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Progress in solid electrochemical gas sensors based on NASICON and oxide electrodes

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Abstract

The mixed-potential type NASICON-based sensor attached with an oxide electrode is generally used at intermediate temperatures and more suitable for monitoring the harmful and toxic gases in the atmospheric environment. This presentation focuses on the exploration of new oxide electrode materials and the design of new sensor structure for increasing the sensing performance of the sensor based on NASICON and oxide electrode.

Key words: NASICON, gas sensor, oxide electrode, mixed potential

1. Introduction

With the increasing of world's population and the acceleration of the industrialization process, lots of harmful gases (CO_2, SO_x, NO_x, H_2S, NH_3, CO and so on) from the power generation, heat supplying, metallurgy, chemical production and motor vehicle lead to the greenhouse effect, acid rain, photochemical smog and other environmental disasters. Therefore, the high-performance environment gas sensors have been urgently desired for detecting and monitoring these hazardous gases. Up to now, various kinds of gas sensors based on semiconductor oxides [1], organic thin films [2] and solid electrolytes [3] have been developed. Among them, the solid electrolyte type sensors exhibit excellent sensing performances, such as high sensitivity, rapid response kinetics, outstanding selectivity and reproducibility. For the solid electrolyte sensors, most researches focused on the sensors based on yttria stablized zirconia (YSZ) and sodium super ionic conductor (NASICON). In general, the YSZ-based sensor was operated at high temperature (600-800°C), so it seems to be inappropriate for detecting the gases in atmospheric environment because of its low sensitivity as well as high power consumption. Contrary to the YSZ-based sensors, the mixed potential type sensors based on NASICON are generally operated at the intermediate temperatures (300-500°C), so they are more suitable for detecting the hazardous gases in the atmospheric environment. According to the sensing mechanism, the NASICON-based gas sensors are mainly divided into three types: the current-type, the equilibrium-potential-type and mixed-potential-type. N. Miura et al. developed the current NO_2 sensor based on NASICON and $NaNO_2$ electrode. The sensor has good linearity within the range of 10ppb-1ppm concentration at 150°C [4]. As for the equilibrium potential type sensors, N. Yamazoe et al systematically researched the CO_2 sensors using a series of composite carbonate, e.g. CO_2 sensors with good moisture resistance have been fabricated by using Na_2CO_3-$BaCO_3$ and Li_2CO_3-$BaCO_3$ as the auxiliary electrode [5, 6]. S. Choi et al. reported SO_2 sensor using Na_2SO_4 and Na_2SO_4-$BaSO_4$ as auxiliary electrodes [7], which showed excellent stability. K. Obata et al. developed the equilibrium-potential-type NO_2 sensor with ITO and $NaNO_2$-Li_2CO_3 as the auxiliary electrode, which had low detecting limit (about 2ppm) and an excellent moisture resistance [8]. For above two types of sensors, the long-time stability and moisture resistance need further be improved, due to the hygroscopicity of the oxysalt auxiliary electrode as well as the interface reaction between the oxysalt and NASICON. Unlike these two types of sensors, the mixed-potential-type sensor based on NASICON uses an oxide as a sensing electrode which has good moisture resistance and not directly involved in the electrode reaction (electrode catalyst), so it has been a hot research topic in recent years. Y. Shimizu et al developed a CO_2 sensor with $NdCoO_3$ and $La_{0.8}Ba_{0.2}CoO_3$ as sensing electrode, which improved the stability and moisture resistance, but the sensitivity need to be improved [9]. They also developed mixed-potential-type NO_x sensor with $Pb_2Ru_{1.9}V_{0.1}O_{7-z}$ as sensing electrode. However, the systematic investigation about the NASICON-based mixed potential type sensor has been scarcely reported.

This paper provides an overview and mainly discusses the mixed-potential-type gas sensors based on NASICON solid electrolyte and metal oxide electrodes developed by our group.

2. Methods

The NASICON was synthesized with $ZrO(NO_3)_2$, $NaNO_3$, $(NH_4)_2HPO_4$ and $Si(C_2H_5O)_4$ by sol-gel process. The sensor was fabricated with an alumina tube of 6 mm long, 0.8 and 1.2 mm in inner and outer diameters. The NASICON precursor was applied on an alumina tube twice and sintered at 900ºC for 6 h in air. Then noble metal (Pt or Au) and oxide layers were formed on the two ends of NASICON layer.

3. Results and Discussion

Table 1 shows some results of the NASICON based gas sensors using oxide electrodes. As shown in the table 1. For improving the performance of sensors, two main approaches have been utilized.

First, some novel oxide electrode materials for sensing H_2S, Cl_2, SO_2, NH_3 have been developed. For example, we have reported the NASICON based H_2S sensor using Pr_6O_{11}-doped SnO_2 electrode as sensing electrode. It showed excellent sensing properties to H_2S at intermediate temperatures. The EMF value of the sensor was almost proportional to the logarithm of H_2S concentration, and the sensitivity(slope) was 74 mV/decade at 300ºC [10], as shown in Fig. 1.

The sensor using $CaMg_3(SiO_3)_4$-doped CdS sintered at 600 °C exhibited excellent sensing properties to 1–10 ppm chlorine in air at 100–250 °C [11]. Its sensitivity (slope) was 392 mV/decade at 200°C. It also showed a good selectivity to Cl_2 against H_2S, SO_2, NO_2, NH_3, CH_4 and CO, as shown in Fig. 2.

A high performance SO_2 sensor was developed by combining NASICON with V_2O_5-doped TiO_2 sensing electrode [12]. The sensor displayed excellent response and recovery characteristics to 1 – 50ppm SO_2 at 300 ºC, as shown in Fig. 3. For increasing the sensitivity of the sensor to NH_3, a porous Cr_2O_3 prepared by doping C was utilized as the sensing electrode [13]. As shown in Fig. 4, the sensor using porous Cr_2O_3 showed much higher sensitivity than that using Cr_2O_3 particle. It can be attributted to the speedy diffusion through the porous sensing layer and lower loss of the NH_3 concentration in the sensing layer.

Second, in order to improve the sensing performance and realize simple sensor array, we also focused on designing new device structures, such as the dual-function sensor using double oxide electrodes and the buried structure device for blocking the electrochemical reactions on the reference

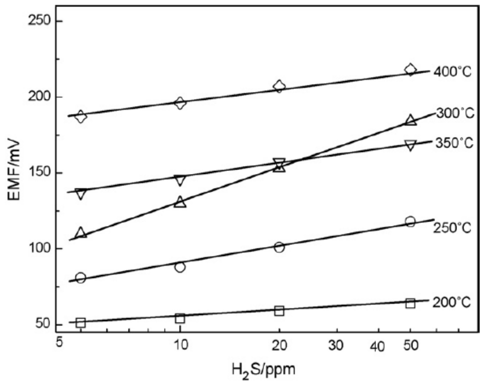

Fig. 1. Dependence of EMF of the sensor attached with Pr_6O_{11}-doped SnO_2 on the H_2S concentration at 200-400°C.

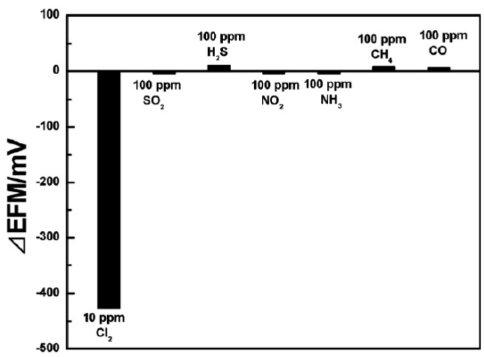

Fig. 2. Cross-EMF responses of the sensor using $CaMg_3(SiO_3)_4$-doped CdS *to various gases at 200 °C.*

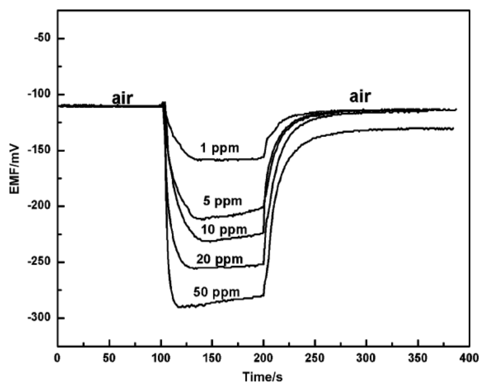

Fig. 3. Response transients of the sensor based on NASICON and V_2O_5-doped TiO_2 sensing electrode *to various concentrations of SO_2 at 300 °C.*

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Table 1 Typical examples of mixed-potential type gas sensors utilizing NASICON and different oxide electrodes

Gas	Sensor structure Air, RE | electrolyte | SE, target gas	Sensitivity (mV/decade)	Gas conc. (ppm)	Operating temperature (℃)
H_2S	Air, Au | NASICON | Au, Pr_6O_{11}-SnO_2, H_2S(+air)	74	5-50	300
Cl_2	Air, Au | NASICON | Au, $Cd_3O_2SO_4$, Cl_2(+air)	-392	1-10	200
SO_2	Air, Au | NASICON | Au, V_2O_5-TiO_2, SO_2(+air)	-78	1-50	300
NH_3	Air, Au | NASICON | Au, porous Cr_2O_3, NH_3 (+air)	-89	50-500	350
NO_2	Air, Pt | NASICON | Au, NiO, NO_2 (+air)	78	5-200	350
CO	Air, Pt | NASICON | Au, $NiFe_2O_4$, CO (+air)	-45	100-1000	350
CO	Air, Au | NASICON | Au, Y_2O_3 CO (+air)	-45	5-50	400
C_7H_8	Air, Au | NASICON | Au, Sm_2O_3 C_7H_8(+air)	-75	5-50	350
NO	Air, Au | NASICON | Au, $NiWO_4$ CO (+air)	70	5-500	350
NH_3/ C_7H_8	NH_3(+air) , Cr_2O_3, Au, | NASICON | Au, Air, Au | NASICON | Au, ZnO-TiO_2, C_7H_8 (+air)	-91/-60	50-500 /5-50	350
Cl_2	Air, | NASICON | Au | NASICON | Au, Cr_2O_3, Cl_2(+air)	-270	1-50	300

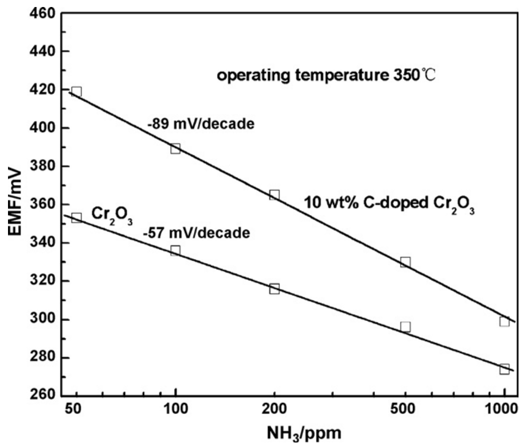

Fig. 4. Dependance of EMF on NH_3 concentration for the sensor attached with the undoped Cr_2O_3 and the 10 wt% C-doped Cr_2O_3.

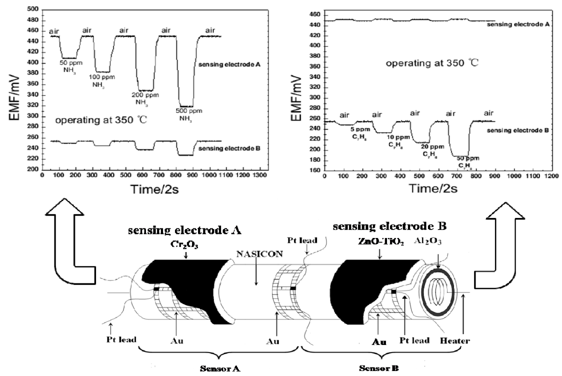

Fig. 5. Structure and response transients of dual-function sensor using Cr_2O_3 and ZnO-TiO_2 for detection of NH_3 and C_7H_8.

electrode. Fig. 5 showed the structure as well as the response transients to different concentrations of NH_3 and C_7H_8 for the dual-function sensor using Cr_2O_3 and ZnO-TiO_2 at 350°C. It can be seen that the electrode A showed higher response to NH_3, but the electrode B displayed a higher response to C_7H_8. The combining of electrodes A and B can realize the simultaneous measurement to these two kinds of gases [14].

A buried structure sensing device was developed by using Cr_2O_3 electrode, which can effectively prevent the reaction of the target gas on reference electrode [15]. Fig.6 shows the dependence of ΔEMF on the Cl_2 concentration for different type of sensor (type A: conventional device, type B: simple buried device and type C: deep-buried device), the sensitivity (-slope) for the type C was -270 mV/decade, which is much higher than those for type (A) (-119 mV/decade) and type (B) (-157 mV/decade).This suggested that covering reference electrode with NASICON in Type B and C can block the contact of RE with the Cl_2 and restrain electrochemical reaction in the reference electrode. The potential difference between the sensing and reference electrode as well as the sensitivity of the sensor has been obviously increased. The other way to enhance the sensitivity is to increase the effective area of the sensing electrode. For the sensor A and B, because the sensing electrode and reference electrode were located at both ends of the same NASICON layer, the area of the sensing electrode was reduced to about one half of the surface area of the first NASICON layer. However, for Type C, since the sensing electrode almost covers the all of the surface area of the second NASICON layer (Fig. 1 (C)), the area of the sensing electrode is greatly enlarged, and the sensitivity of the Type C is obviously enhanced.

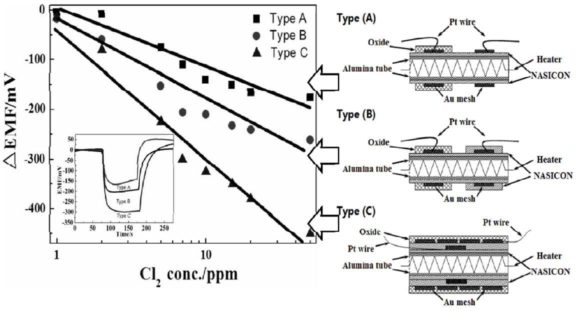

Fig. 6. The buried structure sensor using Cr_2O_3 for detection of Cl_2.

4. Conclusions

The mixed potential type sensors utilizing NASICON and oxide electrodes have been developed and showed a potential for detecting the harmful and toxic gases in the atmosphere.

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