An investigation of the effect of RuO$_2$ on the deactivation and corrosion mechanism of a Ti/IrO$_2$ + Ta$_2$O$_5$ coating in an OER application

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A B S T R A C T

This article describes the investigation into the effect of RuO$_2$ on the deactivation and corrosion mechanism of Ti/IrO$_2$ + Ta$_2$O$_5$ coating in a sodium sulphate solution. Mixed metal oxide coatings within the composition, included in IrO$_2$ + RuO$_2$ + Ta$_2$O$_5$ with different percentages of RuO$_2$ (10, 30 and 50 wt.%) on the titanium substrate, were prepared by thermal decomposition of a chloride precursor mixture at 480 °C. Surface morphology and microstructure of the coatings, were investigated by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Grazing Incidence X-Ray Diffraction (GIXRD) analysis.
The systematic study of the electrochemical properties and corrosion behavior of these coatings was performed by cyclic voltammetry (CV), Accelerated Life Time test (ALT) and Electrochemical Impedance Spectroscopy (EIS). The results showed that the uniform dissolution of the active surface layers was the main mechanism for deactivation of the electrodes, especially the anode with 30 wt.% RuO$_2$. Also, adding RuO$_2$ up to 30 wt.% to the binary coating, because of the increase in active surface area and formation of the solid solution structure between ruthenium and iridium oxides, helped to improve performance and increase the working life of the anode.

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1. Introduction

Nowadays, mixed metal oxide anodes (MMO), are widely used in different industrial applications, because of their excellent characteristics, as alternatives to the old type anodes such as graphite. Some of the important applications of these anodes (MMO anodes) in a variety of electrochemical processes are:

1. Chlorine generation in the chlor-alkali industry [1,2]
2. Industrial wastewater filtration [3,4]
3. Electrowinning [5,6]
4. Fuel cells [7]
5. Cathodic protection [8]
6. Electrochemical oxidation [9,10] and
7. Ozone generation by the electrochemical method [11].

Theses anodes have a low wear rate (3 to 6 mg/A year in all currents and frequencies). In addition, these anodes are highly resistant to erosion and suitable for applications in a variety of environments [12]. Another important feature is that their performance can be improved by optimizing the process of preparing an appropriate anode. Dimensionally stable anodes are made up of two main parts: the substrate and the coating. Valve metals (Ti, Zr, Nb, Ta) and their alloys, copper or steel are introduced as metal substrates [13], but titanium is essential

because of appropriate costs and suitable mechanical and chemical stability [14,15]. Un-coated titanium, however, is not suitable for use as a substrate since the surface of the titanium would oxidise and the titanium would soon cease to function as an anode. Therefore, the use of an electro-catalytic coating is essential in order that the titanium can continue to function. The coating includes:

a) Metals of the platinum group, oxides of metals of the platinum group and mixtures or solid solutions of them as the electro-catalytic part
b) Tin oxide, platinum, metals and oxides of the platinum group as the stabiliser
c) One or more oxides of a valve metal which increases the conductivity [16].

Among the oxides that are commonly used in the oxide coating, RuO$_2$, IrO$_2$ and Ta$_2$O$_5$ with high conductivity and electrochemical activity, are very popular in the oxygen evolution industry as electro-catalysts [17].

It has also been reported [18–21] that a mixed metal oxide anode with a composition of IrO$_2$–Ta$_2$O$_5$ is by far the best anode for oxygen evolution. Its main advantage is its technological ability to support oxygen evolution in a severe acid media while preserving its catalytic activity and good dimensional stability [6,22,23]. However, considering the high price of iridium oxide, on the one hand, and the role of ruthenium oxide as an active oxide in oxygen evolution [6] on the other, adding the ruthenium oxide to the coating is recommended as it will reduce the
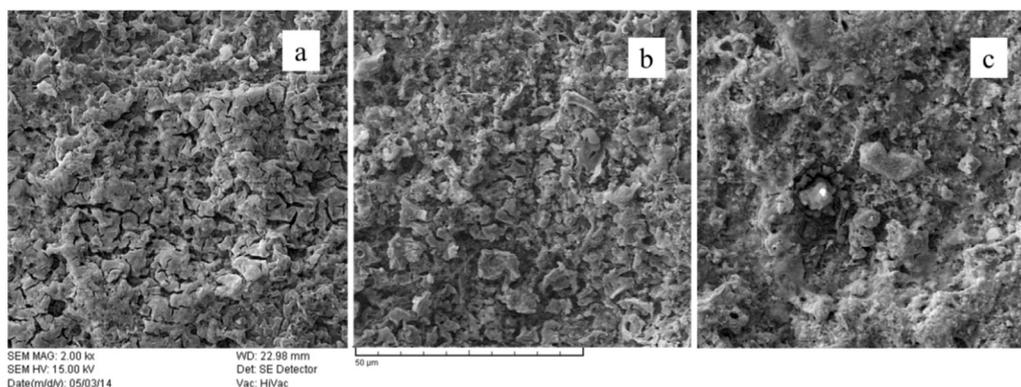
Fig. 1. Scanning Electron Microscope image of the mixed metal oxide coating a) A(10 wt.% RuO$_2$), b) B(30 wt.% RuO$_2$) and c) C(50 wt.% RuO$_2$) before ALT.

costs of production and achieve more favorable electrochemical properties.

Deactivation of anodes is one of the big problems in their operation, which can occur in the coating from dissolution or passivation of the substrate [24]. Referring to the mud cracked morphology which is formed due to the presence of ruthenium oxide on the surface of mixed metal oxide anodes, its content should be such that the resulting morphology doesn't cause the anode to be deactivated too soon. Therefore this should be checked during the anode operation. Nowadays, electrochemical impedance is one of the best techniques used in the study of electrochemical behavior of various materials, and this has been used as part of this study into the corrosion behavior of the samples along with other tests.

2. Experimental

In order to make an anode, a Ti (Gr 2) sheet with a thickness of 3 mm was sandblasted and subsequently degreased in an alkaline solution at 60 °C with an ultrasonic cleaner, at a frequency of 20 KHz. After rinsing, the substrate was chemically etched in a 5 vol.% hydrofluoric acid solution for 3 min. The samples were then rinsed and pickled in 10 wt.% oxalic acid at 80–90 °C for 2.5 h.

Anodes with a composition of IrO$_2$-RuO$_2$-Ta$_2$O$_5$ (with constant Ta$_2$O$_5$ and rather than increasing quantity of RuO$_2$ in the amount of A = 10, B = 30, C = 50 wt.%, the IrO$_2$ was reduced) were prepared by the standard technique of thermal decomposition of the chloride precursors inherent in H$_2$IrCl$_6$, RuCl$_3$, and TaCl$_5$. HCl was used for dissolving the precursors containing Ir and Ru, and C$_2$H$_5$OH was used for dissolving tantalum chloride. The prepared sol was painted on the substrate repeatedly. After each painting step, the layer was dried at 150 °C for 7 min and then calcined at 450 °C for 7 min. The coated samples were finally exposed to calcination at 480 °C for 1 h. The surface morphology of the anode was analysed by Field Emission-Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) in a Vega Tescan-XMU microscope. X-ray Diffraction (XRD) was used to analyse the structure of coatings. The inspection was carried out on a Philips-X'Pert model equipped with CuK$_\alpha$ radiation, 40 keV and radiation angle of 1 degree (grazing incidence) and the X'Pert HighScore Plus software was used to analyse the data and identify phases. Accelerated life test (ALT) on anode were carried out based on NACE Standard TM 0108-2008 [25]. The composition of electrolyte was 1 M sodium sulphate at 30 ± 5 °C. The applied ALT constant current density was 0.1 A cm^{-2}. The service lifetime of anode was considered as the time in which voltage increased up to 4 V. Cyclic voltammetry tests were done by a Potentiostat/Galvanostat Biologic-VSP 300 in the range of 0 to 1.4 V vs SCE (Saturated Calomel Electrode), with a scan rate of 10 mVs^{-1} in 0.5 M sulphuric acid solution. EIS tests were done by a Potentiostat/Galvanostat Biologic-VSP 300 with 100 frequency points in the frequency range of 100 KHz to 10 mHz, with potential amplitude

of ± 10 mv with 20 points per decade in 0.5 M sulphuric acid solution. The data was then analysed using zview2 and EC-Lab software.

3. Results and discussion

3.1. Characterization of the surface of the samples

3.1.1. SEM analysis

Fig. 1 shows the SEM image of the produced mixed metal oxide coating with different amounts of RuO$_2$ added. The anodes showed a typical porous "mud cracked" structure. It can be seen in Fig. 1 that the less compact, wider and more cracked coating, was formed onto anode 'A' (10 wt.% RuO$_2$) with the least amount of RuO$_2$.

Fig. 2 shows that microscopic investigations at high magnification on anode 'B' (30 wt.% RuO$_2$), revealed a mixed metal oxide coating consisting of nano-crystals with a range of the crystals dimensions of 20–40 nm that were dispersed all over the surface.

3.1.2. GIXRD analysis

GIXRD patterns for the coated electrodes are shown in Fig. 3. A set of sharp and nearly symmetrical peaks revealed a crystalline structure assigned to tetragonal rutile.

The sharp peaks at 2θ ~28°, 35°, 38° and 54° indicate that a mixed oxide system had been formed in a solid solution of IrO$_2$ and RuO$_2$ with rutile-type structures. Since the ionic radii of Ru^{4+} (0.076 nm)
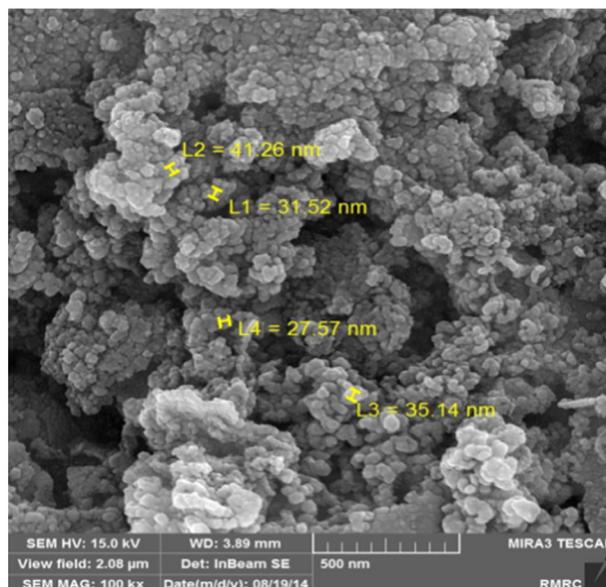

Fig. 2. FE-SEM image of the surface of anode B (30 wt.% RuO$_2$).