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Effect of IrO_2 loading on RuO_2–IrO_2–TiO_2 anodes: A study of microstructure and working life for the chlorine evolution reaction

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Abstract

RuO_2–IrO_2–TiO_2/Ti anodes are widely used in chlor-alkali and chlorate industry. The working life is of particular importance for anodes. The relationship between the content of IrO_2 and working life was investigated. The microstructure of the anode with 0.5 mg/cm^2 IrO_2 is much more homogeneous than those with lower IrO_2 contents. Both the size of particles containing RuO_2 and IrO_2 and the content of rutile TiO_2 phase in anodes decrease with increased IrO_2 content. The working life of anode with 0.5 mg/cm^2 IrO_2 is almost double that of the anode with 0.3 mg/cm^2 IrO_2.

Keywords: Anode; Working life; IrO_2 content

1. Introduction

Electrocatalytic materials based on noble metal oxides of metallic conductivity are widely used as electrodes in many fields of applied electrochemistry, such as chlorine production in the chlor-alkali and chlorate industry, processes involving oxygen generation in electroplating and metal electrowinning, as well as in cathodic protection, etc. [1] Dimensional stable anode (DSA) was considered as one of the most important discoveries in electrochemical field in the 20th Century. In recent years an interesting group of catalysts based upon the oxides of noble metals, in particular ruthenium and iridium, was reported [2]. Electrocatalysts RuO_2–IrO_2–TiO_2 demonstrates high activity together with a considerably higher stability in oxygen and chlorine evolution reaction in comparison with RuO_2 anode. This leads to the development of mixed RuO_2–IrO_2–TiO_2 coating. RuO_2–IrO_2–TiO_2 coated titanium electrodes are now becoming more and more attractive in the chlor-alkali industry as dimensionally stable anodes [3,4].

During the long-term electrolysis of chloride solutions, DSA exhibits a certain service life. The anode service life and coating stability can be evaluated by an accelerated stability test (AST) [5,6], which involves the electrolysis of dilute chloride solution at constant high current densities. The content of noble oxide has great effect on the electrochemical property of as-prepared anodes.

In this paper, the phase compositions and microstructure of RuO_2–IrO_2–TiO_2 anodes were characterized by SEM, HRTEM and XRD, and the effect of content of IrO_2 on the microstructure and service life of as-prepared anodes was discussed.

2. Experimental

2.1. Anode preparation

A solution of $TiCl_3$, $RuCl_3$ and H_3IrCl_6 was used to prepare the corresponding sols, by condensation and forced hydrolysis with simultaneous oxidation in air at elevated temperatures, using a similar procedure described elsewhere. In order to make an anode, the mixture of sols, was applied to titanium plates which was previously sand-blasted and etched. Multilayer painting of the Ti substrate by a mixture of RuO_2–IrO_2–TiO_2

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sols was performed. After each painting step, the layer was calcined at 450 °C for 10 min. The procedure was repeated until the coatings with 0.5, 0.4, 0.3 mg/cm^2 of IrO_2 were obtained, corresponding to anodes A, B and C, respectively. The samples were then calcined at 450 °C for 1 h.

2.2. Microstructure characterization

A JSM 6700F scanning electron microscopy (SEM) with an Inca energy spectrum analyzer, operated at 10 kV, was used to give the secondary electron (SE) image of as-prepared anodes under different magnifications. The surface of these anodes was sputter-coated with gold. The anodes microstructure was analyzed using a JEM 2010F transmission electron microscopy (TEM) operating at 200 kV. For the preparation of TEM samples, anode coatings were scratched from titanium substrate as powders for the observation. And the X-ray diffraction (XRD) patterns of the samples were measured using a Cu Kα radiation system (40 kV, 80 mA, Rigaku, CN-2028).

2.3. Service life test

Electrochemical characterization of the samples was performed by accelerated corrosion test (ACT) measurements. ACT, with a current density considerably higher and an electrolyte solution more dilute than those usually applied in industrial electrochemical conditions, provided information about the electrode stability and lifetime (via the electrode potential–time dependence at constant current density). All the electrochemical experiments were carried out in an electrochemical cell with a Ti counter electrode as the reference. The other experimental parameters were: electrolyte, 0.5 M NaCl, 35 °C. The applied ACT constant current density was 2.0 A cm^{-2}.

3. Results and discussion

3.1. XRD analysis

Ternary mixed oxides were prepared by combining various proportions of IrO_2 with equimolar amounts of RuO_2 and TiO_2. The chemical compositions of different anodes are listed in Table 1. Fig. 1 shows the XRD patterns of these three anodes, which indicates that all the anodes are composed of three phases—titanium, rutile TiO_2 and (Ru, Ir)O_2 phases. The strongest peak is identified as the titanium substrate because the coatings are too thin so that the X-ray can penetrate to the titanium substrate. Besides titanium, rutile TiO_2 is the main phase in all the anodes. The average sizes of rutile phase in anodes A, B and C are 30, 50 and 80 nm, respectively,

Table 1
Chemical composition of as-prepared anodes

	IrO_2 (mg/cm^2)	RuO_2 (mg/cm^2)	TiO_2 (mg/cm^2)
Anode A	0.5	1.0	0.9
Anode B	0.4	1.0	0.9
Anode C	0.3	1.0	0.9

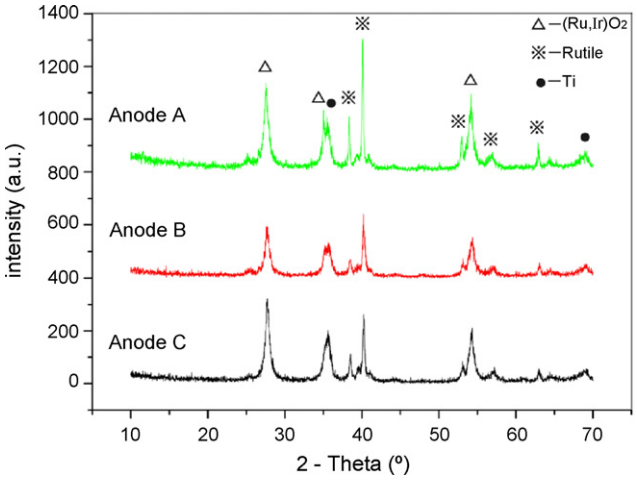


Fig. 1. XRD patterns of as-prepared anodes.

according to Scherrer's equation. The RuO_2 and IrO_2 would coexist in the form of (Ru, Ir)O_2 solid solution. The observation of mutual solubility for the oxides RuO_2 and IrO_2 is not new. Mcdaniel and Schnedider [7] has reported a continuous range of solid solubility for the system RuO_2–IrO_2, based upon results from the high temperature reaction of the component oxides, as both RuO_2 and IrO_2 have the rutile structure and very similar ionic radius with each other (Ru^{4+}: 0.076 nm, Ir^{4+}: 0.077 nm).

The relative peak intensities of (Ru, Ir)O_2 solid solution (1 0 1) and rutile TiO_2 (1 0 1) change with the content of IrO_2 in anodes. The peak intensity of solid solution is higher than that of rutile in anode A, while those in both anodes B and C are lower than that of rutile TiO_2. It lets us to conclude that the content of RuO_2–IrO_2 solid solution of in anode A is higher than those in anodes B and C, i.e., high IrO_2 concentration results in lower percentage of rutile TiO_2 phase.

3.2. SEM analysis

The surface morphologies of anodes are significantly affected by the concentration of IrO_2. SE images of the coating surface at three magnifications are shown in Fig. 2. It can be found that all the anodes consist of mud-cracks structure and flat area. The area of each mud in anodes B and C is larger than that in anode A, and there are also much more mud-cracks structure in anodes B and C than that in anode A. The widths of cracks for these anodes are also different. For anode A, the crack width is about 0.3 μm, but for anodes B and C, the cracks are about 1–3 μm wide. Cracks can provide the space for the smooth release of chlorine gas bubbles. It also provides the channel for the oxygen to result in the passivation of Ti substrate. Therefore, the cracks can deteriorate the electrochemical performance of as-prepared anodes. In anodes B and C, there are many needle-like crystallites along the inner side of cracks with average sizes about 20–30 nm. The needle-like crystallites are not present in anode A. The flat areas of all the anodes are composed of numerous nanosize particles which are not well-grown. Most of theses particles are agglomerated, so it is difficult to know the exact particle size on flat area by SEM.

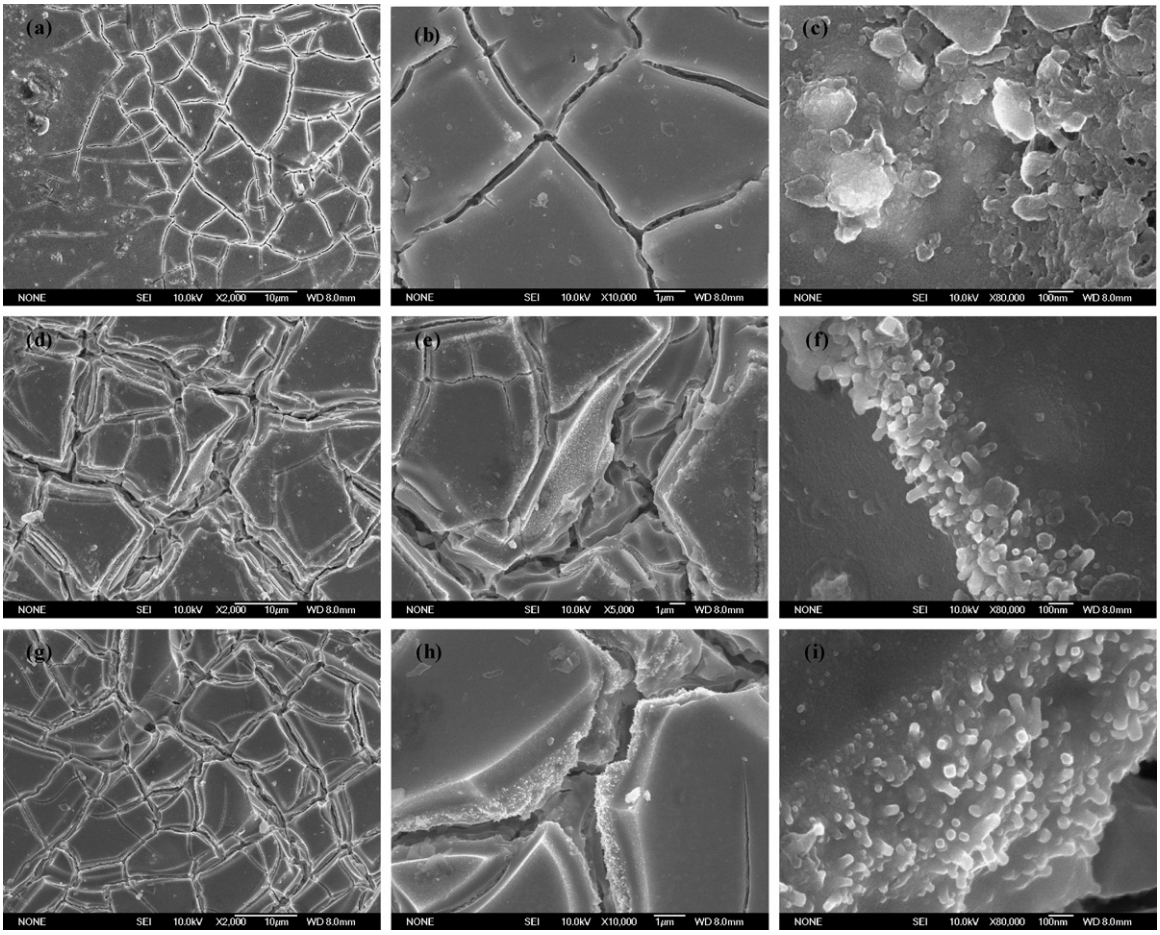
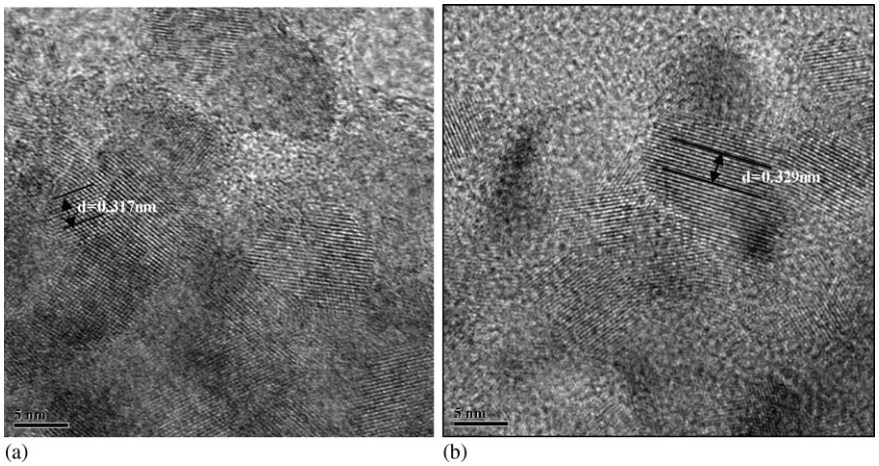


Fig. 2. SEM surface morphologies of as-coated anodes: (a–c), anode A; (d–f), anode B; (g–i), anode C.

3.3. TEM analysis

Fig. 3 shows the TEM images of anode A, which indicates that the sizes of most particles are about 5–8 nm. There are two different sets of lattices for those ultrafine particles. The *d* value of one set of lattice plane is 0.317 nm, which is close to the standard value of ruthenium oxide (1 1 0)—0.3182 nm and iridium oxide (1 1 0)—0.3178 nm. The EDS results show that the ultrafine particles consist of Ru, Ir, Ti and O elements. The fraction of this kind of particles is higher than 60%. The *d* value of the other set of lattice plane is 0.329 nm close to the standard value of rutile, and the corresponding particle contains only Ti and O elements by EDS. So, it could be concluded that one phase is probably the (Ru, Ir, Ti)O_2 solid solution and the other one is rutile TiO_2 phase.

For anode B, there are also two kinds of particles as shown in Fig. 4 with approximately equal amounts. The average size of



(a) (b)

Fig. 3. HRTEM of anode A: (a) (Ru, Ir, Ti)O_2 phase and (b) rutile phase.

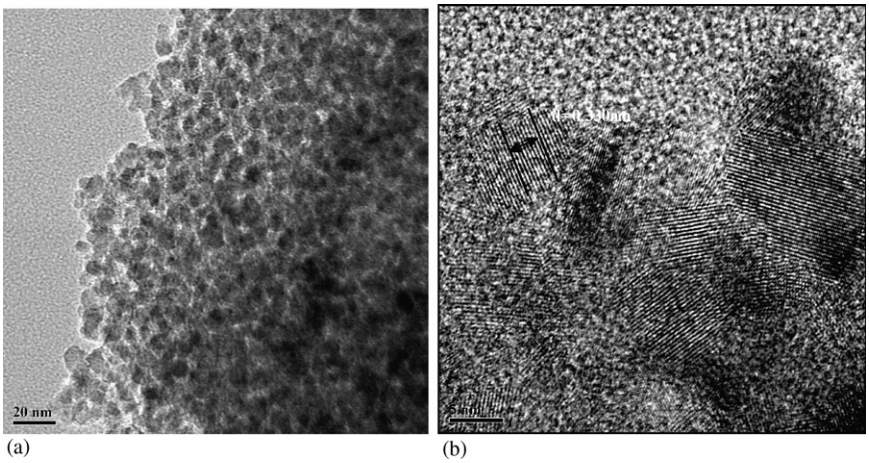


Fig. 4. TEM images showing two phases in as-prepared anode B. (a) (Ru, Ir, Ti)O_2 phase and (b) rutile phase.

the larger particle is about 15–20 nm, which is in agreement with the size of needle-like crystallites as shown in Fig. 2. The EDS results show that this kind of particles consists of Ru, Ir, Ti and O elements. The semi-quantitative results indicate that the content of Ti in the larger particles of anode B is much lower than that in the particles of *d* value 0.317 nm in anode A. So, it could conclude that the presence of TiO_2 would prevent the growth of RuO_2 and IrO_2 containing particles. Another half in the structure is composed of ultrafine particles about 4–5 nm in diameter as shown in Fig. 4(b). The HRTEM results show that the *d* value is 0.336 nm, which is a little larger than the standard value of rutile (1 1 0). The EDS results show that there are mainly two elements—Ti and O, and a few amount of Ru element. Both anodes A and B contain ultrafine particles of about 5 nm in size, however, the phase compositions of the ultrafine particles are quiet different with each other: rutile TiO_2 in anode B, a phase of solid solution containing Ru, Ir, Ti and O elements in anode A. Though the ionic radius of Ti^{4+} is considerably larger than those of Ru^{4+} and Ir^{4+}, however, it still lies just within the Hume-Rothery limit for successful substitution. Both RuO_2 and IrO_2 are metallic conductors, TiO_2 is a wide-gap semiconductor (band gap—3.2 eV), which is known to demonstrate only limited solid solubility with RuO_2 and IrO_2. In the present work, the Ti, Ru, Ir and O coexist in many particles in both anodes A and B, and it also finds that many particles which only contain Ti and O elements in anode B. So, it could assume that (Ti, Ru, Ir)O_2 material is not simply a mixture of fine crystals of TiO_2 and (Ru, Ir)O_2, but some clustering may occur.

Combined with the SEM results, it could be proposed that the flat area of anode B consists of rutile TiO_2 phase, and the particles whose size is 15–20 nm along the innerside of cracks are the (Ru, Ir, Ti)O_2. The distribution of both rutile and (Ru, Ir, Ti)O_2 phases is much more homogeneous comparing with that in anode A.

3.4. Accelerated corrosion test

The time dependence of the relative electrode potential, obtained from the results of the accelerated corrosion test, for as-prepared anodes is shown in Table 2. The working life increases with the increase of concentration of IrO_2. The working life of anode A is almost double that of anode C under the same condition.

The anode lifetime in the stability test is defined by the time at which the potential of an anode suddenly escalates under galvanostatic conditions in simultaneous oxygen and chlorine evolution reaction. Two paths for the loss of the electrocatalytic activity have been suggested [8]:

1. the simultaneous electrochemical oxidation of Ru species in the coating forming the soluble products that move to the electrolyte,
2. the formation of insulating TiO_2 layer at the substrate coating interface which grows by oxidation of the Ti substrate with oxidizing agents as chlorine and especially oxygen are.

The chemical composition of all the anodes before and after accelerated corrosion test is shown in Table 3. The results show that the concentration of RuO_2 is greatly decreased after the accelerated corrosion test. The content of RuO_2 for anode A after the accelerated corrosion test becomes only about 1/2 of

Table 2
Working life of as-prepared anodes

	Working life (h)
Anode A	2250
Anode B	1600
Anode C	1200

Table 3
The chemical composition of as-prepared anodes before and after ACT by EDS

	Before ACT			After ACT		
	TiO_2 (%)	RuO_2 (%)	IrO_2 (%)	TiO_2 (%)	RuO_2 (%)	IrO_2 (%)
Anode A	52.9	34.8	12.5	72.4	15.9	11.7
Anode B	60.0	31.7	8.3	80.9	11.2	7.9
Anode C	65.2	28.9	5.9	87.3	6.7	6.0

the original, it remains only 1/3 for anodes B and C after the accelerated corrosion test. And the concentration of IrO_2 is almost same for all the anodes before and after the test. This indicates that the electrochemical dissolutions for anodes B and C are much more serious than that for anode A. This leads to much longer anode lifetime of anode A than that of anodes B and C.

The different morphologies of the coatings may be responsible for the different lifetime. According to the SEM images shown in Fig. 2, microstructure of anode A, especially those particles containing RuO_2 and IrO_2 on the coating surface is much more homogeneous and smooth than that in the anodes B and C, which leads to larger surface area. Consequently, the real current density (the rate of dissolution of the Ru species) on the anode A is lower. Meanwhile the dense and homogeneous structure of the catalytic coating of the anode A prevents the penetration of the electrolyte toward the titanium substrate, which, besides the lower current density, restrains the quick formation of the less non-conductive intermediate TiO_2 layer. In additional, high percentage of rutile TiO_2 phase before the accelerated corrosion test in the anodes B and C as observed in Fig. 2 would accelerate the loss of the electrocatalytic activity according to path 2.

4. Conclusions

The surface morphologies of as-prepared three anodes with different amounts of IrO_2 are quite different. The microstructure on the anode surface with 0.5 mg/cm^2 IrO_2 are homogeneous which is composed of ultrafine nanoparticles containing RuO_2 and IrO_2, however this kind of nanoparticles can only be found along innerside of cracks for anodes B and C with 0.4, 0.3 mg/cm^2 IrO_2, respectively. The size of ultrafine particles containing RuO_2 and IrO_2 for anode A with 0.5 mg/cm^2 IrO_2 is 5–8 nm, which is less than those (15–20 nm) of anodes B and C with 0.4, 0.3 mg/cm^2 IrO_2. The size of rutile TiO_2 (about 5 nm) is almost the same for all prepared anodes. However, the relative contents of rutile phase are different for all these anodes, the content of rutile phase decreases with the increase of IrO_2 content. Significantly longer lifetime by the accelerated corrosion test is obtained for anode with highest IrO_2 content.

References

[1] S. Trasatti, in: A. Wieckowski (Ed.), Interfacial Electrochemistry: Theory, Experiment and Applications, Marcel Dekker, New York, 1999, p. 769.
[2] Y.E. Roginskaya, T.V. Varlamova, M.D. Goldstein, I.D. Belova, B.S. Galyamov, R.R. Shifrina, V.A. Shepelin, V.N. Fateev, Formation, structure and electrochemical properties of IrO_2–RuO_2 oxide electrodes, Mater. Chem. Phys. 30 (1991) 101–113.
[3] R. Hutchings, K. Muller, K.S. Stucki, A structural investigation of stabilized oxygen evolution catalysts, J. Mater. Sci. 19 (1984) 3987–3994.
[4] M. Guglielmi, P. Colombo, V. Rigato, Compositional and microstructural characterization of RuO_2–TiO_2 catalysts synthesized by the sol–gel method, J. Electrochem. Soc. 139 (1992) 1655–1661.
[5] V.A. Alves, L.A. Silva, J.F.C. Boodts, J. Appl. Electrochem. 28 (1998) 899.
[6] V.M. Jovanovic, A. Dekanski, P. Despotov, B. Nikolic, R.T. Atanasoski, J. Electroanal. Chem. 339 (1992) 147.
[7] C.L. Mcdaniel, S.J. Schnedider, J. Res. NBS 73A (1969) 213.
[8] M. Ito, Y. Murokami, H. Kaji, K. Yohikozawa, Y. Takasu, Surface characterization of RuO_2–SnO_2 coated titanium electrodes, J. Electrochem. Soc. 143 (1996) 32–36.