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

Xishuang Liang 1, Biao Wang 2, Houbo Zhang 1, Quan Diao 1, Baofu Quan 1 and Geyu Lu 1*
1 State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China;
Corresponding e-mail address: lugy@jlu.edu.cn
2 Changchun Institute of Optics, Fine Mechanics and Physics, CAS, 3888 Dong Nanhu Road, Changchun 130033, China.

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 (CO2, SOx, NOx, H2S, NH3, 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 stabilized 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 NO2 sensor based on NASICON and NaNO2 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 CO2 sensors using a series of composite carbonate, e.g. CO2 sensors with good moisture resistance have been fabricated by using Na2CO3-BaCO3 and Li2CO3-BaCO3 as the auxiliary electrode [5, 6]. S. Choi et al. reported SO2 sensor using Na2SO4 and Na2SO4-BaSO4 as auxiliary electrodes [7], which showed excellent stability. K. Obata et al. developed the equilibrium-potential-type NO2 sensor with ITO and NaNO2-Li2CO3 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 CO2 sensor with NdCoO3 and La0.8Ba0.2CoO3 as sensing
electrode, which improved the stability and moisture resistance, but the sensitivity need to be improved [9]. They also developed mixed-potential-type NOx sensor with Pb$_2$Ru$_{1.9}$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$_4$)$_2$HPO$_4$, and Si(C$_2$H$_5$O)$_4$ 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$_2$S, Cl$_2$, SO$_2$, NH$_3$ have been developed. For example, we have reported the NASICON based H$_2$S sensor using Pr$_6$O$_{11}$-doped SnO$_2$ electrode as sensing electrode. It showed excellent sensing properties to H$_2$S at intermediate temperatures. The EMF value of the sensor was almost proportional to the logarithm of H$_2$S concentration, and the sensitivity (slope) was 74 mV/decade at 300°C [10], as shown in Fig. 1.

The sensor using CaMg$_3$(SiO$_3$)$_4$-doped CdS sintered at 600 ºC exhibited excellent sensing properties to 1–10 ppm chlorine in air at 100–250 ºC [11]. Its sensitivity (slope) was 392 mV/decade at 200°C. It also showed a good selectivity to Cl$_2$ against H$_2$S, 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$_2$O$_5$-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$_2$O$_3$ prepared by doping C was utilized as the sensing electrode [13]. As shown in Fig. 4, the sensor using porous Cr$_2$O$_3$ showed much higher sensitivity than that using Cr$_2$O$_3$ particle. It can be attributed 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
Table 1: Typical examples of mixed-potential type gas sensors utilizing NASICON and different oxide electrodes

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sensor structure</th>
<th>Sensitivity (mV/decade)</th>
<th>Gas conc. (ppm)</th>
<th>Operating temperature (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;SUB&gt;2&lt;/SUB&gt;S</td>
<td>Air, RE</td>
<td>NASICON</td>
<td>Au, Pr₅O₁₁·SnO₂, H₂S(+air)</td>
<td>74</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Air, Au</td>
<td>NASICON</td>
<td>Au, Cd₅O₃SO₄, Cl₂(+air)</td>
<td>-392</td>
</tr>
<tr>
<td>SO₂</td>
<td>Air, Au</td>
<td>NASICON</td>
<td>Au, V₂O₅·TiO₂, SO₂(+air)</td>
<td>-78</td>
</tr>
<tr>
<td>NH₃</td>
<td>Air, Au</td>
<td>NASICON</td>
<td>Au, porous Cr₂O₃, NH₃(+air)</td>
<td>-89</td>
</tr>
<tr>
<td>NO₂</td>
<td>Air, Pt</td>
<td>NASICON</td>
<td>Au, NiO, NO₂(+air)</td>
<td>78</td>
</tr>
<tr>
<td>CO</td>
<td>Air, Pt</td>
<td>NASICON</td>
<td>Au, NiFe₂O₄, CO(+air)</td>
<td>-45</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>Air, Au</td>
<td>NASICON</td>
<td>Au, Sm₂O₃, C₇H₈(+air)</td>
<td>-75</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Air, Au</td>
<td>NASICON</td>
<td>Au, NiWO₄, CO(+air)</td>
<td>70</td>
</tr>
<tr>
<td>NH₃/</td>
<td>NH₃(+air), Cr₂O₃, Au,</td>
<td>NASICON</td>
<td>Au, Air, Au</td>
<td>-91/-60</td>
</tr>
<tr>
<td>C₇H₈</td>
<td>NASICON</td>
<td>Au, ZnO-TiO₂, C₇H₈(+air)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Dependence of EMF on NH₃ concentration for the sensor attached with the undoped Cr₂O₃ and the 10 wt% C-doped Cr₂O₃ electrode. Fig. 5 showed the structure as well as the response transients to different concentrations of NH₃ and C₇H₈ for the dual-function sensor using Cr₂O₃ and ZnO-TiO₂ at 350°C. It can be seen that the electrode A showed higher response to NH₃, but the electrode B displayed a higher response to C₇H₈. 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 Cr₂O₃ electrode, which can effectively prevent the reaction of the target gas on reference electrode [15]. Fig.6 shows the dependence of ΔEMF on the Cr₂O₃ 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 Cl₂ 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 all of the surface area of NASICON layer.
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.

![Diagram](https://via.placeholder.com/150)

Fig. 6. The buried structure sensor using Cr$_2$O$_3$ 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.

Acknowledgements

Support by NSFC (Nos. 61074172, 61134010, 61104203) and Program for Chang Jiang Scholars and Innovative Research Team in University (No. IRT1017) and Jilin province science and technology development plan program (20106002) is gratefully acknowledged.

References


