The NO₂ Response of Solid Electrolyte Sensors Made Using ZnFe₂O₄ Electrodes

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A mixed potential sensor based on yttria-stabilized zirconia (YSZ) and a spinel-type oxide sensing electrode (SE) ZnFe₂O₄ is fabricated and examined for NO₂ detection at high temperatures. The devices give a linear correlation between EMF and the logarithm of NO₂ concentration from 100 to 1000 ppm in the temperature 450 and 500°C. The mechanism of the sensor has been discussed on the basis of the particle size of sensing electrode-ZnFe₂O₄. [doi:10.2320/matertrans.M2013413]

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1. Introduction

Nitrogen dioxide, [NO₂], is one of the most harmful gases emitted from combustion of automobile's engines, home heaters, furnaces, plants, etc.¹⁾ Emission and environmental standards of NO_x have been regulated in many countries. In order to solve the NO_x-related polluted problems effectively, it is necessary to develop compact sensors capable of monitoring NO_x.²⁾ Sensors of a great variety of types are well established in process industries, agriculture, medicine and many other areas, still the development of sensing materials with high sensing capabilities is proceeding at an unprecedented rate.³⁾ Many solid-state potentiometric and amperometric NO_x sensors based on the yttria-stabilized zirconia (YSZ) and metal-oxide SE have been developed and reported to date. Some of the NO_x sensing mechanism for these sensors is based on mixed potential. For NO₂ sensing, the following electrochemical reactions ((1), (2) and (3)) proceed at the interface of YSZ/SE and mixed potential appears on the SE.

It is found that the sensors using oxide SE such as Zinc ferrite (ZnFe₂O₄) are able to detect NO and NO₂ in containing oxygen atmospheres in high temperature. Zinc ferrite (ZnFe₂O₄) has a normal spinel structure with a tetrahedral A-site occupied by Zn²⁺ ions and octahedral B-site by Fe³⁺ ions.⁴⁾ This material is easy to synthesize and is environmentally friendly. And it is of interest not only to basic research in magnetism, but also has great potential in technological application.⁵⁾ Recently, ZnFe₂O₄ has been widely applied in the field of NO_x sensors.⁶⁾

Many researches put a lot on ZnFe₂O₄ electrodes which are nanometer and small micrometer size at present.^{7,8)} For example, in Serge Zhuiykov's research, the size of ZnFe₂O₄ particle is smaller than 1 μm. And the values of EMF are 42 and 28 mV at 650 and 700°C respectively.³⁾ Specially, scarcely any published works discuss the effect of SE particle size.

In order to make research integrity about ZnFe₂O₄ SE of NO_x sensors, we focused on ZnFe₂O₄ spinel type oxides and their particle size towards the better NO_x sensing. And the YSZ-based devices are further subjected to detailed performance tests as well as electrochemical measurements in relation to the NO_x sensing mechanism and improvement in sensing performance.

2. Experimental

2.1 Fabrication of sensors

The structure of the sensor consists of a solid electrolyte, an oxide sensing electrode and a noble metal reference electrode as shown in Fig. 1. The electrolyte is made of yttria stabilized zirconia (YSZ, 8 mol% Y₂O₃, self made) chip 10 mm in length, 8 mm in width and 0.3 mm in thickness. Pt pastes are screen printed on one side of YSZ chip for a reference electrode and on the other side for an electrical contact. For the signal collection, Pt wires are attached on printed Pt paste. Then the YSZ with Pt paste are sintered at 1400°C for 2 h, which is named as substrate. The oxide electrode is made from oxide paste, which is prepared as a mixture of oxide powder and organic binder (α-terpineol and ethyl cellulose) with 50:50 mass% ratio. The oxide paste is screen-printed on substrates and then sintered 1200°C for 2 h to form the sensing electrode (SE).

2.2 Measurement of sensing properties

The phases and microstructures of the as-obtained products are characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM). The X-ray diffraction patterns

Fig. 1 The simple diagram of the sensor Electrolyte: yttria-stabilized zirconia; Reference electrode: Platinum; Sensing electrode: ZnFe₂O₄.

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Fig. 2 Experiment setup for NO₂ detection. Fig. 3 X-ray diffraction pattern of ZnFe₂O₄ powders prepared at 1400°C. Fig. 4 Dependence of EMF on the sensors with SE of different balling time at 450°C (a) and 500°C (b) in NO_x atmosphere.

are obtained by an X-ray diffractometer (XRD, DX2700, DanDong HaoYuan Instrument Co. Ltd., China) using Cu K α radiation in a plane $\theta/2\theta$ geometry between 10 and 80° at a scan rate of 1°/min. The morphology of the obtained ZnFe₂O₄-SEs is observed using scanning-electron microscopy (TM-3000, Hitachi, Japan).

The gas-sensing characteristics of the sensors are examined at 450 and 500°C. Both the ZnFe₂O₄ SE and the Pt RE are simultaneously exposed to the sample gas that is prepared by diluting parent gas (NO₂) with the base gas. The gas-flow rate is fixed at 100 mL/min. The dependence of the NO₂ sensitivity is evaluated in the NO₂ concentration range of 100–1000 ppm. The ppm referred to the volume concentration of NO_x in the gaseous mixture. The electromotive force (EMF) output between the ZnFe₂O₄-SE and the Pt-RE of the sensor is monitored as a sensing signal with a digital multimeter (Agilent 3942, AM). The sensitivity to each gas is defined as the difference between the EMF value of the sensor in the sample gas and that in the base gas. Experimental setup used for evaluation of NO₂ sensor is shown in Fig. 2.

3. Results and Discussions

3.1 Crystal structure of sensing

XRD measurement of as-obtained products of ZnCO₃ and Fe₂O₃ sintered at 1400°C reveals that the powder crystallized in a franklinite phase of the ZnFe₂O₄ (JCPDS 22-1012). Additional peaks due to possible impurities are not observed,

which is as shown in Fig. 3. It can be seen from this figure that ZnFe₂O₄ may be prepared by the solid-state reaction of the parent ZnCO₃ and Fe₂O₃ sintered at 1400°C.

3.2 Effect of particle size

Figure 4 depicts the EMF responses to NO₂ concentrations in based gas for the planar YSZ-based sensors using ZnFe₂O₄ oxide SEs of different particle size tested at 450 and 500°C. The devices are sintered at 1200°C for 2 h. The material of ZnFe₂O₄ is balled for 0, 8, 16, 24 h respectively. For the median diameters of them are 13.7, 7.1, 4.0 and 2.5 μ m respectively. SEM images also present this law. In the base gas, the EMF value is close to zero. Thus, the measured EMF values are regarded to the sensitivities NO₂. The gas sensitivity is almost linear to the logarithm of NO_x concentration from 100 to 1000 ppm at tested temperatures for all sensors. Moreover, the signal of mixed-potential sensors changed with different particle size of SEs as clearly shown in Fig. 5. The sensing model includes two processes for NO₂ molecules, diffusion and chemical reaction in the pores of the ZnFe₂O₄ layer and electrochemical reactions at the three phase contact of YSZ, ZnFe₂O₄ electrode and gas phase. During the diffusion in the ZnFe₂O₄ layer, reaction (3) occurs.⁸⁾ As grains became larger, NO₂ gas makes fewer contacts with the surface of the ZnFe₂O₄ grains during operations when it diffuses through the pores, where surface of the grains act as a catalyst for the gas-phase reaction (3). Thus, NO₂ can reach the YSZ/SE interface without serious decomposition to NO. Less possible conversion of NO₂ to

Fig. 5 SEM images of the surfaces of (a) balling-0 h, (b) balling-8 h, (c) balling-16 h and (d) balling-24 h.

NO in the gas phase reaction would lead to high NO₂ contact in the case of the large grain size of SE. So, combining the change of area of TPB and the particle size, when ZnFe₂O₄ is ball milled for 8 h, correlating the medium diameter is 7.1 μm, gives the highest sensitivity. After that point, reactions (1) and (2) that occurred at three phase boundary of sensing electrode, electrolyte and tested gas became more important. Bigger pores and bigger grains product smaller TPB area. With the grain size of SEs increasing, the TPB area of the sensor becomes smaller. Reactions (1) and (2) will become relieved and the EMF will reduce. So the optimized ball milling time is 8 h.

The NO₂ conversion on ZnFe₂O₄-SE is relatively correlating to temperature. The higher the temperature, the higher activity of the catalytic reaction (3) occurs on ZnFe₂O₄-SE interface.⁹⁾ So all signals tested at 500°C are lower than 450°C.

4. Conclusions

- (1) The devices give a linear correlation between EMF and the logarithm of NO₂ concentration from 100 to 1000 ppm in the temperature range 450 and 500°C.
- (2) With size of ZnFe₂O₄ sensing electrode increasing,

EMF increased first and then decreased. The preferred balling time for ZnFe₂O₄ sensing electrode is 8 h. And the correlating media meter of ZnFe₂O₄ is 7.1 μm.

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