

Nanostructured Ti/TiO₂-RuO₂-La₂O₃ anodes prepared by sol-gel process and the effect of electrolyte composition on their stability

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Ti/TiO₂-RuO₂-La₂O₃ anodes were prepared by sol-gel process. The main aim of this work was to study nanostructured TiO₂-RuO₂-La₂O₃ coatings and the effect of electrolyte composition on their stability. For this purpose, coatings with different molar ratios applied on titanium substrate. Then, the morphology and electrochemical properties of the anodes in 0.5 M NaCl and 1 M H₂SO₄ solutions were studied using field emission scanning electron microscopy, energy dispersive X-ray spectroscopy, potentiostatic polarisation, cyclic voltammetry, and accelerated corrosion test (ACT). The results showed that the morphology of all the coatings was cracked-mud microstructure and cracks with a width of 50–500 nm produced in the coatings. It was also observed that corrosion resistance, stability, and electrocatalytic properties of the anodes improve with increased La₂O₃ content. Then, the optimum TiO₂-RuO₂-La₂O₃ composition is obtained with a molar ratio of 70:15:15. Besides, the lifetime and stability of the anodes in NaCl solution were higher than H₂SO₄, so that the reduction of active elements in the coating with a molar ratio of 70:15:15 after ACT was obtained about 64.7 and 77.4% of before ACT in NaCl and H₂SO₄, respectively.

1. Introduction: Mixed metal oxides (MMO) anodes are part of dimensionally stable anodes with the oxide coating, which are widely used in different electrochemical fields, including the chlor-alkali industry and cathodic protection. In comparison to other anodes, these anodes have the following advantages: dimensional stability, high anodic current density, low weight per surface unit, high current efficiency, low cell voltage, and high chlorine production per anodic surface unit [1–6].

Metal conductive oxides are used as catalyst on titanium substrate in MMO anodes, which create excellent mechanical and electrocatalytic properties. In fact, oxygen evolution reaction (OER) and chlorine evolution reaction (CER) are the main anodic reactions in most cathodic processes. The introduction of SnO₂, IrO₂, RuO₂, and La₂O₃ or a combination of them into MMO anodes can improve the performance of the anodes for OER and CER [7–16]. Thus, the fractional replacement of TiO₂ with active oxides, such as SnO₂ or La₂O₃ in RuO₂-based anodes improves the electrocatalytic activity for OER and CER [17–20].

The lifetime and stability of MMO anodes are of great importance, so that the lifetime of anode is when it could be applicable during usage without erosion, corrosion, and electrochemical deactivation. The lifetime of anode ends due to the reduction of electrocatalytic activity, and thereby electrochemical dissolution of coating components, mechanical erosion, or oxygen permeation from the coating into the substrate surface and formation of non-conducting layer of TiO₂ between coating and substrate [21].

Depending on the composition of oxide coatings and under different operating conditions, the anode degradation mechanism can be completely different. Therefore, the degradation mechanism of MMO anodes is significantly affected by parameters, such as surface porosity and heterogeneity, the production process of coating and sintering treatment. Also, one of the effective parameters in the behaviour of anode is the nature of the substrate. Studies have indicated that in RuO₂-based anodes, the first step in the dissolution of active components is the oxidation of RuO₂ to RuO₃. In other words, the degradation mechanism can usually be attributed to the dissolution of active component in the oxide layer or the formation of a non-conducting oxide layer in the interface of the active layer and substrate [22].

Although many research works reported fabrication of MMO anodes by sol-gel process, to the best of our knowledge there has been no report on Lanthanum oxide in this process. The aim of this study is to investigate the effect of La₂O₃ content in the coating and electrolyte composition on the stability of nanostructured Ti/TiO₂-RuO₂-La₂O₃ anodes prepared by sol-gel process. For this purpose, the properties and characterisation of anodes were investigated using field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), potentiostatic polarisation, cyclic voltammetry, and accelerated corrosion test (ACT) in NaCl and H₂SO₄ solutions.

2. Experimental

2.1. Materials: Commercial pure titanium foils (Grade 2) were used as the substrate. The substrates were ultrasonically cleaned (SONICA, SOLTEC, 80 W) with acetone and ethanol, followed by chemical cleaning in hydrochloric acid (HCl) 37% (MERCK) solution.

2.2. Sol preparation: The TiO₂ sol was prepared by the addition of titanium tetraisopropoxide (TTIP, MERCK) to distilled water and HCl 37%. The RuO₂ and La₂O₃ sols were provided by adding precursors RuCl₃·xH₂O and LaCl₃·xH₂O (MERCK) to distilled water. The sols were agitated for 6 h at ambient temperature. Then, the TiO₂, RuO₂, and La₂O₃ sols were mixed in the molar ratios of 70:25:5, 70:20:10, and 70:15:15. Finally, the sols magnetically agitated at ambient temperature for 2 h.

2.3. Sol-gel process: The coating process was performed in different sols for six steps. After each coating step, the substrates were placed in an oven at 100°C for 20 min. Finally, the substrates were subjected to heat treatment at 450°C for 2 h at a temperature rate of 50°C/min.

2.4. Morphological characterisations and electrochemical measurements: The surface morphology and microstructure of anodes were examined by means of FESEM (MIRA3TESCAN-XMU).

In order to study the anodic behaviour of the coatings, the potentiostatic polarisation curves and cyclic voltammetry were obtained

at scan rate of 5 and 20 mV/s, respectively, and in 0.5 M NaCl and 1 M H₂SO₄ solutions. For this purpose, a conventional three electrode electrochemical cell was used, including a platinum plate as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and Ti/TiO₂-RuO₂-La₂O₃ anodes as working electrodes.

The lifetime of anodes was determined by ACT in NaCl and H₂SO₄ solutions at ambient temperature and a constant current density of 1 A cm⁻², and potential curves were recorded using a digital millimetre (FLUKE 187 & 189). Also, before and after ACT, optimal coating surface morphology was evaluated by FESEM and elemental analysis was assessed by EDX. It should be noted that the electrochemical experiments were performed using an AUTOLAB model PGSTAT30 instrumentation and all potentials were measured with respect to SCE as the reference electrode.

3. Results and discussion: Fig. 1 shows FESEM images of TiO₂-RuO₂-La₂O₃ coatings with different molar ratios. The surface of the coatings appears like cracked-mud microstructure. This structure has been developed by the exit of combustion products during the heat treatment. The existence of these cracks, due to the preparation of oxygen entry source and electrolyte, as well as substrate oxidation, can be one of the disadvantages of this microstructure. However, the cracks can have a positive effect on electrocatalytic properties due to the increased specific surface of the coatings, and facilitating OER and CER. Therefore, the reduction of cracks and increasing the density and uniformity of the coating are very important [23–27]. As seen in Fig. 1, the cracks with different width and in the range of 50–500 nm were produced in all the coatings. As a result, increasing La₂O₃ content causes reduction in RuO₂ content and the crack width.

The potentiostatic polarisation curves of Ti/TiO₂-RuO₂-La₂O₃ anodes, obtained in 0.5 M NaCl and 1 M H₂SO₄, are shown in Figs. 2 and 3. The cause of a sudden increase in the current density in the anodic branch of these curves can be attributed to

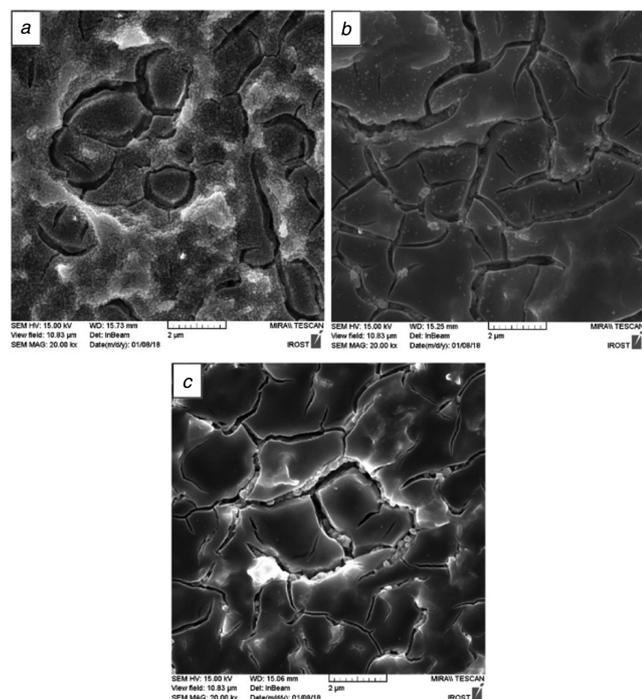


Fig. 1 FESEM micrographs of Ti/TiO₂-RuO₂-La₂O₃ anodes with the molar ratios of
a 70:25:5
b 70:20:10
c 70:15:15

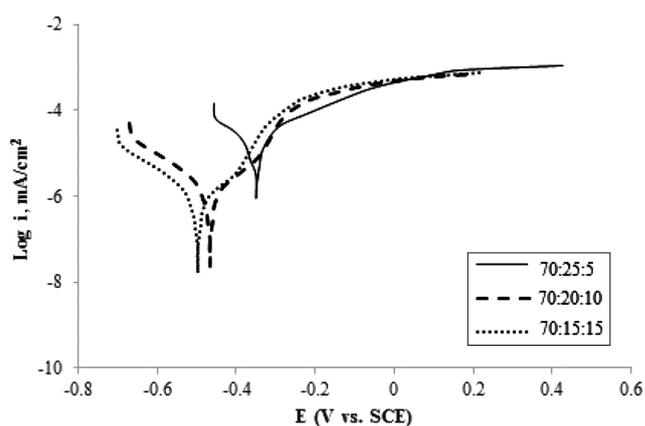


Fig. 2 Polarisation curves of Ti/TiO₂-RuO₂-La₂O₃ anodes with different molar ratios in 0.5 M NaCl

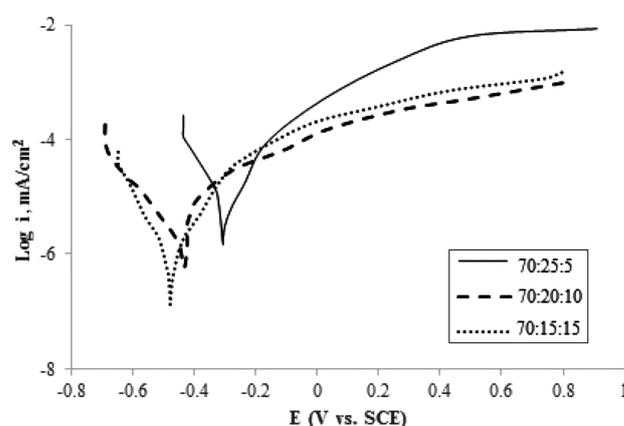
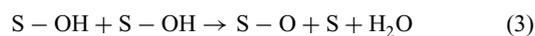
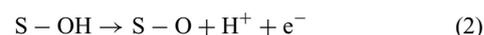


Fig. 3 Polarisation curves of Ti/TiO₂-RuO₂-La₂O₃ anodes with different molar ratios in a 1 M H₂SO₄

OER and CER. It is well known that the standard potentials of O₂/H₂O and Cl₂/Cl⁻ electrodes are 1.229 and 1.358 V (versus the standard hydrogen electrode), respectively. Therefore, in NaCl solution, in addition to chlorine, oxygen is also released. Since OER potential is lower than CER potential, oxygen must be released faster and more than chlorine, but CER is kinetically preferable.

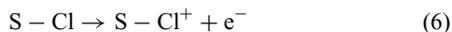
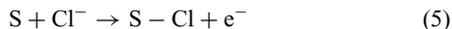
The proposed mechanism for OER in acid medium on an active surface site (S) of coating can be described as equations below [2, 28]:



In this mechanism, (2) and (3) occur in parallel. In fact, the occurrence of one or the other depends on the adsorption strength of the intermediate.

Several different mechanisms have been proposed for CER. The proposed mechanism for CER on an active surface site (S) of

coating is as follows [28]:



Comparing Figs. 2 and 3, it is observed that in H₂SO₄ solution, OER current has begun at more positive potentials and the Tafel slope is more, which is the result of different reaction mechanisms. In fact, in solutions containing proton and chloride ion, protons are involved in the oxidation of active sites which are building the suitable sites for adsorption of chlorine gases. CER in such a situation occurs in a less potential than NaCl solution [13]. Also, Figs. 2 and 3 show that the presence of higher La₂O₃ in the coating improves the electrocatalytic property of the coating, so that the noblest corrosion potential and the lowest corrosion current density are related to Ti/TiO₂-RuO₂-La₂O₃ anode with a molar ratio of 70:15:15. Also, the lowest OER and CER potentials are related to this coating composition. In other words, the tendency to discharge oxygen and chlorine gases in TiO₂-RuO₂-La₂O₃ coating with a molar ratio of 70:15:15 is increased and the reaction is done at a lower potential and with a lower slope, which shows that oxygen and chlorine gases are evolved at its surface at a high rate. Therefore, it has a better electrocatalytic property than other coatings, but in general, the electrocatalytic property of all the coatings for OER is lower than CER.

It is important to know the degradation mechanism of an oxide anode to increase its lifetime and stability. Generally, the lifetime of the anode under ACT conditions, the application of a high current density to the system, and measuring the potential variations against time, is determined. When a fast increase in the potential is observed, the anode is deactivated.

Two reasons are proposed for the loss of electrocatalytic activity of the anode [29, 30]:

1. Simultaneous electrochemical oxidation of active components in the coating and their entrance into the electrolyte.
2. Formation of a non-conducting TiO₂ layer at the interface of the coating and substrate.

The time dependence of the relative anode potential, obtained from the results of ACT, for Ti/TiO₂-RuO₂-La₂O₃ anodes in 0.5 M NaCl and 1 M H₂SO₄ is shown in Figs. 4 and 5. As can be seen, after a constant potential region, a potential increase is observed. Also, it is observed that potential-time curve changes are similar for the anodes in NaCl and H₂SO₄. Researches have indicated that the electrochemical activity loss is related to OER

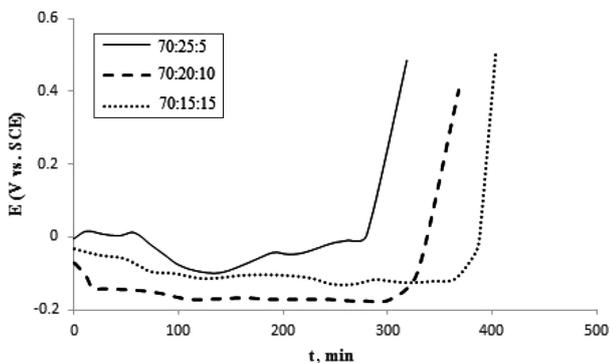


Fig. 4 ACT results of Ti/TiO₂-RuO₂-La₂O₃ anodes with different molar ratios in 0.5 M NaCl

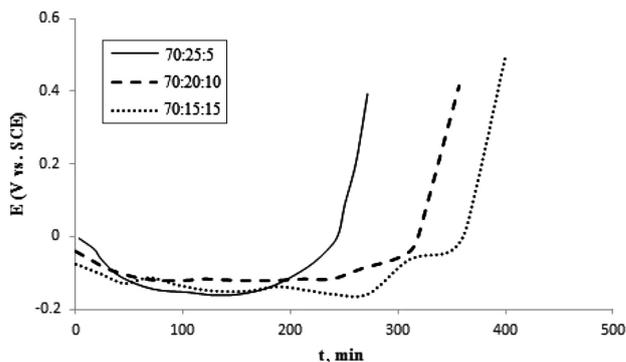


Fig. 5 ACT results of Ti/TiO₂-RuO₂-La₂O₃ anodes with different molar ratios in 1 M H₂SO₄

and CER. In solutions containing chloride, the discharge rate of oxygen is slower than H₂SO₄ solution. Therefore, the required time for the degradation of anode in H₂SO₄ solution is very short.

As seen in Figs. 4 and 5, increasing La₂O₃ content in the coating causes to increase the stability of the anode, as Ti/TiO₂-RuO₂-La₂O₃ anode with a molar ratio of 70:15:15 has a higher lifetime than the anodes with molar ratios of 70:25:5 and 70:20:10. It is also observed that the lifetime of the anodes in a NaCl solution is higher than H₂SO₄.

Figs. 6 and 7 illustrate the cyclic voltammograms of Ti/TiO₂-RuO₂-La₂O₃ anode with a molar ratio of 70:15:15 in 0.5 M NaCl and 1 M H₂SO₄, before and after ACT. The cyclic voltammogram of the anode before ACT in H₂SO₄ (Fig. 6) shows the large peak around +0.6 V which can be related to the oxidation-reduction processes of Ru(III)/Ru(IV) and Ru(III)/Ru, while OER starts at about +1 V. Before ACT, voltammograms are completely

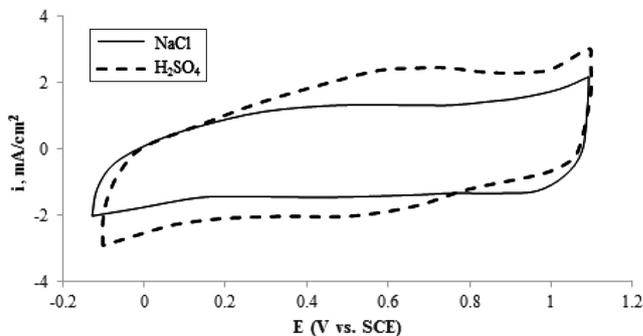


Fig. 6 Cyclic voltammograms of Ti/TiO₂-RuO₂-La₂O₃ anode with a molar ratio of 70:15:15 before ACT in different solutions

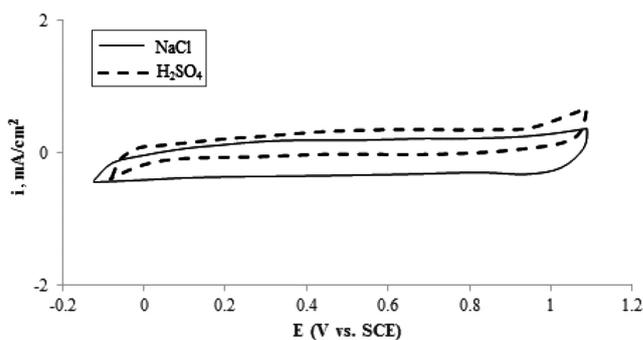


Fig. 7 Cyclic voltammograms of Ti/TiO₂-RuO₂-La₂O₃ anode with a molar ratio of 70:15:15 after ACT in different solutions

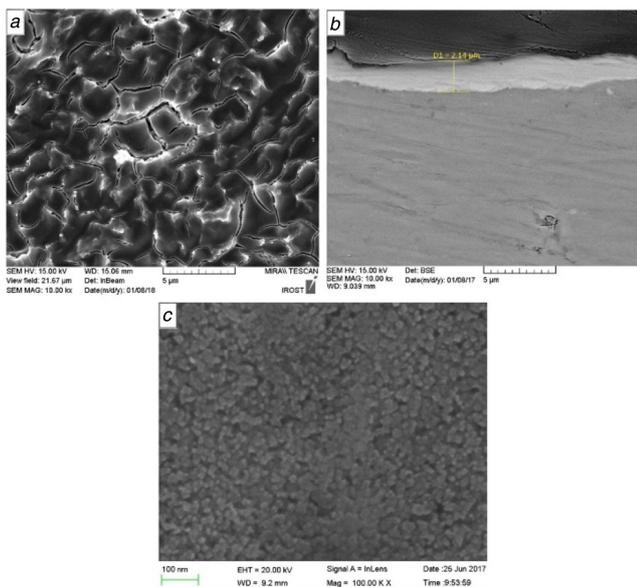


Fig. 8 Surface morphology of $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anode with a molar ratio of 70:15:15 before ACT at various magnification
 a, c FESEM micrographs
 b Thickness of coating

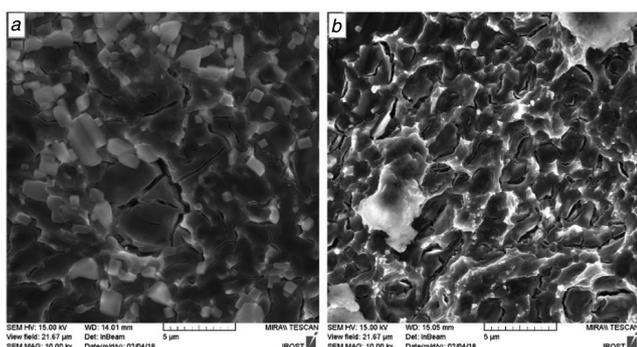


Fig. 9 FESEM micrographs of $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anode with a molar ratio of 70:15:15 after ACT in solutions of
 a 0.5 M NaCl
 b 1 M H_2SO_4

symmetrical in both solutions. The currents are higher in H_2SO_4 compared to NaCl. The pseudo-capacitive ability of coating is more evident in H_2SO_4 solution, which can be attributed to the Faradic processes including proton. After ACT, the curves become almost featureless in both solutions, which is related to decrease the active sites on the anode surface and the corrosion of the more compact part of the active layer.

In order to study the morphology changes of $\text{TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ coating with a molar ratio of 70:15:15 after ACT, FESEM micrographs of the coating before and after ACT in different solutions were investigated. As seen in Fig. 8a, the microstructure of anode surface has cracked-mud structure before ACT, which is a common structure for titanium anodes coated with noble metal oxides. The cross-section of the coating displays an average thickness of about 2.14 μm (Fig. 8b). Also, needle-like crystals of the size of about 10–40 nm are observed on the surface of the coating at higher magnification (Fig. 8c). As can be seen in Fig. 9, the non-active anodes (after ACT) show a different structure. In fact, the cracked structure of the coating gradually disappears during the electrolysis. The chemical composition of $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anode before and after ACT are summarised in

Table 1 EDX analysis results of $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anode with a molar ratio of 70:15:15 before and after ACT in 0.5 M NaCl and 1 M H_2SO_4

	Ti	Ru	La
before AST	72.09	14.23	13.68
after AST in 0.5 M NaCl	90.16	3.47	6.37
after AST in 1 M H_2SO_4	93.68	2.05	4.27

Table 1. EDX results after ACT revealed a significant increase in titanium atomic percentage, which may be a result of an increase in TiO_2 content in the interface of coating and substrate during ACT. Also, the thinning of coating in these regions and the X-ray penetration into the substrate are another reasons for the increase of titanium content after ACT. According to the results of EDX analysis in Table 1, it is also clear that after ACT, the content of active elements in the coating (Ru+La) in NaCl and H_2SO_4 solutions were reduced about 64.7 and 77.4% of before ACT, respectively. Therefore, it can be concluded that the dissolution of active components occurs due to ACT, which is more intense in H_2SO_4 solution in comparison with NaCl.

4. Conclusion: The main objective of this study was to produce nanostructured $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anodes by sol-gel process and to investigate the effect of La_2O_3 content in the coatings, as well as the effect of electrolyte composition on the stability of these anodes. The results of the study showed that $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anodes display a cracked-mud structure and contain cracks with different widths (50–500 nm). It was also observed that the degradation mechanism and lifetime of $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anodes depend on the electrolyte and coating composition. It is found that the corrosion resistance, lifetime, and electrocatalytic properties of the anode increased with increasing La_2O_3 in the coating, so that $\text{Ti/TiO}_2\text{-RuO}_2\text{-La}_2\text{O}_3$ anode (molar ratio 70:15:15) was considered as an optimal anode composition. The results of study of the stability of this optimal anode composition in different solutions indicated that the lifetime and stability of anode in NaCl solution is higher than H_2SO_4 , which is due to the more severe dissolution of active components of the coating in H_2SO_4 , so that the content of active element reduction after ACT in H_2SO_4 was more than NaCl.

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