

Oxygen evolution reaction of Ti/IrO₂–SnO₂ electrode: a study by cyclic voltammetry, Tafel lines, EIS and SEM

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Abstract. The electrochemical characteristics towards oxygen evolution reaction of thermally prepared Ti/IrO_2 -SnO₂ electrodes were examined. Two electrodes prepared with two different IrO_2 compositions were analysed in Na₂SO₄ electrolyte. Cyclic voltammetry, steady state polarization curves, impedance spectroscopy and open circuit potential were performed to investigate the performance and stability of these electrocatalysts. It has found that the surface electrochemistry of Ti/IrO_2 -SnO₂ anodes are governed by the Ir(III)/Ir(IV) couple. The impedance spectroscopy investigation permitted to propose an equivalent circuit to describe the modifications occurred in different potentials during oxygen evolution reaction. The same equivalent circuit was found to describe both electrodes. Moreover, the double layer capacitance and microstructure analysis reflected that the inner surface makes a large contribution to the electrochemically active surface area of Ti/IrO_2 -SnO₂ anodes. It was found that the stability and the electrocatalytic activity mainly depend on changes in the IrO_2 composition of the electrode and its morphology during oxygen evolution reaction.

Keywords. Oxygen evolution reaction; impedance spectroscopy; electrocatalysts; microstructure.

1. Introduction

Oxygen evolution reaction (OER) on dimensionally stable anodes (DSAs) has been a subject of much interest in the electrochemical industry. An interest in Ti/IrO₂ type DSAs for oxygen evolution has been attracted in the last decades also [1,2]. The advantage of these electrodes as one of the most widely employed OER electrocatalyst lie in their high catalytic activity, stability, extremely high durability, high electrical conductivity and corrosion resistance [1-4]. As an 'active' electrode (electrodes which have low over-potentials for the OER), IrO₂ is believed to be less sensitive to poisoning due to simultaneous oxygen evolution [5]. The electrocatalytic activity of IrO2 electrode can be further improved by controlling the electrode preparation parameters and the appropriate selection of the oxide components as secondary metals [6,7]. Various kinds of these anodes can be developed by mixing with 'non-active' electrode materials such as TiO₂, ZrO₂, Nb₂O₅, SnO₂, Ta₂O₅ and they have been extensively studied as oxygen-evolving anodes [4,8–12].

Electrochemical impedance spectroscopy (EIS) is used as a powerful technique in characterization of electrochemical properties of metallic oxide electrodes. Equivalent circuits were used to describe the influence of each component of the oxide layer on the impedance spectrum. Typical electric circuits are modelled to the oxide electrode elements that describe the ohmic resistance associated with solution and the oxide film, as well as the charge transfer resistance of the processes that occur at the oxide/solution interface [2,13– 15]. Moreover, the superior electrocatalytic properties of an anode material towards oxygen evolution can be achieved by high exchange current density and low Tafel slope. The anode activity depends also on the electrochemically active surface area. As a consequence, investigating novel electrode materials with better electrocatalysis properties and lower overpotential for OER is crucial [6].

Since iridium is expensive and scarce, in this research, alternative electrodes mixed with less expensive electrocatalyst SnO_2 were investigated. In our previous work, it has been found that such electrodes provide better efficiencies in degrading organics dissolved in water, and the electroactive surface area and stability are high [17]. The goal of the present work is to find electrochemical properties of OER that developed Ti/IrO₂–SnO₂ electrode in Na₂SO₄ solution. So far, many researchers have been carrying out a large number of investigations on the works of IrO₂-based DSAs in acidic and alkaline solutions for OER [2,13,15]. However, little work is known about investigation for OER of IrO₂

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type electrodes in neutral solutions [16]. Moreover, better performances in OER will allow the electrode to be used as oxidizing organics in wastewater, even the wastewater contains low amount of chloride ions.

To the best of our knowledge, no published study has investigated the electrocatalytic properties of Ti/IrO_2-SnO_2 electrode in Na_2SO_4 solution. To investigate these changes, the surface properties of IrO_2-SnO_2 system with two different IrO_2 compositions were analysed using the OER as a model reaction in a neutral medium. The electrocatalytic properties of these anodes were investigated in terms of cyclic voltammetry, open circuit potential, linear sweep voltammetry and EIS.

2. Experimental

2.1 Electrode preparation

Electrodes with variable compositions of IrO_2 -SnO₂ active layers were prepared by thermal decomposition method. Since a smooth surface with no oxides or scales is required as the substrate for a uniform and well-adhered deposit, commercial Ti plates with a dimension of 10 mm × 10 mm × 2.5 mm (i.e., an effective geometric area of 2.75 cm²), were pretreated and used as the substrate. The substrates were initially sandblasted. Subsequently chemical treatment was carried out using 5% (w/w) oxalic acid solution for 10 min and 37% (w/w) HCl acid for 5 min, respectively. Then, the substrates were dried at 100°C until they reach a constant weight.

Two different precursor solutions were prepared by dissolving $IrCl_3 \cdot 3H_2O$ in ethanol. The Ir metal concentrations in the precursors were 0.1 and 0.3 M, respectively. 0.1 M Ir coating solution was prepared by dissolving 0.4 g of IrCl₃·3H₂O in 6.18 ml ethanol. Similarly, 0.3 M Ir coating solution was prepared by dissolving 0.8 g of $IrCl_3 \cdot 3H_2O$ in 4.12 ml ethanol. 0.01g of polyethylene glycol (1000 ppm) was added to both precursor solutions. The pretreated substrates were dip-coated in above solutions and the wet coating surfaces were air-dried in 80°C airflow to evaporate solvents. Then, coating layers with different compositions were calcinated in an oven at 450°C for 10 min. Electrodes were washed with distilled water to remove the coated polymer. Subsequently, the second precursor solution, 2.5 mM of Sn, was prepared by dissolving 2.43 ml of Sn (1000 ppm) standard solution in 8.2 ml of isopropanol. Then, it was applied on all the previously coated electrode surfaces. The wet coating surface was then air-dried in 80°C air flow to evaporate solvents and calcinated in an oven at 450°C for 10 min. The entire procedure was repeated till the final coating load of 1 mg cm^{-2} is achieved. After reaching the final coating load, the electrodes were post-backed at 500°C in a muffle furnace for 1 h. Our previous work indicated that incorporating polyethylene glycol to precursor solution with Ir makes pores on the layer and subsequent introduction of precursor solution with Sn leads to better performances [17].

2.2 Microstructure analysis

Morphology of two electrodes was investigated using scanning electron microscope (SEM).

2.3 Electrochemical measurements

Electrochemical parameters related to anodic activity were performed for two electrodes by cyclic voltammetry (CV) in the range of voltage scan from -2.5 to 2.5 V at a 0.1 V s⁻¹ scan rate. To assess the electrode stability of the prepared anodes, open circuit potential (OCP) was performed. Anodic performance was measured by using anodic polarization curves. The EIS measurements were conducted covering the frequency range of 10 mHz-100 kHz in the potential range between 1.2 and 1.35 V. The amplitude of sinusoidal potential perturbation was 5 mV. The impedance data were fitted to appropriate equivalent circuits using Nova (1.10.19) software. All the tests were conducted using potentiostat/galvanostat equipment (Autolab, PGSTAT128N) in a three electrode cell. The electrodes under study were used as the working electrode (WE), titanium plate as the counter electrode (CE) and Ag/AgCl electrode was used as the reference electrode (RE). In all the cases, Na₂SO₄ (0.5 M) was used as the electrolyte and experiments were carried out at room temperature (25°C).

3. Results and discussion

3.1 Microstructure

As shown in figure 1a and b, both anodes exhibit a typical porous 'cracked mud' structure in some flat area. This morphology with dried-mud cracks is very classical for thermally prepared DSAs and those cracked mud are oxide particles [11]. It is observed that the coating morphology is affected by the concentration of the precursor solution. As a matter of fact, coatings obtained with diluted solution (0.1 M of Ir) were less cracked while those obtained with a solution of 0.3 M Ir were more cracked.

3.2 Cyclic voltammetry and voltammetric charge analysis

Figure 2 shows the voltammetric curves of two Ti/IrO₂–SnO₂ anodes in 0.5 mol dm⁻³ of Na₂SO₄ at a scan rate of 0.1 V s⁻¹. For these fresh anodes, well-defined peaks were found at 0.8 and 1.2 V. The broad peak observed at 0.8 V is attributed to the surface redox transition of Ir(III)/Ir(IV), while the other peak at 1.2 V is associated with the Ir(IV)/Ir(VI) transition [18,19]. This means that the surface electrochemistry of the electrode is governed by the active component of IrO₂. It is in a good agreement with the production of an oxide layer with a high degree of purity [19]. With the increase of Ir concentration, the voltammetric curve shows similar shape, but higher current density. Aromaa *et al* [20] also reported that the current densities increase with the increasing IrO₂ concentration.



Figure 1. Scanning electron microscopic images of electrodes. (a) Electrode coated with (a) 0.1 and (b) 0.3 M Ir precursor solutions.



Figure 2. Cyclic voltammograms of (- -) 0.1 M Ir-coated electrode, (---) 0.3 M Ir-coated electrode. Scan range = 2.5 to -2.5 V, scan rate = 0.1 V, electrolyte = 0.5 M of Na₂SO₄, reference electrode = Ag/AgCl. Arrow shows the direction of CV for 0.1 M Ir-coated electrode.

The main electrochemical reactions which were occurred in neutral Na_2SO_4 solution are shown in equations (1) and (2) [21].

$$IrO_2 \cdot 2H_2O + e^- + Na^+ \rightarrow Na^+ [IrO(OH)_2 H_2O]^-, (1)$$

$$IrO_2 \cdot 2H_2O + e^- + H^+ \rightarrow IrO(OH) \cdot 2H_2O, \qquad (2)$$

where the Na ion probably has a transient existence within the reduced form of IrO_2 , being replaced by H⁺ with time and IrO_2 is in its hydrous form.

The change in the anodic voltammetric charge density (q_a) obtained from the voltammograms are shown in table 1. The voltammetric charge was determined by integration over the whole potential region *vs.* Ag/AgCl. Voltammetric charge density is an indication of the electrochemically active sites present on the surface of the coating. It is seen that electrode coated with 0.3 M Ir has higher charge compared to that of

Table 1. Anodic voltammetric charge density (q_a) obtained from the voltammograms of the Ti/IrO₂–SnO₂ electrodes.

Composition	Charge density/mC cm^{-2}		
0.1 M Ir	67.93		
0.3 M Ir	102.80		

the electrode coated with 0.1 M Ir. It can be speculated that this difference in charge correlates to more defective/cracked microstructure of electrode coated with 0.3 M Ir due to its higher IrO_2 content. Scanning electron micrographs further confirmed the above speculation (figure 2). Therefore, it is clear from these charges that more electrochemically active sites are present and a large surface area is available for these electrodes.

3.3 Polarization behaviour

OER on the Ti/IrO2-SnO2 anode surface was studied by polarization curves under quasi-steady-state conditions. Results obtained for two electrodes are presented in figure 3. Tafel coefficients obtained in the low and high overpotentials are presented in table 2. Tafel lines show two slopes and the slope becomes increasingly steep in the high overpotential region than in the low overpotential region. It can be seen that the Tafel slope is $23.6 \text{ mV} \text{ dec}^{-1}$ for 0.1 Mcoated electrode and 17.7 mV dec⁻¹ for 0.3 M coated electrode in the low current density region. With increasing Ir content, in the high current density region, this slope has become increasingly steep from 158.9 mV dec⁻¹ for 0.1 M coated electrode to 116.6 mV dec⁻¹ for 0.3 M coated electrode. This increment in the high current density region or high overpotential region is usually attributed to the gas bubble formation and pore clogging. This in turn may block some electrochemically active surface area or change electrochemical reaction mechanism [3,22]. There are several proposed mechanisms which can describe the oxygen evolution reaction in acidic media. The typical values of two slopes in OER for IrO2-based oxide electrodes are reported as 60 mV dec⁻¹ in low overpotential region and 120 mV de⁻¹ in high overpotential region in H_2SO_4 solution [2,23]. However, Tafel slope values which were obtained in this research are different from the reported literature in low overpotential region. Since Tafel slopes indicate the electrocatalyst quality,



Figure 3. Steady-state polarization curves performed in 0.5 mould m^{-3} of Na₂SO₄. (- - -) 0.1 M and (---) 0.3 M Ir-coated electrodes. Scan rate = 0.1 mV s⁻¹.

Table 2. Tafel coefficients at low (b_1) and high (b_2) overpotentials Ti/IrO₂–SnO₂ electrodes prepared by different Ir concentrations in 0.5 mould m⁻³ Na₂SO₄.

Composition	$b_1 (\mathrm{mV}\mathrm{dec}^{-1})$	$b_2 \text{ (mV dec}^{-1})$		
0.1 M Ir	23.6	158.9		
0.3 M Ir	17.7	116.6		

lower value of Tafel slope represents faster kinetics of the reaction [24]. Moreover, agglomerates can be generally found that IrO₂-coated titanium anodes derived from conventional thermal decomposition and has been reported in the literature [25]. In the case of our anode, the electrocatalysts may consist of agglomerates which may have different reaction sites. Therefore, different rate-determining steps for different reaction sites can coexist and the measured Tafel slope may represent an average. Therefore, it is unclear in this case which mechanism is operating on these electrodes and further research in this context can be interesting.

The Tafel slope of 0.3 M coated electrode is 116.61 mV dec⁻¹, which is close to 2.303 (2RT/F). In addition, it has been reported that OER on the thermal IrO₂ in neutral solution is difficult [3,26]. Similar behaviour of OER with two Tafel slopes has been reported for IrO₂–Ta₂O₅ electrodes in 0.5 mould m⁻³ of Na₂SO₄ [3]. The other value of the Tafel slope in high overpotential region (158.9 mV dec⁻¹) is also not complying with the reported standard values. This suggests that the mechanism is presumably a composite one. Additionally, since change in Tafel slope represents a difference in electrochemical reaction mechanism, it can be suggested that these two electrodes have different mechanisms.

3.4 Electrochemical impedance spectroscopy (EIS)

In the study of Ti/IrO₂–SnO₂ as a porous electrode, it is important to identify the main electroactive processes in different domains of applied voltage. In addition, assessing the effects of the transport of electroactive species and reactivity of the catalytic surface are important. EIS is a good tool for obtaining such information, as EIS enables the analysis of electrochemical structures and catalytic activities on the oxide matrix and their interface of the DSAs. Figure 4a and b shows the EIS patterns of the Ti/IrO₂– SnO₂ electrodes with two different IrO₂ concentrations under



Figure 4. Nyquist plots of Ti/IrO₂–SnO₂ electrodes in 0.5 mould m^{-3} Na₂SO₄ at different potentials: (**a**) 0.1 M and (**b**) 0.3 M Ir-coated electrodes. (**II**) 1.25 V and (**A**) 1.3 V *vs.* Ag/AgCl electrode.



Figure 5. Bode plots of of Ti/IrO₂–SnO₂ electrodes in 0.5 mould m^{-3} Na₂SO₄ at different potentials (**a**) 0.1 M and (**b**) 0.3 M Ir-coated electrodes. (**I**) 1.25 V and (**A**) 1.3 V *vs.* Ag/AgCl electrode.



Figure 6. Equivalent circuit model for EIS analysis of Ti/IrO₂–SnO₂ electrodes.

oxygen evolution reaction at different anodic potentials in 0.5 mould m⁻³ Na₂SO₄ solution. It can be observed in both anodes (separately) that the complex plane in the whole frequency, phenomenally domain, shows only one capacitance arc, decreasing with the electrode potential. Moreover, as can be clearly seen, the capacitive region shifts to higher frequencies as the IrO₂ concentration decreases, indicating a lower capacitance value.

The fit results of Bode plots with the above equivalent circuit are also shown in figure 5a and b. The deviation between the experimental data and the simulation result is small, suggesting that the used equivalent circuit is suitable to represent the electrochemical system. The fitting of equivalent electrical circuits (EEC) to the EIS results were performed to establish the possible differences between the physical and chemical characteristics of both electrodes when in contact with a liquid phase. The equivalent circuit $[LR_s(Q_{dl}[R_{ct}(Q_2R_2)])]$, shown in figure 6, has been used to fit the EIS data using Nova 1.10. Similar impedance parameters were obtained from fitting the experimental data to the $R_s(R_2Q_2)(R_{ct}Q_{dl})$ circuit, for platinum activated IrO₂/SnO₂ nanocatalysts [27].

The inductance (*L*) is resulted from the wiring and measuring equipment components. R_s is the solution resistance between the reference and working electrodes, while R_{ct} is the charge transfer resistance for oxygen evolution reaction. The pseudocapacitance used in the model is represented by a constant phase element (CPE) and its impedance is represented by the expression given in equation (3) [28,29]:

$$Z_{\rm CPE} = \frac{1}{Q \left(i\omega\right)^n},\tag{3}$$

where ω is the angular frequency, Q is a frequency independent constant and n is a power factor related to the depression angle. n is in the range varying from 0 to 1.0 and directly associated with the dispersive character of the system. An n value of zero corresponds to a pure resistor.

Here the constant phase angle elements Q_2 and Q_{dl} are used to replace the film capacitance and double layer capacitance for a better simulation of the spectra due to the depression effect, which is attributed to the roughness and inhomogeneity of the electrode surface. R_2 and Q_2 are resistances and pseudocapacitances associated with two solidstate surface redox transitions, which are possibly due to electrochemical porosity occur at the electrode material. The use of pseudo-capacitances instead of pure capacitors is due to the heterogeneous nature of the surface. Both CPE parameters depend on the electrode potential and when *n* values are close to 1, the value of Z_{CPE} approaches the impedance value of a conventional capacitor.

EEC parameters obtained through fitting are listed in table 3. It is not exactly clear the source of the small inductive element, L, possibly resulting from testing wiring, electrical connections and measuring equipment components. The value of this electronic originated inductance was reported as about 1 μ H, which is in good agreement with our fitting result [1,11]. Da Silva *et al* [30] have suggested that the main cause of the inductance can be due to the properties

Table 3. The fitting EIS parameters of Ti/IrO_2 -SnO₂ electrodes prepared by different Ir concentrations at 1.3 V.

Anode	L (µH)	$R_{\rm s}$ (Ω)	Q _{dl} (µ Mho)	$R_{\rm ct}$ (Ω)	n
0.1 M Ir-coated anode	212	17.4	2.65	14.0	0.895
0.3 M Ir-coated anode	182	16.9	2.68	10.7	0.940

of porous nature of the thermally prepared metallic oxide electrode materials.

The change of charge-transfer resistance (R_{ct}) for OER with the composition of anodes was measured at 1.3 V potential, as shown in table 3. R_{ct} was slightly decreased from 14.0 to 10.7 Ω cm⁻² with increasing IrO₂ content, showing the slight enhancement of the catalytic activity of 0.3 M Ircoated anode. Conversely, the reciprocal of R_{ct} represents the electrochemical activity of OER on the surface of the anode. The $R_{\rm ct}$ for 0.1 M coated anode is 0.093 Ω cm⁻², which is much higher than the other anode $(0.071 \ \Omega \ cm^{-2})$. This indicates its poor electrochemical activity. This is consistent with the results of polarization measurement. The film resistance, $R_{\rm s}$, is originated from both the mixed metal oxide coating and the interlayer between the oxide coating and the substrate. The change of the oxide film resistance with two compositions of Ti/IrO2-SnO2 anodes show that the film resistance dropped slightly from 17.4 to 16.9 Ω , when coated Ir content increased from 0.1 to 0.3 M.

As shown in table 3, n values of both anodes are close to 0.9-1, which suggests that the CPE for oxygen evolution on Ti/IrO₂-SnO₂ anodes has the nature of a capacitor. Moreover, the Q_{dl} can be taken approximately as the double layer capacitance C_{dl} , which is also related to the electrochemically active surface area of the oxide coating [14]. However, the values of C_{dl} of both anodes at that potential are almost similar and do not reflect the increment of electrochemically active surface area. This means inner surface makes a large contribution to the electrochemically active surface area of Ti/IrO₂-SnO₂ anodes. However, the cyclic voltammetry study showed that 0.3 M Ir-coated anode has more IrO₂ agglomerates and hence a large electrochemically active surface area. This may be due to the fine crystallites which produce more grain boundaries to enlarge the inner surface area.

The change in double layer capacitance, C_{dl} , as a function of the applied potential is shown in figure 7. At 1.2 V, C_{dl} shows its maximum and then it suddenly drops with increasing potential. It is interesting to observe that its maximum coincides with the peak potential, corresponding to the Ir(IV)/Ir(VI) solid-state redox transitions, observed in the cyclic voltammograms of both anodes. Moreover, it is clearly seen that C_{dl} depends on potential as well as composition. The increment of IrO₂ content in the 0.3 M coated anode resulted in an increase in the C_{dl} value at 1.2 V. Lassali *et al* [14] also observed that the higher C_{dl} value at 1.2 V and a maximum at around 0.9–1.0 V/RHE, corresponding to the Ir(III)/Ir(IV) solid-state redox transitions.



Figure 7. Double layer capacitance C_{dl} as a function of the potential of Ti/IrO₂–SnO₂ electrodes. (() 0.1 M and (\diamond) 0.3 M Ir-coated electrodes.



Figure 8. Open circuit potential of different Ti/IrO_2-SnO_2 electrodes. (- - -) 0.1 M and (—) 0.3 M Ir-coated electrodes.

3.5 Open circuit potential (OCP)

From a practical point of view, electrode stability is always the main concern. Open circuit potential (OCP) measurements were carried out to assess the stability of the anodes under investigation. Figure 8 shows the OCP curves for both anodes immersed in 0.5 M of Na₂SO₄ solution at 25°C. The 0.3 M coated electrode has -0.74 V OCP value, while 0.1 M coated electrode has -0.82 V OCP value. OCP values of both anodes is negative, since surface of IrO₂ is negatively charged. The reason is due to the zero charge of IrO₂ is less than 1 in Na₂SO₄ solution. Alves *et al* [15] observed similar negative values and these values were also dependent on the composition. Moreover, 0.3 M coated anode stabilizes quickly around a higher stationary value than 0.1 M coated anode. This stable potential occurs with the oxidation of the surface of electrode. OCP measurements performed were also in agreement with other results.

4. Conclusions

The surface electrochemistry of Ti/IrO₂–SnO₂ anodes are governed by the Ir(III)/Ir(IV) couple. Ti/IrO₂–SnO₂ anode with 0.3 M Ir has both the largest electrochemically active surface area and electrochemical activity. This is due to the more defective/cracked microstructure of electrode coated with 0.3 M Ir, due to its higher IrO₂ content.

The Tafel slope of 0.3 M coated electrode is 116.61 mV dec^{-1} , close to 2.303 (2RT/F) in high overpotential region, while other electrode has Tafel slope of 158.9 mV dec^{-1} . Therefore, it is unclear in this case which mechanism is operating on these electrodes.

The equivalent circuit that matches our experimental data in terms of impedance measurements is $[LR_{\rm s}(Q_{\rm dl}[R_{\rm ct}(Q_2R_2)])]$. $R_{\rm ct}$ was slightly decreased from 14.0 to 10.7 Ω cm⁻² with increasing IrO₂ content, showing the slight enhancement of the catalytic activity of 0.3 M Ir-coated anode. In the range of potentials investigated here, both CPEs for oxygen evolution on Ti/IrO₂–SnO₂ anodes have the nature of a capacitor. However, the values of $C_{\rm dl}$ of both anodes at 1.3 V potential are almost similar and do not reflect the increment of electrochemically active surface area. This shows that the inner surface makes a large contribution to the electrochemically active surface area of Ti/IrO₂–SnO₂ anodes.

It can be seen that OCP of 0.3 M coated electrode is -0.74 V, while 0.1 M coated electrode is -0.82 V. This analysis also permits to conclude that changes in the IrO₂ composition of the electrode during OER, affect the stability.

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