

Preparation of $\text{RuO}_2\text{-SnO}_2$ nanomaterial by sol-gel technique^①

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Abstract: Ru-Sn binary oxide is one of the most frequently used anode coating material in electrochemical industry, but its composition distribution and microstructure are not homogeneous, so the nanoscale $\text{RuO}_2\text{-SnO}_2$ binary oxide was prepared for improvement by a sol-gel technique. The morphology, microstructure, crystal structure and other properties of the new oxide were studied by EPMA, DTA, XRD, TEM, and electrochemical analysis. The results showed that the Ru-Sn oxide nanomaterial has excellent electrocatalytic properties.

Key words: $\text{RuO}_2\text{-SnO}_2$ nanomaterial; sol-gel technique; electrocatalytic

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1 INTRODUCTION

Precious metal oxides have been the first choice as anode materials in electrochemical industries^[1,2]. Ru-Sn binary oxides have excellent electrocatalysis properties and corrosive resistance. Ru-Sn based oxides are widely used anode coating materials in electrochemical industries. These coatings are usually prepared by thermal decomposition of metal chlorides which are brushed with solvent to titanium substrates. A variety of micro-analyses have revealed that the composition distributions and microstructures of coatings are not homogeneous^[3~6]. In order to develop superior anodes or to clarify the physical and chemical properties of these electrocatalysts, new techniques must be considered. In this regard, the sol-gel process may be chosen first as a new approach because it has many advantages in preparing the oxide coatings with homogeneous structures or even with nanoscaled structures. In spite of this, the studies on anode materials by sol-gel method are very scarce^[7].

The most recent studies have shown that, properties of products may be greatly improved if their grain sizes reach nanoscale. So we exerted ourselves in preparing nanoscale anode materials by every effort^[8~10]. Recently, we reported a technique to prepare RuO_2 nanocrystal by a sol-gel method^[8]. In this paper, a nanoscale Ru-Sn oxide is prepared by a sol-gel method and the characterization of the product is studied.

2 EXPERIMENTAL

2.1 Raw materials

Commercial RuCl_3 and SnCl_4 were used as the raw materials. A required amounts of ruthenium and tin chlorides were reacted with sodium ethylate to

prepare ruthenium ethoxide and tin alkoxylate, respectively^[6,11].

2.2 Reaction process

Certain amount of ruthenium ethoxide was mixed with tin alkoxylate by magnetic stirring in ethanol solution for 10 min and then water was added to it. After 24 h, a gel with the Ru and Sn molar ratio being 40:60 was formed and then dried in an oven at 60 °C for 4 d. The dried gel was sintered to produce Ru-Sn oxide at 450 °C, 600 °C and 800 °C, respectively.

2.3 Instrumental analyses

The differential thermal analysis (DTA) for the dried gel was performed in Perkin Elmer DTA1700. The heating rate was 10 °C/min and the air flow rate was 40 mL/min. The compositions were analyzed by electron probe microanalysis (EPMA). The phase structures were studied by X-ray diffractometry (XRD). The experimental conditions were: CuK_α radiation, Ni filter, 40 kV, 15 mA. The crystal sizes and the microstructures were measured with Hitachi HU-12 transmission electron microscope (TEM).

The electrochemical properties were examined by studying their electrocatalytic activity, which was conducted by three-electrode method to determine their chlorine-evolution voltages in brine using HDV-7b type potentiostat.

3 RESULTS AND DISCUSSIONS

3.1 EPMA analysis

The composition of different regions in the oxide was analyzed by EPMA. The data measured are largely in agreement with the compositions of the starting material.

3.2 DTA analysis

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The DTA curve for the dried gel was detected (see Fig.1). A precipitous peak at about 150 ~ 250 °C can be seen in the curve. It may be contributed from the crystallization process and oxidizing process for the dried gel. The small hill between 400 ~ 800 °C may have something to do with a phase transformation. The valley at 100 °C is a heat absorption from the evolution of water.

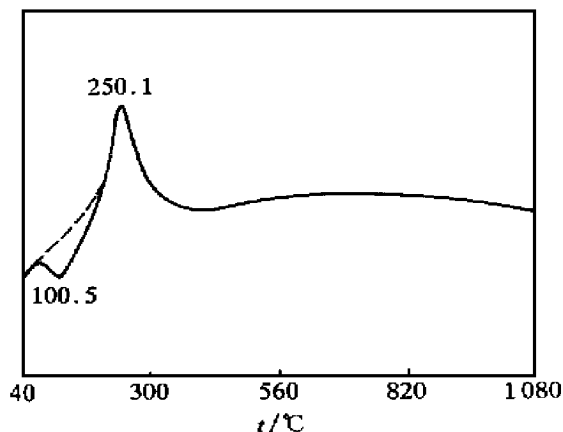


Fig.1 DTA curve of xerogel

3.3 XRD analysis

The XRD patterns of the oxide sample sintered at various temperatures are shown in Fig.2. According to the indexed patterns we observe the three samples sintered at 450 °C, 600 °C and 800 °C containing three phases: rutile RuO_2 , rutile $(\text{Ru}, \text{Sn})\text{O}_2$ and hexagonal Ru. At low sintering temperature 450 °C, only rutile phase is detected. While the temperature rising, the rutile solid solution phase tends to decompose. Firstly, metallic Ru may deposit, for a small amount of hexagonal phase is detected in specimen sintered at 600 °C. Secondly, when the sintering temperature reaches 800 °C, split phenomenon in the characteristic patterns is found. When we examine the characteristic peaks in detail, we find the two

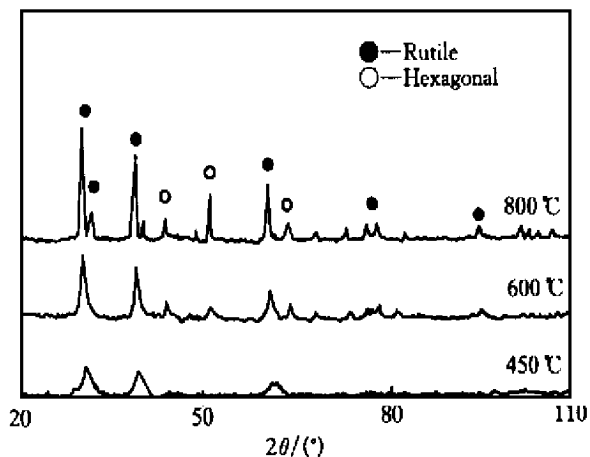


Fig.2 XRD patterns of powders sintered at various temperatures

separated peaks belong to rutile phases. It is obvious that the rutile phase formed at low temperature is not stable. It may further decompose like super-saturated alloys. This phenomenon is not found in RuO_2 - TiO_2 binary system. Rutile phases of precious metal oxides are generally accepted to be the excellent electrocatalytical materials. According to the above experiments, it is not suggested that the RuO_2 - SnO_2 binaries can be heated to higher temperature than 600 °C.

3.4 Electron micrographs and crystal sizes

The crystal morphologies of the oxide samples sintered at various temperatures could be observed by a transmission electron microscope under the accelerating voltage of 75 kV. For the sample sintered at 450 °C, the dotted-like crystals can be seen all over the field of vision (Fig.3(a)). The average size of them is smaller than 5 nm. The oxides sintered at 600 °C are composed of particles whose sizes are also small. Although most of grains reach about 10 nm in size, some of them remain about 5 nm (Fig.3(b)). Even when sintered at 800 °C, the sample is composed of particles with sizes between 10 ~ 15 nm (Fig.3(c)). It is obvious that the nanocrystals are smaller in RuO_2 - SnO_2 binary system than those in RuO_2 or SnO_2 monobasic systems^[8,9]. The reasons may be as follows: firstly, the addition of second element to act as barriers of grain growth; secondly, the decomposition of the grains. The former may take effects mainly at lower temperatures sintering. The latter may come into action merely at higher temperatures sintering. It is worthy noticing that the shapes of quadruprism which are typical appearance of a rutile phase are never observed in the three specimens. It seems that the nanograins had not grown to the normal dimension.

3.5 Electrocatalytical properties

Using constant potential method in saline water, the chlorine-evolution ability can be determined. According to the standard^[12] issued by the Chemical Engineering Ministry of China, the curve of chlorine-evolution voltage vs current density of the specimen sintered at 450 °C was determined (Fig.4). Within the experiments, the rise of voltage follows the increase of current density. The characteristic value is lower than 1.07 V, which most high active anodes can never reach. The high chlorine-evolution property may result from the nano-structured surface layer. The nano material can provide an extraordinarily large specific area of surface for electrochemical reaction, on which much more reactive centers may expose to and contact with the electrolyte in electrolytical cell. Compared with the ordinary material having the same composition (see Fig.4), we may know the

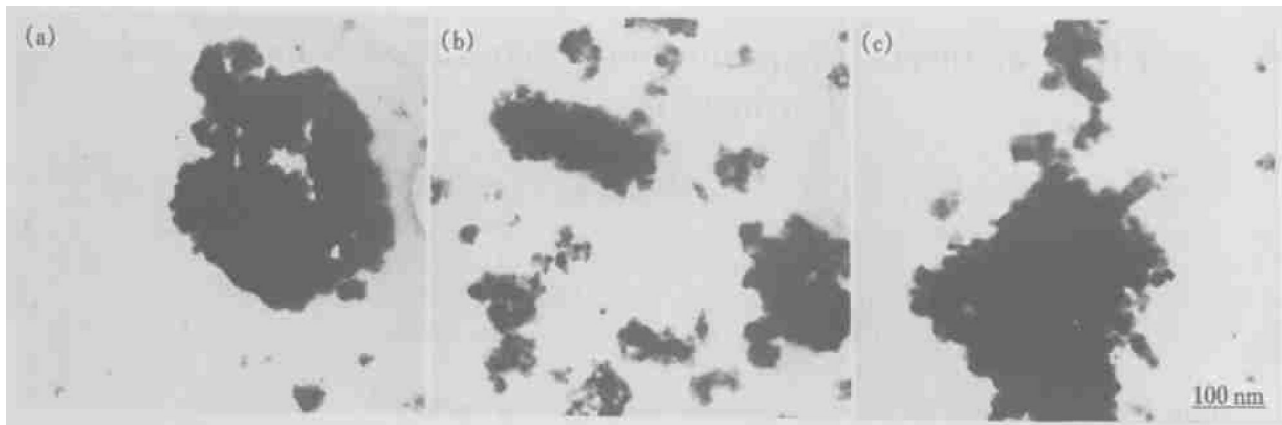


Fig.3 TEM photographs of samples sintered
(a) $-450\text{ }^{\circ}\text{C}$; (b) $-600\text{ }^{\circ}\text{C}$; (c) $-800\text{ }^{\circ}\text{C}$

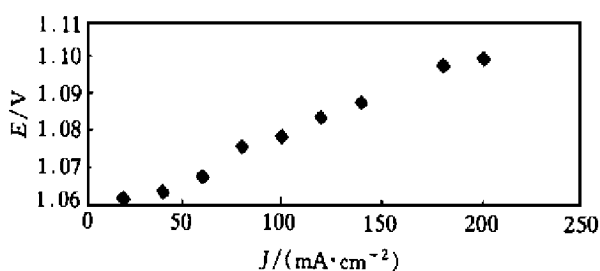


Fig.4 Curve of chlorine-evolution voltage vs
current density of $450\text{ }^{\circ}\text{C}$ specimen

electrochemical effect of nanometer.

4 CONCLUSIONS

In the present paper, a $\text{RuO}_2\text{-SnO}_2$ binary mixed oxide with the Ru-Sn molar ratio being 40:60 was prepared by a sol-gel method consisting of hydrolysis and condensation of metal alkoxides in ethanol and water. Three phases: rutile RuO_2 , rutile $(\text{Ru},\text{Sn})\text{O}_2$ and hexagonal Ru are found in the specimens by sintering the dried gel. One phase structure of rutile binary oxides is obtained when sintered at $450\text{ }^{\circ}\text{C}$. The decomposition of rutile phases takes place when sintered at higher temperatures. All the specimens are composed of nanograins. The nanophase size increases as the sintering temperature rises. The crystal sizes in $450\text{ }^{\circ}\text{C}$ sample are not larger than 5 nm. The $600\text{ }^{\circ}\text{C}$ sample is composed mainly of crystals whose diameters are between 5 ~ 10 nm. The electrocatalytic property of the specimen sintered at $450\text{ }^{\circ}\text{C}$ is excellent, while compared with the ordinary material with the same chemical composition. The results suggest that there is an electrochemical effect of nanometer.

REFERENCES

[1] TANG Dian, CHEN Shi-ren, LIN Xuan, et al. Failure

- analysis of peeling precession for titanium anode coating [J]. Trans Nonferrous Met Soc China, 1995, 5(4): 104.
- [2] TANG Dian. Electrode materials for electrochemical industries [J]. Material Science and Technology, (in Chinese), 1996, 6(1): 89.
- [3] Ardizzone S, Falcicola M and Trasatti S. Effect of the nature of the precursor on the electrocatalytic properties of thermally prepared ruthenium oxide [J]. J Electrochem Soc, 1991, 136: 225.
- [4] Ito M, Murakami Y, Kaji N, et al. Preparation of ultrafine $\text{RuO}_2\text{-SnO}_2$ binary oxide particles by a sol-gel processes [J]. J Electrochem Soc, 1994, 141: 1243.
- [5] Battisti A D, Lodi G, Cappadonia M, et al. Influence of the valve metal oxide on the properties of ruthenium based mixed oxide electrodes [J]. J Electrochem Soc, 1989, 136: 2596.
- [6] TANG Dian, YAN Qi and CUI Xiong. On microstructures of the titanium anodes [J]. Chlorine and Soda Industries, (in Chinese), 1994, (8): 24.
- [7] Kameyama K, Shohji S, Onue S, et al. Preparation of ultrafine $\text{RuO}_2\text{-TiO}_2$ binary oxide particles by a sol-gel processes [J]. J Electrochem Soc, 1993, 140(4): 1034.
- [8] TANG Dian, WEN Shi-xue and CHEN Shi-ren. Preparation of nanoscale ruthenium dioxide [J]. Chemical Engineering and Metallurgy, (in Chinese), 1997, 18(3): 1.
- [9] WEN Shi-xue, CHEN Shi-ren, TANG Dian, et al. Preparation of nanoscale tin dioxide [J]. Chlorine and Soda Industries, (in Chinese), 1996(8): 23.
- [10] TANG Dian, LI Yong-sheng, WANG Yong-kang, et al. Preliminary studies on nanoscale titanium dioxide [J]. Chlorine and Soda Industries, (in Chinese), 1995, (11): 12.
- [11] TANG Dian, WEN Shi-xue and CHEN Shi-ren, et al. Nanomaterials prepared from ruthenium ethoxide by ammonia hydrolysis and their microstructures [J]. Precious Metals, (in Chinese), 1998, 19(3): 1.
- [12] ZHANG Yu-ying. Review of the quality examination results for anodes according to standard [J]. Chlorine and Soda Industries, (in Chinese), 1996, (8): 3.

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