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Effects of Ni addition on the response of La_2CuO_4 sensing electrode for NO sensor

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ABSTRACT

The effects of Ni addition on the response of La_2CuO_4 sensing electrode for NO sensors were described in this work. Various Ni contents (0, 5, 10, 15, 20 wt.%) were added into La_2CuO_4 by ball-milling method, respectively, and a new phase $La_8Cu_{5.6}Ni_{2.4}O_{20}$ was found in the Ni added electrodes. The sensor fabricated with 10 wt.% Ni addition exhibited the highest response to NO at 400 °C. The sintering temperature of the sensing electrodes was elevated to 1100 °C, at which temperature the sensor exhibited high sensitivity to NO and insensitivity to O_2. The existence of the new phase $La_8Cu_{5.6}Ni_{2.4}O_{20}$ may be the crucial reason for the enhancement of sensing properties. In addition, polarization curves were measured to further demonstrate the electrochemically catalytic activity of the sensing electrodes.

1. Introduction

As the continuous increase in car ownership in the last few decades, the environmental problems caused by the emission of exhaust gas have become more and more serious. NO and NO_2 (referred as NO_x) are the main pollution gases in the air pollutants which mostly come from the vehicle exhaust emissions and other combustion processes [1]. Great efforts have been made to control the emissions of NO_x, such as enforcing stricter legislations [2], employing a SCR system [3] and so on. Therefore, there is an urgent demand for high-performance sensing devices to monitor NO_x gases in the emission process.

Amperometric NO_x sensor is the only commercial sensor, but some problems remain to be solved [4], such as complex structure, costly materials and short service life, etc. And the most critical shortage of amperometric sensors is that the measurements are easily affected by O_2 [5]. In recent years, much attention has been widely paid to solid-state potentiometric sensors based on YSZ because of their high stability, cross-selectivity, simplified structure and low costs. The properties of the sensor usually depend on sensing materials and their micro-morphology which is related to the sintering temperatures of the electrodes [6]. A variety of materials have been reported to monitor NO_x. Perovskite oxide with high sensitivity to NO_x, low costs and unique crystal structure has drawn much research attention. However, the response to NO of most perovskite oxide sensing materials is much smaller than that to NO_2. Whereas, in combustion exhausts, NO is the major component of NO_x at high temperatures [7,8], and the share of NO is usually about twenty times as large as that of NO_2 [1]. Among the sensing materials, La_2CuO_4 is thought to be a potential sensing material, owning to its high sensitivity to NO and lack of catalytic activity for NO reduction to N_2 or oxidation to NO_2 [9]. In addition, La_2CuO_4 is insensitive to O_2. The sensitivity to NO in fixed O_2 concentration is 500 times higher than that to O_2 in fixed NO concentration [10]. Ying Chen et al. [11]improved the performance of a potentiometric NO_x sensor by adding YSZ into La_2CuO_4 sensing electrode. At 400 °C, the electrode with 5 vol.% YSZ addition showed a much larger response (52 mV at 700 ppm NO) compared with that of pure La_2CuO_4 sensing electrode (22.6 mV at 700 ppm NO), whereas excessive YSZ (10 vol.% addition) is detrimental to NO response. However, the sensing mechanism of La_2CuO_4 is not completely clear by now. E.D. Wachsman et al. proved that the Mixed Potential Theory is not complete enough to explain the NO_x gases sensing behaviors by investigating the effects of the La_2CuO_4 electrode's microstructure [10], thickness [12], and area [13]on the response of the potentiometric sensor.

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Furthermore, both the sintering temperature and operating temperature of La_2CuO_4 electrode are relatively low in some extent, which is unfavorable for approaching co-firing process with YSZ electrolyte. To sum up, the properties of La_2CuO_4 electrode need to be further enhanced.

Various methods have been applied to improve the sensing performance for the gas sensors, such as doping [14,15], morphology controlling [16–18], seed/buffer layers employment [19] and electrolyte surface preprocessing [20,21]. To promote the sensitivity and selectivity, the widely accepted method is to introduce specific dopants to change the band structure, morphology and grains size of the sensing materials [22]. Yamazoe et al. examined the effects of various additives on sensing properties for gas sensors [23]. Some additives, such as CaO and MgO, were investigated to inhibit grain growth while some other additives, such as ZnO, CuO and MnO, could enhance densification when the sintering temperature was above 800 °C. And additives like Nb_2O_5 and Sb_2O_5 can affect the conductivity of sensing electrodes. For SnO_2 based gas sensors, Nickel addition has been reported to increase the sensitivity by inhibiting the grain growth [24,25]. Besides, Nickel oxide itself is a kind of sensitive material to NO_x. Miura et al. [26,27] investigated the sensing performance of binary metal oxides for NO_x sensor, and found that NiO exhibited the best response (higher than 50 mV at 400 ppm NO_2). And they also found that the response of NiO electrode was enhanced as sintering temperature increases. The 1100 °C-sintered NiO electrode was more sensitive to NO_2 and attained the steady-state more quickly at different NO_2 concentrations, compared with the 1000 °C-sintered NiO electrode. Jian Wang et al. [14] examined an improvement in sensing characteristics by adding noble metal into NiO sensing electrode and the Rh addition gave a significant enhancement of NO_2 sensitivity resulting from the increase of the catalytic activity to the cathodic reaction. Jinsu Park et al. [28] found that the YSZ addition into NiO electrode could raise the amount of the triple phase boundary and improve the response value as well as shorten the response/recovery time.

In the old work of Wachsman group [12,13,29], the sensing behavior of La_2CuO_4 electrode was investigated a lot and the semiconducting effect was included to explain the sensing mechanism. In our work, the properties of La_2CuO_4 electrode were enhanced by different methods. As described in our earlier work, YSZ was added into the La_2CuO_4 sensing electrode to improve the performance of the NO_x sensor, and the electrode was highly sensitive to NO and free from the influence of O_2 concentration. However, it was not helpful for the increase of sintering temperature of the sensing electrode. Meanwhile, the La_2CuO_4 sensing electrode sintered at high temperature showed small responses to NO_x, especially when the sintering temperature is higher than 1000 °C.

In this work, the effects of Ni addition on the performance of La_2CuO_4 sensing electrode have been investigated. The responses to NO of the La_2CuO_4 electrodes with Ni addition sintered at 1000 °C and 1100 °C were monitored. In addition, the NO selectivity against O_2, NO_2, CO, CH_4 and NH_3 was also discussed.

2. Experimental

2.1. Powder synthesis

Amorphous citrate gel combustion method was used to synthesize La_2CuO_4 powders [11]. Firstly, stoichiometrical amounts of analytical grade lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$) and copper nitrate ($Cu(NO_3)_2{\cdot}6H_2O$) were dissolved in deionized water. Then citric acid ($C_6H_8O_7{\cdot}6H_2O$ or CA) of which the molar ratios to nitrate ions (CA/NO^{3-}) is 0.22 was added to the solution. After solvent evaporation with continuous stir at 100 °C, a gel was left behind. Finally, the gel was calcined at 650 °C for 10 h to obtain La_2CuO_4 powders. The La_2CuO_4 powders were mixed with 5 wt.% of yttria-stabilized (5 mol% Y_2O_3) zirconia via ball-milling method, and then 5, 10, 15 and 20 wt.% of highly purified Ni (20−100 nm, 99.9% metals basis) were added, respectively.

2.2. Sensor preparation

The sensing electrodes paste was prepared with the synthesized powders and organic binder (terpineol, ethyl cellulose and span 80, 94:5:1) with weight ratio of 70:30. Tape cast YSZ slices which were sintered at 1480 °C for 2 h in air with a dimension of 10 mm × 10 mm were used to fabricate the sensor. Two pieces of Pt electrodes were printed on the YSZ substrate and one of them was covered with a porous catalyst layer by screen printing. The sensing electrodes were sintered at 1000 °C and 1100 °C for 1 h, respectively. Finally, Pt wires were connected to both electrodes. The schematic of the NO sensor is shown in Fig. 1. The crystal structure of the sintered electrodes was analyzed via X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., Holland) using CuKa radiation and the surface morphology of the sensing electrode was observed by an environmental scanning electron microscope (ESEM, Quanta 200, FEI, Holland).

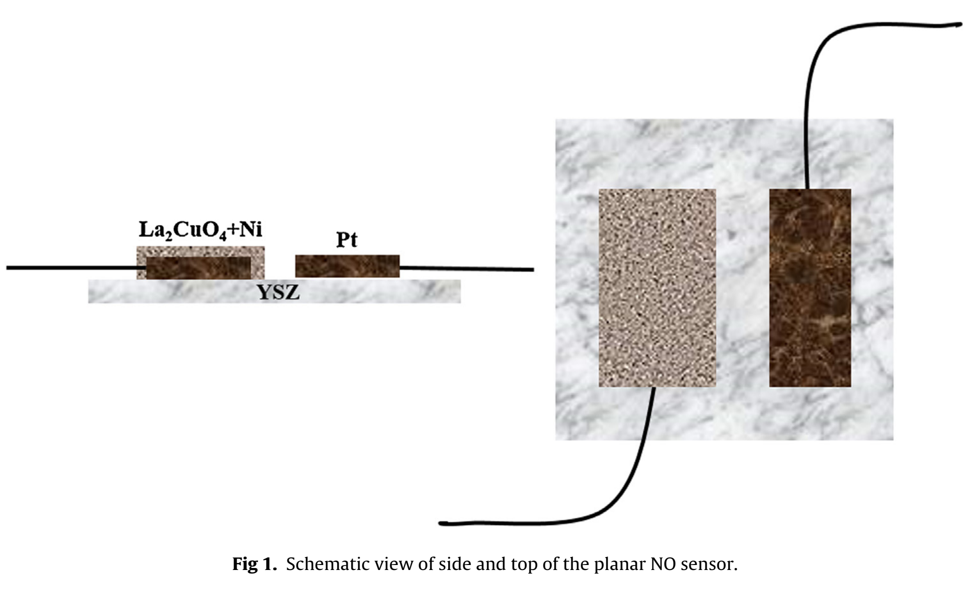

Fig 1. Schematic view of side and top of the planar NO sensor.