

Synthesis and optimisation of IrO₂ electrocatalysts by Adams fusion method for solid polymer electrolyte electrolyzers

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Abstract: IrO₂ as an anodic electrocatalyst for the oxygen evolution reaction (OER) in solid polymer electrolyte (SPE) electrolyzers was synthesised by adapting the Adams fusion method. Optimisation of the IrO₂ electrocatalyst was achieved by varying the synthesis duration (0.5 – 4 hours) and temperature (250 - 500°C). The physical properties of the electrocatalysts were characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD). Electrochemical characterisation of the electrocatalysts toward the OER was evaluated by chronoamperometry (CA). CA analysis revealed the best electrocatalytic activity towards the OER for IrO₂ synthesised for 2 hours at 350°C which displayed a better electrocatalytic activity than the commercial IrO₂ electrocatalyst used in this study. XRD and TEM analyses revealed an increase in crystallinity and average particle size with increasing synthesis duration and temperature which accounted for the decreasing electrocatalytic activity. At 250°C the formation of an active IrO₂ electrocatalyst was not favoured.

Keywords: Water electrolysis, Solid polymer electrolyte, Anodic electrocatalyst, Adams fusion method, Oxygen evolution reaction

1. Introduction

Hydrogen used as a fuel has benefits over the hydrocarbon rich fuels: it has a higher specific energy density by mass and does not present the problem of the emission of pollutants or greenhouse gases, such as CO₂ [1]. However challenges related to the production of hydrogen has delayed the realisation of the hydrogen economy [2]. Solid polymer electrolyte (SPE) or commonly known as proton exchange membrane (PEM) electrolyzers have in recent years received considerable interest as a production method for carbon free hydrogen [3, 4]. SPE electrolyzers are well suited for water electrolysis using intermittent power sources and have been identified by the European Commission as a key technology to transform renewable electricity into hydrogen and oxygen [5]. The main drawback at present is the high cost associated with the SPE electrolyser components such as the expensive precious metal electrocatalysts and the proton conducting

membrane [6, 7]. One way to reduce the cost of the SPE electrolyser is by improving the specific performance and durability of the noble metal electrocatalysts. The oxygen evolution electrode (anode) is the greatest source of overpotential of the system at typical operating current density [3, 7] and is associated with a substantial energy loss. The anodic electrocatalyst therefore needs to be highly stable and active under the operating conditions [8]. IrO₂ is commonly employed as the anodic electrocatalyst as it exhibits a high corrosion resistance to the oxygen evolution reaction (OER) in a strong acidic environment [8, 9]. IrO₂ offers a lower anodic overpotential (100 mV at 1 A cm⁻²) than metallic Pt and a long term stability of at least two years. IrO₂ also shows less efficiency loss due to corrosion or poisoning [10]. However, IrO₂ is scarce and very expensive [11], adding significantly to the cost of the SPE electrolyser system. IrO₂ has a service life of about 20 times longer than RuO₂, but has a slightly lower electrocatalytic activity towards the OER [12]. Therefore it becomes important to improve the electrocatalytic activity of the IrO₂ electrocatalyst. The electrolytic evolution of oxygen is influenced by several factors: crystal field stabilisation energy, mixed and doped oxides, dispersion, crystallinity and particle size [13] therefore it becomes important to develop an electrocatalyst that possess an optimum combination of these attributes. Methods for preparing the noble metal oxides include the Sol – Gel method, a modified polyol method, the Adams fusion method, a sputtering technique and a sulphite complex based preparation method [14]. In this study IrO₂ was synthesised and optimised as an anodic electrocatalyst for the SPE electrolyser by adapting the Adams fusion method. The Adams fusion method is a simple and easy method and is known to directly produce nanosized metal oxides [15]. Physical properties of the electrocatalysts were characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD). Electrochemical characterisation of the electrocatalysts towards the OER was evaluated by chronoamperometry (CA).

2. Experimental

2.1 Synthesis and optimisation of IrO₂

The Adams fusion method, first described by R. Adams and R.L. Shriner [16], entails the fusion of the metal chloride precursor with NaNO₃ in air at elevated temperature. The method has since been used to prepare various noble metal oxides [17 – 19]. In this study a predetermined quantity of the H₂IrCl₆ (SA Precious Metals, South Africa) was dissolved in 10 ml isopropanol (Alfa Aesar, Johnson Matthey) until a metal concentration of 3.5 x 10⁻² M was achieved and magnetically stirred for 1.5 hours. Five grams of finely ground NaNO₃ (Holpro Fine Chemicals, South Africa) was added to the solution, which was then further stirred for 30 minutes. The mixture was then placed in a preheated oven (at 80°C) for 30 minutes to evaporate the isopropanol. The dried catalyst precursor/salt mixture was then reacted in a preheated furnace. The obtained metal oxide was then cooled and washed with ultrapure water to remove the unreacted NaNO₃. The final step was to dry the metal oxide in an oven at 100°C. In order to achieve the most active IrO₂ electrocatalyst, the synthesis duration

(0.5 – 4 hours) and synthesis temperature (250 - 500°C) was varied. First, the temperature of 500°C was chosen (based on the literature) and the synthesis duration was varied from 0.5 to 4 hours. The best synthesis duration obtained was then kept constant while varying the synthesis temperature from 250 to 500°C. No additional annealing step followed to limit the sintering of the nanosized particles. A commercial IrO₂ electrocatalyst was procured from Alfa Aesar (Johnson Matthey) and used as received as a comparison to the best performing synthesised IrO₂ electrocatalyst.

2.2 Preparation of the working electrode

A glassy carbon working electrode (area = 0.196 cm²) was used for all electrochemical measurements. Catalyst inks were prepared by mixing together the IrO₂, ultrapure (UP) water and 5 wt % Nafion solution (Aldrich) in a ratio of 1:2:6. The mixture was then ultrasonically dispersed for 15 minutes. A measured drop of the catalyst ink was deposited using a micropipette onto the thoroughly cleaned glassy carbon surface followed by drying in an oven at 80°C. The IrO₂ loading equated to 0.45 mg cm⁻².

2.3 Characterisation

Physical phases and structures of the electrocatalysts were characterised by X-ray diffraction (XRD) employing the Bruker AXS D8 Advance diffractometer using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. Scanning electron micrographs were obtained with the Hitachi X-650 SEM using GENESIS software, working at 25 keV. Transmission electron micrographs were obtained using a Tecnai G² F20 X-Twin Mat200 kV Field Emission TEM, operating at 200 kV.

2.4 Electrochemical Measurements

CA analysis was performed in a standard three-electrode cell at 25°C and atmospheric pressure. A glassy carbon working electrode (as described in section 2.2), a 3M Ag/AgCl reference electrode, a platinum mesh counter electrode and a 0.5M H₂SO₄ electrolyte solution was used. Autolab potentiostat PGSTAT20 (Eco-Chemie) was used for CA analysis to evaluate the electrocatalytic activity of the synthesised IrO₂ electrocatalysts towards the OER. The electrolyte solution was purged with N₂ for 30 minutes before performing electrochemical measurements. CA was performed by stepping the potentials from 1.2 – 1.6 V and measuring the current (mA) response as a function of time. Each potential step was performed for 30 minutes. All potentials are reported versus the 3M Ag/AgCl electrode.

3. Results and discussion

3.1 Physico-chemical characterisations

The XRD analysis of synthesised IrO₂ (500°C, 0.5 – 4 hours) is shown in Fig. (1). XRD analysis revealed the presence of a rutile oxide phase, showing the preferential (110) and (101) orientations of IrO₂, which are both close-packed planes for the Ir atom [20]. An increase in crystallinity and particle size was

observed as the synthesis duration was increased which is known to contribute to the decrease in active surface area of the electrocatalysts [21]. The particle size may also affect the electronic conductivity, catalyst utilisation and gas/water transport when the electrocatalyst is used as part of a MEA [18]. Calculated using the Scherrer equation, the average particle size was estimated to increase from 4.5 nm (0.5 hour) – 10 nm (4 hour). The XRD analysis of synthesised IrO_2 (2 hours, 250 – 500°C) is shown in Fig. (2). XRD analysis revealed an increasing trend towards crystallisation and larger particle sizes as the temperature was increased. IrO_2 prepared at 250°C and 350°C showed broader peaks, depicting lower crystallinity, or an amorphous nature. Broader peaks are known to be indicative of smaller particle sizes. Rasten *et al.* [22] also found that IrO_2 prepared at 340 °C via the Adams fusion method consisted of nanosized particles with low crystallinity. The 110 phase which is known to be a stable surface of IrO_2 , was not observed for IrO_2 (2 hours, 250°C) but became more prevalent as the synthesis temperature was increased from 350 – 500°C. Calculated using the Scherrer formula, the average particle sizes for synthesised IrO_2 (2 hours, 250 – 500°C) were estimated to increase from 1.5 nm (250 °C) to 5.5 (500 °C). No metallic Ir was observed for all of the synthesised IrO_2 electrocatalysts. The XRD analysis of the best synthesised IrO_2 (2 hours, 350°C) and the commercial IrO_2 electrocatalyst is shown in Fig. (3). The XRD analysis revealed both broad amorphous and sharp crystalline peaks for commercial IrO_2 . The presence of metallic Ir was observed for the commercial IrO_2 electrocatalyst. Metallic Ir is not known to be beneficial for the OER since the reaction always takes place at an oxide surface [17]. Rutile type oxides of Ir are known to be considerably better as oxygen evolving electrodes than the metallic Ir. Oxygen evolution on metal surfaces can only take place when there is high oxygen coverage and at high oxidation potentials, the metal might form a metal oxide [23].

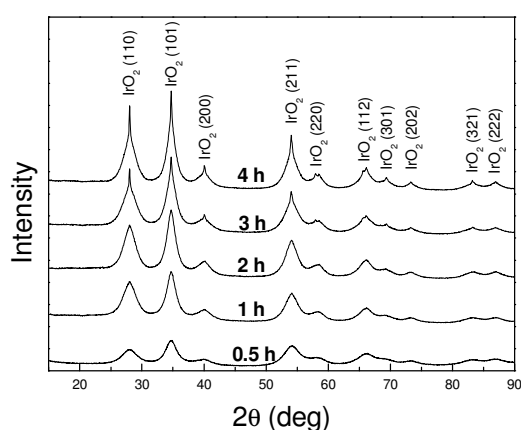


Fig. (1). XRD analysis of synthesised IrO_2 (500 °C, 0.5 - 4 hours).

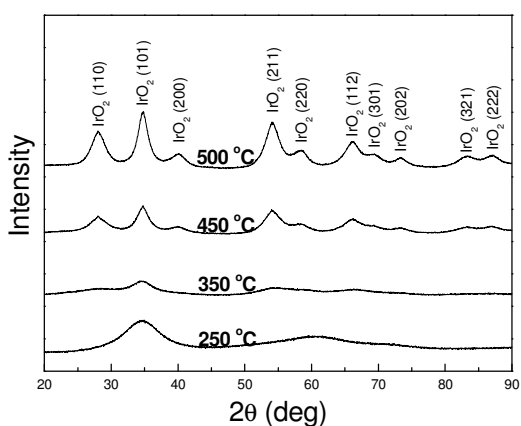


Fig. (2). XRD analysis of synthesised IrO₂ (2 hours, 250-500 °C).

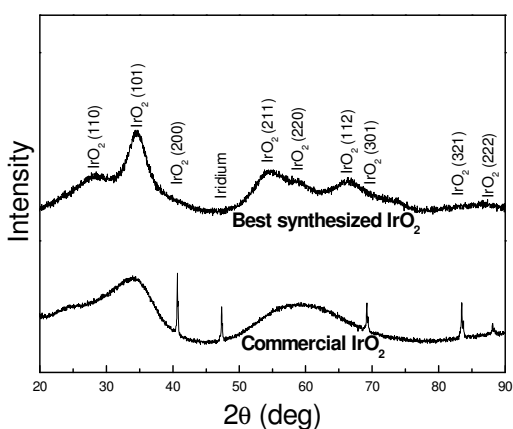
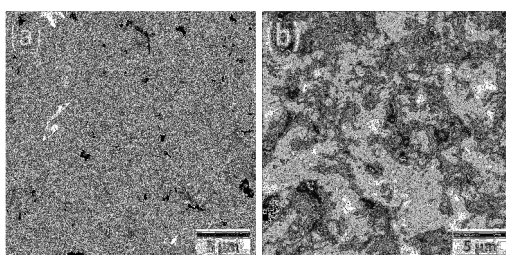


Fig. (3). XRD analysis of the best synthesised IrO₂ and commercial IrO₂.

SEM analysis of synthesised IrO₂ (500 °C, 0.5 – 4 hours) and commercial IrO₂ is shown in Fig. (4). Particle formation and size could not be defined from the SEM images as agglomerates of micrometer scale are visible. A change in morphology was observed for the synthesised IrO₂ as the synthesis duration increased which was probably due to particle agglomeration. The most notable change was observed for IrO₂ synthesised at 500 °C for 2 hours which had morphology more similar to the commercial IrO₂ electrocatalyst. SEM analysis of synthesised IrO₂ (2 hours, 250 – 500 °C) is shown in Fig. (5). Particle formation and size could not be defined from the images. A change in morphology was observed as the synthesis temperature was increased which was probably due to particle agglomeration or sintering due to the increasing temperature.



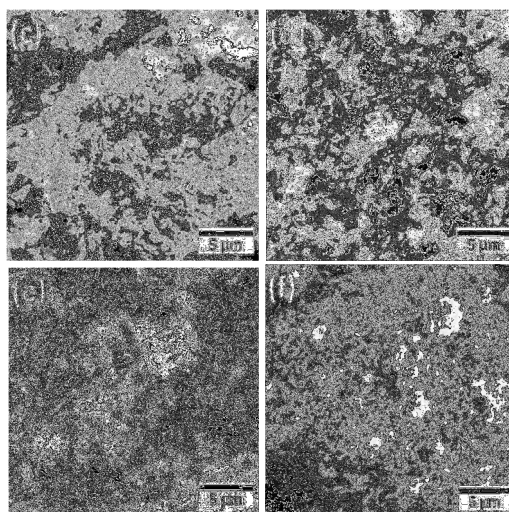


Fig. (4). SEM images of synthesised IrO₂ (500 °C, 0.5-4 hours) and commercial IrO₂ (a) 0.5 hour (b) 1 hour (c) 2 hour (d) 3 hour (e) 4 hour (f) commercial.

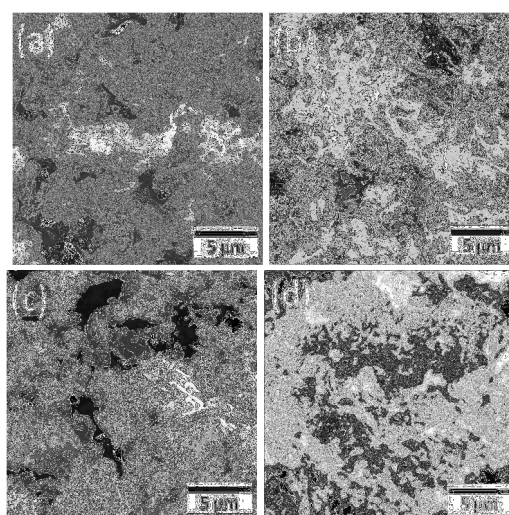


Fig. (5). SEM images of synthesised IrO₂ (2 hours, 250-500 °C) (a) 250 °C (b) 350 °C (c) 450 °C (d) 500 °C.

TEM analysis of synthesised IrO₂ (500°C, 0.5 – 4 hours) and commercial IrO₂ is shown in Fig (6). TEM analysis of the synthesised IrO₂ electrocatalysts was consistent with the XRD analysis, i.e. as the synthesis duration was increased, the average particle size increased. TEM also confirmed that the synthesised IrO₂ electrocatalysts consisted of nanosized particles with the following average sizes; 4 nm (0.5 hour), 5.5 nm (1 hour), 6.5 nm (2 hours), 8 nm (3 hours) and 10.5 nm (4 hours). Larger needle-shaped particles were present for IrO₂ (500°C, 4 hours) indicating a higher degree of crystallisation as the synthesis duration was increased. The TEM analysis of the commercial IrO₂ electrocatalyst revealed the presence of particles larger than 50 nm. Larger particles are associated with a decrease in the active surface area and available active sites. TEM analysis of synthesised IrO₂ (2 hours, 250 – 500°C) is shown in Fig. (7). TEM analysis revealed an increasing particle size with increasing synthesis temperature which is consistent with the XRD analysis. TEM revealed nanosized particles with the following average sizes: 2.5 nm (250°C), 4.5 nm (350°C), 6 nm (450°C) and 6.5 nm (500°C).

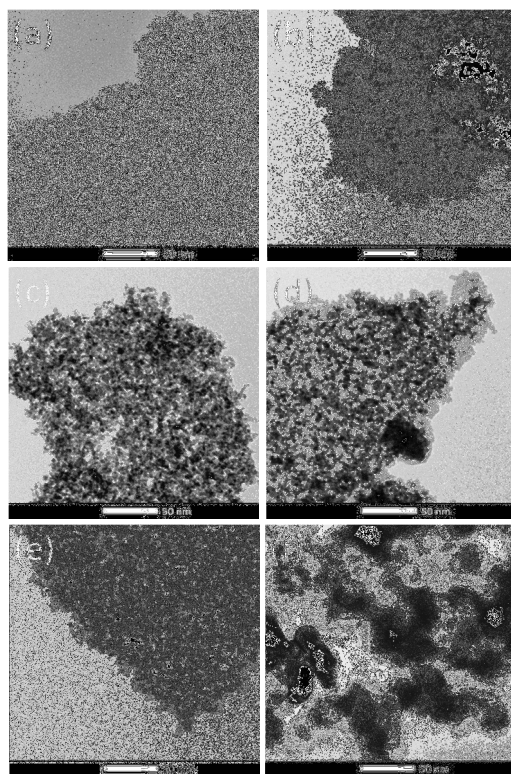


Fig. (6). TEM images of synthesised IrO₂ (500 °C, 0.5-4 hours) and commercial IrO₂ (a) 0.5 hour (b) 1 hour (c) 2 hour (d) 3 hour (e) 4 hour (f) commercial.

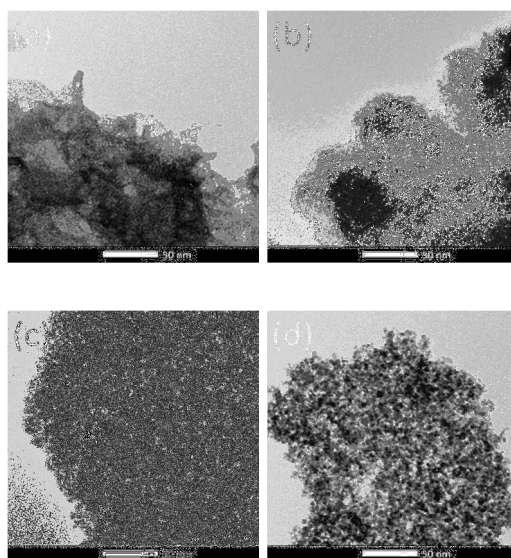


Fig. (7). TEM images of synthesised IrO₂ (2 hours, 250-500 °C) (a) 250 °C (b) 350 °C (c) 450 °C (d) 500 °C.

3.2 Electrochemical characterisations

The CA analysis for synthesised IrO₂ (500°C, 0.5 – 4 hours) performed at 1.6V for 30 minutes is shown in Fig. (8). CA analysis revealed the best electrocatalytic activity towards the OER for the IrO₂ electrocatalyst synthesised at 500°C for 2 hours. As the synthesis duration was increased from 0.5 – 2 hours, the IrO₂ electrocatalyst became more active towards the OER which was followed by a decrease in activity as the synthesis duration was kept longer than

2 hours. The high temperature resulted in a higher degree of crystallisation and larger particle sizes as revealed by XRD and TEM which probably caused a decrease in the active surface area and a decrease in available active sites [21]. The CA analysis for synthesised IrO₂ (2 hours, 250 – 500°C) and commercial IrO₂ performed at 1.6V for 30 minutes is shown in Fig. (9). CA analysis revealed the best electrocatalytic activity towards the OER for the IrO₂ electrocatalyst synthesised at 350°C for 2 hours. IrO₂ (2 hours, 250°C) showed very low electrocatalytic activity towards the OER. XRD analysis revealed the absence of the stable 110 phase which may be the reason for low electrocatalytic activity and the large decrease in current density. Cruz *et al.* [24], although using a different synthesis method, observed a phase transition from an amorphous to a crystalline phase between 240 - 480°C. They found their 200 and 300°C samples to show an amorphous phase whereas the 400 and 500°C samples showed a crystalline phase. Therefore the decrease in electrocatalytic activity of IrO₂ synthesised at temperatures above 350°C is due to an increase in crystallinity and particle size as was revealed by TEM and XRD. A similar observation was made by Rasten *et al.* [22] when they annealed the catalyst between 440 and 540°C. The best synthesised IrO₂ electrocatalyst was found to be almost twice as active towards the OER as the commercial IrO₂ electrocatalyst. The lower electrocatalytic activity of the commercial IrO₂ electrocatalyst can be attributed to the larger particle sizes (> 50nm) and the presence of metallic Ir as revealed by TEM and XRD. At 1.6V, a decrease in current density was observed for the synthesised and commercial IrO₂ electrocatalysts which was not evident at lower voltages (1.2 – 1.5V). At 1.6V, significant amounts of O₂ bubbles due to the OER were observed to adsorb onto the electrocatalyst surface due to the use of a stationary electrode. The O₂ bubbles on the electrocatalyst surface are known to cause an ohmic drop which could explain the oscillations in the measured current [11]. The use of a hydrodynamic electrode would probably have been a more suitable choice to eliminate interference due to adsorption and oxygen film formation.

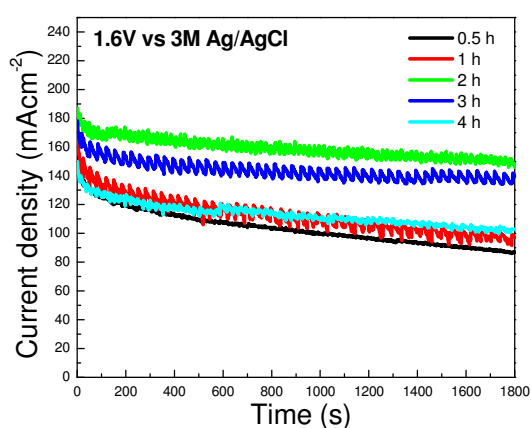


Fig. (8). Chronoamperometry analysis of synthesised IrO₂ (500 °C, 0.5-4 hours).

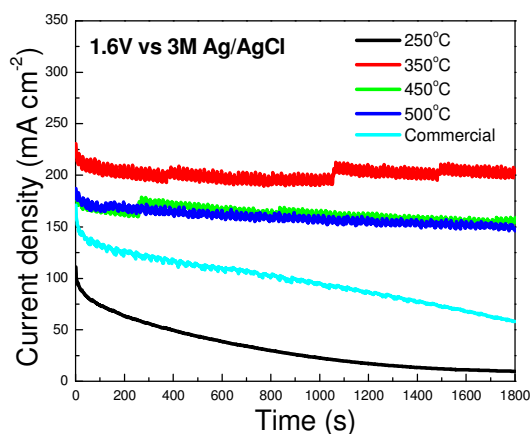


Fig. (9). Chronoamperometry analysis of synthesised IrO₂ (2 hours, 250-500 °C) and commercial IrO₂.

Conclusion

IrO₂ was successfully synthesised and optimised by adapting the Adams fusion method. TEM and XRD were useful in relating the physical structure of the electrocatalysts to the electrochemical performance. XRD and TEM analyses revealed increasing crystallinity and particle size as both synthesis duration and temperature was increased. CA revealed the best electrocatalytic performance for IrO₂ synthesised for 2 hours at 350°C. At 250°C the formation of an active IrO₂ electrocatalyst was not favoured. CA revealed that the best synthesised IrO₂ electrocatalyst were almost twice as active towards the OER as the commercial IrO₂.

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