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Novel NASICON-based H_2 sensor with insensitive reference electrode and buried Au sensing electrode

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ABSTRACT

A mixed potential type sensor based on NASICON (sodium super-ionic conductor) was designed for the detection of hydrogen. Two original ways were combined to promote the sensor's sensitivity. $LaCrO_3$ was applied on Au reference electrode as H_2 oxidation layer to minimize the H_2 response on reference electrode. Additional NASICON layer was coated on Au sensing electrode serving as sensitive electrode for limiting the O_2 diffusion. H_2 temperature-programmed reduction (TPR) measurement was conducted to test the oxidizability of $LaCrO_3$. The effect of O_2 concentration on sensor's sensitivity was discussed to verify the function of additional NASICON layer. The correlation between the thickness of additional NASICON diffusion layer and sensor's sensitivity was also studied. The research showed that the sensor attached with 0.3 mm thick additional NASICON layer exhibited the largest sensitivity to 100–5000 ppm H_2 at 400 °C, the slope was −123 mV/decade. In addition, the sensor exhibited excellent selectivity to H_2 against the other interference gases, such as CO, NO_2, NH_3, C_7H_8, C_2H_4, CH_2O, C_3H_6O and CH_4.

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1. Introduction

Hydrogen (H_2), a kind of clean energy, has been widely used in fuel cells, cars with H_2 engine, industrial processing and others [1,2]. However, its security is very important in practical application, since H_2 is a kind of hazardous, odorless and flammable gas. Based on this, the detection of H_2 has recently attracted considerable interest. Hydrogen sensors based on various sensing principles and materials have been widely investigated and developed, e.g., thin film type H_2 sensor [3,4], semiconductor metal oxides type [5–7], diode type [8], FETs type [9,10], solid electrolytes type [11–15], etc. Among these sensors, the solid electrolyte type H_2 sensor exhibits high sensitivity, speedy response kinetics and excellent stability [11–15]. Lu et al. has developed the mixed potential H_2 sensor based on stabilized zirconia and oxide electrode [16]. Though the H_2 sensing device showed an excellent sensing performance, the high operating temperature (500–700 °C) limited its further application. NASICON ($Na_3Zr_2Si_2PO_{12}$) electrolyte can work at the temperature range of 100–500 °C, and has been widely used as sensing materials for detecting various gases. Besides their relative lower operating temperature, the gas sensors based on NASICON have obvious advantages, such as high selectivity, rapid and reproducible response, low concentration detection. Various NASICON-based sensors, e.g., potentiometric type CO_2 sensor [17–19], amperometric type NO_2 sensor utilizing the nitrite auxiliary electrode [20], as well as mixed potential type sensors using oxide sensing electrode [21–25], have been investigated in the past few years. However, few researches about NASICON-based H_2 sensors have been reported. As for NASICON-based mixed potential type sensors, most attentions have been paid on searching new sensing electrode materials. The study found that NASICON-based sensors attached with Pr_6O_{11}-doped SnO_2 [22], V_2O_5-doped TiO_2 [23], $CaMg_3(SiO_3)_4$-doped CdS [24], or Cr_2O_3 [25] as the sensing electrodes, can give sensitive and selective respond to dilute H_2S, SO_2, Cl_2 or NH_3 in air, respectively.

For the NASICON-based mixed potential sensors in which the sensing and reference electrodes are exposed to the same gases, electrochemical reactions occur at both electrodes, and the difference of the sensing and reference electrode potentials is measured as the sensing signal (sensitivity) [26]. Thus, blocking the electrochemical reactions at the reference electrode could raise the sensitivity of sensor to target gases. Miura et al. used Mn_2O_3 as gas-insensitive reference electrode for yttria-stabilized zirconia (YSZ)-based potentiometric oxygen sensor [27], the oxygen sensor attached with a couple of Au sensing electrode and Mn_2O_3 reference electrode exhibited large responses to CO, H_2 and unsaturated HCs.

In this work, a new kind of H_2 sensor has been fabricated and evaluated. To get a H_2-insensitive reference electrode, $LaCrO_3$ has been applied on the Au electrode because of its oxidation to H_2 at high temperature. Moreover, Au electrode has been used as sensing electrode for the H_2 sensor and an additional NASICON layer has

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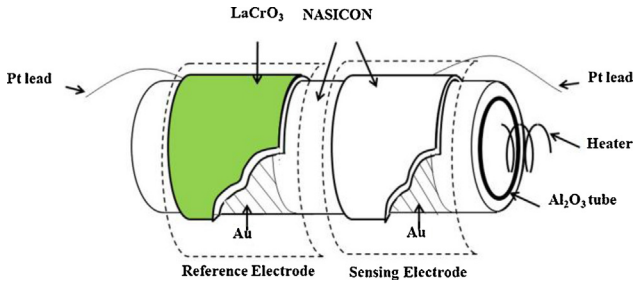

Fig. 1. Schematic structure of the sensor.

been coated on Au sensing electrode for limiting the diffusion of O_2, resulting in a great enhancement of sensor's sensitivity. A sensing mechanism involved in the mixed potential, gas diffusion and H_2 oxidation in the $LaCrO_3$ layer has been proposed.

2. Experimental

2.1. Synthesis of NASICON and $LaCrO_3$

NASICON was synthesized from $ZrO(NO_3)_2$, $NaNO_3$, $(NH_4)_2HPO_4$ and $Si(C_2H_5O)_4$ by sol–gel process and calcined at 900 °C for 6 h [24]. Perovskite-type oxide $LaCrO_3$ was prepared by a citric acid complex method [28]. $La(NO_3)_3$ $6H_2O$ and $Cr(NO_3)_2$ $9H_2O$ were used as sources of La and Cr, respectively. The above metal nitrates in stoichiometric ratios were first dissolved in an aqueous solution with an equimolar amount of citric acid, making [M]:[citric acid] = 1:1. This mixture was evaporated at 80 °C to make a sol–gel of organic metal complex, followed by an overnight drying at 120 °C and pre-decomposition at 400 °C for 2 h. The precursors were finally calcined in air at 800 °C for 5 h, the increasing and decreasing rates were 10 °C/min and 5 °C/min, respectively.

Phase composition of the prepared powder was verified by X-ray diffraction (Rigaku wide-angle X-ray diffractometer (D/max rA, using Cu Kα radiation at wavelength λ = 0.1541 nm)). Temperature-programmed reduction (TPR) measurements were conducted with a Micromeritics AutoChem 2910 Automated Catalyst Characterization System. About 0.1 g of sample placed in the reactor was activated in a flow of synthetic air at 500 °C at a rate of 10 °C/min for 1 h. After the sample was cooled to 50 °C in synthetic air, a mixture of 10 vol% H_2/Ar was introduced into the sample loop at 50 ml/min. The sample was heated at a rate of 10 °C/min to 800 °C. The effluent gas was passed through a viscous solution of isopropanol, cooled by liquid N_2 to remove the water produced during the reduction, and analyzed with a thermal conductive detector.

2.2. Fabrication of the sensor

The schematic structure of NASICON-based sensor is shown in Fig. 1. A thick film of NASICON was formed on the outer surface of an alumina tube as the ionic conductor layer by applying NASICON precursor paste and sintering at 900 °C for 6 h. A couple of ring-shaped Au electrodes were formed on the two ends of the NASICON thick film. An additional NASICON layer and $LaCrO_3$ layer was coated on one and the other Au electrode by sintering NASICON and $LaCrO_3$ paste at 800 °C and 600 °C for 6 h, respectively. The sensors with 0 mm, 0.1 mm, 0.3 mm and 0.6 mm thick additional NASICON layer were marked as sensor A, B, C and D, respectively. A sensor without $LaCrO_3$ layer and with 0.3 mm thick additional NASICON layer was marked as sensor E. For keeping the sensor at an appropriate operating temperature, Ni–Cr coil heater was inserted into the alumina tube.

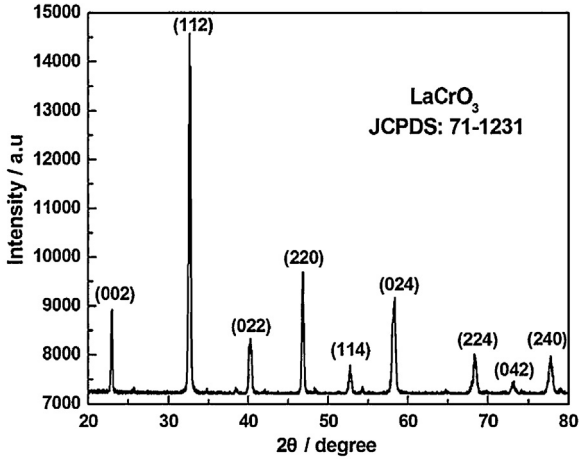

Fig. 2. X-ray diffraction (XRD) pattern of $LaCrO_3$.

2.3. Measurement of sensing properties

Gas sensing properties of the sensors were measured by a conventional static mounting method. The sample gases containing different H_2 concentration were obtained by diluting pure H_2 with air. When the sensor was exposed to air or the sample gas, the electromotive force (V) was measured with a digital electrometer (RIGOL TECHNOLOGIES, INC, DM3054, China) as a sensing signal and the obtained results were registered with a computer connected to the electrometer.

3. Results and discussion

3.1. Characterization of $LaCrO_3$

Fig. 2 shows the XRD pattern of the as-prepared material. It can be seen that the as-prepared oxide retained its orthorhombic crystallographic phases, corresponding to JCPDS PDFs#71-1231 and was testified to be pure perovskite-type oxide $LaCrO_3$. The particle size of $LaCrO_3$ calculated by Debye–Scherrer equation was about 38 nm.

$LaCrO_3$ is applied on Au reference electrode as oxidation layer for H_2, the overall H_2 consumption has effect on sensor's sensing properties. The oxidation behavior of $LaCrO_3$ examined by TPR is shown in Fig. 3. The TPR profile of $LaCrO_3$ sample exhibited two distinct peaks at 335 and 435 °C. When $LaCrO_3$ was heated up to

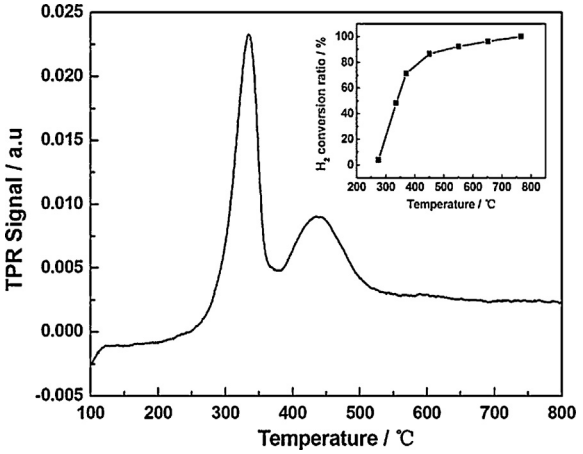

Fig. 3. H_2 TPR profile of $LaCrO_3$ and dependence of H_2 conversion ratio on temperature.

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