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Effect of MgO doping on the $BiVO_4$ sensing electrode performance for YSZ-based potentiometric ammonia sensor

Chao Wang, Jinlong Xu, Bin Yang, Feng Xia, Yiwei Zhu, Jianzhong Xiao*

State Key Laboratory of Materials Processing and Die & Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China

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ABSTRACT

In order to improve the microstructure and sensing property for electrode material $BiVO_4$ of potentiometric ammonia sensor, different MgO-doped (0, 1, 3, 5 and 8 at.%) $BiVO_4$ powders were synthesized by solid-state reaction method. There is no significant difference in XRD spectrum for the different powders, but the particle size of the sensing electrode has an obvious refinement with the doping of MgO. The NH_3 sensitivity of the sensor had a enhancement from 41.7 mV/decade to the highest value of 61.8 mV/decade when Mg-content reaches 5 at.%. The interfacial resistance R_i between the electrode and YSZ decreases with the increment of NH_3 concentration and the Mg-doping based on impedance spectroscopy. The reduction of interface resistance is due to the enhancement of electrode reactions. The dopant MgO improves the conductivity of $BiVO_4$ and the TPB area, and leads to a greater charge exchange rate for the electrode electrochemical reactions. The increased specific surface area due to the grain size refinement gets more NH_3 involved in the reactions. This eventually leads to the increased sensitivity and decreased interface resistance. The optimal operating temperature is 600 °C based on the synthetical effects of various factors such as conductivity, the catalytic and gas adsorption performances of the sensing material.

1. Introduction

Nitrogen oxides (NO_x) from vehicle exhaust gas have resulted in worse pollutions to the natural environment in recent decades. To control the NOx emissions, most of the nations have set stricter standards and developed a number of emission reduction technologies. According to the researches, NO_x could not be removed by conventional three-way catalysts (TWCs) [1,2]. As an effective exhaust treatment technology, selective catalytic reduction (NH_3-SCR) system has already been serialized for the removal of NO_x for heavy duty vehicles and passenger cars in recent years [3]. However, the leak of ammonia from the SCR systems could affect the signal of NO_x sensors and decrease the NO_x conversion efficiency [4]. So it has to involve an ammonia sensor downstream SCR catalyst for the purpose of promoting NO_x conversion and controlling ammonia concentration in the loop-controlled system [5]. The YSZ-based potentiometric NH_3 sensor meets the most requirements of practical applications in automobile exhaust: durability, high sensitivity, low cost and potential for mass manufacturability [6], so it has emerged widely in automobile exhaust gas sensor researches.

As one of the key parts of solid-state electrochemical NH_3 sensor, the sensing electrode material has to provide three-fold functionality: electrically conductive, catalytically selective and electrochemically active [7], and all these functions should maintain long-term stability in the harsh environment of exhaust gas. So far, metal oxide semiconductor becomes one of most frequently used sensitive material in the solid state sensor fields [8]. As a member of this kind of materials, Vanadium oxide (V_2O_5) is a n-type semiconducting oxide and its electric conductivity increases due to formation of oxygen vacancies when part of the V^{5+} species are reduced to V^{4+} [9]. Meanwhile V_2O_5 is one of the important components in catalysts for catalytic reactions in flue gas denitration and exhaust SCR technology, and it has been used as the sensing material for gas sensors [9–12]. Unfortunately, the melting point of V_2O_5 is relatively low (less than 700 °C) compared with other metal oxides. Since the temperature of automobile exhaust reaches more than 800 °C during high-speed cruising, vanadium oxide could melt and volatilize when operated in the harsh exhaust environment under elevated temperature, and this could cause the attenuation of the catalysts containing V_2O_5. Therefore, as one of key components of the excellent catalysts and sensing materials, we hope that the vanadium species can be physical and chemical stable under high temperatures. Bimetallic compounds may solve this problem based on the higher melting point and other properties. Bimetallic oxides are very

* Corresponding author.
E-mail address: jzxiao@mail.hust.edu.cn (J. Xiao).

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promising to be used in the applications of catalysis, electrochemistry, microelectronics and material science because of their excellent properties. These materials have multiple functionalities and could exhibit prominent catalytic activity, selectivity, and stability over monometallic oxides [13–15]. Due to the unique physical and chemical properties, such as wide energy gap change (from 2 to 3.96 eV), high dielectric permittivity and marked photoconductivity, bismuth oxide (Bi_2O_3) has been used in various areas, especially solid oxide fuel cells, sensor technologies, electric and optical materials, superconductor materials, functional ceramics and catalysts [15,16]. And as a member of bismuth-based oxides, bimetallic oxides bismuth vanadate ($BiVO_4$) has attracted enormous attentions due to its excellent properties such as non-toxic, resistance to corrosion, ferroelasticity, and ionic conductivity [17]. Especially, it is sensitive for visible-light irradiation due to its narrow band (Eg = 2.4 eV) and has been widely used in the photocatalytic fields [18]. Wang et al. examined the $BiVO_4$ as sensing material for solid-state potentiometric ammonia sensors, and demonstrated that it was effective for the sensing of NH_3 at high temperatures [19].

Generally speaking, the composition, phase structure and the morphology of the sensing electrode play vital roles in the sensor properties, such as sensitivity, selectivity and response rate, hence researchers usually optimize these factors to improve the performance of gas sensors [20–23]. Magnesium oxide (MgO) is often used as conductive doping agent to improve the electrical conductivity of the semiconductor materials [24], it also could be used as a doping agent for the grain refinement of ceramic materials [25,26]. In this work, the impacts of the dopant MgO on the bismuth vanadate electrode microstructure and the sensing performance for YSZ-based mixed potential NH_3 sensor were studied, the electrochemical impedance spectra (EIS) of the sensor elements were also tested and interpreted to analyze the sensing mechanism by means of an equivalent circuit. The results showed that the MgO-doping played an important role in the grain refinement and NH_3 sensitivity enhancement for the $BiVO_4$ sensing electrode, and the detailed mechanisms are discussed in this paper.

2. Experimental

2.1. Preparation and characterization of $BiVO_4$ and Mg-doped $BiVO_4$ powders

The solid-state reaction method was used to synthesize the $BiVO_4$ and Mg-doped $BiVO_4$ catalyst powders with the raw materials bismuth oxide (Bi_2O_3, 99.5%), ammonium metavanadate (NH_4VO_3, 99.5%) and nanometer magnesium oxide (MgO, 99.5%). These raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Firstly, stoichiometric amounts of the three powder were mixed to form a mixture by milling or grinding for enough time. Then the mixture was sintered at 200 °C, 500 °C and finally at 850 °C for 18 h with intermediate grinding. The obtained powder is luminous yellow. Four different MgO-doped $BiVO_4$ powders were synthesized in this work, they were 1.0, 3.0, 5.0 and 8.0 at.%. The pure $BiVO_4$ powder was synthesized by the same preparation technology with Bi_2O_3 and NH_4VO_3. The synthesized powders were stored in airtight dry environment after been fully grinded. The crystalline phase of as-synthesized $BiVO_4$ and Mg-doped $BiVO_4$ powder sintered at 850 °C were characterized by X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.). It was operated at 40 kV and 40 mA with Cu Kα (λ = 1.5406 Å) radiation at room temperature. Data in the angular region of 2θ = 10–90° was collected in a step-scanning mode, with a step length of 0.017° and scan speed of 8°/min.

2.2. Fabrication of the NH_3 sensor and microstructure characterization of the sensing electrode

NH_3 sensor contains one piece of YSZ electrolyte (5 mol% Y_2O_3-doped ZrO_2, φ16 mm × t 0.3 mm) and sensing/reference electrodes located on the two surfaces of the electrolyte. Reference electrode comprises a porous Pt layer which is screen printed and sintered on the YSZ, whereas the sensing electrode consists of a symmetrical Pt which is covered with a porous layer of the $BiVO_4$ or Mg-doped $BiVO_4$. The sensing material was screen printed use the slurry which consists of the powder and organic binder with the weight ratio of 70:30. The printed sensing electrodes were dried at 80 °C for 2 h and subsequently sintered at 850 °C for 20 min in air. Different Mg-content (0, 1, 3, 5, 8 at.%) samples were prepared in this work. The schematic of the mixed potential ammonia sensor is shown in Fig. 1. The surface morphology of the different sensing electrodes was analyzed by Environmental Scanning Electron Microscope (Quanta 200, FEI, Holland) with the excitation voltage of 10 kV.

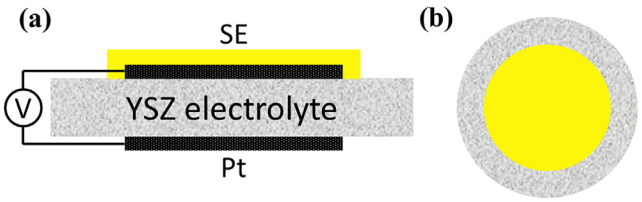

Fig. 1. Schematic of the potentiometric ammonia sensor (a) side view and (b) top view.

2.3. Parameters of the sensor testing

The sensor performance testing apparatus is shown in Fig. 2. Each NH_3 sensor was assembled in the center of a quartz tube heated by a resistance furnace. Both the reference and sensing electrodes were attached to electrochemical workstation (VersaSTAT3, Princeton) use Platinum wires (φ 0.2 mm) welded on the Pt layers for collecting electrical potential signals. The NH_3 sensor was heated up to the working temperatures (500–650 °C) and maintained at a fixed temperature for five minutes prior to the sensitivity tests. During the tests, the sensor was alternatively exposed to the base gas (10 vol% O_2, N_2 balance) and a sample gas (20–320 ppm NH_3 in 10 vol% O_2, N_2 balance) and maintained 100 s. The total flow rate of the base gas and sample gases was 500 ml/min. Two electrodes of a NH_3 sensor were exposed to the same gas atmosphere. The flow and the retention time of the base/sample gases were controlled by mass flow controllers (Beijing Seven Star Electronics Company) with a gas-flow apparatus (MPA-80). The differentials of the electrode potential (ΔV) between sensing and reference electrodes, namely the signals of the NH_3 sensor, were collected by the electrochemical workstation with a computer.

3. Results and discussion

3.1. The influence of MgO doping on the $BiVO_4$ phase composition and electrode morphology

Fig. 3 shows the XRD patterns of as-synthesized $BiVO_4$ and four different Mg-doped $BiVO_4$ powders sintered at 850 °C. Bismuth vanadate (PDF 01-083-1699, monoclinic) was the only phase detected in these samples, and there was no significant diffraction peak of magnesium oxide in the spectrum, indicating that it might be a solid solution state in the matrix material. This could lead to the position replacements for parts of the Bi^{3+} and V^{5+} and the improvement of the conductivity.

Surface morphology micrographs of $BiVO_4$ and 5 at.% Mg-doped $BiVO_4$ sensing electrodes are shown in Fig. 4a and b respectively. It can be seen that both the sensing electrodes consist of irregular shaped particles and construct a three-dimensional porous structure. A certain degree of sintering neck between particles could promote the formation of mesh structure which is beneficial for sensitivity and response speed