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High Performance Mixed-Potential Type NO_x Sensor Based On Stabilized Zirconia and Oxide Electrode

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ABSTRACT

The mixed-potential NO_x sensor based on yttria-stabilized zirconia (YSZ) and oxide electrode is considered as a potential device used for the on-board diagnostics. Over the past decades, many researchers have paid their attentions on such YSZ based potentiometric NO_x sensors and gotten a lot of achievement in developing new type electrode materials. Recently, in order to enhance the sensing performance of the mixed potential type NO_x sensor, we have been focusing on modifying the triple-phase-boundary (TPB) by various techniques, including chemical corroding, the double-tape casting, the pore-forming and laser fabrication method. We also designed and prepared the microstructure of the oxide electrodes by controlling the sintering process for increasing the sensitivity of the NO_x sensor. This paper reviews our works with regard to the above-mentioned two aspects.

1. Introduction

With speedy increase of the vehicles in city, the car exhaust results in severe urban atmosphere pollution. More and more attentions have been focused on the detection of nitrogen oxides (NO_x) which give rise to some environmental disasters such as acid rain and photochemical smog. To monitor and detect the NO_x from car exhaust, the high performance NO_x sensor has been urgently desired. Because the NO_x sensor used for monitoring the car exhaust must work under very harsh condition (high temperature, high humidity and many coexisting gases), the sensor materials used for the NO_x sensor should have excellent chemical and thermal stability. The stabilized zirconia and the metal oxides show the advantage in the stability under the severe atmosphere, so the mixed potential type NO_x sensors based on them have been widely investigated [1–13].

Since the oxide electrodes play an important recognition role for NO_x molecules, most of the researchers have paid more attentions for developing new oxide electrodes. Some single (WO_3 [14–21], NiO [22–25] and Cr_2O_3 [26–28]) and complex (spinel and perovskite type) oxides have been applied as the sensing electrodes of the YSZ-based NO_x sensors. For the study of the oxide sensing electrode, both composition and microstructure of the electrode materials have attracted special attentions, because the composition and microstructure decide the catalytic (electrochemical and chemical) activity and diffusion speed of the gases, respectively. On the other hand, the triple-phase-boundary (TPB) where the electrochemical reactions take place is very important for enhancing the sensing performance. The TPB with a large area can give more electrochemical activity sites, so its constructing strategy has been investigated by some researchers. J. Park et al. raised the area of TPB by mixing NiO with YSZ [12], but such method also covered some activity sites, resulting in the decrease of the electrochemical reaction rate. We have suggested another strategy: forming a rough surface of YSZ plate which does not only give a larger contacting interface between the YSZ plate and the sensing electrode, but also keep a higher activity of the electrode materials. Some rough surfaces of YSZ plates have been fabricated with some special surface treatment techniques by our group, such as HF corroding, the double-tape casting, the pore-forming and laser fabrication methods. In this paper, we will review the development of new sensing electrode materials and the construction of the TPB with large area.

2. Development of the novel sensing electrode materials

The composition of the sensing electrode materials plays an important role on the sensing property of the mixed potential NO_x sensor based on YSZ. The oxide sensing electrodes were testified to have better sensing performance (sensitivity and selectivity to NO_x) than the noble metals [20–27]. Some typical simple and complex oxides oxide electrode materials are summarized in the Table 1. For the simple oxide electrodes, NiO, Cr_2O_3, WO_3, ZnO, In_2O_3, CuO and V_2O_5 have been widely investigated by some groups. Among them, NiO shows very excellent sensing property at elevated temperature. The sensitivity of the NO_2 sensor based on NiO is about 40 mV/decade in the early study. The sensor output (ΔEMF) can be improved by optimizing the sintering temperature of NiO, because an appropriate sintering temperature can form the best balance among the electrochemical and chemical activities as well as porosity for NiO [29]. In addition, the resistance of NiO to water vapor [30] has been studied. The sensor using NiO sensing electrode shows good output even in wet atmospheres with different O_2

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Table 1
Typical example of the SE materials for mixed-potential type NOx sensors.

Sensing electrode materials	Operating temperature (°C)	Reference
NiO	900	[22–25]
ZnO	600 ~ 700	[34]
CuO	700	[12]
WO_3	500 ~ 700	[14–21]
Cr_2O_3	500	[27]
In_2O_3	550	[46]
V_2O_5	440	[33]
Rh-loaded NiO	800	[23]
Tin-doped indium (ITO)	613	[13]
$NiCr_2O_4$	550	[35]
$MnCr_2O_4$	650	[37]
$ZnCr_2O_4$	700	[48]
$ZnFe_2O_4$	650	[49]
$CdCr_2O_4$	500 ~ 600	[36]
CuO + $CuCr_2O_4$	518-659	[47]
$LaFeO_3$	450	[38]
$La_{0.8}Sr_{0.2}FeO_3$	450 ~ 700	[39]
$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$	500	[40]
$La_{0.85}Sr_{0.15}CrO_3$	600	[41]
NiO + YSZ	700	[12]

concentration [31]. Doping of noble metals or oxides in NiO is also a strategy to increase the sensing performance. For example, the Rh-loaded NiO sensing electrode shows higher response to NO_2 than pure NiO, because high distribution Rh nanoparticle has higher electrochemical catalytic activity to the reaction related to NO_x [23]. Besides NiO, WO_3 and Cr_2O_3 also exhibit good sensing performance to NO_2. WO_3 fabricated with difference methods has unique microstructure which leads to different response [32]. However, WO_3 has been testified to be unstable at elevated temperature, so its thermal and chemical stabilities need to be improved by adding the other oxides. Other simple metal oxides, such as V_2O_5 [33], ZnO [31] and CuO [12], have also been reported as the sensing electrode materials.

In order to further increase the sensitivity of the mixed potential type NO_x sensor, some complex oxides oxides were prepared and utilized as the sensing electrodes. Lu and Mirua et al. firstly applied spinel type oxides for detecting NO_x. [35,36]. Specially, $NiCr_2O_4$ and $CdCr_2O_4$ displayed high sensitivity and excellent selectivity to NO_2 and NO at elevated temperature (Fig. 1). Recently, Diao et al. developed a new type spinel oxide electrode $MnCr_2O_4$ as the sensing electrode of the mixed potential type NO_x sensor [37]. The EMF of the sensor based on the $MnCr_2O_4$ is strongly dependent on its sintering temperature. As shown in Fig. 2, the optimal sintering temperature for the $MnCr_2O_4$ is 1000 °C. Generally, with the increasing of the sintering temperature, the electrochemically catalytic activity decreases, but the porosity increases. The former trend to reduce the sensitivity and the latter enhances the diffusion of the target gas into the sensing electrode layer and raises the sensor output. At 1000 °C, the best balance between the

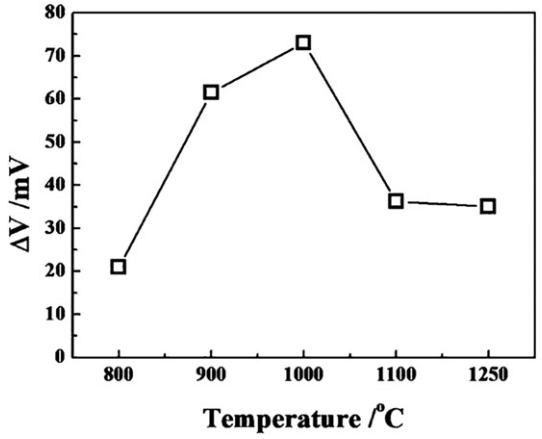

Fig. 2. Response to 100 ppm NO_2 of sensors based on $MnCr_2O_4$ calcined at different temperatures. Source: reprinted from reference [37] with permission from Elsevier.

above factors was obtained, and the largest output was realized. The measurement of the polarized curves for the sensors using the $MnCr_2O_4$ obtained at different the sintering temperature indicates that the $MnCr_2O_4$ sample sintering at 1000 °C gives the largest reduction current related NO_2, at the same time, effectively suppresses the electrochemical oxidation reaction related to oxygen. The perovskite complex oxides oxide was also examined as the sensing electrode. Due to its high chemically catalytic activity, the target gas was largely consumed when it passed through the sensing electrode layer, inducing the sharp decreasing of the NO_x concentration. Therefore, at high temperature, the sensor based on the perovskite complex oxides oxide displayed a small output. However, for $LaFeO_3$ [38], when the other element (such as Sr, Co and Ni) replaced the A or B site partly or completely, an improving response to NO_x was obtained [39–41].

The microstructure of the electrode materials, such as the particle and pore sizes [29], is another key factor determining the sensitivity of the mixed potential type NO_x sensor, because it can influence the adsorption and desorption of the target gases on the sensing electrode materials as well as their diffusion in the sensing electrode layer. Before arriving at the three-phase-boundary, the target gas must passes through the layer of the sensing electrode and is consumed partly due to the chemical reaction in this process. Therefore, the porosity of the sensing electrode is supposed to be of great benefit to enhance the sensing property. Generally, two strategies were applied for improving the porosity of the sensing electrode: enlarging particle size by increasing the sintering temperature and controlling pore size and number by using special hard template. Lu et al. prepared the W/Cr binary oxides in which W was utilized as hard template, because it can sublimate after 800 °C and form stable porous structure even at very high temperature [42]. The porosity and composition of W/Cr complex oxides oxide

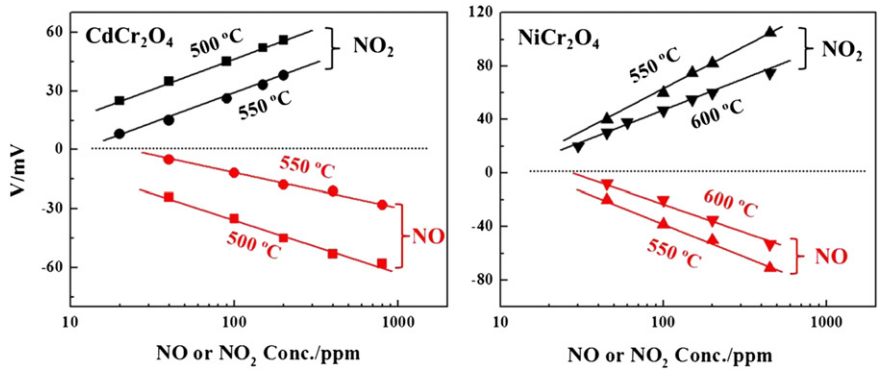

Fig. 1. Dependence of V on the logarithm of NO or NO_2 concentration for the mixed-potential-type device using the $CdCr_2O_4$ or $NiCr_2O_4$ SE. Source: reprinted from reference [35,36] with permission from Elsevier.