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 NOx have been regulated in many countries. In order to solve the NOx-related polluted problems effectively, it is necessary to develop compact sensors capable of monitoring NOx.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 NOx sensors based on the yttria-stabilized zirconia (YSZ) and metal-oxide SE have been developed and reported to date. Some of the NOx sensing mechanism for these sensors is based on mixed potential. For NOx sensing, the following electrochemical reactions ((1), (2) and (3)) proceed at the interface of YSZ/SE and mixed potential appears on the SE.

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\begin{align*}
\text{NO}_2 + 2e^- & \rightarrow \text{NO} + \text{O}^{2-} \quad (1) \\
2\text{O}^{2-} & \rightarrow \text{O}_2 + 2e^- \quad (2) \\
\text{NO}_2 & \rightarrow \text{NO} + 1/2\text{O}_2 \quad (3)
\end{align*}
\]

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 NOx 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 NOx sensors, we focused on ZnFe2O4 spinel type oxides and their particle size towards the better NOx sensing. And the YSZ-based devices are further subjected to detailed performance tests as well as electrochemical measurements in relation to the NOx 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

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

3.1 Crystal structure of sensing

XRD measurement of as-obtained products of ZnCO$_3$ and Fe$_2$O$_3$ sintered at 1400°C reveals that the powder crystallized in a franklinite phase of the ZnFe$_2$O$_4$ (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 ZnFe$_2$O$_4$ may be prepared by the solid-state reaction of the parent ZnCO$_3$ and Fe$_2$O$_3$ sintered at 1400°C.

3.2 Effect of particle size

Figure 4 depicts the EMF responses to NO$_2$ concentrations in based gas for the planar YSZ-based sensors using ZnFe$_2$O$_4$ 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 ZnFe$_2$O$_4$ is ballied for 0, 8, 16, 24 h respectively. For the median diameters of them are 13.7, 7.1, 4.0 and 2.5 µm 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 NO$_2$. 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 NO$_2$ molecules, diffusion and chemical reaction in the pores of the ZnFe$_2$O$_4$ layer and electrochemical reactions at the three phase contact of YSZ, ZnFe$_2$O$_4$ electrode and gas phase. During the diffusion in the ZnFe$_2$O$_4$ layer, reaction (3) occurs. As grains became larger, NO$_2$ gas makes fewer contacts with the surface of the ZnFe$_2$O$_4$ 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, NO$_2$ can reach the YSZ/SE interface without serious decomposition to NO. Less possible conversion of NO$_2$ to
NO in the gas phase reaction would lead to high NO₂ contact in the case of the large grain size of SE. So, combing 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. 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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REFERENCES


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.