



Ammonia sensing characteristics of La₁₀Si₅MgO₂₆-based amperometric-type sensor attached with nano-structured CoWO₄ sensing electrode



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ABSTRACT

An amperometric type NH₃ sensor based on La₁₀Si₅MgO₂₆ electrolyte is reported in this paper. The design of this type sensor is significantly simplified due to the in-situ preparation of the nano-structured CoWO₄ sensing electrode in the pre-sintered porous La₁₀Si₅MgO₂₆ layer by impregnation method. The XRD and SEM investigations show that the CoWO₄ particles with the diameters about 50–100 nm are obtained after calcined at 800 °C for 3 h. The performance of the sensor is investigated with respect to the sensitivity at different temperatures, influence of the CoWO₄ loading and calcination temperatures, reproducibility and selectivity. The complex-impedance measurements are performed to analyze the mechanism of the sensor. The results show that the sensor exhibits good amperometric response-recovery characteristics to NH₃ in the temperature range of 500–650 °C at a constant bias voltage of 400 mV. Good linear correlations between the response currents and the NH₃ concentrations for 30–300 ppm are obtained. The influences of the loading and calcination temperature of the CoWO₄ sensing electrode on the sensing performance of the sensor suggest that the enhanced triple phase boundary is in favor of the improvement of the sensing performances. The present sensor also displays good reproducibility and low cross-sensitivities to various co-existing gases.

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1. Introduction

NH₃ sensors are widely applied in many fields, including environmental monitoring, chemical industry leakage alarm, automotive exhaust detection and disease diagnosis, etc. Especially, in the automobile industry, in order to decrease the NO_x emissions from diesel engine vehicles and trucks, NH₃ is used as a reductant in the selective catalyst reduction (SCR) systems [1,2]. Therefore, NH₃ sensors are necessary for controlling the conversion rate of NO_x, as well as avoiding the air pollution by extra NH₃ [3–5]. Among various NH₃ sensors, solid electrolyte type sensors are seen to be appropriate for NH₃ detection at elevated temperatures.

Up to now, most researches of the solid electrolyte type NH₃ sensor are focused on the mixed potential type sensors based on a

non-equilibrium electrochemical principle because of their advantages of simple structure and sustainability in the harsh conditions of the exhaust gas. The electrolytes used for NH₃ sensors included oxygen ion conductors (such as yttria stabilized zirconia (YSZ, 8 mol% Y₂O₃) [6–10]), trivalent aluminum ion conductors (such as (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ [11]) and NASICON [12]. Among them, YSZ is the most widely used electrolyte due to its advanced merit of good chemical and mechanic stability. Except for the electrolyte, much research has been devoted to the sensing electrodes, which can selectively catalyze the oxidation reaction of NH₃. Various oxide materials, such as V₂O₅ [6], Ni₃V₂O₈ [7], tungstate [8], In₂O₃ [9], NiO [13] and SiO₂/Au [14] have been exploited as the sensing electrodes in the past and showed excellent sensing performance to NH₃.

In addition to the mixed potential type, solid electrolytes sensor also can be operated in amperometric mode. When a fixed voltage is applied between the sensing and reference electrode, the detected gases can be decomposed at the gas/sensing electrode/solid electrolyte three phase boundary (TPB), resulting in a response current as the sensor output. The sensors also can show

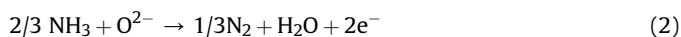
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well selectivity, rapid response and good reproducibility performances, even though there is no limiting current appearance [15]. These amperometric-type sensors have been successfully used for detecting hydrocarbon, NO_x and H₂ [16–21]. However, to our knowledge there is no studies report on the application of the amperometric-type sensor for NH₃ monitoring.

In this paper, we prepare an amperometric-type sensor based on La₁₀Si₅MgO₂₆ (LSMO) solid electrolyte and CoWO₄ sensing electrode for NH₃ detection. This amperometric-type NH₃ sensor can be described by the following electrochemical cells in sample gas: (+) Air + NH₃, CoWO₄/LSMO/Pt, NH₃ + Air (–). When a bias voltage is applied, the following plausible reactions (1) is expected to occur at the Air/Pt electrode/LSMO electrolyte triple phase boundary, accompanied by the transit of the oxygen ion through the LSMO electrolyte to the NH₃/CoWO₄ sensing electrode/LSMO electrolyte triple phase boundary, where reactions (2) is expected to occur [8,9].



Apatite-type lanthanum silicate is chosen as the solid electrolyte due to its high conductivity in the intermediate temperature range, high oxygen transference number across a wide range of oxygen partial pressure, excellent long-term stability and relatively low cost of the raw materials compared with YSZ [22–25]. Meanwhile, the conductivity of the apatite-type lanthanum silicate can be further enhanced by doping Mg on Si site [26,27]. Herein, LSMO with a bilayer structure (including both a dense layer and a porous layer) is used as the electrolyte. CoWO₄ is selected as the sensing electrode due to its excellent electro-catalysis activity as the sensing electrode in the mixed potential type sensor [8]. In the present work, nano-structured CoWO₄ sensing electrode is in-situ prepared by impregnation of CoWO₄ precursor solution in the porous LSMO layer and then heat treatment. The sensing characteristics of the sensor are investigated and discussed in detail.

2. Experimental

2.1. Fabrication of sensors

LSMO powders was synthesized by the solid state reaction process using analytically pure La₂O₃, SiO₂ and MgO powders as the raw materials. In order to remove possible lanthanum hydroxide and/or carbonate phases, Lanthanum oxide powder was pre-calcined at 900 °C for 2 h before weighing. The powder mixtures in stoichiometric ratio of La₁₀Si₅MgO₂₆ were mechanically ball-milled together with pure ethanol for 24 h and then calcined at 1300 °C for 6 h. The as-calcined powders were uniaxially pressed into a cylindrical flat mold utilizing fitted stainless steel disks with a pressure of 20 MPa to obtain disk-shaped samples (13 mm in diameter and 1 mm in height), which were then sintered at 1600 °C for 5 h to form the dense bulk materials.

The slurry produced by dispersing LSMO powder with 30 wt% pore-forming agent (graphite powder) into an organic dispersant (terpineol, 94 wt% and ethylcellulose, 6 wt%) was screen-printed onto one side of above-mentioned dense LSMO electrolyte pellets and then sintered at 1550 °C for 5 h to form the LSMO porous layer.

The CoWO₄ sensing electrode was then introduced into the LSMO porous layer by impregnating an aqueous solution containing 0.12 mol/L Co(NO₃)₂ and 0.01 mol/L (NH₄)₆H₂W₁₂O₄₀, which was prepared by adding Co(NO₃)₂ and (NH₄)₆H₂W₁₂O₄₀ in deionized water at a molar ratio of 1:1 for Co: W. After impregnation, the sample was dried at 100 °C for 20 min, and then calcined at

different temperatures for 3 h, allowing decomposition of the precursors and formation of CoWO₄ nanoparticles. The loading of CoWO₄ was controlled by instilling a given volume of the solution using microliter syringe. The CoWO₄ loading presented below was given in terms of CoWO₄ weight percentage in the porous layer, which was calculated based on the CoWO₄ weight in porous layer divided by the porous layer weight. Pt-layers with an area of 1 cm² were painted on both the sensing electrode side and the back-side of the electrolyte pellet as electrical collector. Pt wires were used to make contact with two electrodes.

2.2. Characterization of sensor materials

The composition of the samples was identified by X-ray diffraction (XRD, Rigaku, D/MAX2500PC) analysis under Cu-Kα radiation with the incidence beam angle of 2° in the range of 10–90°. The microstructure of the samples was investigated by field emission scanning electron microscopy (SEM, Hitachi, S-4800).

2.3. Sensing measurements

Sensing performances of the NH₃ sensor were tested in a gas flow apparatus with heating tube furnace in the temperature range of 500–650 °C. The sample gases containing different NH₃ concentration were prepared by diluting 8000 ppm NH₃ parent gas by the base gas (air). The flow rate of the sample gases (or the base gas) was kept constant at 100 cm³/min using mass-flow controllers. The polarization curves in the potential range of 0–800 mV were measured by means of potentiodynamic method at 5 mV/s. The amperometric responses of the sensor were measured by potentiostatic method at a fixed voltage. The complex-impedance measurements of the sensor were carried out over the frequency range 0.01 Hz–1 MHz with signal amplitude of 5 mV. All the electrochemical measurements were performed by the electrochemical work station (Zahner IM6e).

3. Results and discussion

Fig. 1 shows the representative SEM images of the blank porous LSMO layer used for CoWO₄ impregnation. The original LSMO scaffold shows a homogeneous porous structure with sub-micron pores (Fig. 1A), which make it possible to add CoWO₄ into the electrolyte layer via the impregnation process. The thickness of the scaffold is about 30 μm after 3 times printing, as shown in Fig. 1B.

Fig. 2 shows XRD patterns of LSMO porous layer before and after impregnation of CoWO₄ precursor solution. Before impregnation, all the strong peaks of the sample can be attributed to the hexagonal oxy-apatite structure of La₁₀Si₆O₂₇ via comparison with the standard card (JCPDS 53–0291). After impregnation and calcination at 800 °C for 3 h, the characteristic X-ray peaks of the LSMO porous layer indicate that CoWO₄ (JCPDS 15–0867) has been formed as the decomposition product of the precursor solution. The crystallite size of CoWO₄ is evaluated by the well-known Scherrer formula (Eq (3)) based on XRD results.

$$D = 0.89\lambda/\beta\cos\theta \quad (3)$$

where D is the mean crystallite size, λ is the wavelength of the X-ray radiation and β is the full width at half-maximum of diffraction peak at 2θ. The average crystallite size of the CoWO₄ particles is approximately 36.54 nm. In addition, no impurity phase is observed when CoWO₄ is formed on the LSMO scaffold, indicating that no obvious interface reaction between CoWO₄ and LSMO.

Fig. 3 shows the representative SEM images of the LSMO scaffold

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