ORIGINAL PAPER

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RuO$_2$–TiO$_2$ mixed oxide composite coating for improvement of Al-alloy sacrificial anodes

Abstract It has been recently proved that RuO$_2$ can act as an effective surface activator of aluminum alloy sacrificial anodes. TiO$_2$ has the property of stabilizing RuO$_2$ coating and resisting biofouling on metal surfaces. Hence, a mixed oxide catalytic coating of TiO$_2$ and RuO$_2$ can enhance the galvanic performance of aluminum alloy sacrificial anodes and resists biofouling on the anode surface. In the present work RuO$_2$–TiO$_2$ mixed oxide was coated on aluminum alloy sacrificial anodes. The large and uniform porous nature of the coating was found to facilitate efficient ion diffusion. The coating was found to persist on the anode even after 3 months of galvanic exposure. The anode having an optimum combination of the mixed oxide had 70% TiO$_2$ as the major component in the coating. The catalytic coating significantly improved the performance of the anodes to a large extent.

Keywords Corrosion · Aluminum · Sacrificial anode · Metal oxides · Surface activation · Biofouling

Introduction

Aluminum, due to its high current capacity, is the most suitable metal for fabricating sacrificial anodes for marine applications. Aluminum readily forms an impermeable oxide film on its surface; hence, the inclusion of activators like In, Zn, Bi, Hg, or Sn is essential for its activation [1]. Various new activators have been investigated. These internal activators activate aluminum alloy sacrificial anodes by destructing impermeable alumina film by surface redox reactions [2]. Direct surface activation of sacrificial anodes by metal oxides, having the capacity to exist in various oxidation states of the metal cation, is also an efficient method for achieving good performance [3–5].

RuO$_2$ coating, made by thermal decomposition of the precursors such as RuCl$_3$, can persist on aluminum alloy anode surfaces for long durations and cause the activation of aluminum through its pores [5].

The activation of aluminum alloy sacrificial anodes by RuO$_2$ proceeds through the formation of different ionic clusters by RuO$_2$–Al$_2$O$_3$ interaction. These ionic clusters diffuse through the pores of RuO$_2$ coating. Surface activation by RuO$_2$–TiO$_2$ mixed oxide can occur only if the coating is sufficiently porous for diffusion of the metal ions. TiO$_2$ acts as a stabilizing agent of RuO$_2$ coating and it has high electronic interactions with alumina [6] that normally present on aluminum. The RuO$_2$–TiO$_2$ coating with 20–50% RuO$_2$ content (which is also normally used in dimensionally stable anodes) has exceptionally high uniform mud-crack-type porosity [7]. The RuO$_2$–TiO$_2$ coating, with this range of composition, also shows a high pseudo capacitance value due to the redox reactions of RuO$_2$. At 400°C, the normal firing temperature of RuCl$_3$ on titanium or Al$_2$O$_3$ substrate, ruthenium penetrates deep into the bulk of the substrate and accumulates in the near-surface region [7, 8]. The RuO$_2$ coating on aluminum substrate almost resembles the characteristics of that on titanium substrate. In this context, activation of aluminum and diffusion of ionic clusters through the uniformly porous RuO$_2$–TiO$_2$ film appears to be feasible.

The penetration of ruthenium content into the bulk of the substrate and enrichment of TiO$_2$ in the outer layer of the coating during thermal coating have importance due to the property of TiO$_2$ to resist biogrowth. Its photoinduced biocidal effect has been reported in detail [9, 10]. The photochemical activity of TiO$_2$ can be improved by the synergistic action of metal oxides like RuO$_2$ [11]. Hence, the RuO$_2$–TiO$_2$ coating system can be predicted to resist biogrowth even under daylight.

A steady state potential in the range from −0.900 to −1.000 V should be established by the sacrificial anodes, like aluminum alloy anodes, for effective use. The anodic shift in potential (ennoblement) of the anode due to biofouling is one of the major problems in this process. Noncoulombic metal loss due to microbially influenced

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corrosion (MIC) is the second major problem to be attended for long-term functioning of the sacrificial anodes in marine environments. The present work has the objective to develop high-performance aluminum alloy sacrificial anodes by means of applying RuO_2–TiO_2 mixed oxide coating with a view of controlling these two constrains.

Materials and methods

Anode fabrication

Binary Al+5-wt.% Zn alloy anodes were cast in rectangular shape with a dimension of $5×3×0.3$ cm^3 from commercially available pure 99.0% aluminum and 99.5% Zn at a temperature of around $700±10°C$. The surface of the anodes was polished by using different grades of emery paper and then degreased. $RuCl_3.3H_2O$ (Thomas Baker, India) and $TiCl_4$ (Spectrochem, India) solutions in the required ratio were prepared in isopropanol. The precursor was applied on the anode surface, dried, and fired at $400±10°C$ in presence of air for 30 min.

Physico-chemical characterization

The surface morphology of the coatings was analyzed by using scanning electron microscopy (SEM) without any further treatment of the surface. Surface morphology of the coating after 6 weeks of galvanic exposure was also analyzed to assess the stability. Energy dispersive X-ray (EDAX) analyses of the surface before and after the galvanic exposure were conducted to evaluate the stability of the coating on the anode surface. The coating was scraped from the anode surface and ground well. The powder so obtained was used to determine the crystalline characteristics of the metal oxides by X-ray diffraction (XRD) analysis. CuKa1 radiation was used during XRD analysis.

Electrochemical characterization

The galvanic performance of the anodes in 3% NaCl and in sea water was evaluated based on (1) open circuit potential (OCP) decay measurement, (2) variation of the closed circuit potential (CCP) with time, (3) variation of the galvanic current with time, (4) galvanic efficiency, and (5) self-corrosion. The anodes were coupled with mild steel cathodes and the couples were immersed in 3% NaCl solution and in seawater. The sacrificial anodes with and without galvanic coupling with mild steel cathodes were fixed on a wooden rack for evaluation of galvanic performance in a marine environment. All the connections were insulated and sealed by using M-seal (a commercially available epoxy compound for sealing). The rack was immersed in the Arabian Sea adjacent to Valiyathura pier at Trivandrum. The location of the study was a fixed interior 350 m from the seashore, and the depth of immersion was 5 m from the sea level. The rack was periodically taken out of the sea after placing it in a large tub containing marine water. This procedure helped to measure OCP, CCP, and current without destructing the biofilm. The tub was removed after immersing the rack again in the sea.

The CCP of the anodes, during protection of the steel cathode, was measured as a function of time to assess the capacity of the anodes to provide electrons for cathodic protection. The mild steel cathodes each had a dimension of $11×4×0.5$ cm^3. The anodes were subjected to steady-state polarization, in 3% NaCl solution, by using a galvanostat. A platinum grid was used as the counter electrode during the galvanostatic anodic polarization studies. All potential values were measured with respect to a saturated calomel electrode (SCE) with a Luggin capillary to eliminate IR drop.

The galvanic efficiency of the anodes after 3 months of exposure in 3% NaCl was determined by using the formula:

$$Efficiency(\eta) = (A/B) \times 100; \; where$$

A is the actual charge delivered by the anode during the period of exposure. The current flowing in between the mild steel cathode and the sacrificial anode was continuously measured as a function of time, while the couples were subjected to galvanic exposure for a period of 2 months, by using an ammeter. For this purpose the galvanic couple was provided with a parallel connection having an ammeter, and then the original circuit was disconnected prior to the measurement each time. The measurement did not affect the continuous galvanic action of the anode. The value of A was determined from the plot of current vs time. The area under the graph is exactly proportional to the actual charge delivered by the anode. B is the theoretical charge that would have been delivered by the anode. This charge is calculated by using Faraday's law based on the actual weight loss of the anode due to galvanic exposure.

Biogrowth

The rate of biofouling on the anode surface was monitored for 8 weeks. After 4 weeks, the biofilm formed on the anode surface was brushed into distilled water and then analyzed to detect sulfate-reducing bacteria (SRB), the organism known as the main cause of MIC. The composition of the media used was KH_2PO_4 (0.05 g), NH_4Cl (0.1 g), Na_2SO_4 (0.45 g), $CaCl_2.6H_2O$ (6 mg), $MgSO_4.6H_2O$ (6 mg), sodium lactate (0.6 g), yeast extract (0.1 g), $FeSO_4.7H_2O$ (0.01 g), sodium citrate.$2H_2O$ (0.03 g), and Distilled water (100 mL). The pH ranged from 7 to 5. The bottles containing the scraped biofilm and the medium were filled to the brim and closed to exclude air. Blackening after incubation for 2 weeks, if any, could indicate the presence of SRB.

Fig. 1 The SEM photographs (×500) showing the morphological changes of the optimum (0.175 mg cm^{-2}) RuO$_2$ coating on Al+5% Zn alloy anode due to the incorporation of different percentages of TiO$_2$: **a** 0%, **b** 10%, **c** 50%, **d** 70%
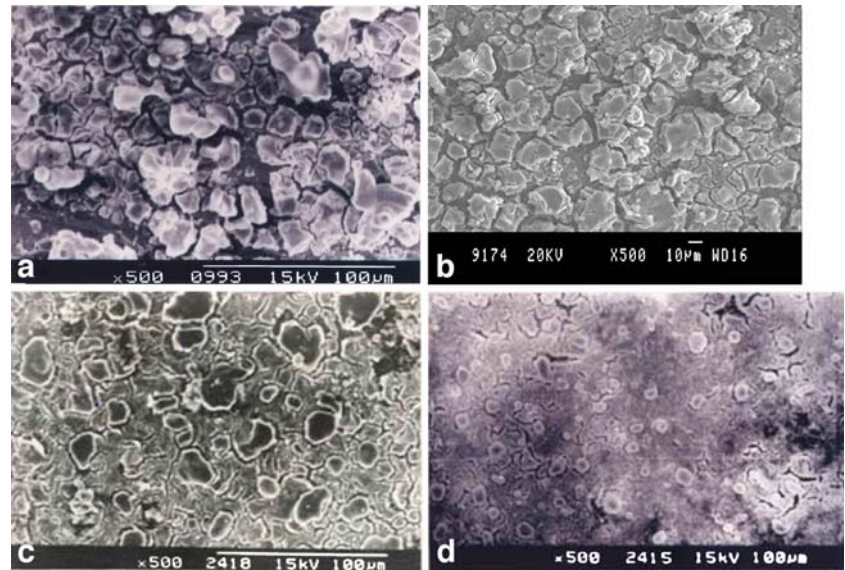
Results and discussion

Preliminary characterization

Morphological change

The main requirements for the effective surface activation of sacrificial anodes by mixed oxide coating are good adherence, optimum porosity, and uniform dispersion to facilitate metal ion diffusion. The optimum concentration of RuO$_2$ on aluminum alloy sacrificial anode surfaces is 0.175 mg cm^{-2} [3, 5]. This optimum concentration was maintained throughout the first stage of the present work, which was intended to find out the optimum total metal oxide composition that facilitates large and uniform porosity. Hence, different amounts of TiO$_2$ were added with the optimum concentration of RuO$_2$. After fixing the optimum total oxide composition, a fine-tuning of the metal oxide ratio was made to study the influence of the metal oxide composition on the coating morphology and galvanic performance of the anode.

Figure 1a shows the surface morphology of the RuO$_2$-coated anode. The anode surface had several uncoated regions or traces of precipitation. Lower concentrations of TiO$_2$ (~10%) with optimum RuO$_2$ led to more uniform pore distribution (Fig. 1b). The pores and grains are more uniformly dispersed with defined boundaries. Incorporation of higher concentrations of TiO$_2$ (>30%) with optimum RuO$_2$ resulted in reduced porosity (Fig. 1c,d).

*Galvanic performance*

The reduction in porosity, resulting due to the incorporation of high percentages of TiO$_2$ along with optimum RuO$_2$, was found to have a high influence on the galvanic performance of the anodes. Consistent with the previous investigations [3, 5], the surface activation by 0.175 mg cm^{-2} RuO$_2$ resulted in higher cathodic OCP (−0.999 V) than that of the bare anode (−0.952 V). The incorporation of lower concentrations of TiO$_2$ (up to ~10%) with optimum RuO$_2$ resulted in a cathodic OCP higher than −0.999 V. However, a further increase in the TiO$_2$ content (>40%) resulted in reduced cathodic OCP values. The CCP values were also found with the same trend during polarization studies. The anodes with lower amounts of TiO$_2$ with optimum RuO$_2$ exhibited more negative CCP at all current densities. The measurements were repeated on several samples and the results were found to be the same. The results are compared in Table 1. It is evident from the table that the incorporation of TiO$_2$ above 40% caused a significant reduction in the galvanic performance of the anodes. The reduced performance at higher TiO$_2$ concentrations can be attributed to the reduced porosity of the film as observed from the SEM micrographs.

Table 1 Comparison of galvanic performance of the anodes as a function of the addition of different amounts of TiO$_2$ with optimum concentration of RuO$_2$ (electrolyte: 3% NaCl, temperature=30°C)

Percentage of TiO$_2$ per cm^2	OCP (V$_{SCE}$)	CCP (V$_{SCE}$) at different current densities (mA cm^{-2})				Self corrosion × 10^{-6} (g cm^{-2} h^{-1})	Efficiency (%)
		3	5	10	15		
0	−0.999	−0.960	−0.957	−0.915	−0.894	7.2491	80
10	−1.060	−0.995	−0.992	−0.991	−0.990	6.9110	84
50	−0.980	−0.980	−0.973	−0.920	−0.898	8.7000	67

Fig. 2 The surface morphology of the optimum RuO_2–TiO_2-coated Al+5% Zn alloy anode before and after galvanic exposure: **a** SEM of the coating before exposure, **b** optical photograph of the coating before exposure, **c** and **d** SEM of the coating at two different magnifications after exposure
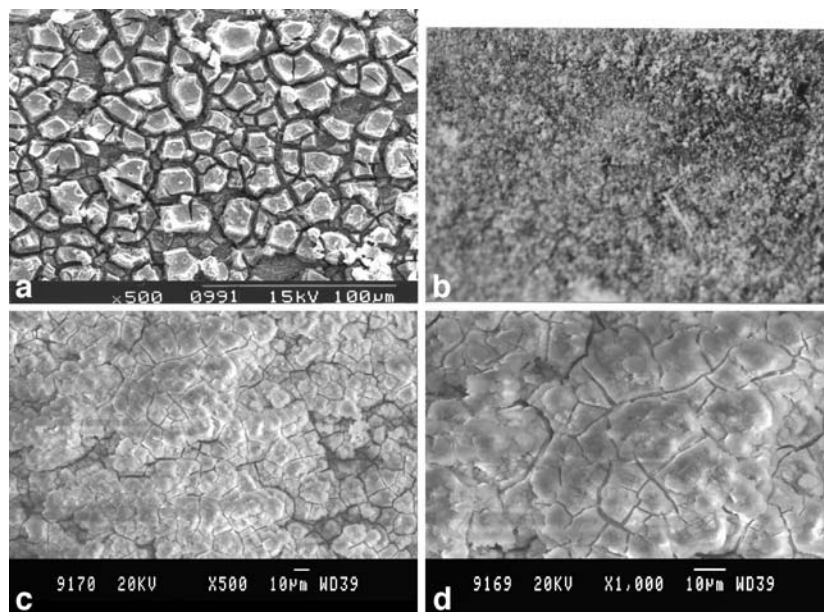

## Optimization of the coating composition

Coating morphology and composition

The results of preliminary studies revealed that a total oxide content of 0.192 mg cm^{-2} activates aluminum alloy anodes without any passivation with maximum efficiency. Hence, the total oxide concentration of 0.192 mg cm^{-2} was kept constant during the subsequent stages, but the percentage concentration of the individual oxides was varied from 0 to 100. Coatings containing 25–35% RuO_2 had high porosity and good morphology. Figure 2a shows the surface morphology of the best coating containing 28% RuO_2. One can argue that the observed porous nature of the coatings might have arisen due to the high vacuum condition used during the SEM analysis. This porous nature of the coatings is due to the probability of the escape of water or other volatile components during the analysis. In this context, the wet electrodes were photographed by using an optical microscope to confirm the actual existence of the observed morphology. Figure 2b shows an optical photograph of the optimum mixed oxide coating. The cracked structure is also visible from the optical photographs.

Fig. 3 The XRD pattern of the RuO_2–TiO_2 coating on the Al+5% Zn alloy sacrificial anode. CuKa1 radiation was used for analysis
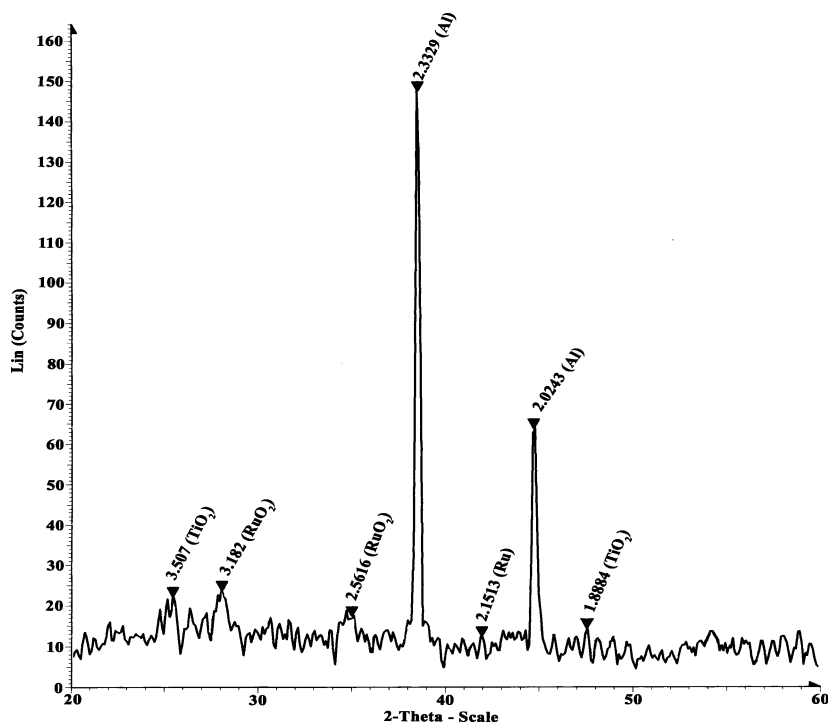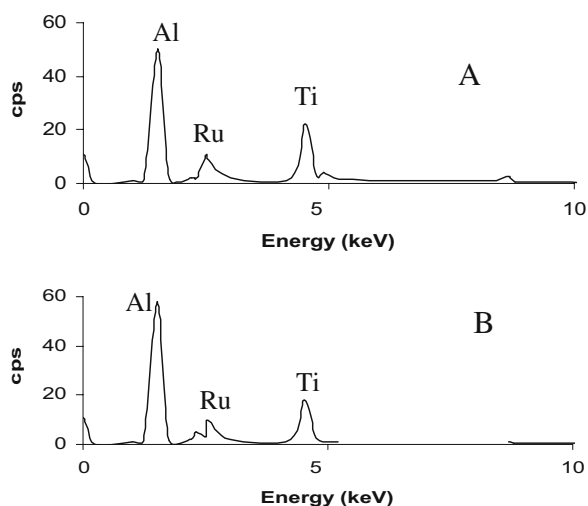
Fig. 4 The EDAX data of optimum RuO_2–TiO_2 coating on Al+5% Zn alloy anode before and after 6 weeks of galvanic coupling with mild steel cathode in 3% NaCl at 30°C: **a** before galvanic exposure, **b** after galvanic exposure

25.379 and 48.145 correspond to anatase TiO_2. The peaks at 28.022 and 34.999 correspond to rutile RuO_2. The high intensity peaks at 38.56 and 44.731 correspond to the aluminum present in the sample, due to deep scratching of the coating. The peak at 41.962 is due to the presence of a small fraction of metallic ruthenium formed due to the possible reduction of $RuCl_3$ during firing.

Coating stability

The morphological studies revealed that the coating was porous enough to allow the free passage of metal ions. The morphology and composition of the coating after 6 weeks of galvanic exposure were studied to assess the coating stability during galvanic exposure. The SEM micrograph of the coating after galvanic exposure exhibited the effective existence of the coating with the same porous structure (Fig. 2c,d). The corrosion products diffused out through the uniform cracks without destructing coating. Based on the EDAX analysis of the coatings before and after the galvanic exposure, it was confirmed that the coating components were only marginally disintegrated due to the galvanic exposure (Fig. 4). These observations show the stability of the coating during corrosion of the anode. After galvanic exposure the percentage of aluminum in the coating was considerably increased due to the release of corrosion products through the pores of the coating.

From a practical point of view, oxide-supported oxide catalysts are extremely complex [12]. TiO_2 is a catalyst support as well as a stabilizing agent of RuO_2. Hence, their interaction normally results in solid solution [13–15]. The formation of $RuTiO_x^+$ cluster ions (x=0, 1, 2) due to the interaction between RuO_2 and TiO_2 has been reported based on secondary ion mass spectrometry study [16]. The solvents used in the coating process also have interactions with the metal ions [17]. The rate of the aforesaid reactions and decomposition of the precursor mixtures are highest in the case of the coating containing 10–30 mol% of ruthenium [18]. This high reactivity facilitates a faster release of heat and gaseous products. This can be attributed as being one of the reasons for the present observation of a uniform and porous coating morphology with ~30% RuO_2 content. Segregation of TiO_2 along the outer layers of the catalytic coating also results in compositional anisotropy and porous coating. This is also the cause for the present observation. Thus, consistent with the SEM observations, the coating with ~30% RuO_2 could be predicted to exhibit uniform mud crack porosity.

It was confirmed, based on the XRD pattern (Fig. 3), that TiO_2 was in the anatase form. The peaks at 2θ values of

Galvanic performances

The anode Based on the primary test results, the amount of total mixed oxide in the coating was kept at 0.192 mg cm^{-2}. The influence of the compositional variation of individual metal oxides on the galvanic performance of anodes was studied under laboratory and marine conditions. The tests were repeated, with a number of samples having the same coating composition, to check the reproducibility of the results. The average values of the results are given in Table 2. Among the various compositions studied, the anodes with the mixed oxide coatings containing 20 to 40% RuO_2 exhibited better galvanic performance. The anode with 28% RuO_2-

Table 2 Galvanic performance of the mixed oxide coated anodes and other anodes in laboratory conditions (electrolyte: 3% NaCl, temperature=30°C)
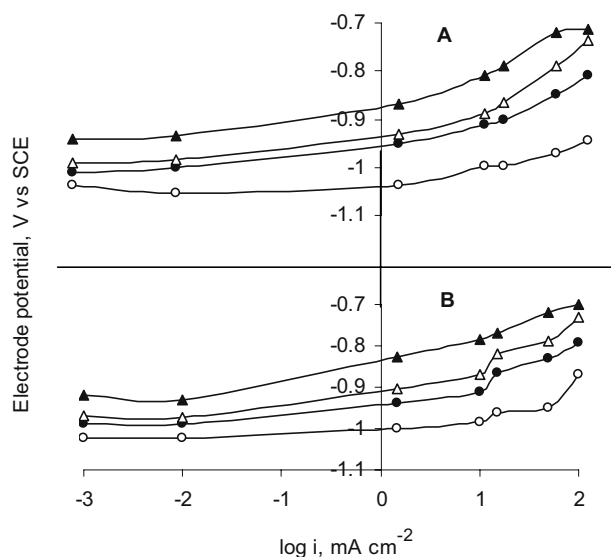
Coating composition (%)		OCP (V_{SCE})	CCP(V_{SCE}) at different current densities (mA cm^{-2})				Self corrosion × 10^{-6} (g cm^{-2} h^{-1})	Efficiency (%)
TiO_2	RuO_2		3	5	10	15		
0	0	−0.952 (−0.949)	−0.950	−0.900	−0.810	−0.739	9.1857 (10.43)	64 (59)
0	Optimum RuO_2	−0.999 (−0.984)	−0.960	−0.957	−0.915	−0.894	7.2491 (9.11)	80 (74)
72	28	−1.098 (−0.997)	−1.000	−1.010	−0.999	−0.998	6.6300 (7.33)	89 (83)
60	40	−1.005 (−0.995)	−0.965	−0.941	−0.910	−0.899	7.1552 (8.55)	82 (76)
25	75	−0.996 (−0.991)	−0.960	−0.952	−0.900	−0.887	7.4221 (8.66)	78 (71)

The values given in parenthesis are those values observed in marine conditions
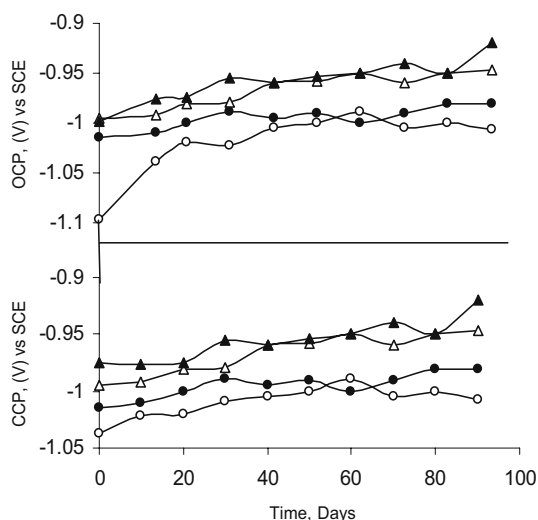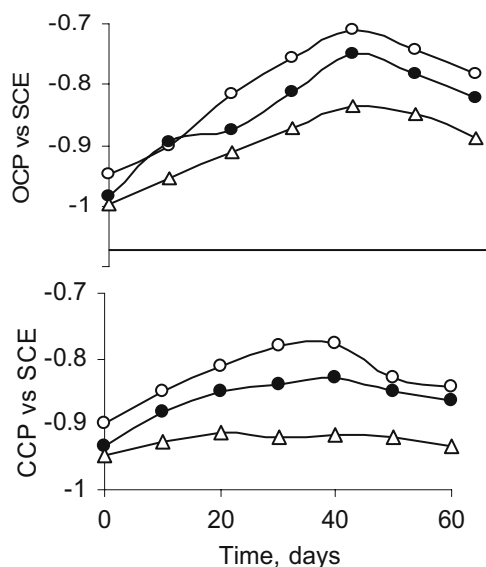
Fig. 5 The variation of OCP and CCP of Al+5% Zn alloy sacrificial anodes coated with different compositions of RuO_2–TiO_2 mixed oxide: ▲ 100% RuO_2, △ 70% RuO_2+30% TiO_2, ● 35% RuO_2+65% TiO_2, ○ 28% RuO_2+72% TiO_2 (electrolyte: 3% NaCl, temperature=30°C)

Fig. 7 The variation of OCP and CCP, under marine conditions, observed for Al+5% Zn alloy sacrificial anodes with and without surface activation: ○ bare anode, ● surface activation by optimum (0.175 mg cm^{-2}) RuO_2, △ surface activation by 72% TiO_2+28% RuO_2 (electrolyte: natural marine water, marine conditions)

containing coating exhibited the best galvanic performance. These anodes exhibited the highest cathodic OCP. The average values of OCP and CCP for a set of samples with the same coating composition were measured as a function of time. Figure 5 compares the variation in the average OCP and CCP values of the bare anodes along with the mixed oxide and optimum RuO_2-coated galvanic anodes. The anode with 28% RuO_2-containing coating showed the least anodic polarization (Fig. 6). At all current densities, the anode showed the highest negative CCP values.
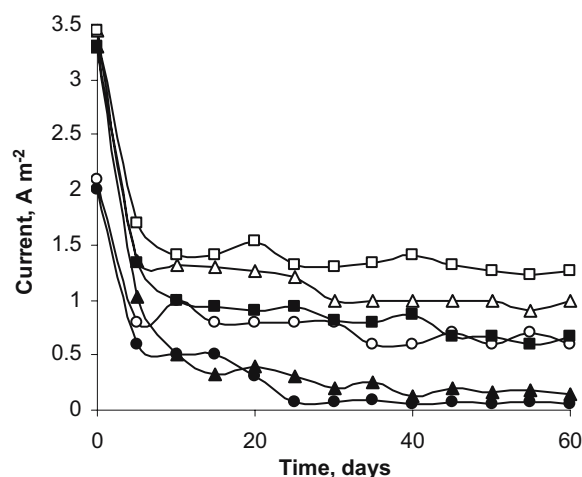
The anodes with 28% RuO_2-containing coating exhibited the highest negative OCP and CCP values (Fig. 7) under marine conditions. The bare and lone RuO_2-coated anodes exhibited high rates of ennoblement due to high biofouling on the anode surface. But the ennoblement did not continue after 45 days. After a period of about 45 days, the potentials slightly shifted to a more negative direction. The potential shift may be attributed to the removal of the biofilm as patches from the anode surface and to the

Fig. 6 The voltammetric curves of Al+5% Zn alloy sacrificial anodes coated with different compositions of RuO_2–TiO_2 mixed oxide: ▲ 100% RuO_2, △ 70% RuO_2+30% TiO_2, ● 35% RuO_2+65% TiO_2, ○ 28% RuO_2+72% TiO_2. **a** and **b** are, respectively, the polarization behavior before and after 6 weeks of galvanic coupling with mild steel cathode in 3% NaCl at 30°C

Fig. 8 The variation of galvanic current between anode and cathode observed for Al+5% Zn alloy sacrificial anodes with and without surface activation under laboratory and marine conditions. Without surface activation: ○ under laboratory condition, ● under marine condition; surface activation by optimum (0.175 mg cm^{-2}) RuO_2: △ under laboratory condition, ▲ under marine condition; surface activation by optimum mixed oxide (28% RuO_2+72% TiO_2): □ under laboratory condition, ■ under marine condition

enhanced biocorrosion caused by the microorganisms present on the anode surface. All the anodes having TiO_2-containing coating did not exhibit considerable ennoblement due to the low rate of biogrowth on the anode surface.

The couple The trend of variation of current with time, between the anode and the cathode under laboratory and marine conditions, is shown in Fig. 8. During the study, the coating having 28% RuO_2 content facilitated high current. After a few days all the anodes attained almost a constant current under laboratory conditions. But all the anodes under marine conditions exhibited constant reductions in the current with time. The reduction in current can be attributed to the biofilm formation on the anode surface suppressing active dissolution of the anode. Due to less biofouling, the decrease in current was least pronounced in the case of the anodes having TiO_2-containing coating. These anodes showed almost the same current as that observed under laboratory conditions.

The cathode The cathodes protected by the RuO_2–TiO_2 surface-activated anodes did not exhibit any tendency to undergo corrosion throughout the period of the study, under marine conditions. Even the initial shiny appearance persisted on the steel surfaces of the cathodes. The corrosion rate was zero when evaluated after a period of 2 months. However, the cathodes coupled with the bare anode or the lone RuO_2-coated anodes exhibited rusting after 1 month of exposure under marine conditions. In this case a mild corrosion on the cathode surface was observed as brown spots after 35 days. There was also mild biofouling. There was no further severe corrosion thereafter. The OCP of the cathodes in the former case was found to be in the range of −0.580 to −0.595 V, while it was in the range of −0.615 V to −0.630 V in other cases, as determined based on the parallel experiments conducted. All these observations are attributed to the reduced current capacity of the biofouled bare and lone RuO_2-coated anodes.

The activation trend The observed high galvanic performances of the metal oxide coated anodes may be attributed to the enhanced activation of aluminum by RuO_2–TiO_2 coating. It was also facilitated by the uniformly porous coating having more dispersivity of RuO_2 when the RuO_2 content was ~30%. Ruthenium oxide can act as a mixed electron–proton conductor and can shift between various oxidation states. Ruthenium oxide can also behave as a good capacitor due to the action of various redox stages of ruthenium with simultaneous proton transfer across the coating originated from the water of hydration [19, 20]. Such oxidation and reduction reactions of ruthenium oxide on the anode surface can destruct the stable alumina film by a mechanism analogous to that of internal activators [2]. To understand the path of activation, the bare and optimum RuO_2–TiO_2 surface-activated anodes were repeatedly polarized in 3% NaCl solution. The anodes were galvanostatically polarized by impressing a current of up to 80 mA cm^{-2}, and then the current was interrupted. The polarization was carried out again after allowing the anodes sufficient time to reach stable potential. The process was repeated several times. After three polarizations, the bare anode became passive, which was evident from the abrupt potential rise into the passive region. The surface-activated anode did not exhibit any passivation tendency, even after six repeated polarizations.

The cyclic voltammograms [17, 18] have revealed that the maximum number of electro-active sites was present when the RuO_2 content in the RuO_2–TiO_2 coating was around 20 to 30 mol%. The coating had a high surface area and uniform pores at this composition. Thus, during polarization, high oxidation state shuttling of ruthenium could be predicted when the RuO_2 concentration was ~30%. Hence, the mixed oxide surface activation could resist severe polarization during the actual functioning of the anode.

Prolonged evaluation

Keeping the total mixed oxide composition of the coating at 0.192 mg cm^{-2}, the individual metal oxide content was varied from 0 to 100%. The anodes coated with the mixed oxide having 20 to 40% of RuO_2 exhibited high galvanic efficiency (more than 80%) and low self-corrosion values under laboratory conditions. These anodes exhibited high efficiency and low self-corrosion values under marine conditions also. The anodes studied under marine conditions were mechanically surface-treated to remove biofilm and insulation. Hence, the efficiency and self-corrosion values, determined under marine conditions, could be treated as apparent. Under laboratory and marine conditions, the anode having the coating containing 28% RuO_2 showed optimum efficiency and least self-corrosion values. The results of the long-term evaluation corresponding to the five compositions are compared in Table 2. The evaluations were repeated and the same trend was obtained in all the cases.

All the anodes showed a well-complementary relation between galvanic efficiency and self-corrosion. Aluminum and aluminum alloys generally suffer from pitting and localized corrosion in NaCl solutions. This is the main cause of low galvanic efficiencies and high self-corrosion values of aluminum alloy anodes [21]. The mixed oxide coating with uniform pore distribution and uniform surface activation can effectively reduce the localized corrosion. Different interactions between the substrate and the coating components, which are faster in the range of 10–30 mol% of ruthenium, create various species at various oxidation states of ruthenium.

The polarization behavior of the anodes after 2 months of galvanic exposure was recorded (Fig. 6b) to assess the retention capacity of the coating to activate aluminum. The same polarization trend as that of the fresh anodes (Fig. 6a) was observed. This observation confirms the activation behavior of the coating even after long-term galvanic exposure.

Biofouling

The tolerance of biofouling is a key factor that determines the worth of sacrificial anodes for marine applications. The rate and nature of biofouling on the anode surfaces were monitored as a function of immersion time in seawater. White calcareous deposition was observed on the surface of all the anodes within 2 days. The RuO_2–TiO_2 mixed oxide coated anodes showed no coverage of marine organisms after 1 week of immersion. However, 50 to 60% of the surface areas of the lone RuO_2 coated or uncoated anodes was found attacked by white slimy organisms. The mixed oxide coated anodes exhibited 20% attacked surfaces after 3 weeks, whereas other anodes exhibited more than 80%. These anodes were also attacked by some green- and brown-colored organisms. After 40 days, the RuO_2–TiO_2-coated anodes showed just less than 30% surface attack. After 45 days, the effluent containing the acidic wastes from the nearby industrial unit (Travancore Titanium) was released into the sea. Hence, some portions of the biofilm from the surfaces of all the anodes were peeled off due to the interaction with the effluent. Even after 2 months of study, the biofilm coverage on the RuO_2–TiO_2-coated anode surface was found below 30%, whereas it was above 80% for the bare and lone RuO_2-coated anodes.

After 4 weeks, the sacrificial anodes were tested for the presence of SRB, the organisms most closely identified with microbially influenced corrosion (MIC). While the absence of SRB was confirmed on RuO_2–TiO_2 surface-activated anodes, other electrodes exhibited an effective presence of SRB consortia. Thus, it was confirmed that TiO_2 in the surface coating could effectively reduce the biofouling and flourishing of microbial groups that interact in complex ways to induce MIC.

Conclusions

The optimum porous TiO_2 mixed RuO_2 catalytic coating on the Al-alloy anodes facilitated the diffusion of Al metal ions. The activation of Al-alloy anodes by RuO_2 was facilitated by the enhanced porosity of the coating. A fine-tuning of the mixed oxide ratio would be necessary to achieve enhanced performance. The anode coated with optimum TiO_2 mixed RuO_2 catalytic coating showed an exceptionally high galvanic performance. The mixed oxide coating on the anode surface was found to have high stability and induce activation even after half the volume of the anode was consumed due to sacrificial action. TiO_2 present in the catalytic coating effectively reduced biofouling on the anode surface. The anodes have the merits of low cost, easy development, high galvanic performance, tolerance in aggressive media, and bioresistance.

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