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The study on high performance titanium electrodes coated with composite active film

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Abstract. Titanium based platinum group composite active electrodes were prepared by thermal oxidation decomposition method at high temperature. Effect of temperature on titanium composite active coating electrodes was investigated. Kinetic study of anodic process of active coating was carried out. The influence of composite active film physicochemical properties on electrochemical catalytic activity and enhancement service life was conducted.

1. Introduction

For many electrochemical processes, all desired products are obtained via cathodic reduction reactions, such as galvanizing of steel plate in steel industry, electroplating in electroplating industry, electrolytic copper foil for printed circuit board, aluminum foil treated by electrolytic surface oxidation, and synthesis of various organic compounds by electrolysis reduction, etc. Meanwhile, oxygen evolution reaction occurs mainly on the surface of the anode. In most industrial production, the lead or lead alloy insoluble anodes occupy a large market. However, the oxidation layer on the surface of lead is easy to corrode and exfoliate, and dissolved into the electrolyte and deposited into the cathode products, causing pollution and reducing the quality of the products. Lead and lead alloy electrodes have high oxygen evolution over potential.

The use of high current density (over 4000 A/m²) not only causes the loss of electrical energy in the form of waste heat, but also increases the dissolution rate of lead. The raw materials (such as copper foil, aluminum foil), lead and alloy electrodes for high density production of electronic products, lead and alloy electrodes are unable to meet the requirements of the production process. A high-performance titanium based composite active coating is studied. The electrode is used as a long life oxygen evolution anode with stable electrochemical performance at high current density.

2. Experimental

2.1. Preparation of sample

The TA1 pure titanium plate with a width of 5mm, a length of 100mm and a thickness of 1mm was etched for 2 hours in a boiling oxalic acid solution with a mass ratio of 8%. After that, it was washed and cleaned with high pure water.

Coating solution: RuCl₃, H₂IrCl₆·6H₂O, H₂PtCl₆·6H₂O, PdCl₂, SnCl₄, MnCl₄, TaCl₅ and CH₃(CH₂)₃OH.



Composite oxide coated titanium electrodes with different compositions were prepared by high temperature thermal decomposition.

2.2. Materials characterization

The surface morphology of the coating was analyzed by scanning tunneling microscope. The electrochemical characteristics of the electrode were tested by electrochemical comprehensive tester. The electrode was composed of composite oxide coated titanium electrode with an area of 8mm² and a reference electrode of Ag-AgCl.

3. Results and discussion

3.1. Effect of sintering temperature on the properties of composite active titanium electrode

The sintering temperature is an important parameter for the development of composite oxide coating electrode [1, 2]. It not only affects the degree of the reaction of chloride in the coating to oxide, but also affects the crystal structure and the surface morphology of the coating. The composite oxide coating electrode is prepared by the thermal oxidation decomposition method of metal chloride under high temperature conditions. The thermal oxidation temperature is too low and the oxidation of metal chloride is incomplete. The electrocatalytic properties of the metal chloride are not available and the thermal oxidation temperature rises. On the one hand, the chlorine content in the coating can be reduced to very low, on the other hand, metal crystal. Particles will inevitably grow and reunite. The growth of crystal particles will cause uneven distribution of surface coating, loose and binding force of composite coating electrodes.

As shown in Table 1, it can be concluded that the main temperature range of thermal decomposition for metal chloride in active coating solution is located at 420~580°C. In the temperature range of 420~580°C, the chloride in the coating is oxidized completely. The temperature is below 420°C, the chloride content in the coating is high. When the temperature is above 580°C, the oxygen content in the coating decreases rapidly. This is because the oxide in the coating is composed of non-stoichiometric oxides, such as IrO₂-X, RuO₂-X and TiO₂-X, which belong to anoxic oxide. At this time, the oxide structure of the coating changes, the oxygen content of the metal oxide coating changes correspondingly. Consequently, the optimum oxidation temperature of the composite coating electrode is 540°C.

Table 1. Oxygen and chlorine contents in coatings at different sintering temperatures.

Temperature °C	Oxygen content wt(%)	Chlorine content wt(%)
200	22.80	27.70
300	27.11	20.52
420	38.05	0.92
460	38.92	0.36
500	38.26	0.39
540	40.04	0.24
580	39.92	0.24

3.2. Study on surface characteristics of composite active coating

The platinum metal iridium, platinum, rhodium and palladium in the surface coating of the composite active coated titanium electrode belong to the cubic crystalline structure of the surface. Ruthenium belongs to the dense crystalline structure of six parties [3]. The ionic radius value of Ru⁴⁺ is 0.65×10⁻⁸cm, the ionic radius of Ti⁴⁺ is 0.64×10⁻⁸cm, and the ionic radius is similar, and it can be stable in the same lattice and form solid isomorphous solid solution.

Figure 1 is an atomic structure model diagram of ruthenium and titanium. In TiO_2 , the outer layer of the electron configuration of Ru is $4d^75s^1$, and the 4 electrons are given to 2 oxygen atoms, and the remaining 4 free electrons are not involved in the CO formation movement. At this time, the solid solution of the ruthenium and titanium coating can be expressed in general formula: $\text{Ru}_\delta\text{Ti}_{1-\delta}\text{O}_{2n}\text{e}_{0.4\delta}$.

The delta represents the number of atoms that Ru replaces Ti; n is the number of atoms in Ti in TiO_2 . In the structure of RuO_2 and TiO_2 solid solution, besides the full band, there are electrons in the band ($\text{e}_{0.4\delta}$). The electrons in this energy band are not bound to the electrons in the full band, only the energy of 0.2eV can be excited to the guide band, so the conductivity of this kind of solid solution is excellent.

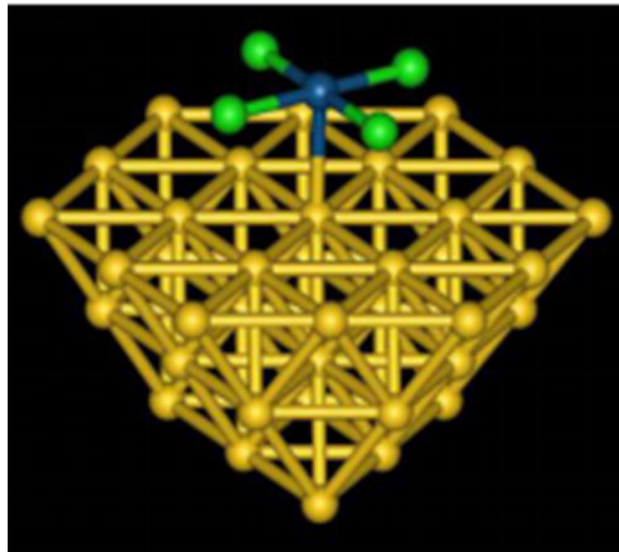


Figure 1. Atomic structure model of Ru and Ti.

Figure 2 is a surface coated STM image. It is observed from the figure that the grain size of the coating surface is very small. There is no obvious crack on the surface of the coating on the 5~20 nm range. In order to obtain the average size of the surface coating grain, the X-ray diffraction phase of the surface grain of the coating was analyzed [4, 5], and the X-ray diffraction data of the surface coating of surface 2 were obtained.

X-ray diffraction data of surface composite coating grains from table 2. The half height width beta of the strongest diffraction peak of the XRD spectrum is obtained. The average grain size of the composite active coating is obtained by using the Scherrer formula: $D = K \lambda / \beta \cos \theta$. Among them, K is Scherrer constant, $K=0.89$; λ is X ray wavelength, $\lambda=0.1540598$ nm. From table 2, the data of 2θ is 34.520. Consequently, $D=0.89*0.1540598*360/[0.54*2\pi\cos(34.52/2)]=15.1$ (nm)

The average grain size of the composite active coating is 15.1 nm and the grain is fine. There is no obvious crack on the surface of the surface coated STM. The solid solution structure of the surface coating and the titanium matrix is compact, and there is no obvious crack [6].

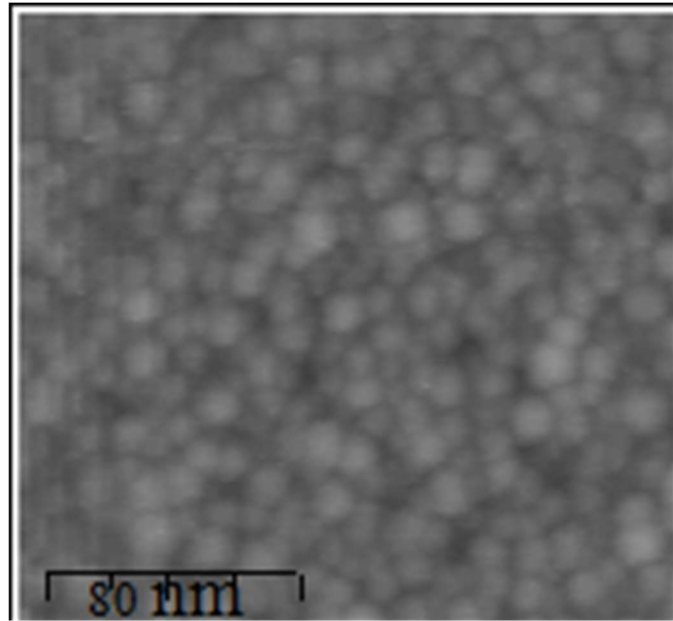


Figure 2. STM micrographs of surfaces coating.

Table 2. XRD pattern of grain crystal of surface coating.

No.	2 θ	INT	Width	d	I/I0
1	27.680	809	0.270	3.220	94
2	34.520	859	0.540	2.596	100
3	38.300	352	0.330	2.348	41
4	40.020	256	0.360	2.251	30
5	53.420	503	0.300	1.714	58
6	56.940	128	0.240	1.616	15
7	58.300	109	0.270	1.581	13
8	62.840	110	0.330	1.478	13
9	65.500	117	0.240	1.424	14
10	68.280	103	0.270	1.373	12

3.3. Electrochemical properties of composite active coating electrodes with different components

The kinetic parameters of oxygen evolution reaction of composite active coating titanium electrode with different compositions were studied. The study electrode area is 8mm², and they are 1 # TiRu electrode, 2 # TiPtIr electrode, 3 # TiPtIrSn electrode, 4 # TiPtIrMn electrode, 5 # TiPdIrMn electrode, 6 # TiIrTaSn electrode and 7 # TiRuIr electrode, respectively. The reference electrode is Ag-AgCl electrode, the auxiliary electrode is platinum electrode, and the study solution is 1mol/L H₂SO₄ solution. The current density is from 7.94*10⁻⁴ A/cm² to 6.31*10⁻³ A/cm², and the temperature is 30°C. According to Tafel formula, the kinetic parameters of oxygen evolution reaction electrode of different research electrodes are included in Table 3.

According to Tafel formula: $\eta = a + b \lg i$, it can be obtained that the sequence of intercept “a” from small to large reflects the order of oxygen evolution activity of composite active coating electrode from strong to weak. The lower the “a” value is, the lower the oxygen evolution potential of the electrode is,

the better the oxygen evolution activity is. The catalytic activity of TiPtIrMn electrode and TiRuIr electrode for oxygen evolution is better. The smaller the slope “b” value represents the smaller the polarization degree of the electrochemical reaction. The β value reflects the influence of the electrode potential on the activation energy of the electrode. When the β value changes in the range of (0, 1), the greater the beta value is, the greater the influence of the activation energy on the electrode is. Among these electrodes, the β n value of TiPtIrMn electrode and TiRuIr electrode, TiPdIrMn electrode and TiIrTaSn electrode are much higher than other electrodes. The exchange current density i^0 is the basic parameter of the electrode process kinetics [7, 8], indicating the rate of oxidation or reduction under the equilibrium potential of the electrode. The i^0 value reflects the reversibility of the electrode reaction. As a result, it can be concluded that the TiPtIrMn electrode and TiRuIr electrode in the electrode are perfect coating electrodes with good catalytic activity for oxygen evolution.

Table 3. Kinetic parameters of various electrodes in oxygen evolution reaction.

Electrode	a, V	b, V	β n	i^0 , A/cm ²
1 [#]	0.4170	0.1275	0.4716	5.363×10^{-7}
2 [#]	0.3160	0.1050	0.5727	9.783×10^{-7}
3 [#]	0.4830	0.0875	0.6872	3.020×10^{-9}
4 [#]	0.2510	0.0675	0.8908	1.912×10^{-7}
5 [#]	0.3790	0.0475	1.2660	1.050×10^{-11}
6 [#]	0.3040	0.0800	0.7516	1.585×10^{-7}
7 [#]	0.2290	0.0650	0.9251	2.999×10^{-7}

Table 4. Results of the strengthened lifetime tests for various electrodes.

Electrode	Current density(A/cm ²)	Life (h)
1 [#]	4.00	5
2 [#]	4.00	565
3 [#]	4.00	712
4 [#]	4.00	896
5 [#]	4.00	220
6 [#]	4.00	278
7 [#]	4.00	34

Different composite active coating electrodes with coating area of 1cm² are used as anode, pure titanium plate is used as cathode, polar distance is 10mm, electrolysis solution is 1mol/L H₂SO₄ solution, temperature is 35°C, and current density is 4 A/cm², the continuous operation of strengthened life value is listed in Table 4. From Table 4, it can be seen that TiPtIrSn electrode and TiPtIrMn electrode have longer service life under the same electrolysis conditions. Combining the data of Table 3 and Table 4, TiPtIrMn electrode has good catalytic activity for oxygen evolution and has a longer service life. It can be used as a long life oxygen evolution anode with excellent electrochemical performance under high current density [9].

4. Conclusion

The main temperature range for thermal decomposition of metal chloride in the active coating solution is located at 420~580°C. The optimum oxidation temperature of the composite active coating electrode

is 540°C. The average grain size of the composite active coating is 15.1 nm, the grain size is fine, the surface coating is compact with the solid solution structure of the titanium matrix, and there is no obvious crack. The TiPtIrMn electrode has good catalytic activity for oxygen evolution and has a long service life. It can be used as a long-life oxygen evolution anode with high current density.

Acknowledgments

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