

The effect of V_2O_5 - WO_3 - TiO_2 electrode thickness on ammonia sensing properties for potentiometric sensor

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Abstract. SCR catalyst V_2O_5 - WO_3 - TiO_2 was synthesized for fabricating sensing electrodes of potentiometric ammonia sensor in this work. As an important sensing electrode structural parameter, the influence of the electrode thickness on sensor properties was investigated. The VWT electrodes with the thickness of 9.8, 15.2 and 24.5 μm were made by different screen printing frequency. As the thickness increased, the NH_3 sensitivity of the sensor decreased from 71.9 to 17.0 mV/decade, and the response/recovery rates also slowed down rapidly. Considering the EIS results, it is believed that with the increase of electrode thickness, more NH_3 molecules are consumed by catalytic reactions in VWT electrode, which reduces the concentration of NH_3 involved in the electrode reaction at the three phase boundary. The weakened reaction reduces the NH_3 sensitivity and increases the interface resistance of the TPB. The increased VWT thickness retards the diffusion of NH_3 molecules, and finally prolongs the response/recovery times.

1 Introduction

Selective catalytic reduction (SCR) technology is widely used in the removal of NO_x from exhaust due to its excellent denitrification efficiency [1, 2]. In order to improve the NO_x conversion efficiency of SCR system and prevent the leakage of reducing agent NH_3 , the demand of a high performance NH_3 sensor used in exhaust is urgent [3, 4]. Among kinds of electrochemical gas sensors, YSZ-based potentiometric sensor becomes a research focus mainly due to the high sensitivity, durability, simple structure and low cost [5]. As an important component of gas sensor, sensing electrode plays a key role in gas adsorption and electrochemical catalysis, and these properties could be influenced by material composition, phase and electrode morphology. As a commercial SCR catalyst, V_2O_5 - WO_3 - TiO_2 (VWT) mixed metal oxides meet the basic requirements of the sensing electrode materials for NH_3 sensors because of the excellent abilities of NH_3 adsorption, catalytic activity and anti-poisoning [6, 7]. VWT has been used as a sensing material for the mixed-potential ammonia sensors and shows excellent ammonia sensitivity [8-11].

In general, NH_3 molecules firstly adsorb on the surface of VWT electrode, and then diffuse through the VWT to the three-phase boundary (TPB) of gas, electrode and electrolyte and participate in the electrode reactions. The different electrochemical reactions due to different catalytic properties of the sensing electrode and reference electrode lead to the corresponding electrode potentials. The potential difference ΔV between two electrodes represents the response signal of the gas

sensor. With the change of the ammonia concentration, varying degrees of electrode reactions result in a corresponding potential difference, so the ammonia concentration of vehicle exhaust can be reflected by the sensor signals.

It is known that VWT has strong gas phase catalytic effect to NH_3 and could consume NH_3 molecules in oxidizing atmosphere at high temperatures [9, 12]. In gas sensor, NH_3 molecules must through the electrode material before reaching the TPB, so as an important electrode structure parameters, electrode thickness could influence the NH_3 sensitivity. In this paper, different thickness V_2O_5 - WO_3 - TiO_2 electrodes were prepared for the YSZ-based potentiometric NH_3 sensors, and the sensitivity, response and recovery times were tested. The influence mechanism of the VWT electrode thickness on NH_3 sensing performances was evaluated combined with the electrochemical impedance spectroscopy.

2 Experimental

2.1 Preparation of V_2O_5 - WO_3 - TiO_2 powder

The impregnation method was used to synthesize VWT with the raw materials anatase TiO_2 , $\text{N}_{10}\text{H}_{40}\text{W}_{12}\text{O}_{41}\text{xH}_2\text{O}$ and NH_4VO_3 . Stoichiometrical amounts of NH_4VO_3 and $\text{N}_{10}\text{H}_{40}\text{W}_{12}\text{O}_{41}\text{xH}_2\text{O}$ were dissolved in the oxalic acid solution. TiO_2 was added to the solution and stirred at 80°C until drying. Then the obtained precipitation was calcined for 3 h at 500°C. The calcined VWT powder

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was stored after full grinding. The V_2O_5 content was 2.0 wt.%, WO_3 was 10 wt.% and the rest was TiO_2 .

2.2 Sensor fabrication and testing apparatus

Each sensor includes one piece of YSZ electrolyte and sensing/reference electrodes located on two surfaces of the YSZ. Reference electrode was a porous Pt layer, and sensing electrode consisted of a Pt layer covered with porous VWT. The VWT layer was screen-printed with the slurry which was the mixture of VWT powder and organic binder. The VWT thickness is controlled by different screen-printing frequency of 1, 2 and 4. After each printing, the VWT layer was dried in the oven before the next printing. The final VWT electrodes were sintered at 700°C for 20min. The morphology of the electrodes was observed by SEM (Sirion 200, FEI, Holland) with an excitation voltage of 10 kV.

Each sensor was exposed to the base gas (10 vol.% O_2 , N_2 balance) and sample gases (10-320ppm NH_3 in 10vol.% O_2 and N_2 balance) at the flow rate of 500 ml/min. The operating temperature was 550°C and the retention time for each sample gas was 100s. The differences (ΔV) of the potential between sensing and reference electrodes were recorded by an electrochemical workstation (VersaSTAT3, Princeton, USA).

3 Results and discussions

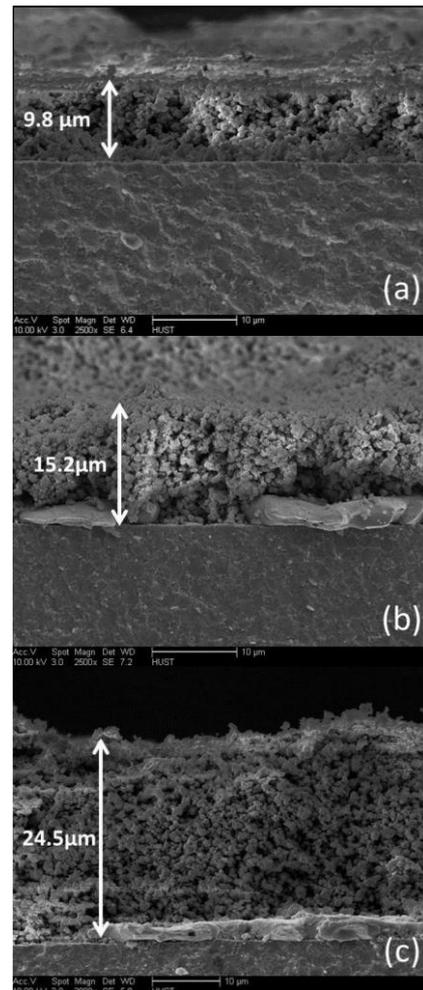


Figure 1. The sectional SEM images of the morphology for VWT electrodes screen-printed with different frequency, (a) once; (b) twice and (c) four times.

3.1 Electrode characterization

The sectional images of the sintered VWT electrodes with different print frequency are shown in Figure 1. With the increase of screen-printing frequency, the thickness of the electrode increases gradually from $9.8\ \mu\text{m}$ to $15.2\ \mu\text{m}$ and $24.5\ \mu\text{m}$. The electrode thickness obtained after sintering does not increase linearly with the printing frequency. This may be due to the permeation of the printing paste into the surface pores of the dried VWT layer. In addition, the screen-printing process could compress the prior printed material and reduce the electrode thickness.

3.2 The influence of electrode thickness on sensing performance

3.2.1 The influence of electrode thickness on NH_3 sensitivity

Response transients to base gas and various NH_3 at 550°C for the sensors with different thickness of VWT electrodes were illustrated in Figure 2a. The sample with the thinnest VWT electrode has the highest response platforms to different concentrations of NH_3 . The

response platforms of the 15.2 μm sensing electrode are greatly reduced and the values of the sensor with 24.5 μm VWT electrode decrease to about a fifth of the thinnest sample. It can be seen clearly that the greater the thickness of the VWT electrode, the more attenuation of the NH_3 sensitivity.

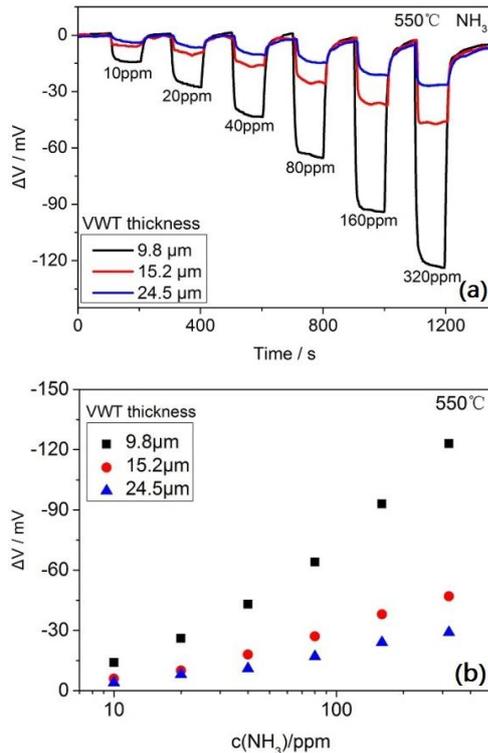


Figure 2. (a) The response transients and (b) response values to different concentration NH_3 at 550°C for the sensors with different thickness of VWT electrodes.

Figure 2b shows the response values (ΔV) to various concentrations of NH_3 for different sensors at 550 °C. It is observed that the ΔV values are almost linear with the logarithm of NH_3 concentrations. This supports the mixed-potential mechanism of the electrochemical gas sensors reported by researchers. The slope of the semi-log plot is defined as the sensitivity for the gas sensor [13, 14]. By the linear fittings, the slopes of the response curves were 71.9 mV/decade, 27.7mV/decade and 17.0mV/decade for the VWT electrodes of 9.8 μm , 15.2 μm and 24.5 μm respectively. The changes of electrode thickness could not affect the TPB area obviously. Therefore, the weakened NH_3 sensitivity may be mainly due to the decreased NH_3 concentration involved in the electrode reactions at TPB. At elevated temperatures, NH_3 molecules could be gas phase catalysed by the VWT material, and the thicker the electrode is, the more serious gas consumption of NH_3 . This results the reduction of the NH_3 molecules participated in the electrode reactions and gives adverse effects on the NH_3 sensitivity.

3.2.2 The influence of electrode thickness on response/recovery times

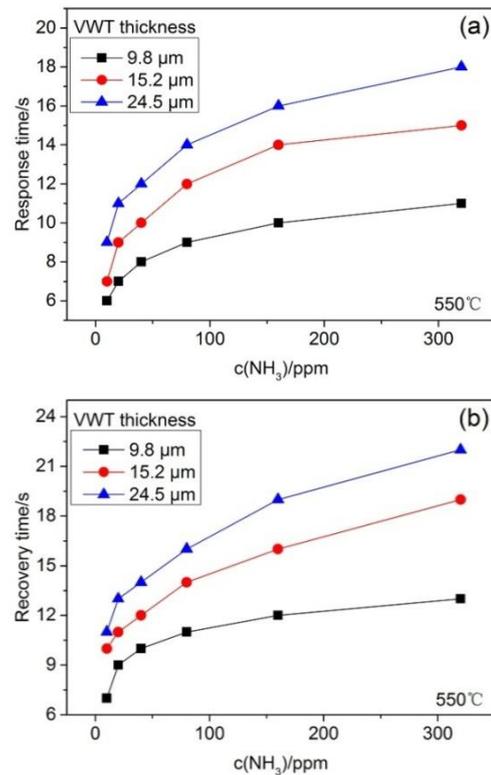


Figure 3. The influence of VWT electrode thickness on the sensor (a) response time and (b) recovery time to different NH_3 concentrations at 550°C.

As one of the most important performance indexes for gas sensor, the response and recovery times were investigated in this work. Figure 3 exhibits the response and recovery times of the sensors with various thickness electrodes to different concentration NH_3 at 550 °C. The response time is defined as the time taken for the ΔV to reach ninety percent of steady-state values after the contact of NH_3 , and the recovery time is the time for the ΔV to reach ten percent from the base line after removing the NH_3 [15]. It can be seen from Figure 3a and Figure 3b that the sample with the thinnest VWT electrode shows the fastest response and recovery of about 6-11s and 7-13s. With the VWT thickness increases from 9.8 μm to 15.2 μm , the response time of the sensor is extended rapidly, especially for the high NH_3 concentration of 320ppm. When the electrode thickness thickenings to 24.5 μm , the response time increases to 9-18s. The recovery time of different electrode thickness sensors has a similar pattern. The above phenomenon shows that the effect of electrode thickness on the response/recovery time is monotonous: with the increase of thickness, the response and recovery times both increase. In the case of the stable TPB state, the response and recovery times of the sensor mainly depend on the gas diffusion velocity from the electrode surface to the TPB. With the increase of the VWT thickness, the exchanges of the gas components between TPB and the atmosphere become slower and it needs more time to achieve balance, so the response and recovery times are extended.

3.3 The influence of electrode thickness on electrochemical impedance spectroscopy

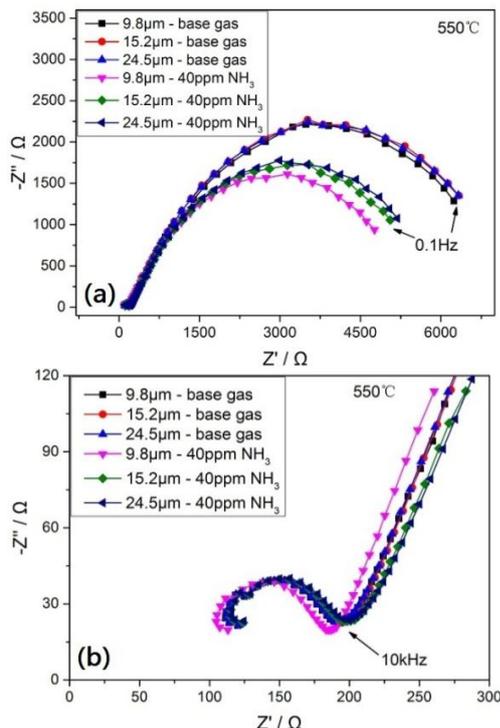


Figure 4. (a) EIS of the sensors with different VWT thickness in base gas and 40ppm NH₃ at 550°C, (b) enlargement of the high frequency region.

In order to explain the influence mechanism of the electrode thickness on sensor performances, the electrochemical impedance spectroscopy (EIS) of the sensors fabricated with different thickness VWT electrodes was tested between 0.1Hz and 1MHz in base gas and 40ppm NH₃ at 550°C, the Nyquist plots are shown in Figure 4a. Each plot consists of a semi-arc which is not obvious in high frequency range and a bigger semi-arc in low frequency range. The enlargement of the high frequency arc is shown in Figure 4b. It can be seen that the size of the arc at high-frequency region could not be affected by the change of electrode thickness and the existence of NH₃. But there is a significant shrinkage toward the Z'-axis for the low frequency arc when 40ppm NH₃ is injected, and the arc gets smaller with the thickness decreases. Each arc of low frequency is not standard, but compressed towards real axis. It might be due to the non-ideal behaviors of the double layer between the electrolyte and electrode [16].

A probable equivalent circuit can be given for the YSZ-based gas sensors, as shown in Figure 5. R_c corresponds to the ohmic resistance of the electric connections in the sensor element. Because of the insensitivity of high frequency arc from gas composition and electrode thickness, the R_b and C_b in high frequency region represent the resistance and capacity of the YSZ. Due to the non-ideal shape, the large arc of the low frequency region can be characterized by a constant phase element (CPE_i) and R_i . CPE_i is used to represent the double layer capacitance of the interface, and R_i is corresponding to the charge transfer resistance which is

related to the ion transfer at TPB, namely interfacial resistance [3]. The R_i is dependent on the electrode electrochemical reactions, so it is deduced that the reactions of NH₃ at the TPB lead to the decrease of R_i . In Figure 4a, with the decrease of VWT thickness from 24.5 μm to 9.8 μm, the interface resistance in NH₃ reduces gradually. It means that the charge exchange caused by electrode electrochemical reactions becomes more intense. The more intense electrode reaction, the bigger sensor response. The sensor with the thinnest VWT electrode exhibits the minimum R_i , mainly due to the least degree of the gas phase consumption of NH₃ molecules. It leads more residual NH₃ molecules could participate in the reactions at TPB and generates higher NH₃ sensitivity.

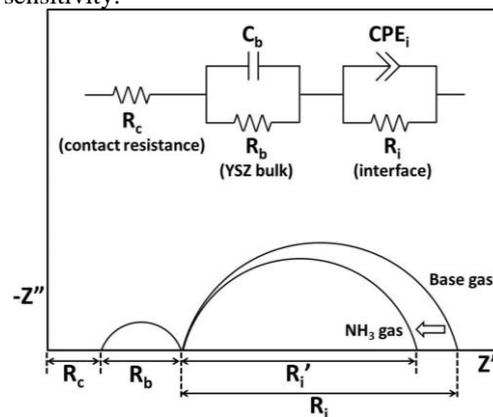


Figure 5. A probable equivalent circuit for the YSZ-based potentiometric gas sensor.

4 Conclusions

In this study, potentiometric ammonia sensors with different thickness of VWT sensing electrodes were prepared. The thickness of the electrode was controlled by different frequency of the screen-printing. With the increase of thickness from 9.8 μm to 24.5 μm, the NH₃ sensitivity of the sensor is reduced from 71.9mV/decade to 17.0mV/decade and the response/recovery times of the responses are increased obviously. Combined with the EIS test results, it is believed that with the increase of VWT thickness, more NH₃ molecules could be consumed by the phase catalytic reactions with VWT, this leads to a lower concentration NH₃ which participate in the electrode reactions on TPB. The weakened electrode reactions and increased TPB resistance are caused by the reduction of the NH₃ concentration, and this eventually leads to the decrease of NH₃ sensitivity. The increased electrode thickness causes the inhibition of NH₃ molecular diffusion from sample gases to TPB, therefore the response and recovery times of the sensor are extended.

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