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Mixed-potential-type NO_2 sensor using stabilized zirconia and Cr_2O_3–WO_3 nanocomposites

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ABSTRACT

A series of mixed W/Cr oxides with different ratio of W and Cr (1:6, 1:2 and 3:2) have been prepared by using polymeric precursor method. By comparing their sensitivities to 20–300 ppm NO_2, it was found that the sensor using oxide with 3:2 W/Cr gave the largest response value. For 3:2 W/Cr oxide, the effect of the sintering temperature on the electrode microstructure was also investigated. As a result, the device sintered at 1000 °C showed the best performance. The response value to 100 ppm NO_2 is 51.6 mV, the response time is within 20 s and the sensing device also shows an excellent selectivity against other coexisting gases. The characteristics of SEM and TEM revealed that the special microstructure of oxide electrode formed by sintering plays a significant role in better sensing performance.

1. Introduction

As the increasing of the exhaust emissions from the automotive vehicles and various industrial processes, more and more attentions have been focused on the detection of nitrogen oxides (NO_x) which give rise to some environmental disaster such as acid rains and photochemical smog. In order to reduce the NO_x emission from cars, some legislations, such as auto emissions standards of European, America and so on, have been strongly enforced. Therefore, the development of high performance NO_x sensors is eagerly required [1]. Solid electrolyte gas sensor using yttria stabilized-zirconia (YSZ) and oxide-based sensing electrode (SE) is one of the most advantageous devices, in terms of their special features such as high temperature operation, chemical and mechanical stability, and relatively low fabrication cost [2–13]. In addition, their sensing properties can be tailored by modifying electrode materials.

Up to now, special attentions have been paid to searching for new oxide electrode materials for increasing the sensitivity to NO_2. The catalytic activity to the reaction of NO_2 decomposition and electrochemical behavior of the SE material are considered to be the main factors to determine the sensitivity [14–19]. The microstructures of the electrodes, such as the particle size, the number of pores and the thickness of the SE layer, considerably affect the sensitivity and response kinetics of the sensor, because these structural factors can influence the adsorption and desorption on the sensing electrode materials of NO_2 as well as its diffusion in the sensing electrode layer [20,21].

In this work, plenty results of micro-structural and gas sensing characterization of W/Cr binary oxides used as sensing electrodes of mixed-potential NO_2 sensors are presented. We focus on the effect of the ratios and microstructure of W/Cr binary oxides on the sensing properties of the stabilized zirconia-based NO_2 sensors at elevated temperature. The microstructure of W/Cr binary oxides was controlled by the sintering temperature and the doping amount of WO_3 to the oxide electrodes for improving the sensitivity.

2. Experimental

2.1. Preparation and characterization of the W/Cr binary oxides

The W/Cr binary oxides were prepared with polymeric precursor method, which provides high-dispersion and inhomogeneous mixing W/Cr nanocomposites. In a typical synthesis process, citric acid and stoichiometric amounts of $Cr(NO_3)_3{\cdot}9H_2O$ and $H_{40}N_{10}O_{41}W_{12}{\cdot}xH_2O$ were dissolved in deionic water, and molar ratio of citric acid and all the metal cations (Cr and W) was 3:1. Then ethylene glycol was added to the above solution of which the citric acid/ethylene glycol mass proportion was 60%:40%. The resulting solution was maintained at 80 °C to form a polymeric gel, and then calcined at 400 °C for 2 h to remove the polymer, finally sintered at 800 °C for 2 h. We prepared three kinds of W/Cr binary

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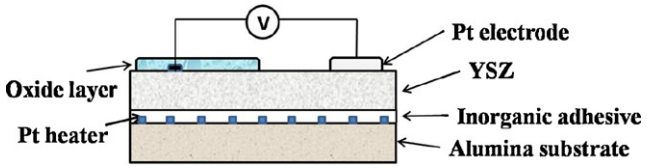

Fig. 1. Schematic cross-sectional view of the planar sensor.

oxides by mixing the W and Cr nitrates with the ratios of 1:6, 1:2 and 3:2. The single Cr_2O_3 and WO_3 were prepared with the same method by using $Cr(NO_3)_3{\cdot}9H_2O$ and $H_{40}N_{10}O_{41}W_{12}{\cdot}xH_2O$, respectively.

XRD patterns of the W/Cr binary oxides were measured by Rigaku wide-angle X-ray diffractometer (D/max rA, using Cu Kα radiation at wavelength λ = 0.1541 nm). Field-emission scanning electron microscopy (FESEM) observations of surface morphology of the sensing electrodes were carried out using a JEOL JSM-7500F microscope with an accelerating voltage of 15 kV. The TEM image was taken by a Philips Tecnai F20 at 200 kV by drop casting the sample dispersions on copper grids.

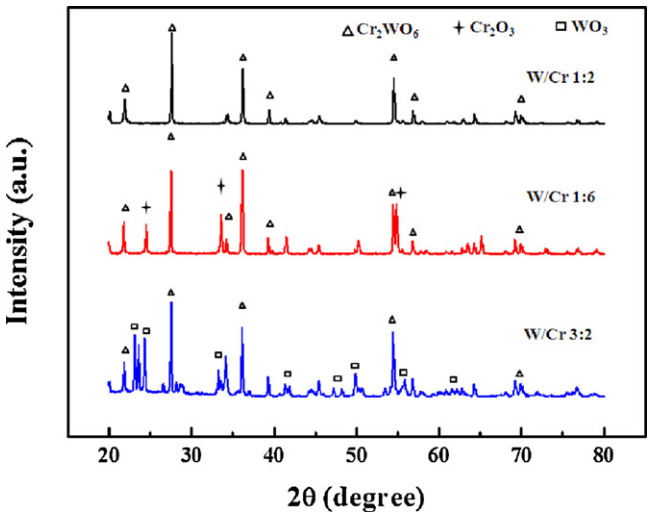

Fig. 2. XRD patterns of W/Cr binary oxides with different ratios sintered at 800 °C.

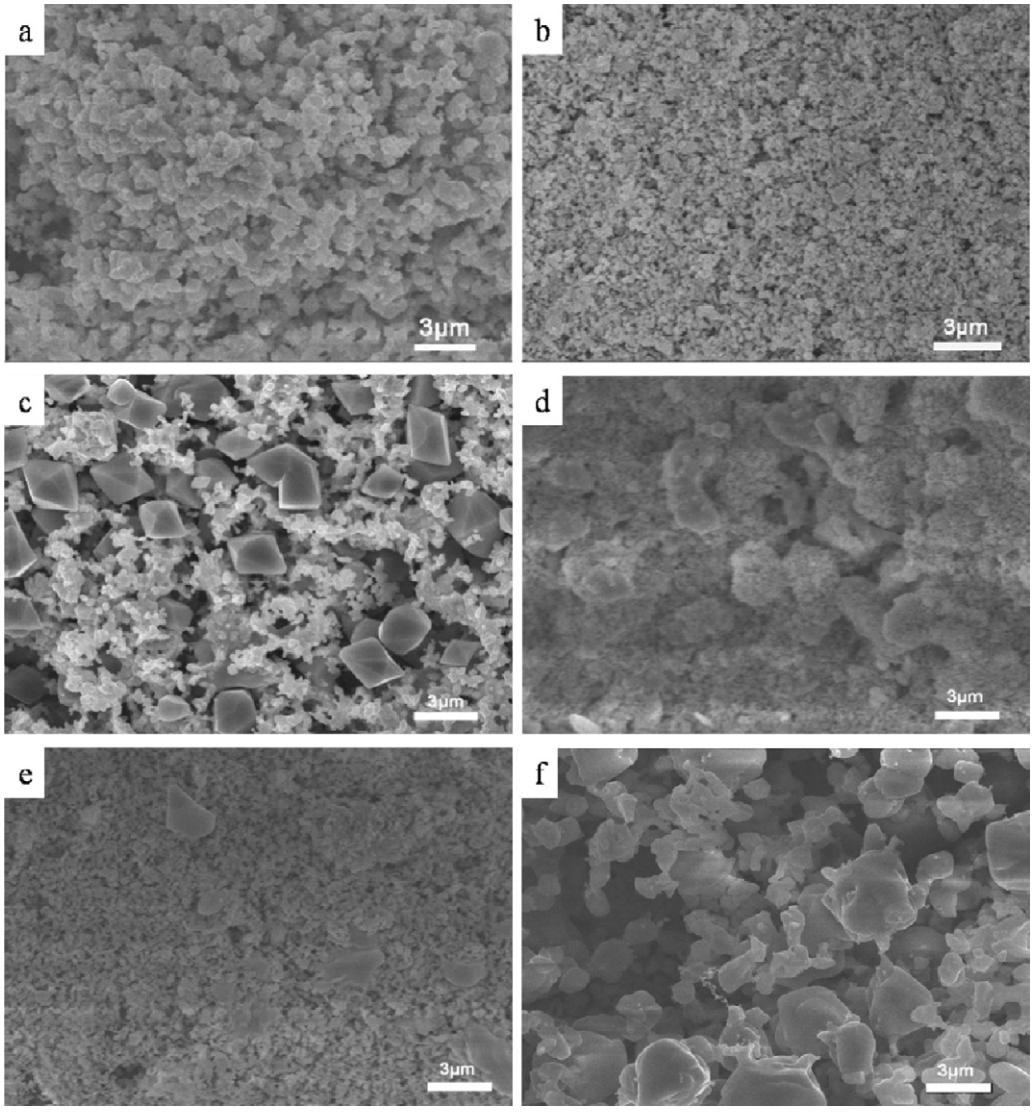

Fig. 3. (i) SEM images of electrode surfaces using W/Cr binary oxides as sensing materials with different ratios: (a) 1:6, (b) 1:2 and (c) 3:2 sintered at 1000 °C; (ii) electrode surfaces using W/Cr binary oxides with the ratio of 3:2 sintered at different temperatures: (d) 800 °C, (e) 900 °C and (f) 1100 °C.

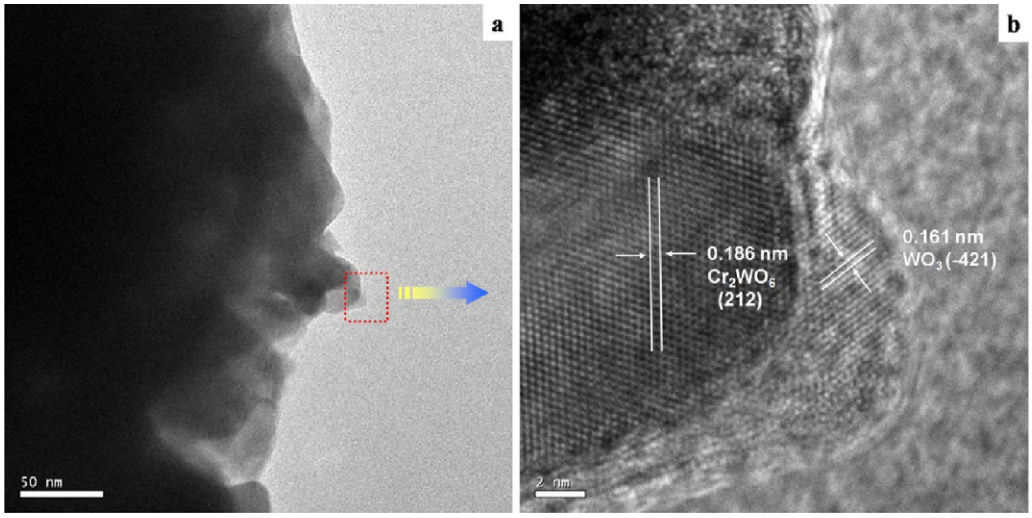

Fig. 4. TEM image (a) and HRTEM image (b) of W/Cr binary oxides with the ratio of 3:2 sintered at 1000 °C.

2.2. Fabrication and measurement of the sensor

The sensor was fabricated using YSZ plate (8 mol% Y_2O_3-doped, 2 mm × 2 mm, 0.2 mm thickness, provided by Tosoh Corp., Japan), as shown in Fig. 1. Two Pt lead wires were attached to the two ends of the YSZ plate with a commercial Pt paste (Sino-platinum Metals CO., Ltd.), and sintered at 800 °C for 2 h. The obtained oxide was mixed with deionized water, fully triturated and the resulting paste was applied on one end of the sensor plate as sensing electrode. Furthermore, to form different surface topography of the sensing electrode material, the device with the 3:2 W/Cr oxide was sintered at 800 °C, 900 °C, 1000 °C and 1100 °C, respectively, and labeled as Sensor A, B, C and D. Then the Pt heater formed on an alumina substrate was attached to the device by using inorganic adhesive, which provides the operating temperature to the sensor.

3. Results and discussion

3.1. Microstructure characteristics

The XRD patterns of W/Cr binary oxides sintered at 800 °C are shown in Fig. 2. In the figure, the patterns of three W/Cr binary oxides are presented, corresponding to terminal products prepared with different ratios of W and Cr nitrates: 1:6, 1:2 and 3:2. When the ratio is 1:2, the diffraction peaks are in good agreement with the JCPDS (File No. 73-2236) data of Cr_2WO_6 tetragonal oxide. When the ratio was changed to 1:6, the pattern contains not only Cr_2WO_6, but also the spectrums of the JCPDS (File No. 84-312) data of Cr_2O_3. On the other hand, when the ratio was adjusted to 3:2, the WO_3 (File No. 72-1465) can be found besides Cr_2WO_6.

The SEM images of the oxide SEs with different W/Cr ratios sintered at 1000 °C are shown in Fig. 3a–c. Fig. 3a and b exhibits agglomerates of elementary particles, but in Fig. 3c the crystals can be seen clearly. To investigate the influence of the temperature on the electrode, the SEM images of the oxides SEs with the 3:2 W/Cr ratio sintered at 800 °C, 900 °C, and 1100 °C are shown in Fig. 3d–f. In Fig. 3d, it can be seen that the surface of the SE is very rugged, since the solid state reactions hardly take place at 800 °C. When the sintering temperature was raised to 900 °C, the solid state reactions related to WO_3 and Cr_2WO_6 seemed to occur, as a result, some small pores and crystals of Cr_2WO_6 started to arise and the surface begins to be flat (Fig. 3e). With the further increasing of the sintering temperature, the Cr_2WO_6 crystal becomes larger and WO_3 partly sublimates, and then the larger Cr_2WO_6 crystals are surrounded by small WO_3 particles at 1000 °C (Fig. 3c). When the sintering temperature rose to 1100 °C, solid solution of Cr_2WO_6 and WO_3 were formed, and the size of the pore became larger (Fig. 3f). Further information about the electrode microstructure of 3:2 W/Cr binary oxide sintered at 1000 °C was obtained from transmission electron microscope (TEM) (Fig. 4). A local region was selected in the TEM image (Fig. 4a), which is the edge of the crystal. The HRTEM image (Fig. 4b) shows the lattice fringes of the crystal with width of 0.186 nm correspond to the (2 1 2) plane of the Cr_2WO_6, and the lattice fringes of the tiny particles around the crystal with width of 0.161 nm correspond to the (−4 2 1) plane of the WO_3. This result clearly indicates the existence of Cr_2WO_6 and WO_3 in the crystals.

3.2. Gas sensing properties

Dependence of the ΔEMF on the NO_2 concentrations for the sensors using W/Cr oxides is shown in Fig. 5. It is seen that the ΔEMFs of all the sensors vary linearly with the logarithm of NO_2 concentration in the examined range of 20–300 ppm at 800 °C. The sensor using W/Cr ratio of 3:2 shows the largest slope and response value. As a comparison, the sensors using Cr_2O_3 and WO_3 as the sensing electrodes were also fabricated and evaluated. Fig. 6 shows the

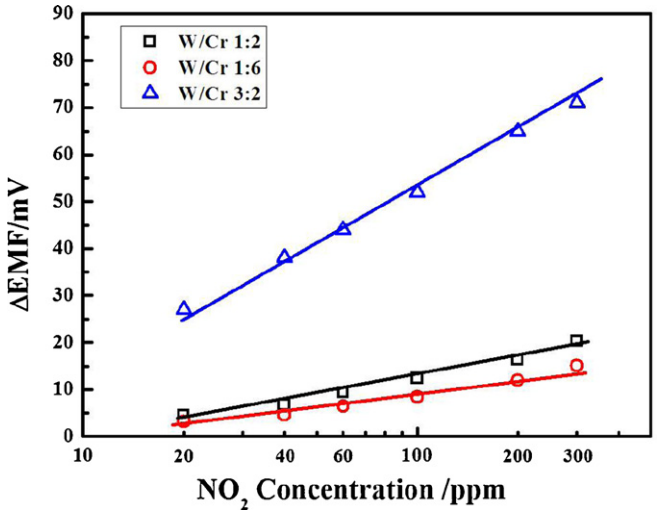

Fig. 5. Dependence of the ΔEMF on the NO_2 concentrations in the range of 20–300 ppm for sensors using different W/Cr oxides sintered at 1000 °C as SE.

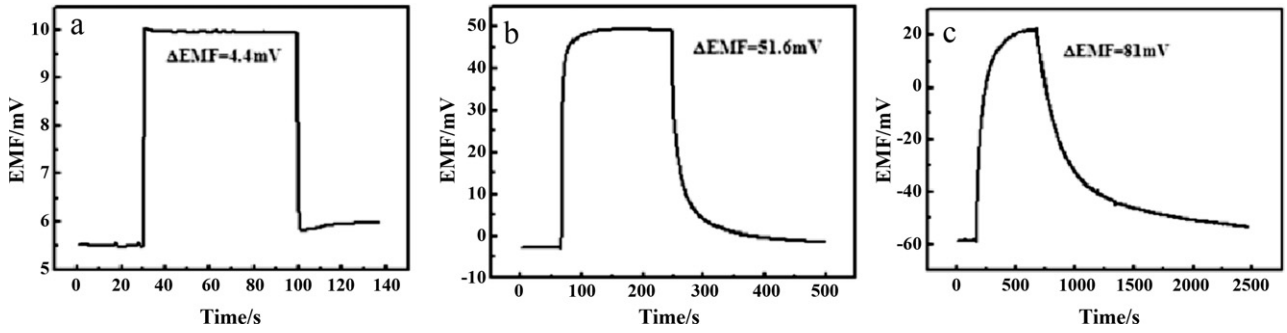

Fig. 6. Response and recovery transients to 100 ppm NO_2 for the planar sensors attached with (a) Cr_2O_3, (b) 3:2 W/Cr oxide as SE sintered at 1000 °C and (c) WO_3.

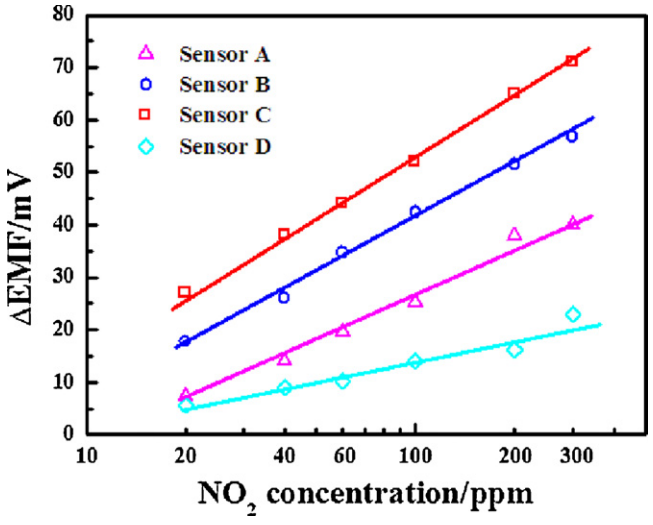

Fig. 7. Dependence of the ΔEMF on the NO_2 concentrations in the range of 20–300 ppm for the sensors with ratio of 3:2 W/Cr oxide as SE sintered at different temperatures: (A) 800 °C; (B) 900 °C; (C) 1000 °C and (D) 1100 °C.

response transients to 100 ppm NO_2 for the three sensors at 800 °C. It can be observed that the sensor with Cr_2O_3 gives the fast response (less than 10 s), but low ΔEMF (about 4.5 mV), the device attached with WO_3 shows a high ΔEMF (about 80 mV), but its response and recovery are too slow. Comparing with the sensors using the single oxides, the sensor attached with Cr_2WO_6/WO_3 nanocomposite has an acceptable response time (about 20 s) and a ΔEMF value (almost 52 mV). In the case of Cr_2WO_6/WO_3 nanocomposite, the excellent electrocatalytic activity of WO_3 seemed to contribute to a high sensitivity to NO_2.

In order to investigate the effects of microstructures formed at different sintering temperatures on the sensitivities of the sensors, the four sensors were evaluated at 800 °C. Fig. 7 shows the dependence of ΔEMF on the NO_2 concentrations for the Sensor A, B, C and D at 800 °C. It is seen that the ΔEMFs of all the sensors are almost linear with the logarithm of NO_2 concentration in the examined range of 20–300 ppm at 800 °C. Sensor C gives the largest sensitivity (slope) compared with the others, in which the device was sintered at 1000 °C. This can be attributed to the special microstructure of Cr_2WO_6/WO_3 sintered at 1000 °C. As expressed above, the pores accumulated by large particles of Cr_2WO_6 and high electrocatalytic activity of WO_3 to NO_2 give rise to a high sensitivity to NO_2 for the Sensor C.

Fig. 8a shows the step-up sensing signal for Sensor C exposed to 2–300 ppm NO_2 at 800 °C. Both at the low and high concentrations, the response and recovery are fast, and the corresponding dependence of the ΔEMF on concentrations is shown in Fig. 8b. The present device was subjected to additional test, in which, it exposed to 100 ppm NO_2 repeated 11 times at 800 °C. As shown in Fig. 9, the response transients as well as the potential difference response to 100 ppm NO_2 are almost reproducible in the successive runs.

The cross-sensitivities to various gases for the Sensor C are exhibited in Fig. 10. It is seen that the present sensor displays rather high selectivity to NO_2: the ΔEMF to NO_2 is more than 50 mV, whereas the ΔEMF values to the other gases are less than 10 mV. Even to 1000 ppm CO and CO_2, the Sensor C also gives a rather low response value. It is speculated that in the course of diffusion of the sample gas through the SE layer, the reducing gases (CO, CH_4 and C_2H_4) seem to be oxidized to CO_2 and H_2O due to the pronounced

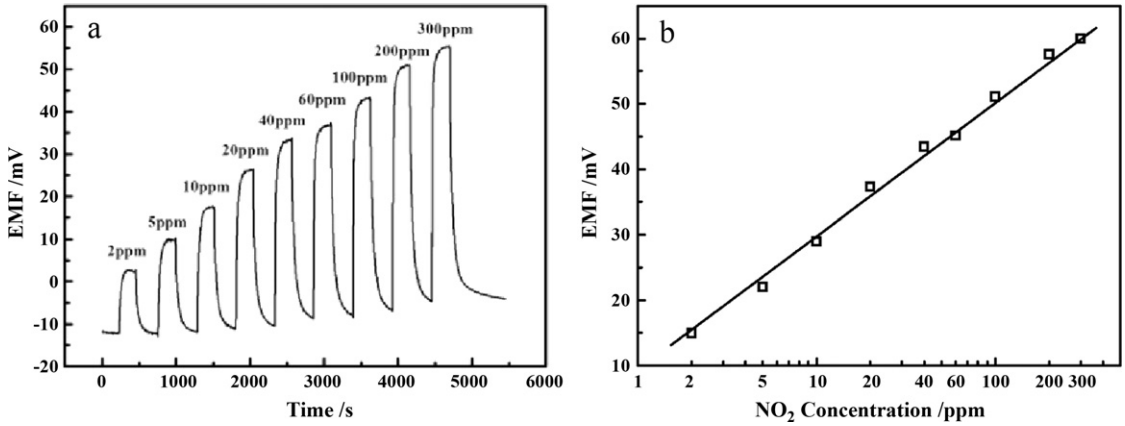

Fig. 8. (a) EMF responses of the sensor with 3:2 W/Cr ratio sintered at 1000 °C to different concentrations of NO_2 in the range of 2–300 ppm and (b) dependence of the ΔEMF on the logarithm of NO_2 concentrations at 800 °C.

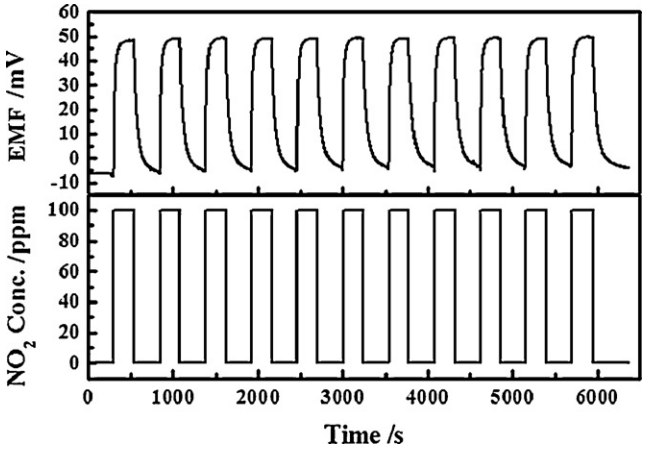

Fig. 9. Repeated response transients of the Sensor C upon switching on- and off-NO_2 at the working temperature of 800 °C.

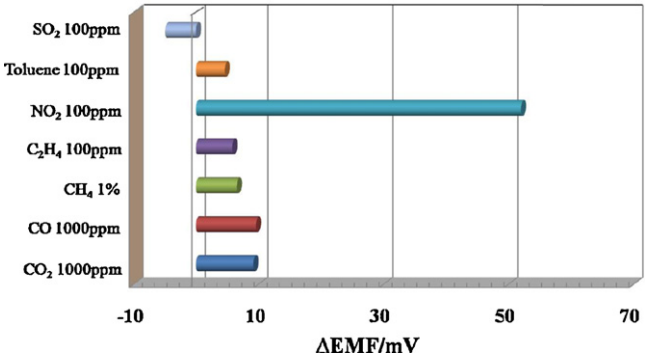

Fig. 10. Cross-sensitivities to various gases for Sensor C at 800 °C with air as balance.

catalytic activity of the Cr_2WO_6 at elevated temperature. Also, the response to NO was investigated. The response to 200–500 ppm NO with air as balance gas is shown in Fig. 11. From the figures, we can see the response value of NO is little rather than that of NO_2.

Additionally, the influence of the humidity on the sensor was measured, because there is a large amount of water vapor in the car emission exhaust. As shown in Fig. 12, values of the ΔEMF to 100 ppm NO_2 obtained with different relative humidity (10%, 20%, 50%, 70% and 90%) are less than 5% difference, which shows that the water has little effect on the NO_2 response for the sensor.

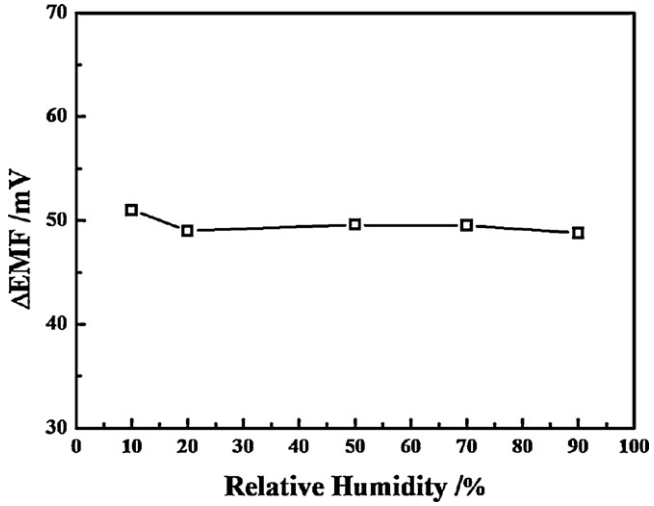

Fig. 12. Response of Sensor C to 100 ppm NO_2 under different humid atmosphere.

The sensing behavior of the potentiometric NO_2 sensor has been explained by the mixed potential mechanism [9,22]. When the SE is exposed to NO_2 in O_2-containing atmosphere, a non-Nernstian potential is produced on the SE, because two electrochemical reactions take place at same time on the SE:

$$O^{2-} \rightarrow 1/2O_2 + 2e^- \text{(anodic)} \quad (1)$$

$$NO_2 + 2e^- \rightarrow NO + O^{2-} \text{(cathodic)} \quad (2)$$

Here, the decomposition reaction related to NO_2 should be mentioned, since it also affects the sensitivity of the sensor.

$$NO_2 \rightarrow NO + 1/2O_2 \quad (3)$$

The reaction (3) is an adverse reaction to the sensitivity of the sensor. When the gas diffuses through the sensing electrode layer, the reaction (3) reduces the NO_2 concentration and results in a low sensitivity. Since the oxide electrode always has the catalytic activity to the NO_2 decomposition more or less and the porous microstructure of the electrode is usually utilized to enhance the diffusion of the NO_2 in the sensing electrode layer as to reduce the consumption of the NO_2 concentration. For the Sensor C, the larger particle size of Cr_2WO_6 enhances the porosity of the nanocomposite oxide and promotes the diffusion of NO_2 in oxide layer. At same time, the outstanding electrocatalytic activity of WO_3 to reaction (2) raises the ΔEMF to NO_2. The above two parameters jointly determined the good sensing performance of the sensor using 3:2 W/Cr oxides.

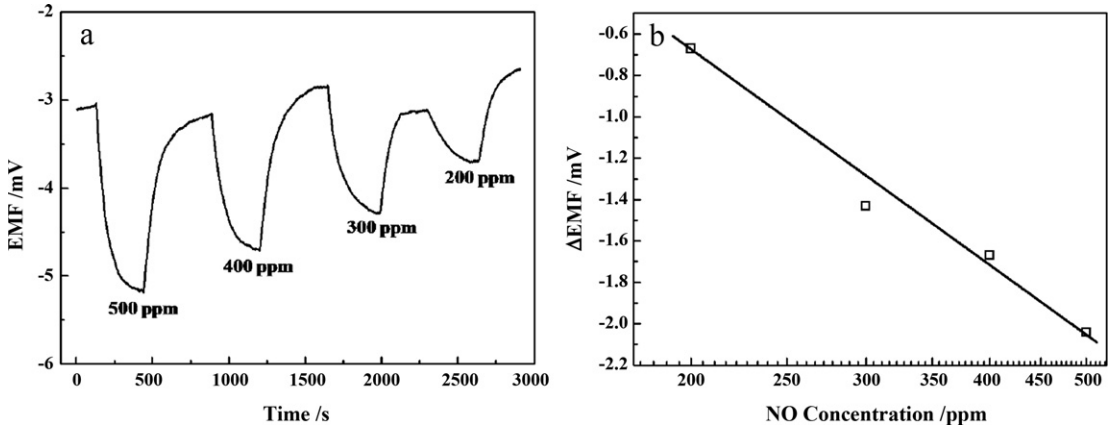

Fig. 11. (a) EMF responses of the sensor with 3:2 W/Cr ratio sintered at 1000 °C to different concentrations of NO in the range of 200–500 ppm and (b) dependence of the ΔEMF on the logarithm of NO concentrations.

4. Conclusions

The W/Cr binary oxides SE layers with different ratios were formed on the YSZ plate. It is found that the sensor using W/Cr binary oxides with the ratio of 3:2 has the optimal NO_x sensing characteristic. Moreover, the sensors sintered at various temperatures (800 °C, 900 °C, 1000 °C and 1100 °C) were prepared and tested. The results revealed that the sensor sintered at 1000 °C exhibits the highest sensitivity and speedy response and recovery rates. The high sensitivity and the fast response rate can be attributable to its special porous microstructure, which results from the sublimation of the WO_3, the growth of the Cr_2WO_6 particles as well as the synergy of the WO_3 and Cr_2WO_6. In addition, the sensor has a rather good selectivity to NO_2. These good sensing properties indicate the promising potential of the sensor in practical application.

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