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A novel amperometric NO_2 sensor based on nano-structured $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$–Ag composite sensing electrode prepared by impregnating method

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ABSTRACT

An amperometric NO_2 sensor using nano-structured $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM)–Ag composite sensing electrode with $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) electrolyte was fabricated. The LSCM–Ag particles in the range of 100–200 nm were prepared in the porous CGO layer by impregnating method. The NO_2 sensing characteristics were examined. The sensor showed high response to NO_2 and the response current was almost linear to NO_2 concentration at 400–600 °C. With the Ag loading level increased, the sensitivity of the sensor increased remarkably and the best performance was observed at the LSCM/Ag molar ratio of 1:0.5. The response current was slightly affected by changing O_2 concentrations in the range of 0–10 vol%.

1. Introduction

As a common air pollutant, NO_2 is mainly emitted as the exhaust gas of automotive engines, boilers, and any other combustion facilities. The development of NO_2 gas sensors with high sensitivity for combustion controlling and environmental monitoring is highly desirable [1–2]. Because of excellent chemical and physical durability, especially at elevated temperatures, special attention has been paid to solid electrolyte type NO_2 sensors, which are available on detection of NO_2 using either the potentiometric, amperometric or impedancemetric mode [3].

As solid electrolyte type NO_2 sensors, the sensing electrodes, which act as catalysts for the NO_2 electrochemical reduction reaction, play a very important role in the sensing performances. In order to improve the properties of the NO_2 sensors further, composite sensing electrodes have attracted many interests of researchers [4–6].

In the present study, Ag modified LSCM was chosen as sensing electrode for an amperometric NO_2 sensor. Ag is used to improve the electronic conductivity, enhance the electrocatalytic properties and is more affordable than Pd, Pt, etc., which has been reported to improve electrode performance for solid oxide fuel cells (SOFCs) [7–9]. The LSCM–Ag composite sensing electrode was synthesised directly in the porous CGO layer via impregnating technique which is a well-known method in the development of heterogeneous catalysts for SOFCs [10–13]. Making use of this method, nano-structured particles can be deposited into the established porous electrolyte framework, which makes electrolyte and electrode materials contact in three-dimensional space leading to increasing the length of the triple phase boundary (gas/sensing electrode/electrolyte). The sensing characteristics of the amperometric sensor using CGO electrolyte and LSCM–Ag composite sensing electrode are reported and discussed here.

2. Experimental

CGO bilayer electrolyte with a dense layer and a porous layer was used for fabricating the sensors. Analytically pure CeO_2 and Gd_2O_3 powders were ball-milled with ethanol for 24 h and then calcined at 1100 °C for 5 h in air. The calcined powders were mixed with 1 at% CuO which was employed as a sintering aid to improve the sinterability. Pellets with 10 mm in diameter and 2 mm in thickness were pressed from above mixture powders, and then sintered at 1300 °C for 5 h to form dense CGO electrolyte. The porous CGO layer was prepared by screen printing CGO ink on a surface of above-mentioned dense CGO pellets and then sintered at 1300 °C for 3 h. The CGO ink used in screen-printing was prepared by dispersing CGO powder with 1 at% CuO and

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30 wt% pore-forming agent (graphite powder) into an organic vehicle (terpinol, 94 wt% and ethylcellulose, 6 wt%).

The LSCM and LSCM–Ag sensing materials were loaded into the CGO porous layer by impregnating technique. 0.1 mol.L^{-1} LSCM precursor solution at stoichiometric ratio of LSCM and 0.1 mol.L^{-1} Ag (NO_3) solution which were prepared from nitrate salts were pipetted into the CGO porous layer and dried in an oven at 100 °C for 0.5 h. The impregnating-drying cycle was repeated until a desired loading of sensing materials was achieved. Finally, the samples were calcined at 800 °C for 3 h. The LSCM loading was about 0.7 mg. The molar ratios of LSCM/Ag were 1:0, 1:0.1, 1:0.5 and 1:0.7, respectively, which were marked as LSCM, LSCM-01Ag, LSCM-05Ag and LSCM-07Ag. A thin Pt layer was painted on the sensing electrode as a collector layer. A Pt-layer as counter electrode was also painted on the back-side of the electrolyte. Pt wires were used to make contact with the sensor. The composition and microstructure of the sample were characterised by X-ray diffraction with Cu-Kα radiation(XRD, D/MAX2500PC) and field emission scanning electron microscopy (SEM, S-4800), respectively.

NO_2 sensing properties were tested in a gas flow apparatus with heating tube furnace. The gas environment consisted of a changing concentration of NO_2 (0–300 ppm) with base gases composed of O_2 (0–10 vol%) and N_2 at a total flow rate of 100 cm^3/min. The amperometric responses of the sensor were measured by potentiostatic method at -500 mV using the electrochemical work station (Zahner IM6e).

3. Results and discussion

Fig. 1A showed the XRD patterns of sensor before and after impregnation. It can be seen that the sample sintered at 1300 °C with 1 at% CuO addition showed single CGO phase. After LSCM–05Ag impregnation and calcined at 800 °C for 3 h, perovskite LSCM phase and Ag phase formed as the decomposition product of the nitrate precursor solution. No additional diffraction peaks were found indicating no reaction among LSCM, Ag and CGO.

The representative SEM images of surface and cross-section of the sensing electrode before impregnation were shown in Fig. 1B–C. It was seen that the original CGO porous layer showed a uniform, porous and three-dimesional network structure with sub-micron pores. The thickness of porous layer was about 25 μm. After LSCM–05Ag impregnation and calcined at 800 °C, as shown in Fig. 1D–E, very fine LSCM–Ag particles were uniformly dispersed in the CGO layer and their size was in the range of 100–200 nm. Because LSCM–Ag adhered firmly to CGO three-dimensional structure, the triple phase boundary length was greatly enhanced, which meant increasing number of gas reaction sites and brought about the improvement of the response for the sensor.

Dynamic responses of the sensor attached with LSCM–05Ag were obtained by changing NO_2 concentration from 20 to 300 ppm at 400–600 °C under a constant bias voltage of -500 mV, as shown in Fig. 2A. Over the whole range of the concentration, the sensor exhibited a rapid increase in the current upon injecting the target gas and the subsequent recovery to an original level after removal of the NO_2 gas. There was almost no baseline shift in the sensor signal, implying good reversibility. With the temperature increasing, the response current increased. Meanwhile, the present sensor also showed faster response at higher temperature, such as, for 300 ppm NO_2 the response time defined as time for reaching the 90% steady current decreased from 300 to 120 s when the temperature increased from 400 to 600 °C.

The variations of the current change ($\Delta I = I_{gas} - I_{base}$, I_{gas} and I_{base} refer to the current when the NO_2 concentration is C ppm and 0 ppm.) as a function of the NO_2 concentration were shown in Fig. 2B. It is clear that good linear relationships between response signal ΔI and NO_2 concentration were achieved. The sensitivities which increased substantially with an increase in operating temperature were 0.027, 0.166 and 0.438 μA/ppm at 400, 500 and 600 °C, respectively.

Fig. 3A showed dynamic responses of the sensor to NO_2 with different molar ratios of LSCM/Ag at 500 °C. It can be seen that with the Ag loading level increased, the response current increased. The maximum response current value was obtained with LSCM–05Ag,

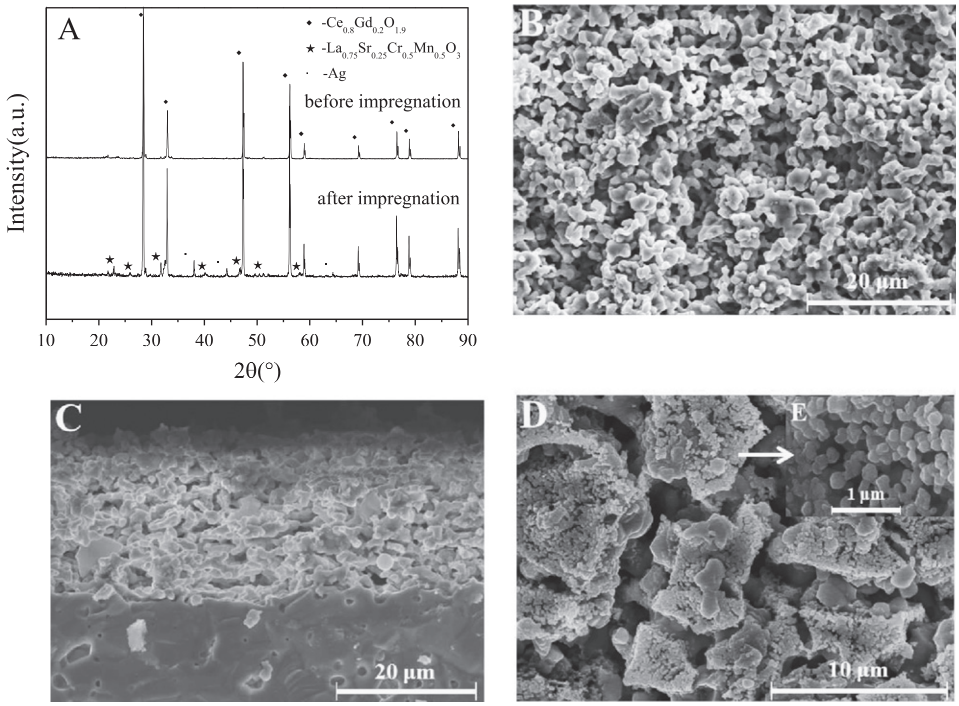

Fig. 1. XRD patterns (A), the representative SEM images of the CGO porous layer: surface (B) and cross-section (C) before impregnation, surface (D) partially enlarged surface and (E) after LSCM–05Ag impregnation.