



# Surface determination and electrochemical behavior of IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings in oxygen evolution reaction application

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## ABSTRACT

Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> anodes were prepared using a sol-gel route, followed by thermal decomposition. X-ray diffraction (XRD), field emission-scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM) analysis and voltammetric charges calculation were performed to explore the surface properties of the coating. The electrochemical behavior of the anodes were investigated by cyclic voltammetry (CV), linear sweep voltammogram (LSV), Tafel lines and electrochemical impedance spectroscopy (EIS) measurements. The long-term stability of the anodes were evaluated using accelerated life test (ALT). It indicated that the compositions of the coating are rutile-type IrO<sub>2</sub>, RuO<sub>2</sub> and IrO<sub>2</sub>-RuO<sub>2</sub> solid solution. SiO<sub>2</sub> existed in an amorphous state in the ternary oxide coating. The IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings with compact structure and a large amount of acerosse crystals of the IrO<sub>2</sub>-RuO<sub>2</sub> solid solution dispersing were detected by FESEM analysis. The generation of the acerosse crystals significantly increased the surface area that increased the electrocatalytic activity of the coating. The active surface area of the coating was "outer" active surface dominated. The rate-determining step of the coating for oxygen evolution reaction in sulphuric acid solution can be regarded as the rearrangement of the intermediate. An increase of Ru content can improve the electrocatalytic activity, however, decrease the service lifetime of the anodes. The anode with a molar ratio of Ir:Ru:Si = 9:21:70 is most suitable for OER due to its high electrocatalytic activity, a certain lifetime and low cost.

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## 1. Introduction

Oxygen evolution reaction (OER) as a counter reaction plays a key role for the water electrolysis, organic synthesis and metal electrowinning [1–6]. The OER is a complex multistep reaction, which requires a considerably large overpotential to the actual process that distinctly reduces the process efficiency. Noble metallic oxides such as RuO<sub>2</sub> and IrO<sub>2</sub> have attracted intensive attention due to their high electrocatalytic activity for OER [7,8]. However, their application is limited by low service life in aggressive aqueous solutions and high cost [9]. An ongoing aim of electrocatalytic research is to increase the electrocatalytic activity and stability while reducing the cost.

OER on the dimensionally stable anodes (DSA) has been a subject of interest due to their low over-potential and inert properties [10–12]. The electrochemical properties of the electrodes are

related to both the active surface area and the intrinsic catalytic nature [13,14]. The active surface area is determined by the morphology of the oxide coating, while the intrinsic catalytic nature can be attributed to the active components. To modulate the electrochemical properties of the electrodes, the electrochemical active components are generally used together with other "non-active" stabilizers, such as SnO<sub>2</sub>, Sb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> to form a mixed oxide coating [15–18]. Among the mixed oxide coatings, a composition of IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> has been reported to be the most suitable active coating for OER due to its high electrocatalytic activity and in particular its high stability in aggressive aqueous solutions [19]. The active component IrO<sub>2</sub> and the inert component Ta<sub>2</sub>O<sub>5</sub> can form a stable solid solution that prolong the service life of the electrode [20].

Silica is a group IV oxide with the properties of high stability in aggressive aqueous solutions, low cost and homogeneous dispersion when mixed with other metal oxides. Zhang et al. [13] explored the electrocatalytic activity of the IrO<sub>2</sub>-SiO<sub>2</sub> binary oxide coatings. It indicated that the electrocatalytic activity of the Ti/IrO<sub>2</sub> amode can be improved by adding silica, which is attributed to an

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increase of active surface area. Moreover, an improvement of service life of the Ti/IrO<sub>2</sub> anode by incorporating an appropriate amount of silica was reported by Wang et al. [21]. It can be concluded that silica is a promising modifier for mixed metal oxide coatings.

Both IrO<sub>2</sub> and RuO<sub>2</sub> are rutile-type oxides. The ionic radii of Ru<sup>4+</sup> and Ir<sup>4+</sup> are 0.076 nm and 0.077 nm, respectively, which are very similar. The IrO<sub>2</sub>-RuO<sub>2</sub> mixed binary oxide system can form a rutile-type solid solution during the calcining process. According to the study of Mazhari Abbasi et al. [19], the formation of the rutile-type IrO<sub>2</sub>-RuO<sub>2</sub> solid solution can improve the electrocatalytic activity of the IrO<sub>2</sub>-based and the stability of the RuO<sub>2</sub>-based electrodes.

In the present work, IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings with different molar ratios of Ir to Ru were coated on titanium substrates using a sol-gel route, followed by thermal decomposition. The surface properties of the ternary oxide coatings were characterized using X-ray diffraction (XRD), field emission-scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM) analysis and voltammetric charges calculation. The electrochemical behavior of the anodes were investigated using cyclic voltammetry (CV), Linear sweep voltammogram (LSV), Tafel lines and electrochemical impedance spectroscopy (EIS) measurements. The service life (SL) of the anodes were evaluated using accelerated life test (ALT).

## 2. Experimental

### 2.1. Electrodes preparation

To prepare Ti-coated anodes, Ti plates with a dimension of 10 mm × 10 mm × 1 mm were used as substrates. The Ti plates were pretreated by means of degreasing in an alkaline solution at 60 °C for 30 min, chemical etching in 10 wt.% oxalic acid at 90 °C for 2.5 h and cleaning with an ultrasonic cleaner in deionized water for 10 min. Anodes with IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings coated were prepared using a sol-gel route, followed by thermal decomposition. H<sub>2</sub>IrCl<sub>6</sub>, RuCl<sub>3</sub> and tetraethoxysilane (TEOS) were mixed directly to form a gel. The obtained gel was dissolved in 1:1 vol ratio N-butyl alcohol and iso-propanol solution to get a sol solution. The molar ratios of Ir:Ru:Si were identified as 9:21:70 and 21:9:70, respectively. The concentration of the TEOS was 0.14 mol L<sup>-1</sup> and the concentration of the RuCl<sub>3</sub> and H<sub>2</sub>IrCl<sub>6</sub> ranged from 0.018 to 0.042 mol L<sup>-1</sup>. The obtained sol solution was painted on the Ti substrate repeatedly. After each painting step, the wet-coated surface was dried at 120 °C for 15 min and then calcined at 500 °C for 15 min. This procedure was repeated 25–30 times. Finally, the coated samples were calcined at 500 °C for 1 h. The oxide coating loaded on the Ti substrate was about 1.5 mg cm<sup>-2</sup>.

### 2.2. Mineralogical and microstructure characterization

The mineralogical composition of the ternary oxide coatings were measured using XRD and EDS analysis. XRD measurements were performed with a continuous scanning device using Cu-K $\alpha$  radiation at 100 mA and 40 kV, a scanning velocity of 10° 2 $\theta$ /min, and a 2 $\theta$  range of 10–90°. The obtained XRD patterns were analyzed using Jade 6.0 which is a mineralogical analysis software based on the PDF-2004 mineralogical database. The surface morphology of the ternary oxide coating were detected using FESEM and AFM measurements.

### 2.3. Electrochemical measurements

The electrochemical measurements were carried out in 0.5 mol L<sup>-1</sup> sulphuric acid solution at a temperature of 25 °C using

the CHI660E electrochemical workstation. The Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> anode with a working area of 1.0 cm<sup>2</sup> was used as a working electrode (WE), a platinum plate was used as a counter electrode (CE). The reference electrode (RE) used in this work was a saturated calomel electrode (SCE). Linear sweep voltammogram (LSV) plots were obtained at a scan rate of 5 mV s<sup>-1</sup>. Cyclic voltammetry (CV) measurements were carried out between 0 and 1.2 V vs. SCE with different potential scan rates between 100 and 5 mV s<sup>-1</sup>. The interval of the scan rate was identified as 10 mV s<sup>-1</sup>. The ohmic drop was compensated by EIS measurements. EIS measurements were performed in the frequency range of 10<sup>5</sup> to 10<sup>-1</sup> Hz. The AC amplitude used in EIS measurement was 5 mV root mean squared. The impedance data obtained from the EIS measurements were analyzed using ZSimpWin software. To explore the long-term stability of the anode, ALT was carried out at a constant current density of 2 A cm<sup>-2</sup> in 0.5 mol L<sup>-1</sup> sulphuric acid solution. The service lifetime of the anode was determined when the voltage increased for 5 V as compared with the initial value.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1 gives the XRD patterns of the Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> anodes with different molar ratios of Ir:Ru:Si. IrO<sub>2</sub> and RuO<sub>2</sub> with rutile-type could be observed in the XRD patterns. The deviation of the peaks of IrO<sub>2</sub> and RuO<sub>2</sub> indicated that a solid solution of IrO<sub>2</sub> and RuO<sub>2</sub> with rutile-type was formed during the calcining process [19]. The generation of the rutile-type solid solution may improve the electrocatalytic activity and stability of the RuO<sub>2</sub>-based and IrO<sub>2</sub>-based coatings for OER. Metallic Ti can be observed at about 41°, 53° and 72°. The diffraction peaks of SiO<sub>2</sub> were not detected in the XRD patterns, indicating that SiO<sub>2</sub> existed in an amorphous state in the ternary oxide coating.

### 3.2. FESEM analysis

Fig. 2 gives the FESEM analysis of the Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> electrodes. The IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings with compact structure and fine crystals dispersing could be observed over the whole molar ratios range (Fig. 2 (a)–(c)). To further explore the surface morphology of the ternary oxide coating, FESEM analysis were performed at higher magnification and shown in Fig. 2 (d)–(f). As shown in Fig. 2(d)–(f), the acerosed crystal with a dimension of 70–110 nm could be observed on the IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> ternary oxide coatings. The dimension of the acerosed crystal was unchanged with the variety of the molar ratios of Ir to Ru. According to the EDS analysis, the acerosed crystal was the IrO<sub>2</sub>-RuO<sub>2</sub> solid solution.

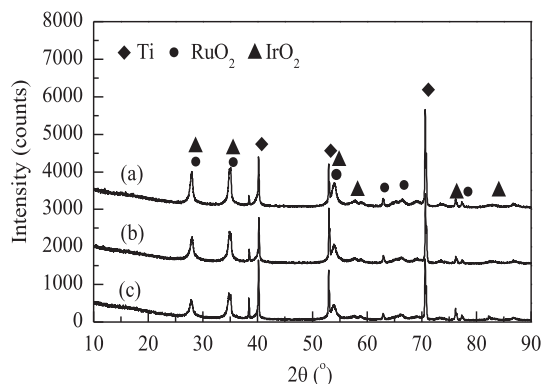


Fig. 1. XRD patterns of the Ti/IrO<sub>2</sub>-RuO<sub>2</sub>-SiO<sub>2</sub> anodes (a) Ir:Ru:Si = 9:21:70, (b) Ir:Ru:Si = 15:15:70, (c) Ir:Ru:Si = 21:9:70.

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