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Ammonia sensor based on NASICON and Cr_2O_3 electrode

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ABSTRACT

A compact tubular sensor based on NASICON (sodium super ionic conductor) and porous Cr_2O_3 sensing electrode was designed for the detection of ammonia. The sensor gave excellent sensing properties to 50–500 ppm ammonia in air at 250–450 °C. The EMF value of the sensor was almost proportional to the logarithm of ammonia concentration, the sensitivity (slope) was −89 mV/decade at 350 °C. It was also seen that the sensor showed a good selectivity to ammonia, and an excellent resistance to water vapor. The sensor had speedy response kinetics to ammonia, the 90% response time to 50 ppm ammonia was 30 s, and the recovery time was 60 s.

1. Introduction

Ammonia is produced and utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, food processing, medical diagnosis, fire power plants, etc. A leak in the system can result the health hazards [1]. Hence, the development of ammonia sensors is very important for the detection of ammonia. At present, some types of ammonia sensors, e.g., conductive type using metal oxide [1–4], organic thin film type [5,6] and optical fiber sensor [7], have been proposed. The solid electrolyte type sensors have been investigated for detecting CO_2, H_2S and SO_2 due to their highly selectivity, rapid and reproducible response [8–10]. But this type of sensors has been few studied for the ammonia gas sensor.

NASICON is one of the most important solid electrolyte materials and Cr_2O_3 has been used for the ammonia or nitrogen oxide-sensitive material in some references [1]. In the present work, we tried to construct a compact solid electrolyte ammonia sensor by combining NASICON prepared by sol–gel process with porous Cr_2O_3 electrode. The sensing mechanism was also suggested by investigating the catalytic behavior of ammonia on porous Cr_2O_3.

2. Experimental

2.1. Synthesis of NASICON and analysis of Cr_2O_3

The NASICON precursor was prepared from $ZrO(NO_3)_2$, $NaNO_3$, $(NH_4)_2HPO_4$ and $Si(C_2H_5O)_4$ by sol–gel process [8,9]. The porous Cr_2O_3 sensing material was obtained by mixing multiple carbon nanotubes (Shenzhen Billnt Corporation, China, 10–30 nm for diameter) with Cr_2O_3, full grinded in the agate bowl and sintered at high temperatures. The adulteration proportion for carbon nanotubes was 10 wt%. The structure of NASICON was identified by X-ray diffraction (a Rigaku wide-angle X-ray diffraction D/max rA, using Cu Kα radiation at wavelength $\lambda = 0.1541$ nm) analysis. The surface morphology of NASICON and sensing electrode was identified by the scanning electron microscope (SEM) (JEOL JSM-7500F Field Emission Scanning Electron Microscope). To investigate the sensing mechanism of the NH_3 sensor, XPS (VG ESCA LAB MK II, Mg Kα, 10^{-7} Pa) was utilized to analyze the adsorbed species on the surface of porous Cr_2O_3 after exposing to 2000 ppm ammonia at 350 °C for 10 h.

2.2. Fabrication of the sensor

A sensor device was fabricated by using an alumina tube of 6 mm long, 0.8 and 1.2 mm in inner and outer diameter, respectively [8,9], as shown in Fig. 1. A thick film of NASICON was formed on the outer surface of the alumina tube by dipping NASICON precursor paste prepared by sol–gel process many times and sintering at 900 °C for 6 h. A couple of Au electrodes with mesh-shape were made on the two ends of the thick film of NASICON. For forming the sensing electrode of the ammonia sensor, porous Cr_2O_3 paste was applied on an Au electrode, followed by sintering at 600 °C for 3 h. Finally, a Ni–Cr coil was set in the inner of the alumina tube as a heater.

2.3. Measurement of sensing properties

Gas sensing properties of the sensor were measured by a conventional static mounting method. The sample gases containing different concentrations of NH_3, CO, NO, CH_4 and H_2, C_7H_8 and

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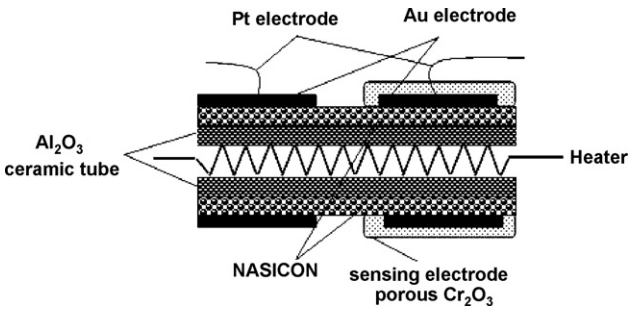

Fig. 1. Structure of NASICON-based electrochemical device attached with a layer of porous Cr_2O_3 (electrode).

HCHO were obtained by diluting pure gases with O_2 (21%) and N_2 (79%). The electromotive force (EMF) was measured with a digital electrometer (Advanced, TR 8652) connected with a registering computer.

3. Results and discussion

3.1. XRD and SEM analysis of NASICON

XRD analysis was used to confirm the phase compositions of NASICON and measure the mean crystallite size of NASICON, as shown in Fig. 2. From Fig. 2, NASICON was confirmed to have single phase of rhombohedral (JCPDS: 33-1314). In addition, the mean grain size of NASICON calculated with Debye–Scherrer equation was about 20 nm. SEM image of the NASICON surface shown in Fig. 3 exhibited that the crystallite size of NASICON was distributed in uniformly and the surface was comparatively compact.

3.2. Sensing properties of the ammonia gas sensor

In this paper, the influence of C doping of the sensing electrode on the characteristics of the sensor was studied firstly. The contrast between the sensor based on the pure Cr_2O_3 and 10 wt% C-doped Cr_2O_3 was studied. Fig. 4 shows that, both the sensors based on pure Cr_2O_3 and 10 wt% C-doped Cr_2O_3 exhibited well characteristics to ammonia at 350 °C. Whereas the 10 wt% C-doped Cr_2O_3 sensor showed much high sensitivity (−89 mV/decade) than the pure Cr_2O_3-based sensor (−57 mV/decade). From Fig. 5, it was seen that a lot of apertures appeared on the surface of the 10 wt% C-doped

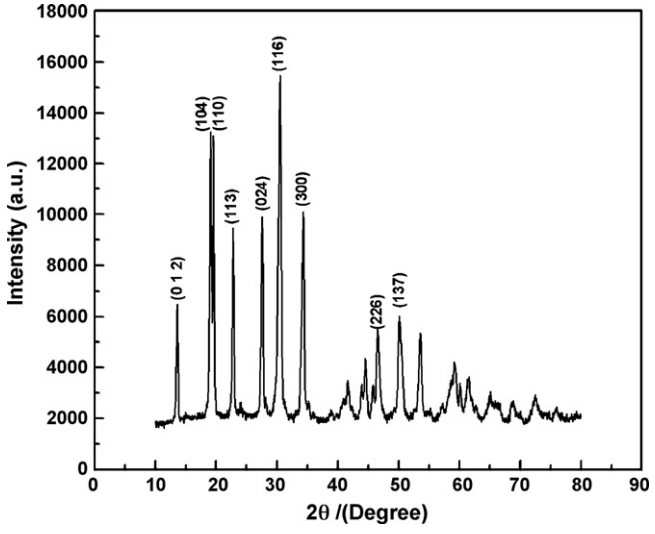

Fig. 2. XRD pattern of NASICON.

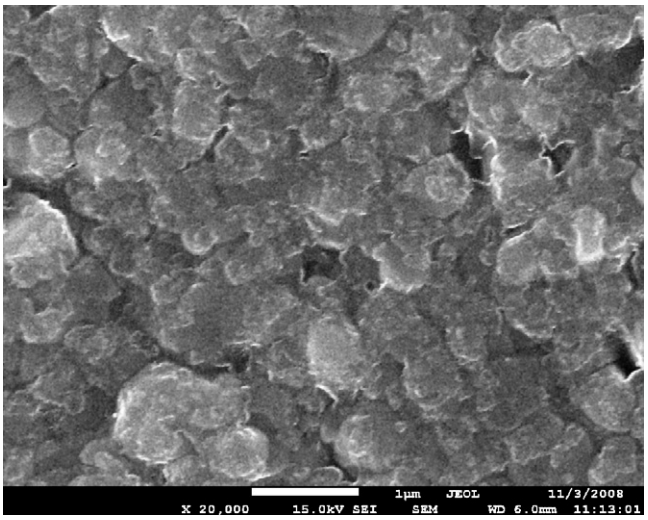

Fig. 3. The SEM image of the NASICON surface.

Cr_2O_3, this could arised from that the carbon reacted with the oxygen in the air when the sensing electrode was doped with carbon, and came into being the porous Cr_2O_3. Therefore, the adsorption and diffusion of ammonia through the porous Cr_2O_3 electrode were much facile than that through the pure Cr_2O_3. This could increase the amount of the ammonia molecule that participated in the chemical reaction. So that the carbon doping in the sensing electrode increased the sensitivity of the sensor to ammonia.

The sensitivity of the sensor depended on the operation temperatures, too. Fig. 6 shows that the EMF of the device attached with porous Cr_2O_3 is perfectly linear to the logarithm of ammonia concentration, and the slopes were −58, −93, −89, −44 and −42 mV/decade at 250, 300, 350, 400, and 450 °C, respectively. With increasing the operating temperature, the slope tended to become large below 300 °C. At 300 °C, the largest value of the slopes occurred, but above 300 °C the slope tended to become small. This could arise from the amount of the ammonia molecular diffused through the porous Cr_2O_3 electrode to the interface of NASICON and porous Cr_2O_3 and adsorbed at the three terms interface of air, porous Cr_2O_3 and NASICON increased along with the gradually increased operating temperature at low temperatures (<300 °C). In

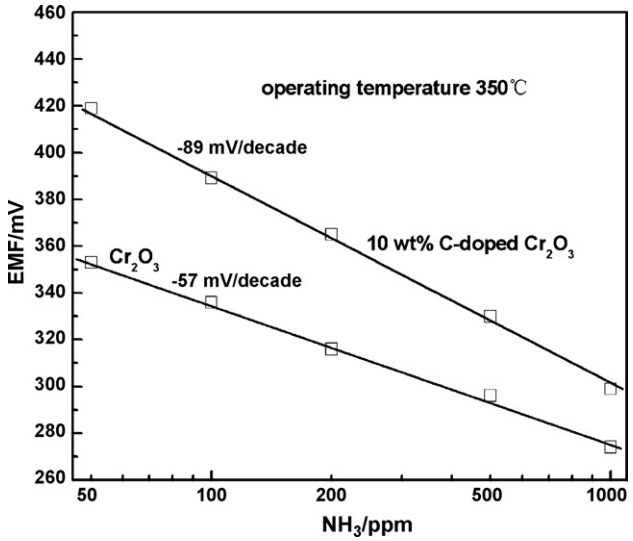

Fig. 4. NH_3 sensing properties of sensor attached with the undoped Cr_2O_3 and the 10 wt% C-doped Cr_2O_3.

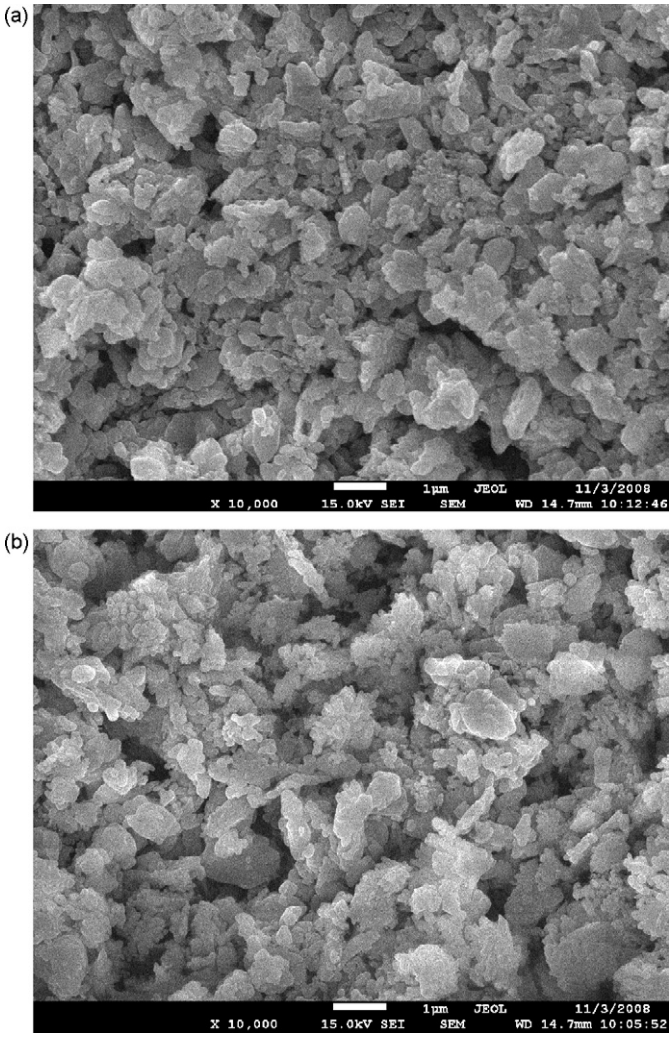

Fig. 5. The SEM images of (a) the undoped Cr_2O_3 and (b) the 10 wt% C-doped Cr_2O_3.

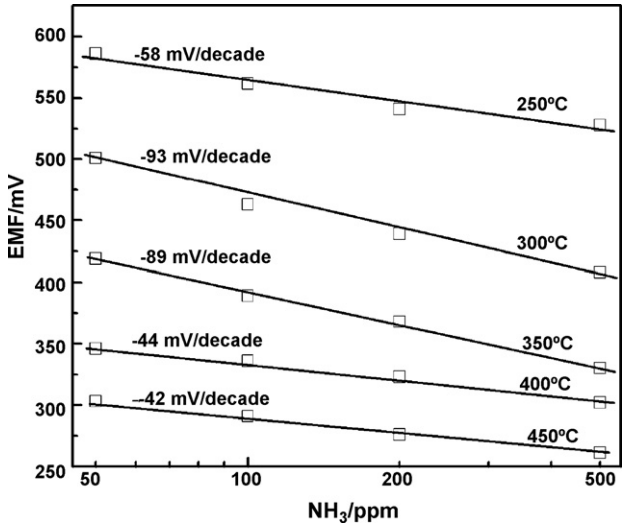

Fig. 6. NH_3 sensing properties of the device attached with porous Cr_2O_3 at different operating temperatures.

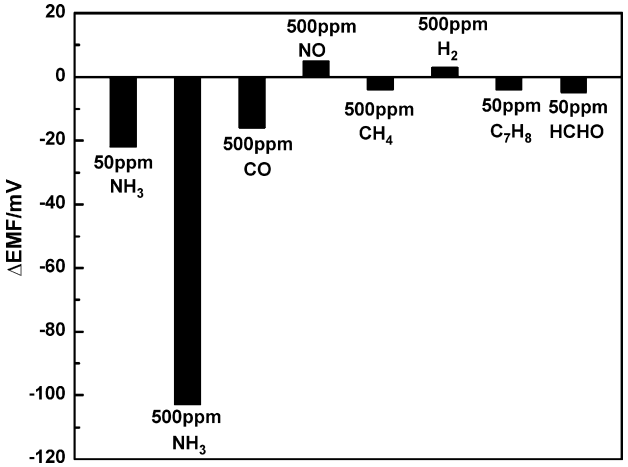

Fig. 7. Sensitivities of the device attached with porous Cr_2O_3 to various gases at 350 °C.

addition, a couple of electrochemical reactions (1) and (2) happen at the sensing electrode simultaneously, the chemical reactions at the three terms interface described by reactions (1) and (2) could be affected by the operating temperatures.

$$4NH_3 + 6Na_2O\,(\text{in NASICON}) \rightarrow 2N_2 + 6H_2O + 12Na^+ + 12e^- \quad (1)$$

$$12Na^+ + 3O_2 + 12e^- \rightarrow 6Na_2O\,(\text{in NASICON}) \quad (2)$$

The occurring of the chemical reaction needed definite activated energy. At low temperatures (<300 °C), it did not reach the activated energy, so that the ΔEMF and the sensitivity of the sensor to ammonia increased along with the increased temperature. But above 300 °C, the desorption of ammonia molecular exhibited more significant and the amount of ammonia molecule that adsorbed on the sensing electrode became less and less along with the increasing temperature. Just this result weakened the reactions (1) and (2). Hence the sensitivity of the sensor to ammonia decreased with the further increased operating temperature. However there were no distinction for the sensitivities of the sensor when operated at 300 and 350 °C. From the perspective of selectivity, 350 °C was selected for the operating temperature.

The cross-sensitivities of the device attached with porous Cr_2O_3 to other various gases, i.e. CO, NO, CH_4, H_2, C_7H_8 and HCHO were measured at 350 °C, and the results obtained are shown in Fig. 7. The cross-sensitivities were rather small or almost none, indicating its excellent ammonia selectivity.

We also tested the effect of water vapor on the EMF value of sensor at 350 °C, as shown in Fig. 8. There were large changes for the EMF value of the sensor at the humidity range of 0 RH%–20 RH%. And it changed small at the range of 20 RH%–75 RH%. Whereas it changed largely at high water humidity (>75 RH%). This might be due to that there was water came into being in reaction (1) above. The existence of water could affect the process of reaction (1) and thereby the changes of the EMF value for the sensor at lower water humidity (<20 RH%). At the range of 20 RH%–75 RH%, the effect of water on the EMF value was less because of the weak adsorption of water on the sensing electrode(porous Cr_2O_3). However, at higher humidity (>75 RH%), the influence of water on reaction (1) was strengthened further which led to the large changes of EMF value. And the specific relations between the humidity and EMF value of the sensor was very complicated and would be investigated in the future study.

The device attached with porous Cr_2O_3 gave speedy response kinetics to dilute ammonia. Fig. 9 showed the response and recovery transients to various concentrations of ammonia at 350 °C, and the 90% response time to 50 ppm and 500 ppm NH_3 was 35 and 30 s, respectively, and the recovery time was 60 and 65 s, respectively.

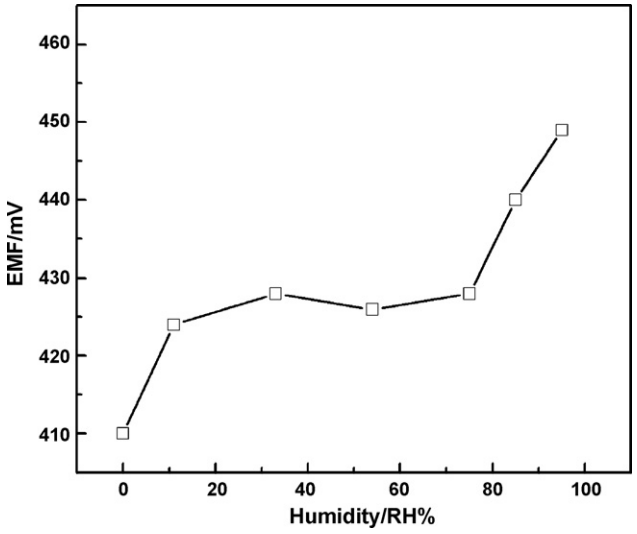

Fig. 8. The effect of water vapor on the EMF value of sensor at 350 °C.

3.3. Sensing mechanism of the NH_3 sensor

For explaining the sensing behavior of the device, XPS was applied for measuring the chemical shift of the related elements (e.g., O1s, Cr2p and N1s) on the surface of porous Cr_2O_3 before (sample 1) and after (sample 2) exposure to 2000 ppm NH_3 at 350 °C, the basic pressure of the XPS chamber was better than 1×10^{-7} Pa, as shown in Fig. 10. As a result, it was found that the chemical binding energies of O1s, and Cr2p did not change before and after exposure to 2000 ppm NH_3. There is no N element in sensing electrode after chemical reaction. This shows that NH_3 comes into being gas status after reacting with sensing electrode. The resultants might be N_2, N_2O, NO or NO_2 and the most possible resultant is N_2 according to the activated energy.

As described, the sensor using NASICON and porous Cr_2O_3 electrode gave a good linear relationship between EMF and the logarithm of the concentration of ammonia as switching on dilute ammonia. Lu, Miura and Yamazoe have established a sensing mechanism involving mixed potentials for a group of sensors combining stabilized zirconia with oxide electrodes, such as NOx, H_2, CO sensors [11–13]. Therefore, a similar sensing mechanism would be attempted to apply for the present sensors.

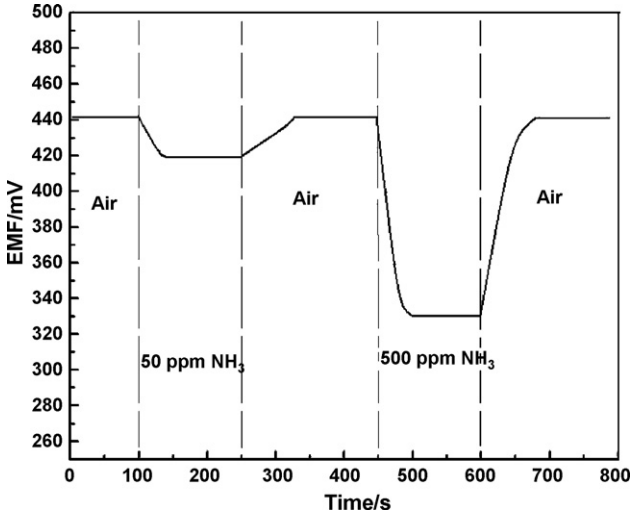

Fig. 9. Transient response and recovery characteristic when taking a switching change from air to different concentrations of ammonia.

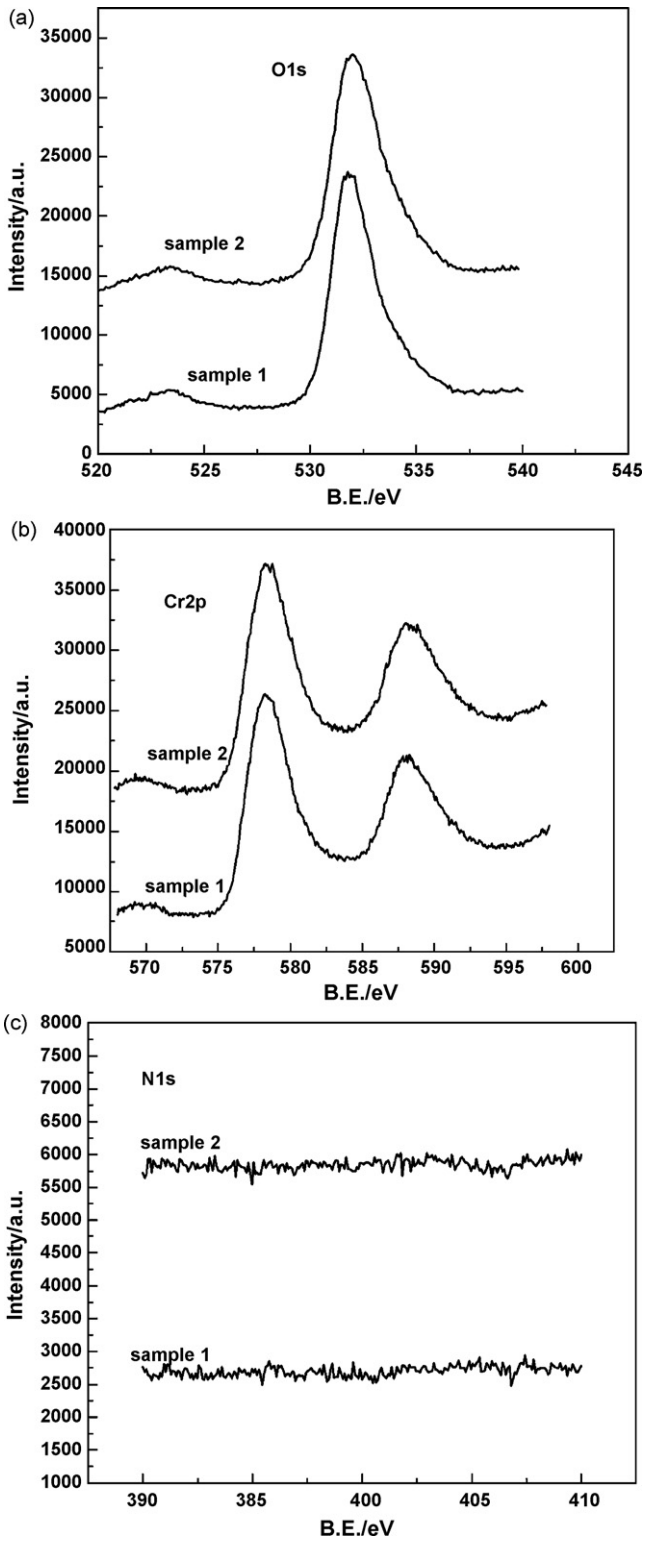

Fig. 10. XPS spectra of porous Cr_2O_3 before (sample 1) and after (sample 2) exposure to 2000 ppm NH_3 at 350 °C.

The sensor could be expressed with the following electrochemical cell:

$$NH_3 \text{ in air, porous } Cr_2O_3, \text{ Au|NASICON|Au, } NH_3 \text{ in air} \quad (3)$$

We consider that a couple of electrochemical reactions (1) and (2) above happen at the sensing electrode simultaneously.

These two electrochemical reactions construct a local cell at the sensing electrode, and when the rates of the reactions were equal to each other, they arrive at a dynamic equilibrium, and the electrode potential at the sensing electrode was the mixed potential [12]. By treating Eqs. (1) and (2) with the same process described in [11–13], we could obtained the following equation.

$$E_M = E_0 + nA \ \ln C_{O_2} - mA \ln C_{NH_3} \quad (4)$$

Here

$$E_0 = \frac{RT}{2(3\alpha_1 + 2\alpha_2)F} \ln \frac{B_2}{B_1} + \frac{3\alpha_1 E^0_{NH_3} + 2\alpha_2 E^0_{O_2}}{3\alpha_1 + 2\alpha_2}$$

$$A = \frac{RT}{2(3\alpha_1 + 2\alpha_2)F}$$

Here C_{O_2} and C_{NH_3} are the concentrations of O_2 and NH_3, and B_1, B_2, m and n are the constants, F the Faraday constant, R the gas constant and T the absolute temperature, $E^0_{NH_3}$ and $E^0_{O_2}$, represent electrode potential at equilibrium, α represent the transfer coefficient, respectively, for reactions (1) or (2). E_M is the electrode potential of the sensing electrode at the equilibrium state, so it is called a mixed potential. The constants A, n and m changed with the operating temperature [14], so that the EMF value of the sensor decreased along with the increased operating temperature at the same concentration in Fig. 6. When the concentration of oxygen is fixed, the mixed potential changes linearly with the logarithm of the concentration of NH_3, as described in Eq. (5)

$$E_M = E'_0 - mA \ln C_{NH_3} \quad (5)$$

Here, $E'_0 = E_0 + nA \ln C_{O_2}$

Eq. (5) could explain the experimental results very well. Similar reactions above occur at the contacting electrode possibly. But the EMF is smaller than that of the sensing electrode. So the electrochemical reactions occurring at the sensing electrode are dominant to that of the contacting electrode.

4. Conclusions

A compact solid electrolyte sensor using a thick film of NASICON and porous Cr_2O_3 electrode has been examined to show good sensing properties to dilute ammonia. The slope between the EMF and the logarithm of ammonia concentration was −89 mV/decade, and the 90% response time to 50 and 500 ppm ammonia was 35 and 30 s, respectively, and the recovery time was 60 and 65 s, respectively. In addition, the sensor also showed excellent selectivity to ammonia against the disturbing gases, and the operating temperature of the sensor was 350 °C. Mixed potential theory could explain the sensing behavior of the sensor. However, further study on the sensing mechanism is yet to be done for understanding the electrochemical behavior at the sensing electrode very well.

Acknowledgements

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