

## Novel $(\text{Ir}_x\text{Sn}_y\text{Sb}_z)\text{O}_w$ Material as Catalyst for The Oxygen Evolution Reaction

N. J. Pérez-Viramontes<sup>1</sup>, C. Guzmán-Martínez<sup>1</sup>, M. Galván-Valencia<sup>1</sup>, S. M. Durón-Torres<sup>1\*</sup>

<sup>1</sup>Universidad Autónoma de Zacatecas, Programa de Maestría en Ciencias de la Ingeniería, Campus Siglo XXI, Carretera Zacatecas-Guadalajara Km. 6.0, Ejido la Escondida, Zacatecas, Zacatecas, México, 98160.  
\*Tel: +524929256690 Ext. 4655; e-mail: duronsm@prodigy.net.mx

---

### ABSTRACT

The synthesis of a novel material of general composition  $(\text{Ir}_x\text{Sn}_y\text{Sb}_z)\text{O}_w$  for use in solid polymer electrolyte water electrolyzers (SPEWE) was accomplished from the simultaneous synthesis of the electrocatalyst and the support by means of thermal decomposition of chlorides precursors  $\text{H}_2\text{IrCl}_6$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SbCl}_5$  in ethanol. Different  $\text{H}_2\text{IrCl}_6$  proportions in the reaction mixture were tested to observe their effect on the amount and electrocatalytic activity of the material obtained. The electrochemical properties of the different syntheses were measured by using: cyclic voltammetry (CV), linear scan voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Electrochemical tests were conducted using as support electrolyte  $\text{H}_2\text{SO}_4$  0.5 M in a conventional three-electrode cell. A mechanical mixture of  $\text{IrO}_2$  with Vulcan carbon and iridium oxide with antimony doped tin oxide were also tested respect to the oxygen evolution reaction to compare the properties of catalyst/support obtained. The results indicate that synthesized materials could represent a suitable candidate to be used use as anode in SPWE to catalyze the oxygen evolution reaction (OER).

---

**Keywords:** Water Electrolysis; Electrocatalyst; Oxygen Evolution Reaction.



## 1. Introduction

Hydrogen has been considered as the most promising fuel for clean energy obtaining carbon free energy to meet growing global energy demand. The capacity to generate clean and pure hydrogen as its storage and distribution is one limitation for its use. A promising method for hydrogen production is water electrolysis, which is less efficient than a direct chemical route but produces virtually no pollution or toxic byproduct when electrical energy is produced by renewable energy [1–3]. Water electrolyzers electrical energy used to divide the liquid water into oxygen and protons (anode reaction). Solvated protons migrate toward the cathode, which are reduced to molecular hydrogen (cathodic reaction). The anode and cathode are separated by an electrolyte, in the case of the polymeric electrolyte membrane water electrolyzer (PEMWE), the electrolyte is solid. PEMWEs have received special interest due to the high current densities that reached, the energy efficiency and the purity of the hydrogen produced, in comparison with the alkali electrolysis.[4,5]

Oxygen evolution reaction (OER) is the limiting step in the development and requiring electrolyzers, suitable catalysts for performing a suitable reaction rates. Electrocatalysis plays an important role in the development of materials for electrolyzers. In conventional PEMWE type oxides are used with rutile structure,[6] such as iridium oxide ( $\text{IrO}_2$ ) or ruthenium ( $\text{RuO}_2$ ) as catalysts to promote the OER.[7–9] The use of these metals has been necessary due to the highly acidic environment found in the polymeric membrane, which may cause corrosion of other materials. Great efforts are being to improve the catalytic activity of such catalysts, due to their nature of precious metals. A method of dispersing metal nanoparticles on a support in order to maximize the specific surface area and hence the specific activity of the catalyst.

Therefore, another aspect to consider is the catalyst support on which will disperse the catalyst, it must have a good performance to high operation potentials electrolyzers ( $E > 1.6 \text{ V vs NHE}$ ),[4] since, for example, the Vulcan carbon (which in general is a good catalyst support due to their large surface area) suffer phenomena of corrosion under these operating conditions, which can cause degradation and loss of electrical contact with the electroactive material, i.e. the material is not reliable for use as the anode catalyst support to get it carry out efficiently the OER alternative. The stability and durability of the catalyst support in the OER is the main challenge in the development of electrocatalysis.

The materials used as supports for catalysts should possess several important features: i) a highly superficial surface to provide better dispersion of the catalyst nanoparticles, ii) high electrical conductivity to allow high efficiency for transporting electrons to the ions involved in the electrochemical reactions, iii) mechanical and chemical stability, iv) good metal support interaction to improve the intrinsic catalytic activity of the catalyst phase.[10,11] Studied materials are based in oxides and other ceramic, which include  $\text{TiO}_{2n-1}$ , [11]  $\text{TiC}$ ,  $\text{SiC-Si}$ ,  $\text{SnO}_2$  [12,13] and  $\text{SbSnO}_2$  [5].  $\text{SnO}_2\text{-IrO}_2$  mixtures have been extensively investigated for the oxygen evolution reaction in acid environment. Such mixtures have been obtained by thermal decomposition of the corresponding metal salts onto plates of titanium, reported a significant increase in surface area remarkable iridium oxide together with an increase in the surface charge of the mixed oxide in comparison with the pure oxides, reducing the load of the noble metals [3,8,14,15]. The object of present study is the synthesis of a mixed oxide powder with  $(\text{Ir}_x\text{Sn}_y\text{Sb}_z)\text{O}_w$  composition for its use in PEMWE.

## 2. Experimental

### 2.1 Mixed oxide preparation.

A 50 mL of a solution 0.25 M was prepared adding metal precursors ( $\text{H}_2\text{IrCl}_6$ ,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SbCl}_5$ ) in absolute ethanol. This solution was heated at  $50^\circ\text{C}$  in nitrogen atmosphere for 2 h. After this time the solution was calcined at  $450^\circ\text{C}$ , the powder obtained was washed three times with deionized water and dry for 5 h at  $80^\circ\text{C}$ [8],[16–18].

### 2.2 Electrochemical characterization



The electrochemical probes was conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> in a typical three electrodes cell, employing a sulphate electrode (0.63 V vs NHE) as a reference electrode, a platinum mesh as a counter electrode and glassy carbon with a thin layer of ink as a work electrode. The ink consist in powder 95 wt.% and 5 wt.% Nafion (Aldrich) mixture, these were prepared by mechanically mixing vulcan carbon (VC) and IrO<sub>2</sub> and a mechanical mixture of IrO<sub>2</sub> and SbSnO<sub>2</sub>(ATO), both of 50:50 weight of catalyst and support, inks of mixed oxides synthesized by thermal decomposition were prepared with the same proportions of powder and Nafion. Measurements were performed using a potentiostat / galvanostat (EG&G, PAR Versastat 3) and a precision rotor (PINE MSR) for controlling the rotation speed. Cyclic voltammetry (CV) was used to meet the electrochemical profile of synthetic materials, performing sweeps potential of -0.600 V to 0.800 V vs reference electrode at a scan rate 50 mV s<sup>-1</sup>, where the electrolytic cell was saturated with nitrogen. To evaluate the oxygen evolution reaction was employed linear scan voltammetry (LSV) rate of 5 mV s<sup>-1</sup>, a potential range of 0.500 V to 1.000 V vs reference electrode with 1000 rpm rotation rate. Electrochemical impedance spectroscopy were carried out in potentiostatic mode at 1.47 V of potential with an alternate signal amplitude of 10 mV and a frequency limits of 100 kHz and 10 mHz. The shown data are referenced versus normal hydrogen electrode (NHE).

### 3. Results and discussion

#### 3.1 Cyclic voltammetry

The cyclic voltammograms obtained for the supported iridium oxide in the ATO, IrO<sub>2</sub> supported on vulcan carbon and the synthesized composite oxide Ir<sub>x</sub>Sb<sub>0.05(1-x)</sub>Sn<sub>0.95(1-x)</sub>O<sub>2</sub> (x=0.1,0.4), in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> are shown in Fig. 1. The oxide electrodes have the normal iridium oxide shape. The current density (j/ mAcm<sup>-2</sup>) is greater for IrO<sub>2</sub> supported on vulcan carbon, the mixed oxides have similar shape. The off-peak potential for oxygen appears to a potential of 1.40 V for iridium oxide supported on vulcan carbon, 1.42 V form mixed oxide and 1.45 V for IrO<sub>2</sub> supported on antimony doped tin oxide, consistent with that reported[8]. The results show that the synthesis of the mixed oxide by the thermal decomposition promotes rate reaction.



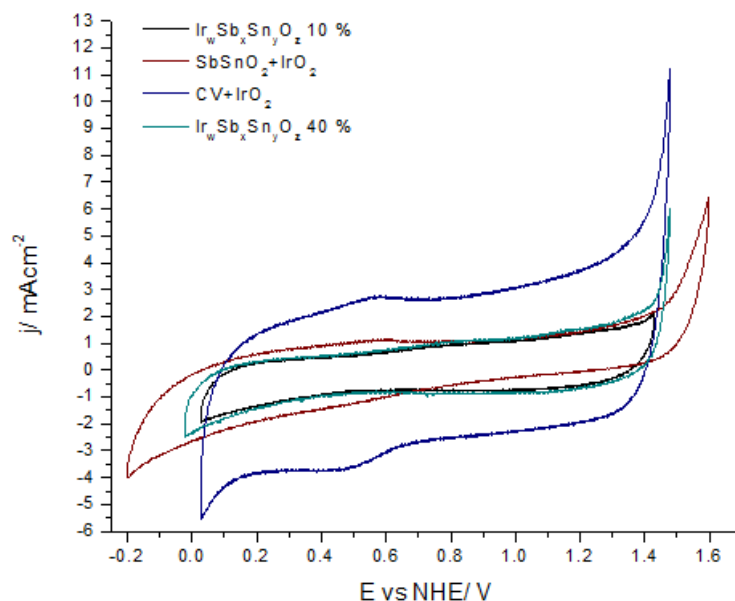


Fig 1. Cyclic voltammogram CV+IrO<sub>2</sub>, Ir<sub>x</sub>Sb<sub>0.05(1-x)</sub>Sn<sub>0.95(1-x)</sub>O<sub>2</sub> (x=0.1, 0.4) and SbSnO<sub>2</sub>+IrO<sub>2</sub> at 50 mV s<sup>-1</sup>.

### 3.2 Linear voltammetry

Linear scan voltammetry was performed for OER for IrO<sub>2</sub> supported in vulcan carbon and ATO, in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 5 mVcm<sup>-1</sup>. Same probes was conducted for mixed oxide Ir<sub>x</sub>Sb<sub>0.05(1-x)</sub>Sn<sub>0.95(1-x)</sub>O<sub>2</sub>, (x= 0.1, 0.4). These test are show in Fig. 2. Its observed that the OER starts at 1.43 V in both mixed oxides, 1.40 V CV+IrO<sub>2</sub> and 1.48 V for SbSnO<sub>2</sub>. Mixed oxide linear voltammogram slope changes with respect to VL of the mechanical mixture of iridium oxide and vulcan carbon, suggesting a change in reaction mechanism. This suggests that the OER is favored when the mixed oxide obtained by thermal decomposition is used as anode. Comparison between the mixed oxide electrodes indicate that, although the oxygen evolution reaction start at similar potential in both electrodes, the current density is higher for the electrode with the highest percentage by weight of iridium.



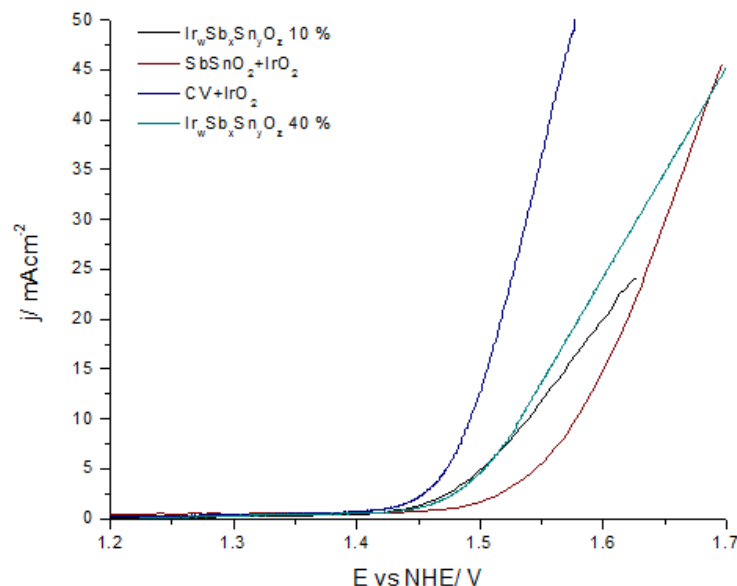


Fig 2. Linear scan voltammogram of CV+IrO<sub>2</sub>, Ir<sub>x</sub>Sb<sub>0.05(1-x)</sub>Sn<sub>0.95(1-x)</sub>O<sub>2</sub> (x=0.1, 0.4) and SbSnO<sub>2</sub>+IrO<sub>2</sub> at 5 mV s<sup>-1</sup>.

In addition above, Tafel plots were drawn from LSV curves for OER after ohmic drop (IRs) correction due to the electrolyte resistance (Rs). This correction was done by subtracting the IR to the applied potential. The Rs values were obtained by electrochemical impedance spectroscopy (EIS) for each electrode. Rs values were in the 3 Ω – 7.5 Ω interval which are mainly attributed to the solution resistance.

In addition to the above, polarization curves were developed from LSV curves for OER, for it, first was made the ohmic drop correction (IRs) due to the electrolyte resistance (Rs). Rs values were obtained by electrochemical impedance spectroscopy (EIS) for each electrode, the values ranged from 0.91 Ω – 4.28 Ω range which is mainly attributed to the resistance of the solution. Fig. 3 shows the Tafel plots for OER for all the electrodes in study, the value of Tafel slope are show for each material. For the mixed oxides, the Tafel slope (b) are 79 mVdec<sup>-1</sup> for x=0.1 and for x=0.4, the Tafel slope has a value of 78 mVdec<sup>-1</sup>, was found that the Tafel slope on Ir–Sn oxide DSA electrodes was 70 mV dec<sup>-1</sup> for iridium contents of 50–100 mol% Ir, and 100–170 for lower iridium contents, [8],[19]. There are several proposed mechanisms which can describe the oxygen evolution reaction in acidic media. According to the above, the following reaction mechanism is proposed[20]:



where S stands for active sites on oxides surface, and S–OH, S–O are two adsorption intermediates. The different Tafel slopes predict which is the rate determining step of reaction (rds). This mechanism predicts the following Tafel slope: 120 mV dec<sup>-1</sup> if (1) rds, 60 mV dec<sup>-1</sup> for (2), 40 mV dec<sup>-1</sup> for (3) and 15 mV dec<sup>-1</sup>. The Tafel slopes close to 60 mVdec<sup>-1</sup> obtained for this materials suggests the dissociation of the surface complex[18][21].



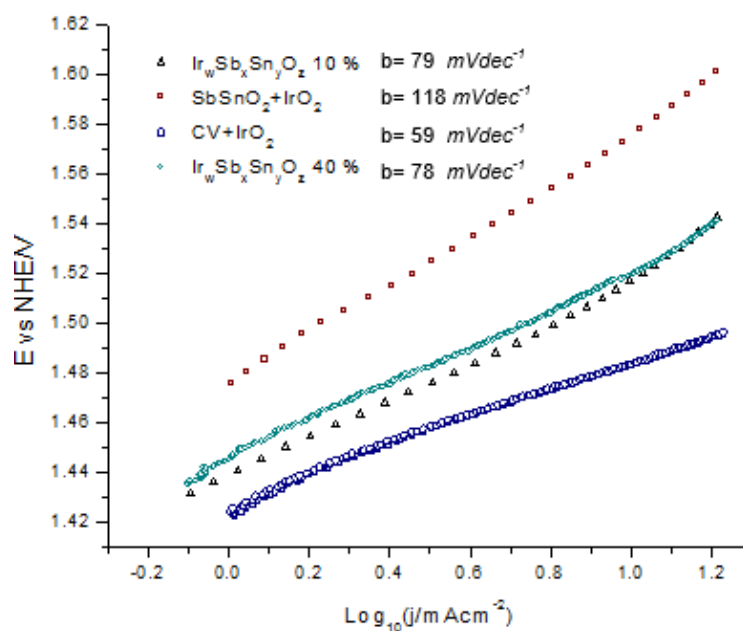


Fig 3. Tafel plots for OER of  $\text{CV} + \text{IrO}_2$ ,  $\text{Ir}_x\text{Sb}_{0.05(1-x)}\text{Sn}_{0.95(1-x)}\text{O}_2$  ( $x=0.1, 0.4$ ) and  $\text{SbSnO}_2 + \text{IrO}_2$  after  $\text{IR}_s$  correction.



### 3.3 Electrochemical impedance spectroscopy

EIS measurements for oxygen evolution was carried out on mixed oxides ( $x=0.1, 0.4$ ) electrodes, in electrochemical cell,  $N_2$  saturated  $0.5\text{ M}$   $H_2SO_4$  solution, at potentiostatic mode with an anodic potential of  $1.47\text{ V}$ . Nyquist plots for mixed oxides are shown in Fig 4. The depressed semicircles presented in that figure were adjusted by EIS Spectrum Analyser to the equivalent circuit presented in Fig 5[22][23].

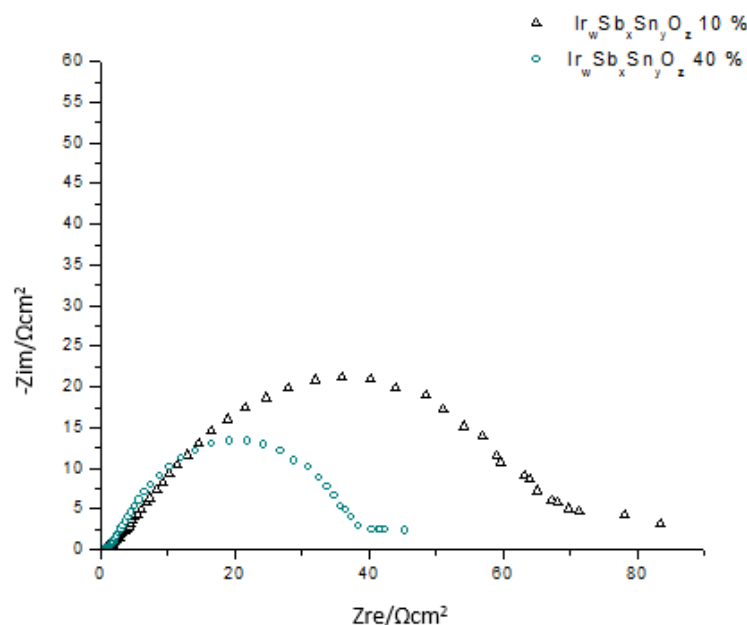


Fig 4. Nyquist plots of  $Ir_xSb_{0.05(1-x)}Sn_{0.95(1-x)}O_2$  ( $x=0.1, 0.4$ ) at anodic potential value of  $1.47\text{ V}$ , in  $N_2$  saturated  $0.5\text{ M}$   $H_2SO_4$  solution.

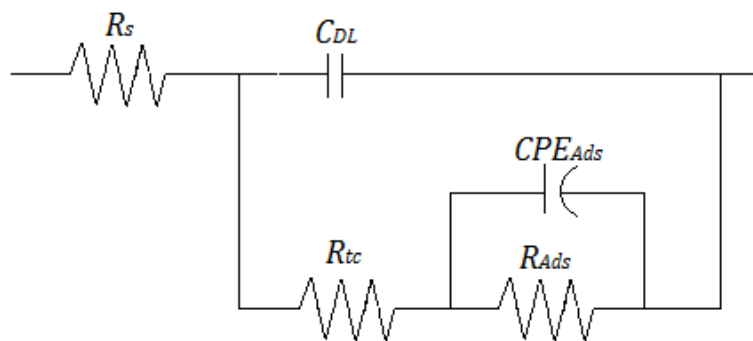


Fig 5. Equivalent circuit used to fit the EIS data for OER on mixed oxide,  $Ir_xSb_{0.05(1-x)}Sn_{0.95(1-x)}O_2$  ( $x=0.1, 0.4$ ) electrodes [22].





Where  $R_s$  is the electrolytic solution resistance,  $R_{tc}$  is the resistance of charge transfer, associated with OER in parallel with the capacitance of double layer ( $C_{DL}$ ),  $R_{Ads}$  and  $CPE_{Ads}$  are the elements associated to adsorption process in OER. The values of  $R_s$  and  $R_{tc}$  calculated for the mixed oxides electrodes are resumed in Table 1 along with other OER kinetic parameter values.

Table 1. Summary of polarisation measurements, EIS probes for OER on mixed oxides  $Ir_xSb_{0.05(1-x)}Sn_{0.95(1-x)}O_2$  ( $x=0.1, 0.4$ ) electrodes.

	$E_{REO}(vsNHE)/V$	$j/mAcm^{-2}$ *1.47 V	$R_s/\Omega cm^2$	$R_{tc}/\Omega cm^2$	$b/mVdec^{-1}$
$Ir_{0.1}Sb_{0.45}Sn_{0.855}O_2$	1.45	2.11	0.22	4.9	79
$Ir_{0.4}Sb_{0.03}Sn_{0.570}O_2$	1.45	5.06	0.19	2	78

The results obtained by EIS are consistent with the results obtained by LSV, where is observed that OER for both mixed oxides are similar, nonetheless current density is greater for the electrode with the highest percentage weight of iridium oxide, which is reflected in the resistance to charge transfer.

#### 4. Summary and perspectives

Electrochemical studies were performed for the OER on mixed oxides electrodes,  $Ir_xSb_{0.05(1-x)}Sn_{0.95(1-x)}O_2$  ( $x=0.1, 0.4$ ), which were obtained from thermal decomposition of metal precursors. Cyclic voltammetry show that oxide electrodes have the normal iridium oxide shape. Linear scan voltammetry show that the mixed oxide is synthesized by thermal decomposition a promising material for use in solid electrolyte electrolyzer, due it has potential for the reaction of oxygen evolution close to that obtained with the use of vulcan carbon as support and iridium oxide as catalyst. Tafel slopes obtained for the electrodes prepared from mechanical mixtures of catalyst and supports give an indication of the reaction mechanism for the oxygen evolution reaction, and its limiting step. The results obtained by EIS are consistent with results obtained using LSV, here the values of the resistance to charge transfer of electrodes were obtained, being higher for electrodes with a lower percentage by weight of iridium.

Subsequently arises perform physicochemical characterization of materials with which will be analyzed the composition, the particle size and the phases present in the mixed oxide is obtained by thermal decomposition.

#### References

- [1] J.A. Turner, A Realizable Renewable Energy Future, Science. 285 (1999) 687–689. doi:10.1126/science.285.5428.687.
- [2] J.A. Turner, Sustainable hydrogen production, Science. 305 (2004) 972–974. doi:10.1126/science.1103197.
- [3] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, P. Saha, et al., Novel (Ir,Sn,Nb)O<sub>2</sub> anode electrocatalysts with reduced noble metal content for PEM based water electrolysis, Int. J. Hydrog. Energy. 37 (2012) 3001–3013. doi:10.1016/j.ijhydene.2011.11.055.
- [4] S.A. Grigoriev, V.I. Porembsky, V.N. Fateev, Pure hydrogen production by PEM electrolysis for hydrogen energy, Int. J. Hydrog. Energy. 31 (2006) 171–175. doi:10.1016/j.ijhydene.2005.04.038.
- [5] J. Xu, Q. Li, M.K. Hansen, E. Christensen, A.L. Tomás García, G. Liu, et al., Antimony doped tin oxides and their composites with tin pyrophosphates as catalyst supports for oxygen evolution reaction in proton exchange membrane water electrolysis, Int. J. Hydrog. Energy. 37 (2012) 18629–18640. doi:10.1016/j.ijhydene.2012.09.156.
- [6] S. Sunde, I.A. Lervik, M. Tsyppkin, L.-E. Owe, Impedance analysis of nanostructured iridium oxide electrocatalysts, Electrochimica Acta. 55 (2010) 7751–7760. doi:10.1016/j.electacta.2009.11.009.
- [7] S. Ardizzone, C.L. Bianchi, G. Cappelletti, M. Ionita, A. Minguzzi, S. Rondinini, et al., Composite ternary SnO<sub>2</sub>–IrO<sub>2</sub>–Ta<sub>2</sub>O<sub>5</sub> oxide electrocatalysts, J. Electroanal. Chem. 589 (2006) 160–166. doi:10.1016/j.jelechem.2006.02.004.
- [8] A. Marshall, B. Børresen, G. Hagen, M. Tsyppkin, R. Tunold, Electrochemical characterisation of Ir<sub>x</sub>Sn<sub>1-x</sub>O<sub>2</sub> powders as oxygen evolution electrocatalysts, Electrochimica Acta. 51 (2006) 3161–3167. doi:10.1016/j.electacta.2005.09.004.





- [9] A. Marshall, B. Børresen, G. Hagen, M. Tsyppin, R. Tunold, Hydrogen production by advanced proton exchange membrane (PEM) water electrolyzers—Reduced energy consumption by improved electrocatalysis, *Energy*. 32 (2007) 431–436. doi:10.1016/j.energy.2006.07.014.
- [10] X.-M. Wang, Y.-Y. Xia, The influence of the crystal structure of TiO<sub>2</sub> support material on Pd catalysts for formic acid electrooxidation, *Electrochimica Acta*. 55 (2010) 851–856. doi:10.1016/j.electacta.2009.09.037.
- [11] P. Paunović, O. Popovski, E. Fidančevska, B. Ranguelov, D. Stoevska Gogovska, A.T. Dimitrov, et al., Co-Magneli phases electrocatalysts for hydrogen/oxygen evolution, *Int. J. Hydrog. Energy*. 35 (2010) 10073–10080. doi:10.1016/j.ijhydene.2010.07.143.
- [12] C. Du, M. Chen, X. Cao, G. Yin, P. Shi, A novel CNT@SnO<sub>2</sub> core–sheath nanocomposite as a stabilizing support for catalysts of proton exchange membrane fuel cells, *Electrochem. Commun.* 11 (2009) 496–498. doi:10.1016/j.elecom.2008.12.034.
- [13] H. Chhina, S. Campbell, O. Kesler, An oxidation-resistant indium tin oxide catalyst support for proton exchange membrane fuel cells, *J. Power Sources*. 161 (2006) 893–900. doi:10.1016/j.jpowsour.2006.05.014.
- [14] M. Rubel, R. Haasch, P. Mrozek, A. Wieckowski, C. De Pauli, S. Trasatti, Characterization of IrO<sub>2</sub>/SnO<sub>2</sub> thin layers by electron and ion spectroscopies, *Vacuum*. 45 (1994) 423–427. doi:10.1016/0042-207X(94)90314-X.
- [15] C.P. De Pauli, S. Trasatti, Composite materials for electrocatalysis of O<sub>2</sub> evolution: IrO<sub>2</sub>+SnO<sub>2</sub> in acid solution, *J. Electroanal. Chem.* 538–539 (2002) 145–151. doi:10.1016/S0022-0728(02)01055-0.
- [16] S. Fierro, A. Kapalka, C. Comninellis, Electrochemical comparison between IrO<sub>2</sub> prepared by thermal treatment of iridium metal and IrO<sub>2</sub> prepared by thermal decomposition of H<sub>2</sub>IrCl<sub>6</sub> solution, *Electrochem. Commun.* 12 (2010) 172–174. doi:10.1016/j.elecom.2009.11.018.
- [17] L. Ouattara, S. Fierro, O. Frey, M. Koudelka, C. Comninellis, Electrochemical comparison of IrO<sub>2</sub> prepared by anodic oxidation of pure iridium and IrO<sub>2</sub> prepared by thermal decomposition of H<sub>2</sub>IrCl<sub>6</sub> precursor solution, *J. Appl. Electrochem.* 39 (2009) 1361–1367. doi:10.1007/s10800-009-9809-2.
- [18] J.-M. Hu, J.-Q. Zhang, C.-N. Cao, Oxygen evolution reaction on IrO<sub>2</sub>-based DSA® type electrodes: kinetics analysis of Tafel lines and EIS, *Int. J. Hydrog. Energy*. 29 (2004) 791–797. doi:10.1016/j.ijhydene.2003.09.007.
- [19] E.N. Balko, P.H. Nguyen, Iridium-tin mixed oxide anode coatings, *J. Appl. Electrochem.* 21 (1991) 678–682. doi:10.1007/BF01034045.
- [20] Y. Matsumoto, E. Sato, Electrocatalytic properties of transition metal oxides for oxygen evolution reaction, *Mater. Chem. Phys.* 14 (1986) 397–426. doi:10.1016/0254-0584(86)90045-3.
- [21] L.M. Da Silva, J.F.C. Boodts, L.A. De Faria, Oxygen evolution at RuO<sub>2</sub>(x)+Co<sub>3</sub>O<sub>4</sub>(1–x) electrodes from acid solution, *Electrochimica Acta*. 46 (2001) 1369–1375. doi:10.1016/S0013-4686(00)00716-7.
- [22] E. Barsoukov, J.R. Macdonald, *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2 edition, Wiley-Interscience, Hoboken, N.J, 2005.
- [23] V. Ávila-Vázquez, J.C. Cruz, M. Galván-Valencia, J. Ledesma-García, L.G. Arriaga, C. Guzmán, et al., Electrochemical study of Sb-doped SnO<sub>2</sub> supports on the oxygen evolution reaction: Effect of synthesis annealing time, *Int. J. Electrochem. Sci.* 8 (2013) 10586–10600.

