The gas sensing properties of some complex metal oxides prepared by self-propagating high-temperature synthesis

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The gas-sensing properties of spinel and orthorhombic ferrites (NiFe2O4, CoFe2O4 and LaFeO3 respectively) as well as cubic nickel–zinc stannates Zn2-xNi1xSnO4 (with x = 0, 0.8) prepared by self-propagating high-temperature synthesis (SHS) are reported. This is the first report of using an SHS derived powder for gas sensing applications. The gas response of the materials was investigated against a range of gases (ethanol, ammonia, propane, CO, ethane, ethene) at a variety of operating temperatures. Good gas response behavior was found in the case of the cubic nickel–zinc stannates with excellent selectivity toward ethanol.

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1. Introduction

There is a need for new materials for chemiresistive gas sensors. Current materials suffer from significant cross sensitivity issues [1]. Complex metal oxides such as ferrites have not been extensively explored [2]. Heterogeneous combustion (or self-propagating high-temperature synthesis (SHS)) is a relatively new, but widely used synthetic method for the production of functional oxide ceramics, cermet and composites [3,4]. An SHS synthesis involves the rapid reaction of the starting mixture in a combustion wave with the direct formation of the product occurring almost instantly. Here we report the SHS synthesis of nickel and cobalt spinel ferrites (NiFe2O4, CoFe2O4), orthorhombic lanthanum ferrite (LaFeO3) as well as zinc–nickel stannate (Zn2-xNi1xSnO4 with x = 0 and 0.8). We have fabricated gas sensors from these materials and have evaluated their resulting gas sensing properties.

2. Experimental

The combustion process was carried out in air with mechanically ground mixtures of appropriate metal (Fe, Co or Zn), metal oxides (used as diluents) and NaClO4. All the reagents were obtained from the Aldrich Chemical Company and used as supplied. Precursor materials were combined in stoichiometric quantities according to the following reactions:

NiO + Fe + 0.5Fe2O3 + 0.375NaClO4 → NiFe2O4 + 0.375NaCl

Co + Fe2O3 + 0.25NaClO4 → CoFe2O4 + 0.25NaCl

La2O3 + 2Fe + 0.75NaClO4 → 2LaFeO3 + 0.75NaCl

Zn + ZnO + SnO2 + 0.5NaClO4 → Zn1.2Ni0.8SnO4 + 0.5NaCl

0.8NiO + 1.2Zn + SnO2 + 0.3NaClO4 → Zn1.2Ni0.8SnO4 + 0.3NaCl

The SHS reaction was driven by the exothermic oxidation of Fe, Zn or Co metal. Sodium perchlorate was used as the internal oxidizing agent in the reaction. Appropriate metal oxides act as a heat sink. This starting material (~1–2 g) was pressed isostatically with a pressure of 1 t into pellets with diameter of 13 mm and thickness of 2 mm. A REKROW RK-2060 Micro Torch (UK) was used to ignite the pellets. This promoted an orange-yellow propagation wave, which traveled at a velocity between 1.0 and 1.5 mm s−1 and reached a maximum temperature of 1350–1500 K. The products from the reaction were ground and washed with deionized water to remove sodium chloride from the product. The resulting powders were sintered at 1420 K–2 h (1)–(2) and at 1670 K–36 h (3) respectively (4 and 5 were not sintered). The powders were then sieved through a 150 μm sieve and mixed into an ink using a previously reported method [5]. The as-prepared inks were printed directly on gold inter-digitated patterned electrodes on 3 × 3 mm alumina chips and calcined in a furnace at 600 °C for 2 h to burn out the organic phase of the ink and fix the powders to the sensor chip surface. The fired chips had 50 μm platinum wire spot-welded onto the gold contacts of the chip, which are used to suspend the sensor on stainless steel pins in molded polyethylene sulfide housings.

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3. Results and discussion

The prepared sensors were then analyzed by X-ray powder diffraction and scanning electron microscopy (SEM). X-ray powder diffraction (Fig. 1) showed that single phase cubic spinel structures were produced for the sintered ferrites (1)–(2) as well as for pure and substituted stannates (4)–(5). The lanthanum ferrite (3) was found to be orthorhombic with the following lattice parameters: \(a = 5.560\), \(b = 5.551\), \(c = 7.854\) Å. The cubic spinels had the following lattice parameters: (1) \(-8.331\) Å; (2) \(-8.339\) Å; (4) \(-8.657\) Å and (5) \(-8.608\) Å. These lattice parameters were identical to those reported in the literature within experimental error [6–9].

Scanning electron microscope imaging of the samples (Fig. 2) indicated an open porous morphology with an average particle size of 1 \(\mu\)m for the CoFe\(_2\)O\(_4\), Zn\(_2\)SnO\(_4\) and Zn\(_{1.2}\)Ni\(_{0.8}\)SnO\(_4\) samples (Fig. 2B, D and E respectively). The NiFe\(_2\)O\(_4\) and LaFeO\(_3\) samples (Fig. 2A and C respectively) had significantly different morphologies and larger crystallite sizes. The NiFe\(_2\)O\(_4\) morphology consisted of large crystals with extended layer growth, leading to the production of a large number of step and kink sites (Fig. 2C).

Gas sensing experiments on the screen-printed sensors were performed on an in-house test-rig [10] designed to maintain up to six sensors at constant operating temperature (varied between 300 and 600 °C) via a heater driver circuit connected to each sensor’s heater track. Resistance measurements were taken using a Keithley multimeter. The sensors were tested with a range of gases (ethanol, ethane, propane, propylene, ammonia and carbon monoxide, all from BOC gases) in environmentally relevant concentrations [11], all diluted using synthetic air.

Fig. 3 shows the five sensors concentration dependent responses to ethanol gas at their optimum operating temperatures. All of the sensor materials gave n-type responses to ethanol (Gas response, \(G_n = \) Resistance in test mixture/Resistance in air) with the exception of the LaFeO\(_3\) sensor, which gave a p-type response (Gas response, \(G_p = \) Resistance in air/Resistance in test mixture). All of the sensors gave measureable responses to ppm levels of ethanol gas, although in the case of the Zn\(_2\)SnO\(_4\) and Zn\(_{1.2}\)Ni\(_{0.8}\)SnO\(_4\) sensors this was appreciably higher in magnitude than the others; responses of ~9 to 20 ppm ethanol rather than 2 or less. The CoFe\(_2\)O\(_4\), NiFe\(_2\)O\(_4\) and LaFeO\(_3\) sensors show only a limited dynamic range, while the Zn\(_2\)SnO\(_4\) and Zn\(_{1.2}\)Ni\(_{0.8}\)SnO\(_4\) sensors have an extended dynamic range, with gas responses of almost ten being achieved on exposure to 20 ppm ethanol.

**Fig. 1.** X-ray diffraction patterns of the sensor materials.

**Fig. 2.** Scanning electron microscope images of the sensors. A) NiFe\(_2\)O\(_4\). B) CoFe\(_2\)O\(_4\). C) LaFeO\(_3\). D) Zn\(_2\)SnO\(_4\). E) Zn\(_{1.2}\)Ni\(_{0.8}\)SnO\(_4\).

**Fig. 3.** Gas response (\(G_n\) or \(G_p\) for LaFeO\(_3\)) of the sensors to ethanol at their optimal operating temperatures.
Fig. 4 shows the response of the sensors to a variety of gases in environmentally important concentrations. In all cases the sensors show some selectivity toward ethanol, in the case of the Zn$_2$SnO$_4$ and Zn$_{1.2}$Ni$_{0.8}$SnO$_4$ sensors this was especially significant with gas responses at least double that of 50 ppm ammonia.

The enhanced response of the Zn$_2$SnO$_4$ and Zn$_{1.2}$Ni$_{0.8}$SnO$_4$ sensors can be attributed in part to the open and porous microstructure of the as prepared sensors (Fig. 2). The responses of the CoFe$_2$O$_4$, NiFe$_2$O$_4$, and LaFeO$_3$ sensors were broadly similar despite the samples having significantly different microstructures. Interestingly the LaFeO$_3$ sensor gave significant gas responses, particularly to ethanol gas, in spite of the poor porosity of the sample. The relatively high sensitivity in this case is attributed to the large number of step and kink sites that may allow for the preferential adsorption and ionization of oxygen at the material interface.

Only a small amount of gas sensing work on NiFe$_2$O$_4$, LaFeO$_3$, and Zn$_2$SnO$_4$ has been previously reported [2,12–14]; in all cases a limited number of gases were examined and poor sensitivity and selectivity were found [15,16]. Where sensors were found to be selective toward a particular gas, large concentrations were examined [17,18], far in excess of what can be reasonably expected as environmental pollutants [11], typically in the region of 200–1000 ppm. The complex metal oxide sensors prepared here by an SHS route give far greater sensitivity and selectivity (Fig. 4) than those previously prepared.

4. Conclusion

A novel self-propagating high-temperature synthesis of these materials has been performed and their application as gas sensors for environmental monitoring has been demonstrated. SHS gives good control over phenomena such as particle size and morphology that allows gas sensor performance and gas selectivity to be greatly improved. This route shows great promise for the production of complex oxide materials for gas sensing applications that show improved selectivity and sensitivity.

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