

PROGRESS IN STUDIES OF ELECTROCATALYSTS AND DOPED CARBON ANODES IN ALUMINIUM ELECTROLYSIS CELLS^①

Liu, Yexiang Wang, Xiangmin Huang, Yongzhong

Wang, Huazhang Yang, Jianhong

Department of Nonferrous Metallurgy, Central South University of Technology, Changsha 410083

ABSTRACT

The second generation electrocatalysts with little or without lithium salt have been studied in laboratory. The promising electrocatalysts which can be used on prebaked anodes in Hall-Heroult process can reduce anodic overvoltage (η_a) up to 200 mV, and those which can be used on Söderberg anodes can reduce η_a up to 148 mV. Some arguments about the lithium salt-containing anode paste are discussed.

Key words: aluminium electrolysis lithium salt-containing carbon anodes new electrocatalysts

1 INTRODUCTION

Aluminium electrolysis industry consumes huge amount of electric energy. It is now facing urgent aspect—the rising of energy prices. Electrocatalysis is a hopeful way to save energy. We [1-5] have been studying the electrocatalytic effects of doped carbon anodes in Hall-Heroult process since 1985. After tested in industrial cells, 2000 HSS cells have used lithium carbonate containing anode paste in their production in China so far. This technique being employed by many smelters is not an accidental phenomenon. It has really shown the merit of saving energy. This paper will report progress related to our studies on the doped carbon anodes and offer explanations to some questions.

2 PROGRESS RELATED TO STUDIES ON SECOND GENERATION ELECTROCATALYSTS

We started the studies on the second genera-

tion electrocatalysts after the lithium carbonate doped anode paste found application in industry. The aims of these studies are as follows.

(1) To reduce the cost of electrocatalyst. The consumption of Li_2CO_3 is around 3 ~ 4 kg/t-Al, owing to the high price of lithium carbonate (more than 30 000 yuan/t), the economical efficiency is not so good. It is necessary to find a type of electrocatalysts containing little or no Li_2CO_3 , and the additives should be no harm to the metal quality and the cell operation.

(2) To improve the electrocatalysts introducing method. The previous mixing method was not satisfactory, because it was not really a doping method.

(3) To seek for a type of electrocatalysts used in prebaked anode which should maintain electrocatalytically active after baking at 1 250 °C.

A number of new type electrocatalysts were selected from fifty dopants by these studies. They are suitable for both Söderberg anodes and prebaked anodes. Some of these electrocatalysts are listed in Ta-

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bles 1 and 2.

Table 1 Results of electrocatalysts used for Söderberg anode

Electrocatalysts	Overvoltage reduced * /mV
K-Ca Salts	148
Li Salts	147
Li-Mg Salts	80
Li-Mg-Ca Salts	74
Mg-Al Salts	68
Mg-Fe Salts	54

* Comparison was made between doped anodes and undoped ones at $0.8 \text{ A} \cdot \text{cm}^{-2}$ anode current density.

Table 2 Results of electrocatalysts used for prebaked anode

Electrocatalysts	Overvoltage reduced * /mV
Ba-Fe Salts	208
Mg-Al Salts	170
K-Ca Salts	150
Li Salts	8

* as Table 1.

The experimental procedures presented elsewhere^[1-5]. The possible mechanism of electrocatalytic effect have also been discussed. We suggested that the active sites which transformed from dopants were formed at the anode surface. Through the preparation of electrodes, active sites should possess electronic conductivity and huge surface area, which are beneficial to promote the main anodic reaction. That is to say, these sites would accelerate the electrons exchange velocity of oxygen evolution reaction (CO_2 formed), thereby decrease the excessive energy consumption, thus decrease the anodic overvoltages. However, the dopants selection and the electrodes preparation need technical know-how.

3 EXPLANATION CONCERNING DIFFERENCES IN EXPERIMENTS AND MEASUREMENTS

Feng, Naixiang *et al.*^[6, 7] argued that no measurable effect of the lithium carbonate addition was

found on the anodic overvoltage or on the rate of the anodic reaction. However, in our studies, we can obtain the measurable η_a reduction almost every time when testing the lithium salt doped anode in laboratory cells. The main differences were in the preparation of electrodes, and the experimental conditions and methods employed. The dopants should be distributed homogeneously in the electrode, and possess huge surface area after special treatment. However, the preparation method is also a know-how at the moment. We are willing to provide some well prepared electrode samples to those who are interested in the measurements of η_a on their request. We believe that they can get quite the same measuring results as we did.

"Doping" is one of the chemical modified electrode methods through which the modified electrode possess many new functions, such as electrocatalysis, selectivity and stability and so on. Using our know-how, an isolate porcelain thin piece exhibited electronic conductivity after doping and heat-treatment.

We agreed that the graphite crucible which contained the cryolite-alumina melt should be shielded by alumina tube, otherwise not only horizontal current would disturb the measurements, but also the composition of melts would be changed.

It should be pointed out that the measurement of η_a on an operating reduction cell is very difficult and is hard to obtain reproducible results. The reasons are as follows: (1) The operating anodes on an industrial cell are far from electrochemically steady state; (2) The real current density changes with time and different measuring locations on the anode, especially with the fluctuation of current supply. As is well known, the η_a varies with current densities; (3) The η_a measuring method is not very good until now. Among existing methods W. Haupin's is the best one, which was employed in our in-situ measurement. The measured η_a data were instant. It was required to keep the experimental conditions and the measuring technique as constant and strict as possible. An expert group invited by CNNC made the η_a measurement in industrial cells in Shandon Aluminium Smelter and Liancheng Aluminium Smelter in 1989 for judging the experiments and tests both in our laboratory

and these two smelters. They obtained effective measurement results.

4 EVALUATION RELATED TO ENERGY SAVING EFFECT USING LITHIUM SALT-CONTAINING ANODE PASTE

Until now, many aluminum smelters still continue employing lithium salt-containing anode paste in their cells, and it is one of the major energy saving measures. But, Sen^[7] questioned that there was no effect on reducing the cell voltage, because the average cell voltage was not decreased. However, the data cited in Sen's paper showed the energy saving effects in the aluminium smelters which use lithium salt-containing paste. According to the following well known equation, one can calculate the energy consumption W and make the comparison:

$$W = 2980V_{ca}/CE, \text{ kWh/T-Al}$$

where 2980 is constant, related to electrochemical equivalent of aluminium; V_{ca} is the average cell voltage (V) and CE is current efficiency(%)

This expression demonstrates that the energy consumption can be reduced by either lowering the average cell voltage or increasing the current efficiency. Thus, Shandon Aluminium Smelter obtained the annual energy reductions 81, 203, 232 and 292 kWh/t-Al respectively from 1987 to 1991. Hushun Aluminium Smelter was more effective and obtained annual energy reduction 231, 300, 245 and 330 kWh/t-Al respectively from 1987 to 1991. Table 3 listed some parameters of one of the potlines (No100) of Hushun Aluminium Smelter.

Sen evaluated the energy saving results merely by average cell voltages and did not pay attention to the increase of CE. As a matter of fact, the reduced anodic overvoltages were in several decades to 200 mV, and they are hard to detect by a voltmeter which is mounted on the reduction cell

and with a 0.2 V precision. Besides, the cell voltages are controlled and regulated by computer in existing smelters, and maintained in a certain region. Once there is a η_a reduced in a reduction cell, it would be compensated by an enlarged anode-cathode distance (ACD). As is well known, an greater ACD is beneficial to the CE. As Table 3 showed, CE was increased annually.

Table 3 Some parameters of reduction cells of potline No100 in Hushun Aluminium Smelter

Parameters	Years				
	1987	1988	1989	1990	1991 Jan. ~ Jun.
Ave. Cell Voltage/V	4.367	4.359	4.377	4.367	4.370
CE(%)	88.91	89.43	90.24	89.68	90.27
D. C. Energy Consumption /kWh·(t-Al) ⁻¹	14759	14528	14459	14514	14429
Li ₂ CO ₃ Containing in Bath(wt.-%)	—	—	2.83	2.75	2.70
Energy Saving /kWh·(t-Al) ⁻¹		231	300	245	330

Electrocatalysis and functional electrode materials are attracting more and more attention because they can lead to energy reductions in many technological fields including electrometallurgy. We will continue our work in this direction.

REFERENCES

- 1 Liu, Y X; Thonstad, J. *Electrochim Acta*, 1983, 28 (1): 113-116.
- 2 严大洲, 刘业翔, 肖海明. 中南矿冶学院学报, 1989, 20(5): 505-511.
- 3 Liu, Y X; Xiao, H M; Xiong, G G. *Light Metals*, 1991 (Warrendale, PA. TMS), 489-494.
- 4 Liu, Y X; Xiao, H M; Chan, Z M. *Light Metals*, 1989 (Warrendale, PA. TMS), 275-280.
- 5 Liu, Y X; Wang, X M; Huang, Y Z; Wang, H Z. *Light Metals*, 1993 (Warrendale, PA. TMS), 599-601.
- 6 Feng, Naixiang *et al.* *Carbon*, 1991, 29(1):39-41.
- 7 沈时英. 轻金属, 1993, (12):26-28.