Influence of ZnO Doping on Property of SnO₂ Ceramic Electrodes

Qi-Lin WANG¹,a, Xin-You HUANG¹,b*, Jia YIN¹, Jing-Feng SUN²,c, Meng-Xian FENG¹, Lei CHEN¹

¹School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu Province, China; ²Jiangsu Xinpu Electronic Science and Technology Co., Ltd, Changzhou 213000, Jiangsu Province, China

a869649101@qq.com, bhuangxy@ujs.edu.cn,

Keywords: Tin oxide ceramics, ZnO doping, Electroconductibility, Density, Electrical resistivity.

Abstract. The tin oxide ceramics electrode were prepared by the traditional solid phase sintering method. Influence of different ZnO doping amount on the microstructure and electroconductibility of the ceramics by SEM and XRD and other analytical instrument and the relationship between composition, performance and structure were obtained. The results show that when ZnO doping quantity increased, the electrical resistivity of tin dioxide ceramics decreased firstly and then increased, the density of tin dioxide ceramics decreased firstly and then increased. When sintered temperature was 1450°C, the doping quantity of ZnO was 0.5wt.%, the electrical resistivity of tin dioxide ceramics was best, crystal growth was most complete, the electrical resistivity was 10.203 mΩ·cm and the density is 5.358g/cm³.

Introduction

There are two main types of fused glass electrode, the one kind is molybdenum electrode, and the other kind is tin oxide ceramic electrode[1]. Tin oxide ceramics is a kind of electrode materials which is mainly used in the area of electric glass-melting furnaces and enamel furnace. It did not only require good electrical conductivity and must have good sintering performance, it has anti-corrosion capability and good certain density at the same time[2]. The metal ion in the glass is replaced by molybdenum metals, restricting the electrode’s performance[3]. Tin oxide is an n-type semiconductor, it is widely-utilized because of corrosion resistance and high temperature resistance[4,5]. It is necessary to improve the performance of the tin oxide electrode due to the development of glass electric melting technology. As a conclusion, a high quality electrode materials with high performance is urgent needed.

The researches of tin oxide doping vario-property have achieved good effect. The properties of tin oxide electrical ceramics doped with La₂O₃ is researched by Chun-Ming Wang[6]. And the results show that the electrically conductive properties of tin oxide ceramics can be changed, which is synthesized by the traditional solid phase sintering method, doping 0~1mol% of La₂O₃ and sintering at 1350°C for 80 minutes. Lou-Ming Zhang[7] et al. added CoO, Nb₂O₅, Cr₂O₃, La₂O₃ and Ta₂O₅ into SnO₂ and sintered in the oxidizing atmosphere. The result shows that the density of sample is related with the sintered temperature and the heating rate. However, the research of improving conductivity and sintering performance of tin oxide doped with ZnO has not been reported.

In this work, the tin oxide ceramics electrode was prepared by the traditional solid phase sintering method, doping with a certain amount of Sb₂O₃, La₂O₃ and variable ZnO to improve the performance of tin dioxide ceramics. ZnO doping mechanism for tin oxide ceramics was investigated.

Experimental

Sample Preparation

The preparation of SnO₂ electrode ceramics was based on the following procedure: SnO₂, La₂O₃[8], Sb₂O₃[9] and ZnO were chosen as the raw materials; A certain amount of SnO₂, a
quantitative proportion of La₂O₃, Sb₂O₃ and a different amount of ZnO were added in the mortar, then mixed and grinded for 2.5h; The fine raw material would be produced through fully mixing and grinding; The powder was sieved by 40 mesh screen; Heating the powder to 1050°C in the high temperature furnace and presintering for 2 hours; 8wt.% mass fraction of polyvinyl alcohol (PVA) solution were added into the powder and mixed, then the powder was dry-pressed to round tablets under 30MPa pressure; Sintering and removing the binder of the samples in the high temperature furnace. The heating producer was as follow: first, heating the samples to 500°C slowly and preserving for 0.5h in order to remove the binder materials. Then, heating the samples up to 1400°C, 1430°C, 1450°C and 1470°C, respectively and keeping warm for 8h. At last, the sintering round tablets was cleaned in water by ultrasonic equipment and dried. And then the density and electrical conductivity of the samples were measured.

Sample Characterization

The model TH2512 intelligent low dcresistance tester is used to determine the resistance and calculate the resistivity of the samples. The sintering performance of the sample was demonstrated by the density which is characterized by the density balance instrument. The phase structure of the samples were analyzed by X-ray diffraction (XRD, Model D/MAX-2500X, Japan) meter and XRD patterns of the samples were obtained. Scanning electron microscope (SEM) (Model JSM-7001F) was used to characterize the microstructure, the SEM micrographs of the ceramic samples were obtained.

Results and Discussion

Effects of ZnO doping on the Phase Composition of SnO₂ Ceramics

Fig.1 shows the XRD patterns of SnO₂ ceramics doped with different amounts of ZnO and sintered at 1450°C. As can be seen from Fig.1, three peaks can be found at 26.7°, 34.0° and 51.9°, which is indexed to the (110), (101) and (211) diffraction planes of SnO₂ [11,12], respectively. The XRD spectra don't change obviously when the doping quantity of ZnO is 0.1wt.% and 0.3wt.%. The similar XRD patterns of samples indicates that ZnO doping only filled into the lattice of SnO₂ with the form of displacement, instead of changing the rutile structure of SnO₂ [13]. The diffraction intensity increases when the doping quantity of ZnO is 0.5wt.% and 0.7 wt.% , which is because the generated Zn₃SnO₄ [14] filled the gap of SnO₂ lattice, promoting the sintering densification of tin oxide ceramics.

![XRD patterns of SnO₂ ceramics doped with different doping amounts of ZnO](image)

Effects of ZnO Doping on the Microstructure of SnO₂ Ceramics

Fig.2 shows the SEM morphology and microstructure of SnO₂ ceramics doped with different amounts of ZnO and sintered at 1450°C. Figure 2 shows that the samples’ porosity is significantly increased when the doping quantity of ZnO is 0.1wt.% . Meanwhile, crystal growth of SnO₂ ceramics doped with 0.3wt.% is not completely compared with 0.1wt.% , which shows sintering performance is not good. Grain is full and angular when the doping quantity of ZnO is 0.3wt.%,
which shows that the crystal grows completely. With the increased quantity of doped ZnO, the crystal edges become fuzzy and the gaps decrease gradually. The reason is probably because the doped ZnO reacted with SnO2 and forming Zn2SnO4 and filling the empty space between the particles[15], which can promote the sintering densification.

![SEM photos of SnO2 ceramics doped with different ZnO doping amounts](image)

**Fig.2 SEM(×3000) photos of SnO2 ceramics doped with different ZnO doping amounts (a, b, c, d, e represent ZnO doping amount: 0.1wt.%, 0.3wt.%, 0.5wt.%, 0.7wt.%, 0.9wt.%)**

The Influence of ZnO Doping on Resistivity of SnO2 Ceramics

Fig.3 shows the resistivity of SnO2 ceramics doped with different ZnO doping amounts. As can be seen from Fig. 3(a) and Fig. 3(b), when ZnO doping amount increased, the resistivity of the samples decreased firstly and then increased when the sintering temperature is 1400°C, 1430°C, 1450°C and 1470°C, respectively.

Analyzing the three pictures of Fig. 3, the best sintering temperature was 1450°C. When the sintering temperature was 1450°C, the electrical resistivity of tin dioxide ceramics was the best (10.203 mΩ·cm) when the doping quantity of ZnO was 0.5wt.%. The electric conductivity of SnO2 ceramics could improve by doping ZnO, because the radius of Zn2+ (0.074nm) is bigger than Sn4+ (0.071nm) and they have different electrovalence[16]. Therefore, the adjacent oxygen atoms break away and forming a large number of oxygen vacancy[13,17] when the Zn2+ replace Sn4+. Meanwhile, a large number of electrons were generated when ZnO promoted SnO2 crystal growth simultaneously, the electrical resistivity of tin dioxide ceramics decreased.
The Influence of ZnO Doping on the Density of SnO2 Ceramics

Fig.3(a) The resistivity of SnO2 ceramics doped with different doping amounts of ZnO

Fig.3(b) The resistivity of SnO2 ceramics doped with different doping amounts of ZnO

Fig.3(c) The lowest resistivity of SnO2 ceramics doped with different amounts of ZnO

The Influence of ZnO Doping on the Density of SnO2 Ceramics

Fig.4 The best density of ceramics doped with different ZnO doping amount
As shown in Fig. 4, the density of tin dioxide ceramics decreased and then increased when the quantity of ZnO increased. The minimum density of tin dioxide ceramics was 5.29 g/cm³ when the doping quantity of ZnO was 0.3wt.%. This is because of the big grain granularity and high void fraction. The density of the samples increased when the quantity of doped ZnO increased. When the doping quantity of ZnO was 0.9wt.%, the density of tin dioxide ceramics was the maximum value (5.58 g/cm³). That is because the Zn₂SnO₄ was generated during the sintering procedure, filling the empty space between the particles gradually, leading to increase density and a better sintering performance.

Conclusions

ZnO doped SnO₂ ceramic electrodes were synthesized by the traditional solid phase sintering method. ZnO doping didn’t change the XRD patterns obviously. When the doping quantity of ZnO was 0.3wt.%, SEM photos display a better crystallinity and a few porosity. The density of SnO₂ ceramics electrodes decreased firstly and then increased when the doping quantity of ZnO increased. In addition, the evolution of resistivity of tin dioxide ceramics doped with ZnO exhibited the same tendency as the density. When the doping quantity of ZnO was 0.5wt.%, the electrical resistivity of tin dioxide ceramics showed a better performance than other samples sintered at 1450°C.

References


