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Impedancemetric NO_2 sensor based on Pd doped perovskite oxide sensing electrode conjunction with phase angle response

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ABSTRACT

A novel impedancemetric NO_2 sensor was developed using the sensing electrode of Pd doped perovskite oxide conjunction with phase angle (Θ) response. The $La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3-\delta}$ particles with nano-structure were in-situ prepared in the porous skeleton of $La_{9.95}K_{0.05}Si_6O_{26.95}$ bilayer electrolyte by the simple impregnation method. The sensing performances of the NO_2 sensor were investigated with the total impedance value $|Z|$ or Θ extracted from the impedance spectroscopy as the sensing signal, respectively. The results shows that the Θ response can provide higher sensitivity, shorter response time and better stability compared to the $|Z|$ response for the same sensor, especially at high frequency and temperature. Compared with the sensor with $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ sensing electrode, the Pd doping in the sensing electrode makes the sensitivity of the sensor be effectively improved. The response signals depend on NO_2 concentrations from logarithmic relationship for $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ sensing electrode to linear relationship for $La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3-\delta}$sensing electrode. Meanwhile, the sensor with LSFP-SE also exhibits the enhanced stability and anti-interference ability to various coexistence gases.

1. Introduction

Environmental issues are one of the major challenges for mankind [1,2]. Due to the serious damage of NO_2 to environment and human beings, strict occupational exposure limits (OEL) for NO_2 (such as 5 ppm in ACGIH) have been proposed by governmental agencies and non-governmental groups. In order to meet OEL requirements, NO_2 which mainly comes from combustion processes (such as automotive engines and power stations) must be treated before the emission. Therefore, NO_2 sensor is essential for monitoring and controlling NO_2 treatment process [3,4]. Solid-state electrochemical NO_2 sensors attract an increasing attention due to the good sensitivity and selectivity, especially the excellent stability in the harsh conditions [5]. In fact, the solid-state electrochemical NO_2 sensor is a type of galvanic or electrolytic cell, which consists of the electrolyte, sensing electrode and reference electrode. Therefore, the work modes for this type of sensor are multiple, which is more distinctive than other types of NO_2 sensors. When the solid-state electrochemical NO_2 sensor works as a galvanic cell, an electric potential difference (ΔV) of the cell is measured as the response signal, often referred to as mixed-potential type sensor [6–8]. A fixed voltage also can be applied on the solid-state electrochemical NO_2 sensor which works as an electrolytic cell. The current associated with the reduction of NO_2 at the sensing electrode is measured that is the amperometric type sensor [9–11].

In addition, an impedancemetric sensing approach also can be applied to the solid-state electrochemical NO_2 sensor [12–14]. Compared with the amperometric-type, the impedancemetric-type can avoid the sustained polarization of the sensor, which is beneficial for better long-term stability. In addition, the impedancemetric-type sensor can measure total NO_x due to the homodromous response to NO_2 and NO, which is superior than the mixed-potential type sensor and amperometric type sensor with opposite response to NO_2 and NO. Meanwhile, compared with the chemiresistive sensors, the impedancemetric-type sensor can provide more tunability due to the controllable parameters, such as frequency and voltage amplitude. More importantly, the impedancemetric-type sensor can be applied in elevated

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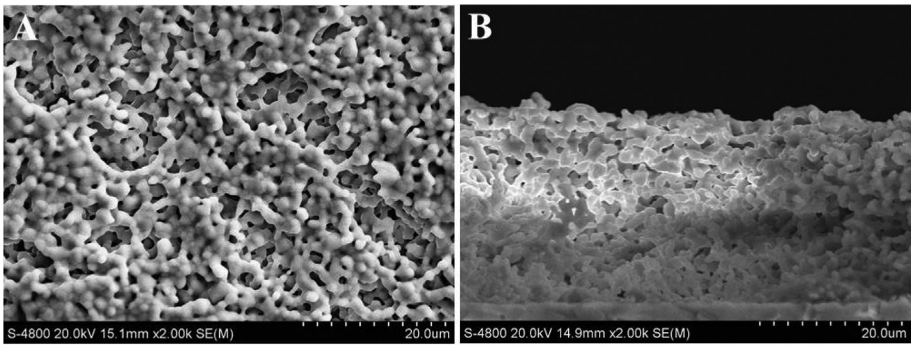

Fig. 1. SEM micrographs of the LSKO porous layer before LSFP impregnation (A) surface and (B) cross-section.

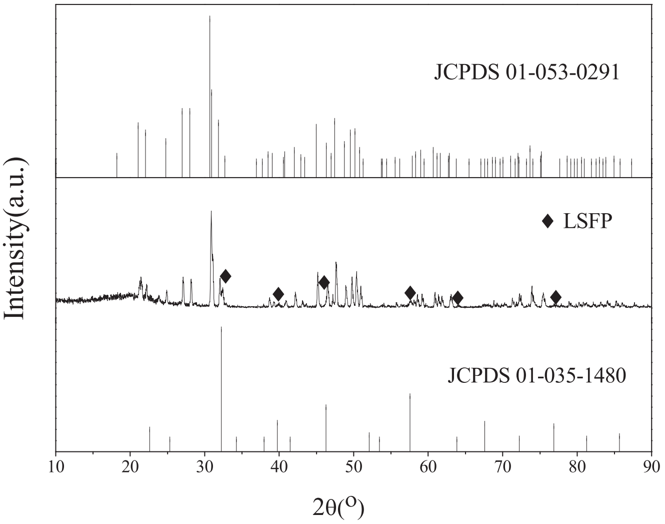

Fig. 2. XRD patterns of the LSKO porous layer after LSFP impregnation and calcination at 1173 K for 3 h with LSKO and LSFP standard patterns as comparison.

temperatures, which is another obvious advantage over the chemiresistive sensors.

In general, the impedance modulus |*Z*| at a fixed frequency is used as the response signal of the impedancemetric-type sensor. However, due to the influences of gas concentration on impedance at the low frequency regime, the frequencies of ≤1 Hz regime are typically chosen for the |Z| response, leading to longer response time [15]. For the impedance spectroscopy, there is another important parameter, that is, phase angle (Θ) calculated from Equation (1). Compared with |*Z*|, Θ generally provides more stable response and higher signal-to-noise ratio at higher frequencies [16–18]. Therefore, Θ should be more promising as response signal for the impedancemetric type sensor.

$$\Theta = \arctan\,(Z''/Z') \tag{1}$$

In term of the sensing electrode, perovskite oxides (ABO_3) have been considered as the promising alternative for the solid-state electrochemical NO_2 sensor due to the excellent selectivity of NO_2 adsorption/decomposition and good structure stability at oxidizing or reducing atmosphere [19–21]. Another advantage for perovskite oxides is the excellent tolerance to extensive aliovalent doping. Doping noble metal, like Pd, Ag, Au, into B site is an effective approach to improve the catalytic activity of the electrode materials and has been approved in solid oxide fuel cells (SOFC) and three-way catalysts (TWCs) due to the production of crystal lattice defects or O^{2-} vacancies in the lattice [22–25]. However, the researchers have paid little attention about the Pd doped perovskite oxide as sensing material of solid-state electrochemical NO_2 sensor.

In this paper, Pd doped iron containing perovskite oxide ($La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3\text{-}\delta}$, LSFP) was in-situ prepared by the impregnation method and used as sensing electrode (SE) for the lanthanum oxyapatite based impedancemetric NO_2 sensor. The sensing performance of the LSFP electrode was investigated by monitoring the modulus |*Z*| and phase angle (Θ), respectively. The Θ response of the sensor exhibits superior sensing characteristic in the sensitivity, stability and response time.

2. Experimental

2.1. Preparation of $La_{9.95}K_{0.05}Si_6O_{26.95}$ bilayer electrolyte

The apatite-type $La_{9.95}K_{0.05}Si_6O_{26.95}$ powders were synthesized by solid-state reaction. The raw materials (La_2O_3, SiO_2 and K_2CO_3) were ball-milled, calcined at 1300 °C in air for 12 h. To form dense $La_{9.95}K_{0.05}Si_6O_{26.95}$ electrolyte, the pre-prepared powders were pressed into disks (diameter: 13, thickness: 3 mm) and then sintered at 1550 °C for 5 h in air. The porous electrolyte layer was prepared by screen-printing $La_{9.95}K_{0.05}Si_6O_{26.95}$ ink on one side of the dense $La_{9.95}K_{0.05}Si_6O_{26.95}$ electrolyte and sintered at 1550 °C. The $La_{9.95}K_{0.05}Si_6O_{26.95}$ ink was obtained by mixing $La_{9.95}K_{0.05}Si_6O_{26.95}$ powder, graphite powder (30%, as the pore-forming agent) and organic dispersants (terpineol, 94 wt% and ethylcellulose, 6 wt %) using ball-milling.

2.2. Preparation of $La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3\text{-}\delta}$ sensing electrode

$La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3\text{-}\delta}$ sensing electrode was introduced into the porous layer of the $La_{9.95}K_{0.05}Si_6O_{26.95}$ electrolyte by in-situ impregnation method. The precursor solution consists of 0.1 mol/L metal salt nitrates with La, Sr, Fe and Pd molar ratio 0.7:0.3:0.95:0.05. The complexing agent of citric acid was added to the solution with the 1:1.5 mol ratio of total metal ions/citric acid. The precursor solution was impregnated into the porous layer with 4 μL at a time, dried at 100 °C, and finally formed $La_{0.8}Sr_{0.2}Fe_{0.95}Pd_{0.05}O_{3\text{-}\delta}$ by calcination at 900 °C for 3 h. The loading was about 5 wt% of the $La_{9.95}K_{0.05}Si_6O_{26.95}$ porous layer by the repeating number of impregnation and calcination.

The phase composition of the samples was identified by X-ray diffraction (XRD, Rigaku, D/MAX2500PC) analysis under Cu-K_α radiation with the incidence beam angle of 2° in the range of 10–90°. The microstructure of the samples was investigated by field emission scanning electron microscopy (SEM, Hitachi, S-4800). The elements mapping of the samples was analyzed by the energy-dispersive X-ray spectroscopy (EDS, FEI Quanta 650 FEG).