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Effect of electrode microstructure on the sensitivity and response time of potentiometric NOx sensors based on stabilized-zirconia and $La_{5/3}Sr_{1/3}NiO_4$–YSZ sensing electrode

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ABSTRACT

The microstructure of a potentiometric NOx sensor's electrodes considerably affects the sensor performance. In the present paper, nanometric $La_{5/3}Sr_{1/3}NiO_4$ and different YSZ concentrations (5 wt%, 10 wt% and 20 wt%) composite powders were synthesized with microwave-assisted complex-gel auto-combustion method for fabricating NOx sensor electrodes. The sensor electrodes were sintered at 1000 °C, 1100 °C and 1200 °C respectively to obtain a variety of electrode morphology. The electrode porosity decreased with the increased YSZ addition. The sintering temperatures have effect on the porosity and distribution. All the sensors could produce a steady-state response voltage at the lower temperatures. Sensor fabricated with 10 wt% YSZ additional composites and sintered at 1000 °C exhibited the biggest response to NO at 400 °C.

1. Introduction

Nitrogen oxides (NOx) are major air pollutants generated from the reaction of nitrogen and oxygen in the air during combustion processes, such as in power plants and automotive engines [1,2]. It is eagerly required to control the emission of such gases and develop high-performance sensors for continuously monitoring these gases in the emission process and ambient atmosphere. Among these sensing devices, solid-state sensors, especially zirconia-based solid-state sensors, are of particular interest due to their compact size, easy use, and low cost.

Over the last two decades, many solid-state potentiometric (mixed-potential-type) sensors based on YSZ solid electrolyte and metal oxide sensing electrodes have been extensively examined for NOx monitoring. Some researchers found that the microstructure of a potentiometric sensor's electrodes considerably affects the sensitivity and response time of the sensor. For example, potentiometric sensors based on $LaFeO_3$ responded well to NO_2 at 400–500 °C and it was observed that decreasing the $LaFeO_3$ grain-size improved both the sensitivity and the response time [3–5]. Conversely, Elumalai et al. [6] observed a decrease in NO_2 sensitivity with decreasing electrode grain size for NiO electrodes operating at 700–800 °C. They showed with catalysis measurements that decreasing the grain size of NiO powder increases the heterogeneous reaction of NO_2 to NO and O_2. Martin et al. found that the porous Cr_2O_3 could affect the sensing performance of the sensor by changing the surface topography of sensing electrode [7]. In summary, the relationship between sensitivity and electrode microstructure is critical to the optimization of sensor performance.

In this study, $La_{5/3}Sr_{1/3}NiO_4$ and different YSZ concentrations were synthesized via a facile microwave-assisted complex-gel auto-combustion synthesis method. Sensors fabricated with the $La_{5/3}Sr_{1/3}NiO_4$–YSZ sensing electrode were sintered at various temperatures to obtain different microstructure. Then, the response performance characteristics (sensitivity and response time) of these sensors were investigated.

2. Experimental

2.1. Powder synthesis

A series of $La_{5/3}Sr_{1/3}NiO_4$–YSZ composite powders (YSZ = 5 wt%, 10 wt%, 20 wt%), in which the YSZ phase was intended to contain

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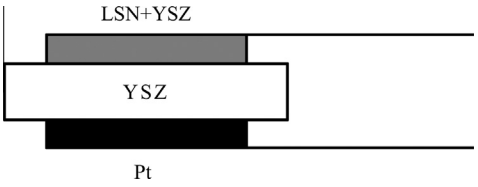

Fig. 1. Sensor configuration.

5 mol% Y_2O_3, were synthesized by the microwave-assisted complex-gel auto-combustion synthesis method [8]. Firstly, stoicheiometric amounts of $La(NO_3)_2{\cdot}6H_2O$, $Sr(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}5H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were dissolved in an appropriate amount of deionized water to form an aqueous solution, CA and EG were added into the solution, in which the molar ratios of CA to metal ions (CA:M) and EG to CA were 3:2 and 3:2, respectively. Then, fit the solution pH to 7 with aqueous ammonia (28%). After that, the solution was continuously stirred at room temperature for 4 h to form a sol. The sol was heated at 80 °C to obtain the dried gel. The as-obtained gel was ignited after about 15 s of microwave irradiation in a microwave oven (Galanz: 2.45 GHz, 1180 W, 20 L). Once on ignition, the combustion took place fiercely, resulting in a fluffy combustion product, which was then subjected to an annealing treatment in air at 800 °C for 2 h. The crystalline phase in the samples after annealing at 800 °C for 2 h was characterized by an X-ray diffraction (XRD, Panalytical X'pert PRO MRD, Holland) using Cu Kα radiation.

2.2. Sensor fabrication

Tape cast YSZ disks with a diameter of 16 mm were used for sensor fabrication. For fabrication of the sensing electrodes paste, $La_{5/3}Sr_{1/3}NiO_4$–YSZ composite powders were ball-milled with terpineol, ethyl cellulose and span 80 for 24 h. A square electrode (0.1×0.1 cm^2) of the $La_{5/3}Sr_{1/3}NiO_4$–YSZ mixture was printed on one side of a YSZ substrate and a Pt electrode (0.1×0.1 cm^2) was printed directly opposite the $La_{5/3}Sr_{1/3}NiO_4$–YSZ electrode (Fig. 1). Thin Pt wires (0.1 mm in diameter) were connected to both electrodes. Finally, the sensors were sintered at 1000 °C, 1100 °C and 1200 °C for 2 h, respectively. Sintered electrode microstructures were observed by an environmental scanning electron microscope (ESEM, Quanta 200, FEI, Holland).

2.3. Testing parameters

Sensor experiments were conducted in a gas-flow apparatus (MPA-80). Gas environments were controlled using mass flow controllers (Beijing Seven Star Electronics Company). The total flow rate was set at a constant 200 ml min^{-1}. The fabricated sensors were exposed to 10% O_2 balanced by N_2. NO was exposed to the sensors in the following concentrations: 0, 100, 200, 500, and 700 ppm, holding each concentration for 150 s. The test temperatures were from 400 to 600 °C at 50 °C increments.

The voltage between the sensing and counter electrodes was measured during the step changes using an electrochemical workstation (VearsaSTAT3, Princeton, USA). Both electrodes of the sensor were in the same gas atmosphere.

3. Results and discussion

3.1. Powder characterization

Fig. 2 demonstrates the XRD patterns for the samples of the powders after an annealing treatment. It can be seen that the

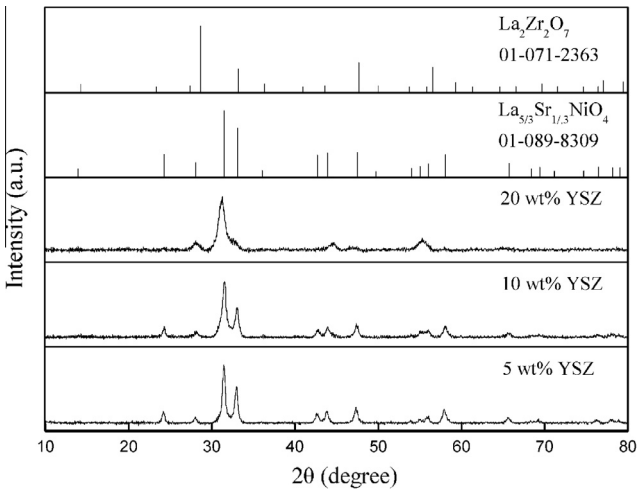

Fig. 2. XRD patterns for the samples of the powders after annealing at 800 °C for 2 h.

samples with 5 wt% and 10 wt% YSZ additions major composition is $La_{5/3}Sr_{1/3}NiO_4$.Because there are a little element Zr and Y in 5 wt% and 10 wt% YSZ additions, which makes them invisible in the XRD. In the case of 20 wt% YSZ, the peak intensity of 33° (2θ) weakens significantly, and some smaller peaks disappear. The lanthanum rich compounds and the YSZ reactive to form the insulating pyrochlore phase ($La_2Zr_2O_7$) [9].

3.2. Electrode microstructure

The electrode microstructures of $La_{5/3}Sr_{1/3}NiO_4$ and different YSZ concentrations composite powders are studied with electron microscopy. Fig. 3(a)–(c) shows the effect of different YSZ amounts on the morphologies of the sensing surfaces at 1000 °C. In the 5 wt% YSZ added $La_{5/3}Sr_{1/3}NiO_4$ (Fig. 3(a)), the electrode exhibits a porous and meshes structure. With the increase of YSZ addition, the porosity decreases, and the electrodes appear sheet structure. The average grain sizes of the three electrodes are all about 65–90 nm. The effect of sintering temperature is also studied with the 10 wt% YSZ-added $La_{5/3}Sr_{1/3}NiO_4$ powders (Fig. 3(b)–(e)). The electrode sintered at 1100 °C looks more compact with obvious lamellar structure then of 1000 °C. When the sintering temperature is 1200 °C, there are some small particles (about 40 nm) around the larger particles, and the porous structure appears again.

3.3. Sensor response

The potentiometric responses at 400 °C and 450 °C for the samples prepared with $La_{5/3}Sr_{1/3}NiO_4$ and different YSZ additional composite powders are compared in Fig. 4. All the sensors show a quick step response at 400 °C and 450 °C. At 400 °C (Fig. 4(a)), sensor prepared with 10 wt% YSZ added $La_{5/3}Sr_{1/3}NiO_4$ shows the largest response (27 mV at 700 ppm of NO), whereas sensor fabricated with 20 wt% YSZ added $La_{5/3}Sr_{1/3}NiO_4$ shows the lowest (16.5 mV at 700 ppm of NO). At 450 °C, sensors fabricated with 10 wt% YSZ added $La_{5/3}Sr_{1/3}NiO_4$ also shows the largest response (17.6 mV at 700 ppm NO) and sensor fabricated with 20 wt% YSZ added $La_{5/3}Sr_{1/3}NiO_4$ shows the lowest. These results are both reproducible and reversible. The response times are calculated from the transient potentiometric measurements by taking the times required for the voltages to reach 90% of their final steady-state values. At 400 °C, the responses of sensors fabricated with different sensing electrodes are generally rapid, with a new