with acetone have nearly 50% lower ECSA: 13 ± 1 m²g⁻¹_{Ir}. The decrease of the ECSA of the NPs washed with acetone is attributed to the loss of Ir during washing. Supernatant of Ir NPs in acetone shows a slightly brown colour not observed for acid washed colloids. This indicates that some Ir remained in the acetone washing phase.

At molar ratio $\text{PVP}_{\text{unit}}/\text{Ir} = 0.2$, the ECSA is 27.2 ± 5.7 m²g⁻¹_{Ir} similar to what is obtained for Ir-no-PVP washed with 2 M HCl. This shows that very low $\text{PVP}_{\text{unit}}/\text{Ir}$ ratios do not affect the catalytic properties of Ir NPs. However, at $\text{PVP}_{\text{unit}}/\text{Ir} = 1.7$, the ECSA is 39 ± 12 m²g⁻¹_{Ir}, possibly due to an improvement in the dispersion of the NPs over the working electrode, as we discuss further below. The broad peaks observed here can be attributed to poorly cleaned surfaces, as a result of an excess of surfactant strongly adsorbed on the NPs surface. The NPs with molar ratios above $\text{PVP}_{\text{unit}}/\text{Ir} = 1.7$, do not show hydrogen adsorption nor desorption, so their ECSA is evaluated to zero. As the $\text{PVP}_{\text{unit}}/\text{Ir}$ increases, the catalytic performance abruptly decreases as most of the active sites are blocked by the surfactant. A commercial Ir black is used as benchmark. It is characterised by a ECSA of 40 ± 5 m²g⁻¹_{Ir}, consistent with what it is has reported previously by Alia and co-workers.^[40] Estimating the ECSA of OER catalysts is an important challenge. In the case of Ir NPs, the formation of Ir-oxides complicates the ECSA estimation, as there is no

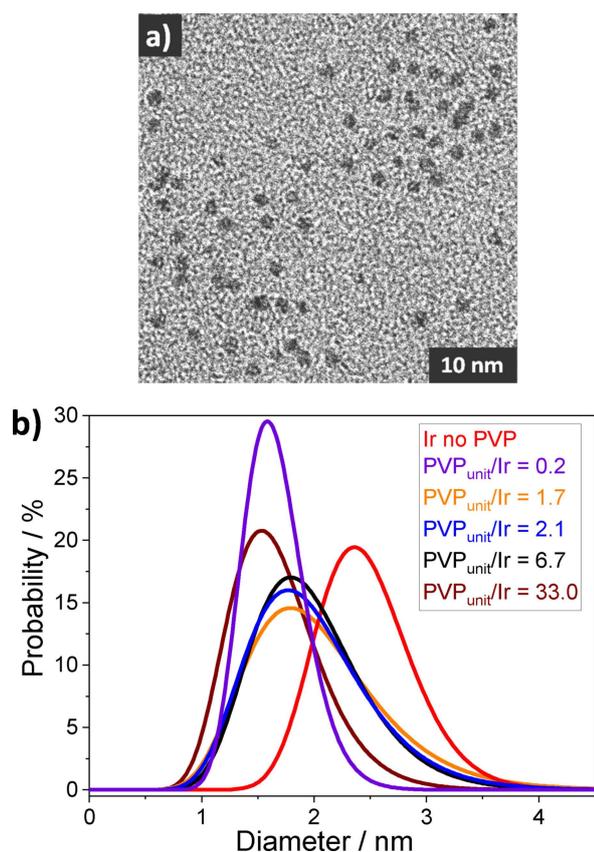


Figure 1. a) TEM micrograph of Ir NPs obtained by a surfactant-free synthesis. b) Size distribution obtained by SAXS analysis of surfactant-free Ir NPs and with different $\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratios (see Fig S1-S3 for complementary TEM and SAXS data).

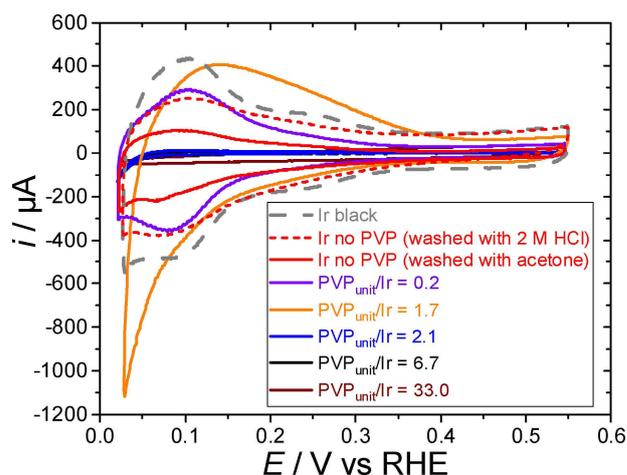


Figure 2. Cyclic voltammograms in the hydrogen adsorption region of Ir NPs obtained under different synthesis conditions as indicated. Nominal mass on the electrode: $71.3 \mu\text{g}_\text{Ir} \text{cm}^{-2}$. All the experiments were performed at room temperature in $0.5 \text{ M H}_2\text{SO}_4$ bubbled continuously with Ar and without rotation of the working electrode.

hydrogen adsorption on such surfaces, leading to a possible underestimation of the real active surface.^[12,41]

Figure 3a shows the catalytic performance of the Ir NPs in the oxygen evolution region from rotating disc electrode (RDE) measurements. Ir-no-PVP NPs washed with 2 M HCl have an electrocatalytic activity of $187 \text{ Ag}^{-1}_{\text{Ir}} \pm 44 \text{ Ag}^{-1}_{\text{Ir}}$ ($13 \pm 3 \text{ mA cm}^{-2}$) at 1.55 V vs RHE. This value is comparable to other commercial and synthesised Ir NPs reported in the literature.^[11,40] A similar value is obtained with commercial Ir black NPs with a mass activity of $170 \text{ Ag}^{-1}_{\text{Ir}} \pm 46 \text{ Ag}^{-1}_{\text{Ir}}$ ($12 \pm 3 \text{ mA cm}^{-2}$) at the same potential. In spite of the lower estimated ECSA, the nanoparticle catalyst produced in this study show an activity comparable to that of Ir black NPs (see Figure 3b).

Ir-no-PVP NPs washed with acetone have lower mass activities, which can be explained by the loss of Ir in the washing steps. For $\text{PVP}_{\text{unit}}/\text{Ir}$ ratios, the Ir NPs show activities proportional to the ECSA. $\text{PVP}_{\text{unit}}/\text{Ir}=0.2$ shows similar catalytic performance to Ir-no-PVP washed with 2 M HCl: $163 \pm 46 \text{ A g}^{-1}_{\text{Ir}}$ ($12 \pm 3 \text{ mA cm}^{-2}$), $\text{PVP}_{\text{unit}}/\text{Ir}=1.7$ shows the highest activity with $233 \text{ Ag}^{-1}_{\text{Ir}} \pm 94 \text{ Ag}^{-1}_{\text{Ir}}$ ($17 \pm 7 \text{ mA cm}^{-2}$) at 1.55 V vs RHE, but

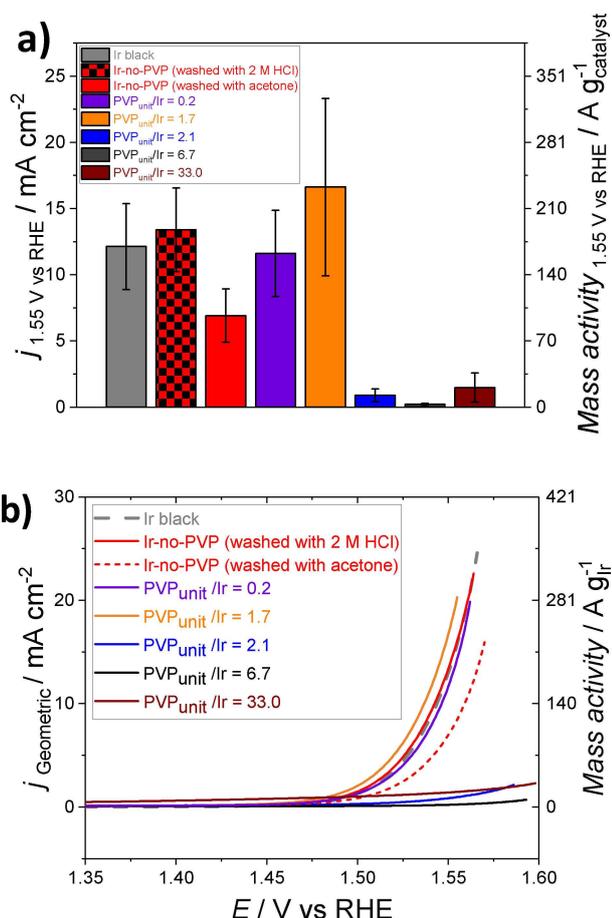


Figure 3. a) Comparison of the mass activity at 1.55 V vs. RHE. b) Cyclic voltammograms in the oxygen evolution region. Mass activity is calculated based on the nominal mass of Ir on the electrode ($71.3 \mu\text{g}_{\text{Ir}} \text{ cm}^{-2}$). All the experiments were performed at room temperature in 0.5 M H_2SO_4 bubbled continuously with Ar and a rotation speed of 1600 rpm of the working electrode.

also a high relative standard deviation of $\pm 40\%$, nearly the double of the one obtained with Ir-no-PVP washed with 2 M HCl ($\pm 24\%$). The CVs obtained with $\text{PVP}_{\text{unit}}/\text{Ir} > 1.7$ are similar to those obtained without using catalyst, which confirms the strong blocking effect of the surfactant.

These results illustrate that, despite the high applied potentials, there is no evidence of partial oxidation or complete removal of PVP. This highlights the challenges in removing the surfactant yet typically added in most colloidal syntheses, but severely impairing the catalytic properties for the OER. Our results show that there is no need of surfactant to obtain active catalysts and low amount of surfactant can be beneficial as discussed below. In Figure S5, the catalytic performances of the NPs prepared with different amount of PVP are compared to catalysts reported in the literature for OER. The highest mass activities are achieved for surfactant_{unit}/metal ratios close or equal to zero and decrease as the ratio increase.

Figure 3a shows that the addition of small amount of PVP ($\text{PVP}_{\text{unit}}/\text{Ir}=1.7$) seems to give a slightly higher catalytic activity; however, the results are not very reproducible (largest error bars). The assessment of electrocatalysts certainly depends on the preparation method of the catalyst (in this case, surfactant vs no surfactant). It equally depends on the 'ink' formulation.^[38] This formulation includes the way the catalysts are washed, re-dispersed and deposited for electrochemical assessment. These steps can strongly affect the activity measured for what is initially a same catalytic material.^[42] This is observed here with the higher activity obtained with Ir-no-PVP catalyst washed with HCl vs. acetone. In many cases, a binder like Nafion is added to the ink for RDE measurements.^[42] Firstly, because it is used in the PEM technology. Secondly, it contributes to stabilise the catalyst on the glassy carbon surface in RDE measurements.^[43] At relatively low $\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratios ($\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratio of 0.2 and 1.7), PVP does not fully block the active sites which accounts for the higher catalytic activity compared to NPs obtained with higher $\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratios. In addition, the activities for $\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratio of 0.2 and 1.7 and 'no' surfactant Ir NPs are comparable as a likely result from complex 'positive' effects of 'low' PVP amount. It cannot be excluded that PVP contributes to a better dispersion of the NPs on the working electrode. This is indirectly observed on the TEM micrographs in Figure S1, where the dispersion on the grids of the NPs slightly increases with higher $\text{PVP}_{\text{unit}}/\text{Ir}$ ratios. However, PVP is unlikely to improve the catalytic activity. Thus, at $\text{PVP}_{\text{unit}}/\text{Ir}=1.7$ molar ratio, the catalytic activity improves possibly by a better preparation for electrochemical testing, e.g. improving the NP film compared to the case with $\text{PVP}_{\text{unit}}/\text{Ir}=0.2$.

At the same time, the higher standard deviation of the measurements, especially for $\text{PVP}_{\text{unit}}/\text{Ir}$ molar ratio of 1.7, stresses the difficulty in reproducing such activity performance. With this molar ratio, it is more difficult to prepare electrode tips in a reproducible manner due to the properties of the catalyst ink. PVP can modify the ink due to its properties to increase the solvent viscosity or its capacity to act as a 'binder'.^[24,28] Figure S6 and S7 show how the use of PVP during the Ir synthesis modifies the dispersion of the resulting NPs.

Residual amount of PVP will affect the ink and so the loading of the Ir NPs on electrode surfaces. This lack of reproducibility is in line with a common challenge in benchmarking the performances of catalysts.^[18,44] Reproducibility issues often rise with the complexity of the catalyst preparation. For a fundamental understanding as well as larger scale implementation, simpler syntheses with as few chemicals as possible present clear benefits.^[45] At lower PVP_{unit}/Ir molar ratio (e.g. 0.2), no benefits could be gained compared to using no surfactant. Surfactant-free NPs are therefore worth for further investigation. In light of these considerations, we focus the rest of our discussion on surfactant-free and NaOH-free prepared NPs (Ir-no-PVP washed in 2 M HCl) and the most active Ir NPs, PVP_{unit}/Ir = 1.7.

The stability of Ir-no-PVP (washed with 2 M HCl), PVP_{unit}/Ir = 1.7 and Ir black NPs were evaluated using both chronoamperometry, holding a geometric current density of 10 mA cm⁻², and chronopotentiometry, at 1.55 V vs RHE, for 10 h. The chronoamperometric studies show similar performance between Ir-no-PVP and Ir black, whereas PVP_{unit}/Ir = 1.7 NPs show a faster decrease of activity at the beginning and important current variations ('noisy' set of data) due to inefficient removal of O₂ bubbles formed during the experiment (Figure S8). Yet, the activity measured before and after chronoamperometry reported in Figure 4, shows clear differences: Ir-no-PVP NPs display a loss in activity of 45% compared to 55% for Ir black NPs at 1.55 V vs RHE. This may indicate that the number of active sites available decreases faster in Ir black than the Ir-no-PVP. This also could be related to the NP size and the possible formation of O₂ bubbles inside the catalyst film or the NPs,^[46] where the biggest NPs (Ir black, see Figure S2) are the most affected. Despite the lack of efficient bubble management during the chronoamperometric experiment, PVP_{unit}/Ir = 1.7 NPs show an increase of 10% in activity at 1.55 V vs RHE. This suggests that some of the surfactant and Ir NPs were removed

during the cyclic voltammetry performed after the chronoamperometry, progressively increasing the available active surface on the working electrode.

In the chronopotentiometric measurements, the principal limitation is the solubility of the catalyst as Ir forms soluble species above 1.8 V vs RHE ($\eta = 0.57$ V).^[40] Figure 5 shows that, for Ir black, the OER overpotential slowly increases until reaching a value of ca. 0.57 V after ca. 8 h. Thereafter, a sudden sharp increase in overpotential to 1.23 V occurs, which corresponds to the overpotential observed for bare glassy-carbon electrodes under same conditions (see Figure S9). Therefore, the lack of activity obtained after the stability test, as shown in Figure 5b, demonstrates that the catalyst was not active any longer or possibly completely dissolved or delaminated from the GC electrode in the electrolyte. El-Sayed and co-workers recently reported that the sudden increase of the potential in chronopotentiometric experiments could be attributed to the formation of bubbles inside the catalyst film that cannot be removed by rotation.^[46] The deactivation by formation of bubbles cannot be ruled out from our stability measurements.

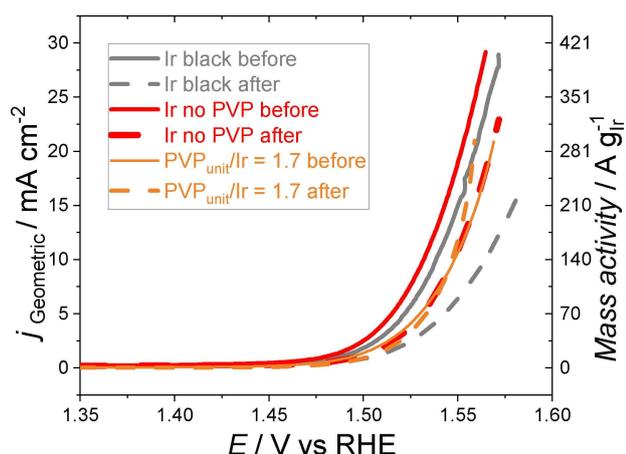


Figure 4. Cyclic voltammograms in the oxygen evolution region before and after 10 h chronoamperometric experiments. Mass activity is calculated based on the nominal mass of Ir loaded on the electrode (71.3 μg_Ir , cm^{-2}). All the experiments were performed at room temperature in 0.5 M H_2SO_4 bubbled continuously with Ar and a rotation speed of 1600 rpm of the working electrode.

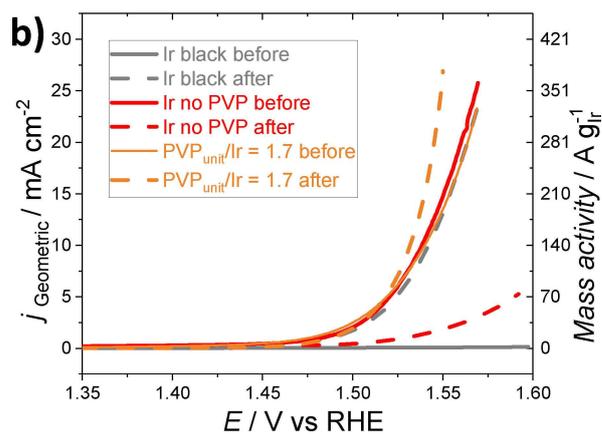
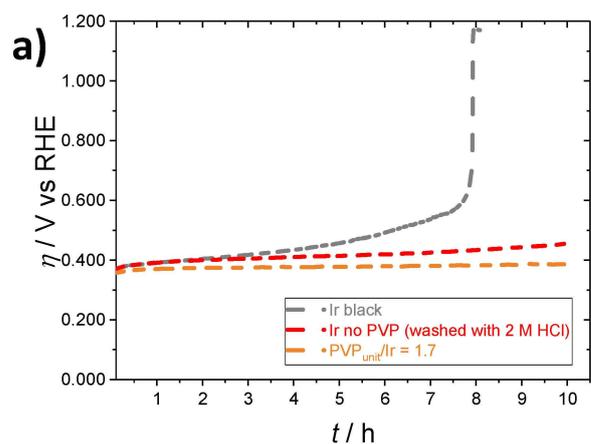


Figure 5. a) Chronopotentiometric measurements at geometric current density, $j = 10$ mA cm^{-2} for 10 h. b) Polarisation curves in the oxygen evolution region before and after 10 h chronopotentiometric experiments. Mass activity is calculated based on the nominal mass of Ir loaded on the electrode (71.3 μg_Ir , cm^{-2}). All the experiments were performed at room temperature in 0.5 M H_2SO_4 bubbled continuously with Ar and a rotation speed of 1600 rpm of the working electrode.

Chronopotentiometric studies have to be analysed carefully as they can give misleading interpretation of the catalytic performance of different materials. We recently showed that the initial overpotential in chronopotentiometric studies determines the apparent stability of Ir NPs as the rate of degradation is much faster at higher overpotentials.^[19] In this work, the initial overpotentials of the different Ir NPs are similar (Figure 5a). Thus, we can assume that the observed differences in stability are related to the differences in Ir NP preparation and amount of PVP used.

In contrast to Ir black, Ir-no-PVP NPs present improved stability, showing only a minor increase in overpotential throughout the whole experiment. Even if the sudden increase in overpotential observed for Ir black is due to the delamination of the catalyst layer, Ir-no-PVP NPs is also more stable in the first 8 h of the chronopotentiometric measurements. The best performance is observed with PVP_{unit}/Ir=1.7 NPs, showing almost a constant overpotential during the 10 h of current hold. It seems that a low amount of PVP used during NP synthesis acts as a protection layer which decreases the detachment and/or dissolution of Ir NPs. There is an important enhancement of the double in the catalytic performance of these NPs after chronopotentiometry (Figure 5b). It is possible that a higher amount of PVP is removed during the current hold than in the chronoamperometric experiment (Figure 4 vs. Figure 5b), leaving more and more active sites available. Overall, our results highlight both the favourable activity and better stability for the small surfactant-free and NaOH-free Ir NPs and the PVP_{unit}/Ir=1.7 NPs compared to commercial Ir black NPs in acidic conditions.

In summary, Ir NPs of ca. 2 nm in diameter are obtained using ethylene glycol as solvent without the need for a base. Using a high amount of surfactant is detrimental as it blocks the active surface of the Ir NPs. In contrast, we show that the surfactant-free and NaOH-free synthesis is simple and does not require extended washing steps to obtain active and stable Ir NPs for the OER in acidic media. The resulting NPs show improved performances compared to commercial NPs. Optimisation of this synthesis procedure with careful tuning of the composition and/or morphology might make surfactant-free Ir-based catalysts promising for long-term applications. In addition, the overall synthesis method is a valuable building block to study parameters that can affect catalysts for the OER beyond the catalyst synthesis. We show that Ir NPs synthesised with low amount of surfactant (e.g. PVP_{unit}/Ir ≤ 1.7) achieve similar to higher catalytic activities for the OER in acid than surfactant-free Ir NPs. This is attributed to a positive stabilisation of the NPs on the electrode.

Experimental Section

Nanoparticle synthesis: The nanoparticles (NPs) were produced by heating 20 mM IrCl₃·xH₂O (99.8%, Alfa Aesar) in 2 mL ethylene glycol (99+%, Sigma-Aldrich) with or without polyvinylpyrrolidone (PVP, Alfa Aesar) with a PVP_{unit}/Ir ratio as indicated. The mixture was stirred at medium speed and heated up under reflux conditions for

15 min at 100 W using a microwave oven (CEM Discover SP). No controlled atmosphere was used.

Size characterisation: The as-produced NPs were diluted in methanol and deposited on a transmission electron microscope (TEM) copper grid (Quantifoil). TEM was performed at 200 kV on a 2100 Jeol microscope. The size distribution of NPs was evaluated with 150 to 300 individual NPs per sample.

Small angle X-ray scattering experiments were performed on the as-produced solutions diluted with ethylene glycol at 2 mM Ir with a fitting procedure as previously described.^[30,34]

Preparation of the catalyst ink: The Ir NPs produced by the surfactant-free were washed twice with 4 mL of 2 M HCl (Suprapur, Merck) and centrifuged at 2400 relative centrifugal force (rcf) for 5 min. The supernatant was removed after centrifugation. In the case of the NPs synthesised with PVP, the NPs were washed with acetone (technical grade, Kautex) and centrifuged at 2400 rcf for 5 min. The supernatant was removed after centrifugation. In both cases, the washed NPs were dispersed in a solution of deionised water (resistivity > 18.2 MΩ cm, total organic carbon < 5 ppb) and isopropanol (IPA, technical grade, VWR chemicals) (1:1) (H₂O:IPA) and 0,096 wt.% of Nafion at a nominal concentration of 2.8 mg_{Ir} mL⁻¹. The commercial Ir NPs (Ir black, Premetek Co.) were weight and dispersed in the solution (1:1) (H₂O:IPA) 0,096 wt.% of Nafion at a nominal concentration of 2.8 mg_{Ir} mL⁻¹.

Electrode preparation: A glassy carbon electrode tip (5 mm diameter) was sonicated with deionised water, acetone, IPA, methanol (HPLC grade, VWR chemicals) and again with deionised water for 5 min, respectively. The tip was polished using alfa alumina suspension (Struers) with 1 μm and then with 0.3 μm particle diameter. After each polishing, the tip was sonicated three times in deionised water for 5 min. The tip was dried using N₂. 5 μL of the catalyst ink was dropped on the glassy carbon tip under rotation at 200 rpm during 5 min and left in a saturated IPA atmosphere until the tip was completely dry.^[38]

Electrochemical set up: The measurements were performed using a computer controlled potentiostat (Eci 200 Nordic electrochemistry) and a half cell configuration using Pt wire as the counter electrode, glassy carbon rotating disc as the working electrode and a reversible hydrogen electrode connected to the cell by a Luggin capillary as the reference electrode. All the experiments were performed at room temperature with 0.5 M H₂SO₄ (electrolyte grade, Merck) bubbled continuously with Ar and resistance corrected.

Hydrogen underpotential deposition measurements: The electrochemically active surface area (ECSA) of metallic Ir nanoparticles was determined using hydrogen underpotential deposition. 20 cycles were performed between 0.025 and 0.550 V vs RHE without rotation of the working electrode. The last cycle was used to determine the ECSA by integrating the average charge of the hydrogen desorption and adsorption peaks between 0.060 V and the end of the desorption peak/beginning of the adsorption peak. The equation for its calculation can be found in the SI.

Activity measurements: Three cycle voltammograms were taken between 1.00 to 1.60 V vs. RHE with a scan rate of 10 mV s⁻¹ and rotation speed of 1600 rpm. The reported catalytic activity measurements where established from the second cycle. The activity was measured taking the current density and mass activity at 1.55 V vs. RHE. The activity value corresponds to the average between the cathodic and anodic sweep.

Stability measurements: Chronoamperometric studies were performed by holding the potential at 1.55 V vs. RHE for 10 h and rotation speed of 1600 rpm. Chronopotentiometric studies were

performed by holding the current at 1.963 mA (current density of 10 mA cm⁻²) for 10 h with a rotation speed of 1600 rpm.

Acknowledgements

M.E.-E. gratefully acknowledges the Villum Foundation for the award of a Villum Young Investigator grant (Project number 19142). J.A.A.R. acknowledges the Siemens Foundation for the award of the project grant in 2018. J.Q. has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 703366 (SELECTRON). Dr S. B. Simonsen and Dr L. Theil Kuhn from the Technical University of Denmark (DTU) are thanked for access to TEM facilities.

Keywords: Electrocatalysis · Iridium · Nanoparticles · Synthesis design · Water splitting · Energy conversion

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Manuscript received: November 22, 2019
Accepted manuscript online: December 10, 2019
Version of record online: January 7, 2020