The Sensing Mechanism Study of Potentiometric NO₂ Sensor Based on Varying WO₃ Electrode Thickness

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Abstract. In order to understand the NO₂ sensing mechanism, YSZ-based (Y₂O₃-doped ZrO₂ electrolyte) potentiometric sensors with varying WO₃ sensing electrode thickness were investigated. The NO₂ sensing performances were evaluated at 500 °C, 550 °C and 600 °C. All sensors showed linear relationships between voltage response and NO₂ concentration. The sensor with moderate WO₃-SE thickness (34.9 μm) exhibited higher sensitivity than any other sensors with thinner or thicker WO₃-SE. This behavior was attributed to different gas adsorption sites and a different degree of catalytic decomposition of NO₂ to NO occurring at the WO₃ (Pt)/YSZ interface.

1. Introduction

The air that we breathe on a daily basis is being continuously polluted by fast growing industrialization. Nitrogen oxides, denoted as NOₓ gases, are poisonous and are highly important gas pollutants. Strict legislation has been published worldwide to limit the emission of NOₓ. This is compelling scholars around the world to look for responsive and portable sensors that are compact, simple, cost effective, robust, have a long lifetime, and are sensitive to detecting NOₓ in ambient conditions. Solid-state sensors can meet the demand because of their compact size, ease of use and low cost [1]. In addition, solid-state sensors can be easily designed by adjusting electrode materials. Many solid-state potentiometric sensors based on semi-conducting metal oxides (WO₃ [2], Cr₂O₃ [3–5], SnO₂ [6,7], ZnO [8,9], In₂O₃ [10,11], LaFeO₃ [12], etc.) have been reported.

In many semi-conducting metal oxide-based sensors, a WO₃ based sensor is more promising because of its excellent sensitivity to NOₓ without significant sensor signal drift. Lu et al. examined many single-metal oxides and found that WO₃ gave the optimal sensing performance to NOₓ at 500–700 °C [2]. Dutta et al. reported that a potentiometric NOₓ sensor with a WO₃ sensing electrode and a Pt or Au reference electrode showed stable, fast and reproducible responses to NO₂ at 600–700 °C [13]. Di Bartolomeo et al. reported a similar planar sensor that showed a fast and stable response to NO₂ at 450–700 °C [14]. The same linear correlation was also reported in a potentiometric tubular sensor with a Pt/YSZ electrode [1]. Yoo et al. did some work on a WO₃-based potentiometric planar sensor. They investigated its sensing behavior and related mechanisms using TPR/TPD techniques [15]. They found that this sensor was even more sensitive to 10 ppm NO₂ [16]. In their later work, Yoo et al. built three different sensors with a (Pt, Au, Pd, and TiO₂)/WO₃ electrode, and found NO₂ sensing was strongly affected by the catalytic activity of the electrode materials (Pt > Au > Pd > TiO₂) [17]. Based on the excellent performance of the WO₃ based sensor, WO₃ was used as a sensing electrode material in this work.
Some previous publications on potentiometric sensors have found that sensor sensitivity is dependent on sensing electrode thickness. Elumalai et al. investigated YSZ-based (Y2O3-doped ZrO2 electrolyte) NOx sensors with different thicknesses of (NiO and Cr2O3)-SEs, and found that NO2 sensitivity was strongly affected by sensing electrode thickness, and the sensor with the thinnest SE layer had the highest sensitivity to NO2 [18,19]. Macam et al. completed similar work on La2CuO4 sensing electrode thickness, and found that NO2 sensitivity increased with decreasing thickness [20]. All of these studies concluded that the sensor with the thinnest SE layer has the highest sensitivity to NO2.

In order to stabilize the fabrication process and optimize the performance of the WO3 based sensor, we investigated YSZ-based potentiometric sensors with different thicknesses of WO3-SE. We found a contrasting result, in which the sensor with a moderate thickness of WO3-SE had the highest NO2 sensitivity. La2CuO4, Cr2O3 and NiO have highly catalytic activity for NO2 decomposition [18,20] and WO3 is inert for NOx component equilibration and has lower catalytic activity for NO2 decomposition [21]. Further, the diffusion path for NOx component equilibration should be longer, therefore it is possible that the sensor with the moderate thickness of WO3-SE has the highest sensitivity. There seems to be no report of the sublimation of La2CuO4, Cr2O3 and NiO, but WO3 is an easily sublimated material [22,23]. The WO3-SE thickness may be changed during the sintering process, so it is possible that the effect of WO3-SE thickness is different to the effect of the La2CuO4, Cr2O3 and NiO sensing electrode thickness.

Motivated by this, in order to understand the NO2 sensing mechanism, we examined the sensing performance of a YSZ-based planar potentiometric sensor with a Pt/WO3 electrode by varying WO3 sensing electrode thickness. Sensing performance was obtained by measuring the difference in potential responses (ΔV). The results presented in this paper are useful to control the sensing electrode thickness to improve the reproducibility of the sensor response. In addition, it is interesting for researchers engaged in practical applications of gas sensors.

2. Materials and Methods

Each planar sensor contains an 8 mol% Y2O3-doped ZrO2 (8YSZ) electrolyte and reference/sensing electrodes located on both surfaces of the electrolyte. The 8YSZ electrolyte with the dimensions of 10.0 × 10.0 × 0.3 mm was sintered at 1500 °C for 2 h in air. The reference electrode and Pt-collector were screen printed with porous Pt slurry on both surfaces of the YSZ electrolyte, dried at 80 °C for 2 h and sintered at 1200 °C for 2 h. For the preparation of the sensing electrode, commercial WO3 powder (99.9% purity, <200 nm, Alfa Aladdin, Shanghai, China) was mixed with 50 wt% binder as screen-print slurry. The mixed slurry was screen printed onto the Pt-collector, then dried at 80 °C for 2 h. Thicker WO3-SE was prepared by screen printing additional layers onto the dried electrode, and were then sintered at 815 °C for 3 h. Pt wires were then connected to both electrodes. The schematic of the planar NO2 sensor is shown in Figure 1. The surface morphology as well as the thickness of WO3-SE was observed by means of a field emission scanning-electron microscope (FE-SEM, JSM7600F, JEOL, Tokyo, Japan) operating at 10 kV.

![Figure 1. (a) Schematic of the fabricated sensor; (b) Top view of the sensor; (c) Bottom view of the sensor.](image-url)
Sensor performance was tested in a gas flow apparatus under various gas environments controlled by mass flow controllers (MPA-80, Beijing Seven Star Electronics Company, Beijing, China). The gas flow apparatus was connected to a quartz tube equipped with a furnace operating at 500–600 °C. The gas environment consisted of a changing concentration of NO\textsubscript{2} varying from 100 to 500 ppm and a base gas (10 vol.% O\textsubscript{2} + N\textsubscript{2} balance) at a total flow rate of 0.2 L/min. Both sensor electrodes were exposed to the same gas atmosphere. The open circuit potential between the sensing and reference electrode was measured with an electrochemical workstation (Versa STAT 3, Princeton, NJ, USA).

The electrochemical impedance spectroscopy (EIS) was tested in the frequency range from 0.1 Hz to 1 MHz by the electrochemical work station, with 10 mV exciting voltage at 550 °C.

3. Results

3.1. Morphology of the WO\textsubscript{3}-SE Layer

SEM (Scanning Electron Microscope) micrographs of the cross-sections of WO\textsubscript{3}-SE are shown in Figure 2. It can be seen that the thickness throughout the electrode is fluctuating. Therefore, four measurements were taken across the cross-section of the electrode and averages were calculated for each electrode. The average thicknesses were 15.8, 25.7, 34.9 and 46.7 \(\mu\text{m}\). These results show that there is no linear relationship between the number of layers of screen printed WO\textsubscript{3}-SE and the corresponding thickness. Figure 3 shows the SEM micrographs of the WO\textsubscript{3}-SE surface. It can be seen that the WO\textsubscript{3}-SE becomes more and more compact with an increasing number of WO\textsubscript{3}-SE layers. It can also be seen that the Pt collector of the sensor with one layer and two layers of WO\textsubscript{3}-SE are not fully covered with WO\textsubscript{3}, and such a phenomenon is more serious in the sensor with one layer WO\textsubscript{3}-SE. This is confirmed in Figure 4, which shows the typical SEM micrographs of the cross-sections of one layer and two layers of WO\textsubscript{3}-SE, where some parts of the Pt collector are exposed to the air and not covered with WO\textsubscript{3}-SE. A part of the Pt collector was exposed to air and was not covered by WO\textsubscript{3}-SE.

![Figure 2. SEM micrographs of the cross-sections of WO\textsubscript{3}-SE. (a) one layer; (b) two layers; (c) three layers; (d) four layers.](image-url)
Figure 3. SEM micrographs of WO$_3$-SE surface. (a) one layer;(b) two layers;(c) three layers;(d) four layers.

Figure 4. The typical SEM micrographs of the cross-sections of one layer and two layers WO$_3$-SE. (a) ×500; (b) ×3000.

3.2. Evaluation of Sensing Characteristics

Figure 5a-c shows the response transients of the planar sensor with various thicknesses of WO$_3$-SE and different NO$_2$ concentrations (+10 vol.% O$_2$ + N$_2$ balance) measured at 500–600 °C. The voltages in these plots are an average of the responses at each concentration. The average voltage was calculated from three values measured at each NO$_2$ concentration of 100, 200, 400 and 500 ppm. Each sensor is designated by its average WO$_3$-SE thickness. The highest voltage was always obtained using a moderate thickness (34.9 μm) of WO$_3$-SE at different operating temperatures and NO$_2$ concentrations. The thickest (46.7 μm) WO$_3$-SE had the lowest voltage at 500 °C and 550 °C, while the thinnest (15.8 μm) WO$_3$-SE had the lowest at 600 °C. The thinnest (15.8 μm) and second thinnest (25.7 μm) WO$_3$-SE had moderate sensitivity and the voltage of the latter was always higher than the former at different operating temperatures and NO$_2$ concentrations. The response rate of the sensors were almost the same at each temperature, irrespective of the thickness of the WO$_3$-SE. The response and recovery rates all increased because of higher reaction kinetics as the temperature increased. In the case of the moderate thickness (34.9 μm) of WO$_3$-SE, the 90% response and the 90% recovery rates were typically about 20 s and 140 s at 550 °C and 500 ppm NO$_2$ concentrations, respectively. It can be seen that the NO$_2$ sensitivity decreased significantly for each sensor with the increasing operating temperature.
Figure 5. NO₂ voltage response versus time for different thicknesses of WO₃-SE at (a) 500 °C; (b) 550 °C; (c) 600 °C.

Figure 6 displays the dependence of the voltage response on the logarithm scale of the NO₂ concentration for each WO₃-SE. It shows that in each case the voltage response increased linearly with the increasing NO₂ concentration on a logarithmic scale. This is typical for a mixed-potential-type sensor. For each sensor of a different thickness, the NO₂ sensitivity decreased as the temperature increased. The highest voltage response was obtained from the sensor with a moderate thickness (34.9 μm) of WO₃-SE at each temperature. The lowest voltage response was obtained from the sensor with the thickest WO₃-SE at 500 and 550 °C.

Figure 6. Voltage response versus log (NO₂ concentration) for different thicknesses of WO₃-SE at (a) 500 °C; (b) 550 °C; (c) 600 °C.
Figure 7 displays the electrochemical impedance spectroscopy at 550 °C in the base gas and sample gas for sensors with different thicknesses of WO$_3$-SE. It could be seen that there was a smaller semicircle which is not obvious in the high frequency range and a bigger semicircle in the low frequency range. The shape and size of the small arc at high frequency region are similar for the sensors with different layers of WO$_3$-SE, whether in the base gas or the sample gas. But there is a significant shrinkage toward the real Z’-axis for the large arc at low frequency when NO$_2$ is injected.

As is well known, the conductivity of an n-type semiconducting oxide decreases upon exposure to an oxidizing gas like NO$_2$. The arc diameter decreased a little from base gas to sample gas, but the order did not change. The order of the arc diameter was contrary to the order of the voltage response results. The arc diameter was the largest for the sensor with the thickest (46.7 μm) WO$_3$-SE. The arc diameter was the smallest for the sensor with a moderate thickness (34.9 μm) of WO$_3$-SE. The arc diameter can reflect the resistance of the electrode reaction [24]. This implies that there was different catalytic activity for the electrochemical reaction occurring at the WO$_3$(Pt)/YSZ interface. This is consistent with the SEM results that the Pt collector of the sensors with the thinnest (15.8 μm) and second thinnest (25.7 μm) WO$_3$-SE were not fully covered with WO$_3$, and some part of the Pt collector was directly exposed to the gas phase, while the Pt collector of the sensors with moderate (34.9 μm) and the thickest (46.7 μm) WO$_3$-SE were fully covered by WO$_3$. Gas should first pass through the WO$_3$-SE, then reach the WO$_3$(Pt)/YSZ interface. The thickness of the WO$_3$-SE will affect the amount and component of the gas phase, so there are different degrees of electrochemical reactions at WO$_3$(Pt)/YSZ interfaces for sensors with different thicknesses of WO$_3$-SE.

![Figure 7. Electrochemical impedance spectroscopy in the base gas and in sample gas at 550 °C for different thicknesses of WO$_3$-SE.](image)

4. Discussion

WO$_3$ is an n-type semiconducting oxide. Gas molecules can be easily adsorbed by porous WO$_3$-SE. O$_2$ is adsorbed and transformed into O$_2^-$, O$^-$ and O$_2^{2-}$ by capturing free electrons in WO$_3$-SE, as seen below:

$$O_2 \text{ (gas)} \rightleftharpoons O_2\text{ (ads)} \quad (1)$$

$$O_2\text{ (ads)} + e^- \rightleftharpoons O_2^-\text{ (ads)} \quad (2)$$

$$O_2^-\text{ (ads)} + e^- \rightleftharpoons 2O^-\text{ (ads)} \quad (3)$$

$$O^-\text{ (ads)} + e^- \rightleftharpoons O_2^{2-}\text{ (ads)} \quad (4)$$

When WO$_3$-SE is exposed to NO$_2$ gas, NO$_2$ can be adsorbed directly into the WO$_3$-SE or react with the adsorbed O$_{\text{ (ads) } }$ through the below reactions [25–27]:

$$\text{NO}_2\text{ (gas)} \rightleftharpoons \text{NO}_2\text{ (ads)} \quad (5)$$
The above adsorption and reaction process is a dynamic equilibrium process. WO$_3$ is also used as a catalyst. When NO$_2$ is adsorbed and passed through the porous structure, NO$_2$ can be catalytically reduced to NO and O$^2^-$ as reaction (7).

Pt is a highly efficient catalyst through which NO$_2$ can also be catalytically reduced to NO and O$^2^-$ as reaction (7). However, the catalyst activity of Pt can be reduced because of the formation of Pt oxides/chemisorbed oxygen when exposed to NO$_2$ [28,29], thus reaction (7) at the reference electrode is very weak. Further, there is saturated oxygen adsorption, thus the influence of reaction (7) can be negligible. The main reaction at the reference electrode is reaction (8). Thus, the overall chemical reaction in the sensor is reaction (9).

Figure 8 is a diagrammatic sketch of the electrode–electrolyte interface and the reactions occurring at these sites. When the sensor is exposed to NO$_2$, O$^2^-$ (ads) can be created by reaction (7) at the WO$_3$ (Pt)/YSZ interface. Thus, the amount of O$^2^-$ accumulated at the WO$_3$ (Pt)/YSZ interface is more than that at the YSZ/Pt interface [13]. A $P_{O_2}$ gradient across the YSZ is created, so there is a positive voltage response. This is consistent with the NO$_2$ voltage response results in Figures 5 and 6.

Figure 9 is a diagrammatic sketch of the effect of WO$_3$-SE thickness at the WO$_3$ (Pt)/YSZ interface. As WO$_3$ is a low temperature sublimation material [22], there was a blank area not covered with WO$_3$ in the sensor with the thinnest (15.8 $\mu$m) and second thinnest (25.7 $\mu$m) WO$_3$-SE. This was more serious in the former, thus there were less adsorption sites at the WO$_3$ (Pt)/YSZ interface, and a lesser $P_{O_2}$ gradient across the YSZ and a lower voltage response. Thus, the NO$_2$ voltage response is smaller.
When the sensor was covered with moderate (34.9 μm) and the thickest (46.7 μm) WO3-SE, the Pt collector was fully covered with WO3. The adsorption sites at the WO3 (Pt)/YSZ interface are similar, thus similar amounts of O2− accumulated at the WO3 (Pt)/YSZ interface. There should be similar voltage response, but the results in Figure 5 are very different in that the sensor with the thickest (46.7 μm) WO3-SE had a much smaller voltage response.

For the YSZ-based gas sensor with a semiconducting oxide sensing electrode, the heterogeneous gas-phase reaction in the SE-oxide and at the SE-oxide/YSZ interface were all very vital for gas-sensing performance [30,31]. WO3 exhibited higher NO2 decomposition activity with a faster commencement of NO2 decomposition from 450 °C [15]. The thicker the WO3-SE, the easier it was for NO2 to be catalyzed to achieve a state of equilibrium. In the screen printing process of multilayered WO3-SE, the upper layer of the electrode material will fill the pores in the lower layer, resulting in more and more compact WO3-SE. This can be confirmed from Figure 3, where the thickest WO3-SE (46.7 μm) is more dense than the moderate (34.9 μm) WO3-SE. The denser and thicker the WO3-SE, the harder it is for NO2 to diffuse to reach the WO3 (Pt)/YSZ interface, the greater the chance for NO2 to make contact with the electrode material, and the easier it is for the catalytic reaction to achieve an equilibrium state at the WO3 (Pt)/YSZ interface. Therefore, for the sensor with the thickest WO3-SE (46.7 μm), it was more difficult for NO2 to reach the WO3 (Pt)/YSZ interface, and the NOx component arriving at the interface was more likely to be in an equilibrium state, thus less O2− from the NO2 decomposition accumulated at the interface. As a result, the NO2 voltage response was also low for the sensor with the thickest WO3-SE. The sensor with moderate WO3-SE thickness (34.9 μm) had enough gas adsorption sites and a moderate gas diffusion path, thus more NO2 was adsorbed and arrived directly at the WO3 (Pt)/YSZ interface, and more O2− accumulated at the WO3 (Pt)/YSZ interface. As a result, a larger $P_{O_2}$ gradient was created, and the largest voltage response was obtained.

Thus, it can be said that the thickness of SE plays a very important role in deciding the sensitivity of a sensor. A complete and effective SE is a necessary condition for obtaining a highly gas-sensitive response. Under this condition, the thinner the SE, the higher the sensitivity.

5. Conclusions
YSZ-based planar potentiometric sensors with different thicknesses of WO3-SE were prepared and their NO2 sensing performance was tested at 500-600 °C. It was shown that the thickness of WO3-SE can strongly influence NO2 sensitivity. The sensor with moderate WO3-SE thickness (34.9 μm) had the highest sensitivity because it had enough gas adsorption sites at the WO3 (Pt)/YSZ interface and a moderate gas diffusion path. NO2 sensitivity is basically dependent on the gas adsorption sites and the NOx component at the WO3 (Pt)/YSZ interface.
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7. References
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