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Nanosized perovskite oxide $NdFeO_3$ as material for a carbon-monoxide catalytic gas sensor

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Abstract
In this paper, research on a CO catalytic gas sensor based on nano-crystalline perovskite oxide $NdFeO_3$ designed for exhaust gas measurement is presented. Nano-crystalline oxide $NdFeO_3$ was synthesized by a sol–gel citrate technique. The gas sensing characteristics of this sensor were investigated in the concentration range of CO between 0 and 5 vol.% in air. The influences of C_3H_8, C_4H_{16} gases, relative humidity and air-flow rate on the cross-sensitivity of the CO sensor were also studied.

Keywords: nano-perovskite oxides, catalytic gas sensors, exhaust gas measurement

Classification numbers: 4.02, 5.06

1. Introduction

Combustion-related emission gases usually include CO_2, CO, hydrocarbons (HCs), volatile organic compounds (VOCs), NO_x and O_2 [1]. According to Euro-VI, the limit values for CO, NO_x and HCs are 1, 0.06 and 0.1 g km^{-1}, respectively. The exhaust gases are a harsh and corrosive environment. For example, the vehicle exhaust gases CO, HCs and NO_x have concentrations up to level of 10, 0.2 and 0.1 vol.%, respectively [2–7]. They are highly active and poisonous gases. For this reason, control and measurement of the concentrations of these gases are very important in reducing environmental pollution.

A catalytic gas sensor is a kind of sensor suitable for detecting gases with concentrations of several per cent by volume and even for direct use in harsh as well as high-temperature environments [8–13]. This sensor is fabricated on the basis of the catalytic principle: a catalytic exothermic reaction between oxidation–reduction gases and solid oxides produced the heat proportional to the gas concentration at a certain operating temperature. The great advantages of this sensor are stability and reliability because the sensor has gas-sensing characteristics with linear dependence of response signal on gas concentration. Furthermore, the sensor also has a compensation part for restricting the influences of the change in temperature and humidity in working ambience.

The nano-perovskite oxides ABO_3 (A: La, Nd, Sm and Gd; B: Fe, Co and Ni; and O: oxygen) have high catalytic activities and high sensitivity with CO and HCs. Their applications in gas sensors were studied in [7, 14–22]. Moreover, the valuable properties of these oxides could be strong, stable and resistible in harsh environments. Here, we have investigated the nano-oxide $NdFeO_3$-based catalytic sensor application for detecting CO in the concentration range 0–5 vol.%.

2. Experimental

The powder oxide $NdFeO_3$ was synthesized by the sol–gel citrate method. $Nd(NO_3)_3.6H_2O$, $Fe(NO_3)_3.9H_2O$ and citric acid were dissolved in ethylene glycol at a molar ratio of $\{Nd^{3+}, Fe^{3+}\} : \{\text{citric acid}\} : \{\text{ethylene glycol}\} = 1 : 1 : 4$. The solution was stirred at 80 °C for 4 h to get a homogeneous mixture and then the mixture was dried at 150 °C to obtain the form of gel precursor. After that, the gel was ground to a fine powder. Finally, the powder was calcined at 700 °C for

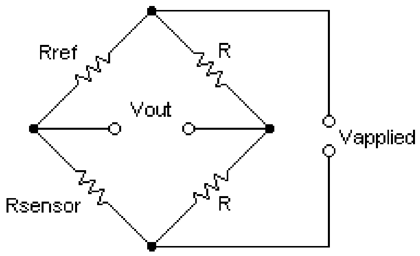

Figure 1. The electrical circuit for the operation of a catalytic gas sensor.

3 h to get a powder $NdFeO_3$ that could be used for subsequent analyses.

The synthesized powder sample $NdFeO_3$ was characterized for its structure and morphology by x-ray Diffraction (Siemens D5000) using CuKα radiation ($\lambda = 1.54$ Å), and scanning electron microscopy (SEM HITACHI S-4800).

To manufacture the sensor, the powder $NdFeO_3$ was mixed with the organic binder and then pasted on a Pt coil to create a gas sensing bead (or active bead). The Pt coil is about 0.5 mm in length and 0.1 mm in diameter. The diameter of the Pt wire was 30 μm. The active bead is circular and 0.6 mm in diameter. In a similar way to fabricating the active bead, a compensation bead (or reference bead) has a Pt coil covered by Al_2O_3. The active and reference bead were calcined by gradually applying voltage to the two ends of the Pt coil with values from 0 to 2 V for 1 h and then the voltage was kept at 2 V for 2 h.

The electrical circuit used to measure the gas response of catalytic sensors is a Wheatstone bridge, as shown in figure 1. Here, R is a fixed resistor with value 500 Ω, and R_{sensor} and R_{ref} are the resistances of the active bead and the reference bead, respectively. A direct current voltage source (dc voltage, or $V_{applied}$) was applied to operate the sensor. The output signal of the sensor was the voltage V_{out} of the Wheatstone bridge. In the working state, the value of V_{out} was zero in air ambience and change in ambience with a trace of reducing gases.

The gas-sensing characteristics were measured by a gas testing system in which the gases were blended according to the continuous gas flow-through mixing principle. The main equipment used in this system includes a programmable direct current voltage supply (Unicorn, model UDP-1510), mass flow controllers (AALBORG, model GFC-17) and data acquisition (Keithley, model 2700), all controlled by PC. The analytical gas source is the Singapore Oxygen Air Liquide Pte Ltd (SOXAL). The influence of relative humidity on cross-sensitivity of the sensor was examined by comparative measurement with a relative humidity meter of HBTM-7MK-C, Russia.

3. Results and discussions

From an x-ray diffraction (XRD) pattern of the synthesized powder $NdFeO_3$ shown in figure 2, the sample is the orthorhombic single phase of the perovskite type.

The morphology of the sample with very homogeneous agglomerates made of nano-sized crystallites ranging from 30 and 50 nm has been observed in the SEM image in

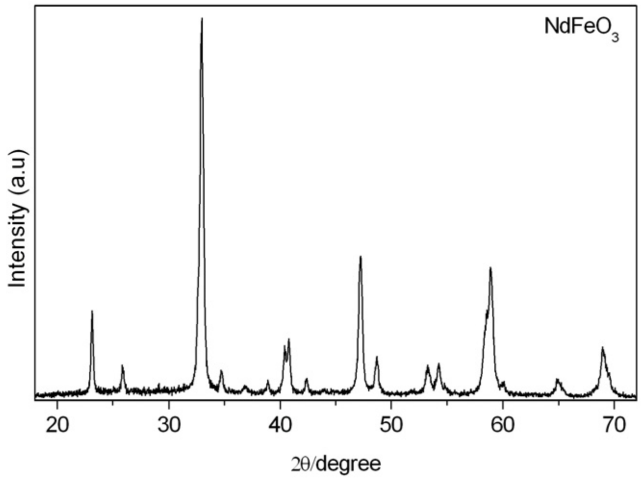

Figure 2. XRD pattern of the powder $NdFeO_3$ synthesized by the sol–gel citrate technique.

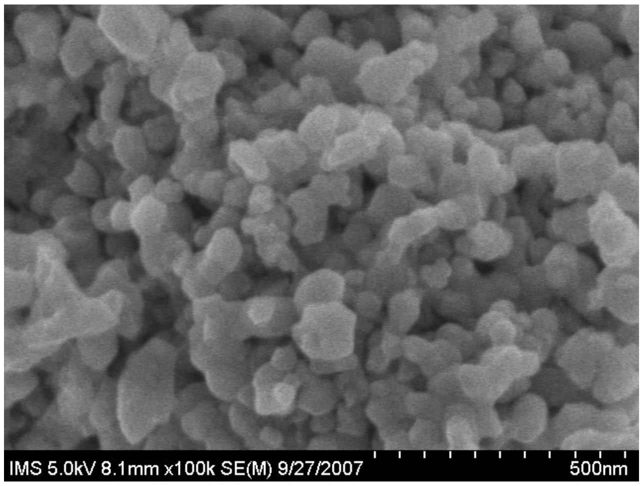

Figure 3. SEM image of the powder $NdFeO_3$ calcined at 700 °C.

figure 3. The $NdFeO_3$ crystallite size is about 13 nm, which is calculated from the strongest peaks of the x-ray pattern. This powder has a very high porosity and this is an advantage for improving the gas-sensing characters.

For the application of the $NdFeO_3$-based catalytic sensor to detect CO gas in exhaust gas environments, we carried out investigation of the gas response dependence on the applied voltage of the sensor in air ambiences having traces of CO, C_3H_8 and C_6H_{14} with concentrations of 1, 0.2 and 0.2 vol.%, respectively. The ambience with C_3H_8 gas is used for this investigation because it is the typical hydrocarbon gas in LPG (liquefied petroleum gas), and n-hexanes (C_6H_{14}) are significant constituents of gasoline, which are usually used in combustion systems and cause air pollution problems. Figure 4 indicates the dependences of gas response (V_{out}) of the sensor on applied voltage (dc voltage) within 1–3.5 V in air (triangle symbol), 1 vol.% CO (square symbol), 0.2 vol.% C_3H_8 (circular symbol) and 0.2 vol.% C_6H_{14} (star symbol). Correspondingly to each gas, the sensor could have a working voltage region at which the gas response reaches maximum value. The working voltage region of the sensor in C_3H_8 and C_6H_{14} is higher than in CO, as clearly shown in figure 4, which is explained as follows. The catalytic active

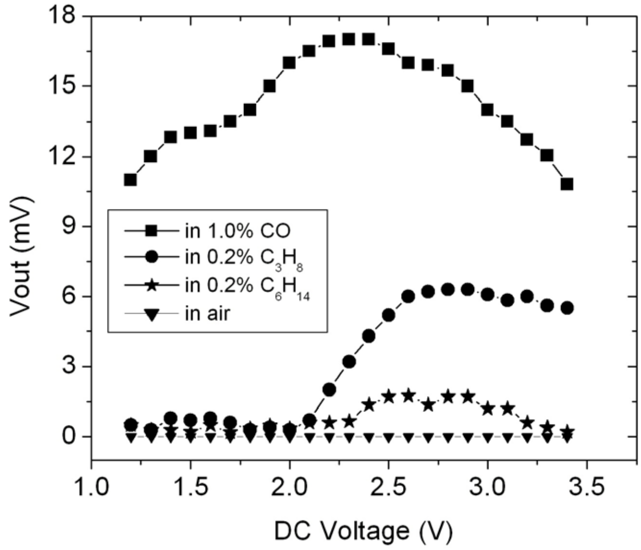

Figure 4. The gas response (V_{out}) dependences on applied voltage (dc voltage) in the air with a trace of some reducing gases.

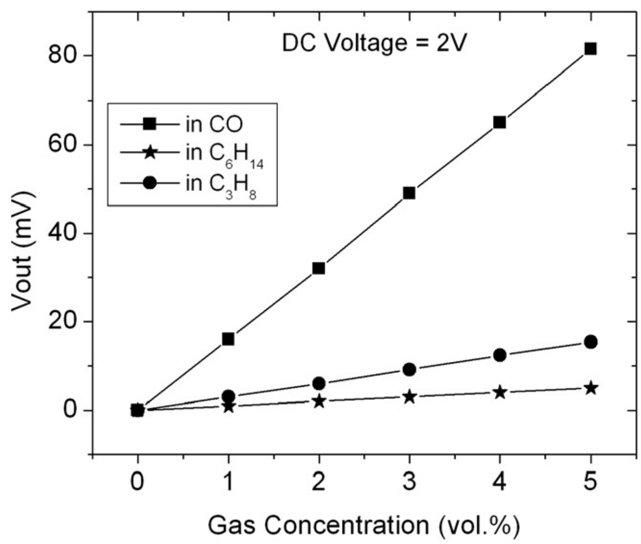

Figure 5. The characteristic of the response (V_{out}) to gas concentrations of CO, C_3H_8 and C_6H_{14}.

temperature of CO gas with sensing oxide materials is usually lower than those of HCs gases [23–25]. Specifically, while the operating voltage is below 2.0 V, the gas response (V_{out}) to C_3H_8 and C_6H_{14} of the sensor is very small (around 1 mV). Thus, it is advantageous to enhance the selectivity of the CO sensor in emission gas environments.

From analyzing the results in figure 4, the applied voltage is selected below 2 V for this sensor to detect CO in emission gas environments existing of HCs. Figure 5 shows the response (square symbols) of the sensor to CO with concentrations ranging between 0 and 5 vol.% in air at an applied voltage of 2 V. This is a typical linear characteristic of a catalytic-based gas sensor. Also from figure 5, the response of the sensor to C_3H_8 (circular symbol) and C_6H_{14} (star symbol) in the concentration range of 0–5 vol.% at an applied voltage of 2 V is lower than that to CO. Specifically, in the concentration range of C_3H_8 and C_6H_{14} around 0–1 vol.% in the emission gases environment, the response of the sensor is below 1 mV. As a whole, the analyzed results in figures 4 and 5 indicate that the sensor has a high selectivity for CO gas at a working voltage of 2 V and is suitable for applications in emission environments.

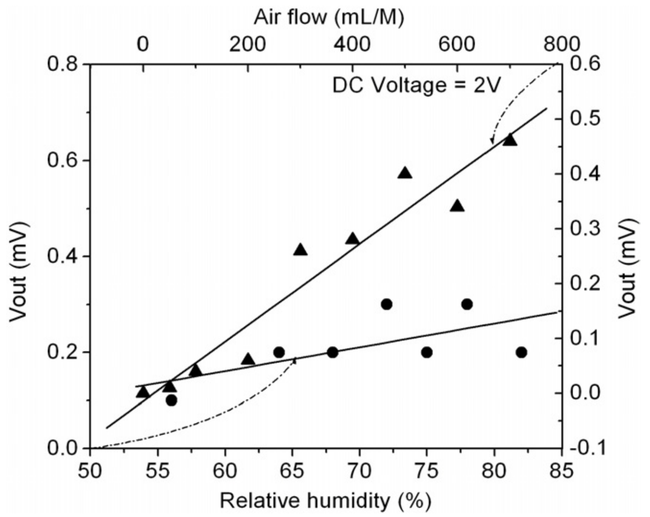

Figure 6. The influences of relative humidity (circular symbols) and air flow rate (triangular symbols) on the cross-sensitivity of the sensor at an applied voltage of 2 V.

To examine the direct use of this sensor in the emission environment, we have investigated the influences of relative humidity (RH) and air-flow rate on the cross-sensitivity of the sensor. Figure 6 plots the response V_{out} to relative humidity of around 50–90% RH (fitted line with circular symbols) and air flow rate (fitted line with triangular symbols). These results showed that the influences of humidity and air-flow rate on the cross-sensitivity of the sensor could be neglected. These inconsiderable influences are explained by the structure of the catalytic gas sensor in which there exists an Al_2O_3 reference bead operating as a compensation part.

4. Conclusions

Nano-crystalline oxide $NdFeO_3$ with an orthorhombic structure was synthesized by a sol–gel citrate technique. The catalytic gas sensor $NdFeO_3$ is suitable for detecting the CO concentration range 0–5 vol.% in emission gas environments. The influences of propane C_3H_8, n-hexane C_6H_{14}, relative humidity and air flow rate on the cross-sensitivity of the sensor could be neglected by applying a working voltage of 2 V.

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