A novel amperometric NO$_2$ sensor based on nano-structured La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$–Ag composite sensing electrode prepared by impregnating method

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**Article info**

**Article history:**
Received 27 October 2012
Accepted 17 January 2013
Available online 30 January 2013

**Keywords:**
NO$_2$ sensor
Amperometric
Impregnating method
Nano-structure
La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$–Ag

**Abstract**

An amperometric NO$_2$ sensor using nano-structured La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_3$–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%.

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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/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$_2$O$_3$ 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...
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 impregnation technique. 0.1 mol.L⁻¹ LSCM precursor solution at stoichiometric ratio of LSCM and 0.1 mol.L⁻¹ Ag (NO₃) 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.

NO₂ sensing properties were tested in a gas flow apparatus with heating tube furnace. The gas environment consisted of a changing concentration of NO₂ (0–300 ppm) with base gases composed of O₂ (0–10 vol%) and N₂ at a total flow rate of 100 cm³/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.

Fig. 1A showed dynamic responses of the sensor to NO₂ 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, 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.

The variations of the current change (\( ΔI = I_{gas} - I_{base} \)) as a function of the NO₂ concentration were shown in Fig. 2B. It is clear that good linear relationships between response signal \( ΔI \) and NO₂ 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 NO₂ 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,