DESIGN AND DEVELOPMENT OF A HIGH PERFORMANCE ANODE FOR CHLORINE-EVOLUTION①

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ABSTRACT The literatures were analyzed, ingredients were designed, the mono/double layered structures were experimented. It was found that the excellent titanium anodes could be obtained by adding cobalt into the intermediate layer. So an anode material with both high activity and corrosion resistance was developed.

Key words titanium anode coblt chlorine-evolution

1 INTRODUCTION

Chlorine-evolution anodes have been widely used in industrial productions. The anodes can be roughly classified as two types: the higher life-time with lower activity and lower life-time with higher corrosion resistance. The former are applied to the chlorine and soda industry and the later mainly the hypochlorite production. The priorer anode with better properties is looked forward to for chlorine-evolution industry usage.

To search for the high active and low corrosion resistant anode materials, the ingredient studies have never stopped since the invention of the dimensionally stable anodes. Up to now, about 75% of the two thousand articles collected in the Dialog System have pertinence to element and composition selecting[1]. The most studies have laid particular stress on active functional or corrosion resistant functional elements. There are still other dubious elements which can not be made good use of. In the paper, the study focuses on adding cobalt as an alloying element, and an anode with both higher activity and corrosion resistance was successfully developed.

2 INGREDIENT DESIGN AND SPECIMEN PREPARATION

2.1 *Ingredient Design*

2.1.1 Literature Recall and Analysis

Through the Dialog System 242 articles of the required literatures concerning elements of Co, Ir, Ru, were summed up. It could be concluded: (1) Ruthenium dioxide must be considered firstly as the active material. (2) Iridium dioxide may be considered as the indispensable material when high corrosion resistance is expected[2]. Iridium is the essential element in some recently developed domestic anodes[3] and in Pt-Ir/Ti anode which was referred to as the highest active one[4]. (3) Cobalt is a controversial element, whose excellent chlorine-evolution properties were observed very early[5-7]. But it could not be made in industrial use of, for it might deteriorate anode's durability when added[8]. A contrary situation has been found to the surprise in some other papers, which used Co as oxygen evoluting element to increase the life-time of the anode[9-11]. The contradictory results in fact provided a turning point to a possible excellent anode.

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2.1.2 Idea for Ingredient Design

The design for active layer was based on the generally accepted idea to select Ru, Ir, Ti, Sn as the main elements. The compositions also referred to the previous literatures including ours[12].

Double-layered structure was emphasized. The distributions of the elments Co and Ir were designed to investigate the layer distributing effects.

The cost of the anodes designed must meet the requirements of industrial productions. So G^* was introduced to indicate the equivalent loading of precious metals (the ratio of Ru and Ir was about 1:4 currently):

$$G^* = G_{Ru} + 4G_{Ir},\ g/m^2$$

G^* values were 10 to 22, the former and the later are adopted in chlorine and soda industry and hypochlorite production relatively.

2.2 *Specimen Preparation*

The anode specimens and products were prepared by a thermal decomposition method, which included a succession of degreasing, etching, brushing, drying oxidizing and annealing. The details can be found elsewhere in previous patent[13].

The 22 types of specimens with mono/double layer coating were experimented. After the ingredient was initially determined, the further experiments were conducted to determine the suitable compositions and techniques. The 7 typical ingredients of the specimens were listed in Table 1.

3 EXAMINATIONS AND ANALYSIS FOR VARIOUS SPECIMENS

3.1 *Experiment and Data Processing*

3.1.1 Corrosion Resistance

The accelerating life-time test (ALTT) was used to indicate the corrosion resistance of a specimen, which was electrolyzed in 4 mol/L H_2SO_4 with a current density of 400 A/dm^2. Life-time τ was recorded.

3.1.2 Electrochemical Properties

In this paper, brine electrolyzing without diaphragm was performed. Cell voltage E and equivalent chlorine content G_{Cl} were recorded, the current efficiency η, voltage efficiency ξ and electrolysis efficiency ζ were calculated.

3.2 *Analysis and Comparison*

The data of the 7 typical specimens about their properties of activities and corrosion resistances were listed in Table 2, in which G^* values were also listed for the sake of preparation. As for the mono-layered specimens, it could be found that the properties were greatly changed by adding Co. In the coating based on Ru dioxide the adding of Co could result in destroying the corrosion resistance, in the meantime the highest activity could be established, while comparing Ru-Ir-Ti-Sn-Co (specimen 3#) with Ru-Ti-Sn (specimen 1#) that is the type currently used in chlorine and soda industry. Whereas in the coating based on Ir dioxide, the adding of Co made things go

Table 1 Ingredients of typical titanium anode spesimens mole fraction

No	Types	Intermediate			Surface					G^* /g·m^{-2}
		Ir	Ru	Co	Ru	Ir	Ti	Sn	Co	
1	Ru,Ti,Sn	0	0	0	33	0	62	0	5	10
2	Ir,Co	0	0	0	0	67	0	0	33	8
3	Ru,Ir,Ti,Sn,Co	0	0	0	26	14	49	5	6	12
4	Ru,Ir,Ti,Sn,Co	67	0	33	27	14	53	6	0	10
5	Ru,Ir,Ti,Sn,Co	100	0	0	25	14	50	5	6	20
6	Ru,Ir,Ti,Sn,Co	70	0	30	25	16	50	5	6	20
7	Ru,Ir,Ti,Sn,Co	67	0	33	27	14	53	6	0	21

Table 2 Properties of typical specimens

No	G^* /g·m^{-2}	E /V	G_{Cl} /g·L^{-1}	η /%	ξ /%	ζ %	τ /h
1	10	3.95	4.16	62.9	42.9	27.0	1.2
2	8	3.97	3.52	53.2	42.8	22.8	5.0
3	12	3.56	4.24	64.1	47.8	30.6	1.0
4	10	3.90	4.17	63.0	43.7	27.5	5.6
5	20	3.72	4.14	62.6	45.8	28.7	14.0
6	20	4.12	4.31	65.2	41.3	26.9	13.2
7	21	4.13	4.13	62.5	43.4	27.1	21.5

into the other terminus, which could be found for Ir-Co(specimen 2#) that the highest life-time value reached and it was accompanied by the lowest activity value. This result was analogous to literature report[9].

As for the double-layered specimens, the states were somehow complicated when Co was added. At the first situation when adding Co to their surface layers, no sign of deterioration in both corrosion resistances and activities appeared. The specimens 5# and 6# with Ru based coatings maintaining high levels of their life-time value and electrolysis efficiency(Table 2).

When Co was added to intermediate layers, good effects could be found obviously. To compare with lower G^* specimens, the specimen added Co(4#) not only had higher activity than that of Ru-Ti-Sn(1#), but also had almost the same corrosion resistance as that of Ir-Co(2#). If we turned to look the data of the higher G^* level specimens, we might also be excited to know that the specimen 7# had much higher lift-time value than those of the specimens 5# and 6#.

4 CHARACTERISTICS OF DEVELOPED ANODE PRODUCTS

4.1 *Corrosion Resistance*

4.1.1 ALTT in H_2SO_4

Specimens were cut from the batches of the anode products with G^* value of 15 and tested according to a national standard (GB 12176-90) and a standard of the Ministry of Chemical Engineering (HG/T 2471-93). The test condition of former is 1 mol/L H_2SO_4, 200 A/dm^2, and later 0.5 mol/L H_2SO_4, 100 A/dm^2. The data of ALTT were listed in Table 3, in which the excellent result could be seen. The life-time of the developed anode was 2.5 times higher than the technical requirment for A-grade products used in hypochlorite production, and 17 times higher than the requirement for A-grade products for chlorine and soda industry.

Table 3 Life-Time τ of ALTT in H_2SO_4

Developed anode	τ /h	τ /min
Tested Datum	50	15 200
Requirment	⩾20	⩾800
Reference	GB 12176-90	HG/T 2471-93

4.1.2 ALTT in Brine

In the JS-45 type hypochlorite production equipment, the cut specimens were eletrolyzed in 3% NaCl with a flow quantity of 0.1～0.2 L/A·h. The results were shown in Fig. 1. The life-time τ of the anode would be 54 thousand h if i was 15 A/dm^2[14].

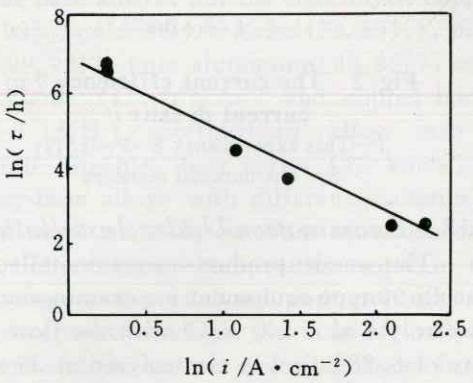

Fig. 1 The life-times τ *vs* current desity i

4.2 *Activity*

4.2.1 Chlorine-Evolution Potential and Polarization Rate

The Chlorine-Evolution Potential (CEP) and Polarization Rate(PR) were tested *vs* SCE in saturated brine according to the Ministry of Chemical Engineering (HG/T 2471-93). It

could be seen that this high life-time anode had excellent activity which obviously surpassed the technical requirements for chlorine and soda industry (Table 4).

Table 4 Data of CEP and PR

Developed anode	CEP /V	PR /mV
Tested Datum	1.11	38
Requirement	≤1.13	≤50

4.2.2 Current Efficiency

Current efficiency was tested in a cell without diaphragm. The test conditions were as follows: 0.5 NaCl, 1 000 C/L, 30±1 ℃. The current efficiency was shown in Fig. 2, which was superior to that of the most active Pt-Ir/Ti anode referred in literature[14] and the requirement of the national standard was also drawn.

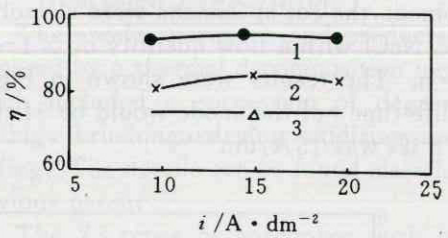

Fig. 2 The current efficiency η *vs* current density i

1—This experiment; 2—Pt-Ir/Ti; 3—The national standard

4.3 *Examination Under Installation*

The anode products were installed into the JS-90 type equipment for examination. The electrolyte of 3.5% NaCl with the flow quantity of 8.88 L/h was electrolyzed at 35±1 ℃. Equivalent chlorine content G_{Cl}, current efficiency η, electrical power consumption per kilogram of chlorine W, utilization rate of NaCl U were determined (Table 5). They fulfilled all the requirements of the national standard.

5 CONCLUSIONS

(1) The Co-containing mono-layered titanium anode coatings based on Ru dioxide possessed very high activity and very low corrosion resistance. And the opposite situation occurred to ones based on Ir dioxide.

Table 5 Data of examination under installation

E /V	G_{Cl} /g·L^{-1}	η /%	W /kW·kg^{-1}	U /%
3.7	11.2	88.8	3.14	32

(2) The adding Co to the surface layer of the double-layered would not destroy its corrosion resistance. When adding Co to the intermediate layer, the life-time of the anode would increase greatly with the same activity level, so a good performance anode for the chlorine-evolution could be expected.

(3) An excellent anode material was developed successfully, which reached both high activity and corrosion resistivity.

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