

Study of Two Vanadium Based Materials as Working Electrode for Developing A Selective Mixed-Potential Ammonia Sensor [†]

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Abstract: Mixed potential ammonia gas sensors were fabricated by using two sensing materials of $\text{Ni}_3\text{V}_2\text{O}_8$ and $\text{Au-V}_2\text{O}_5$ as working electrodes, YSZ as electrolyte and platinum as reference electrode. The results have shown that the $\text{Ni}_3\text{V}_2\text{O}_8$ sensors show cross-sensitivity toward NO gas. However, $\text{Au-V}_2\text{O}_5$ working electrodes displayed a high sensitivity to NH_3 as well as fast response and recovery times at high temperatures. Furthermore, the results indicate that the selectivity of $\text{Au-V}_2\text{O}_5$ sensors increases by increasing temperature.

Keywords: mixed potential sensor; ammonia gas sensor; working electrode; vanadium oxide; $\text{Ni}_3\text{V}_2\text{O}_8$

1. Introduction

According to new European driving cycle, over the past years, while the vehicular emissions of NO_x and CO have decreased, ammonia emissions have been considerably increased [1]. Today, one of the main research subjects of electrochemical gas sensors to control and monitor automotive exhaust emissions is developing a high-performance single sensor capable of monitoring NO_x , NH_3 , CO , and hydrocarbons at the same time.

Selective Catalytic Reduction (SCR) using ammonia gas (NH_3) as a reductant is recognized as the most effective NO_x control technology in the world. More recent applications of this system include reduction of NO_x emissions generated from diesel engine vehicles and trucks, calcining ovens, gas turbines firing landfill and digester gas. In order to optimize the conversion rates of NO_x and to avoid the air pollution of excessive ammonia, an NH_3 sensor is required to control the SCR system for maintaining NH_3 slip at an acceptable level [2].

Solid-state gas sensing technology is considered one the high effective approaches for gas sensing in harsh environments because of simple structure, good selectivity, high sensitivity and especially excellent stability. In recent years, the development of potentiometric sensors has become quite a revolution in sensor technology for monitoring environmental gases [3,4].

Concerning ammonia gas sensors, vanadium-based materials have been reported as promising materials owing to their catalytic acidic sites caused by vanadium content. Vanadium dioxide (V_2O_5), have been recognized as sensitive material to NH_3 even at ppb levels [5,6].

2. Materials and Methods

In this study, solid-state electrochemical planar sensors were fabricated by screen-printing method using commercial yttria-stabilized zirconia (YSZ), commercial vanadium oxide (V_2O_5)

powder and commercial Au and Pt inks. Homemade inks are elaborated for YSZ and Au-V₂O₅, by addition of V₂O₅ to Au ink for the latter.

Ni₃V₂O₈ material was synthesized from nickel nitrate (Ni(NO₃)₂·6H₂O) and ammonium metavanadate (NH₄VO₃) through sol-gel method [7].

In order to determine the decomposition temperature of the precursors and the more suitable sintering temperature of the obtained composite, thermogravimetric and differential thermal analysis (TGA-DSC) were performed. The DSC profile in Figure 1 reveals a sharp exothermic peak at 355 °C, corresponding to a rapid weight loss in TGA curve. This could indicate the oxidation of organic additives and burning out of the nitrate radicals in the precursor. According to TGA curve, about 44% weight loss takes place before 700 °C. The last exothermic peak, centered approximately at 800 °C, can be due to the crystallization of Ni₃V₂O₈.

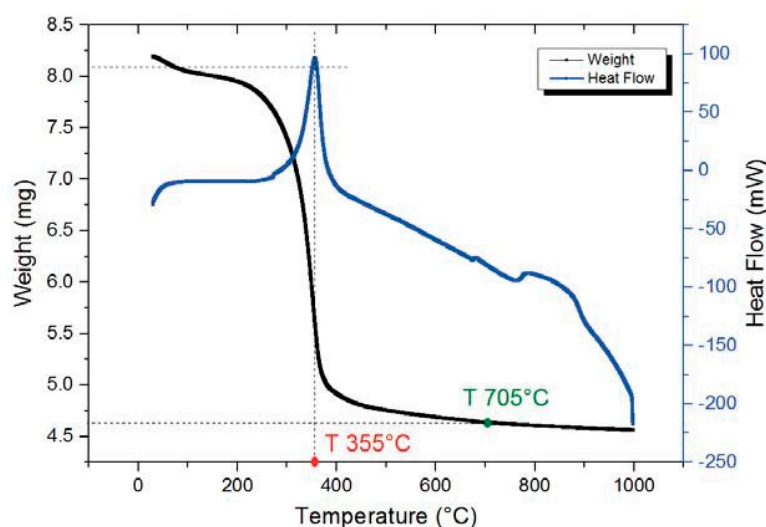


Figure 1. TGA-DSC analysis of Ni₃V₂O₈ precursor.

The crystal structure of Ni₃V₂O₈ powder sintered at 1000 °C for 2 h is verified by X-ray diffraction spectrometry (XRD). The used diffractometer is from Siemens company (D5000) equipped with a radiation source of Cu K α 1 + α 2. The XRD pattern shown in Figure 2 is obtained with radiation in $\theta/2\theta$ geometry between 10° and 65° with a scan rate of 1 degree/min. The resulted spectrum indicates a single-phase pattern attributed to Ni₃V₂O₈ without any impurity peak.

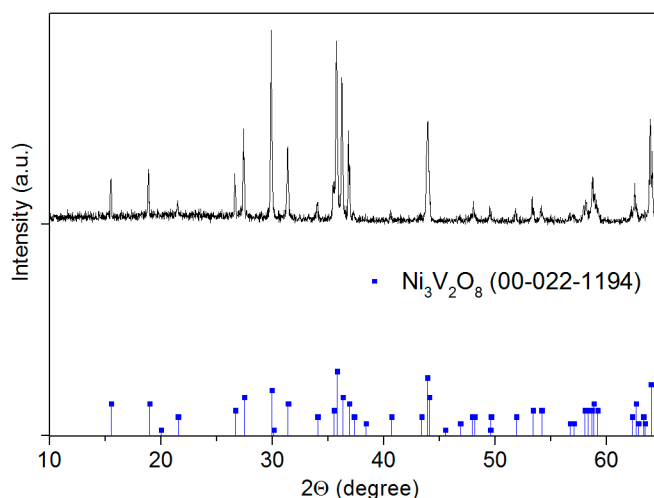


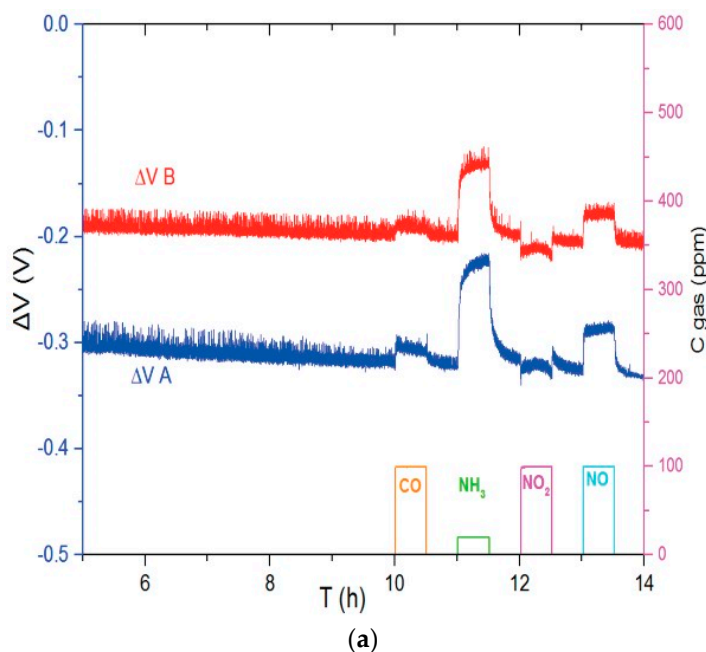
Figure 2. XRD patterns for Ni₃V₂O₈ powder sintered at 1000 °C for 2 h.

The sensors were then developed on an alumina substrate equipped with a Pt Heater. An YSZ layer ($2 \times 5 \text{ mm}^2$) was first deposited and annealed at 1380°C . The electrodes, Pt and either $\text{Au-V}_2\text{O}_5$ or $\text{Ni}_3\text{V}_2\text{O}_8$ were printed on each side of the YSZ layer and connected to gold tracks to measure the sensor signal, ΔV , which is the difference of potential between the reference (Pt) and the working (V-based) electrode. The sintering temperatures were respectively 600 , 850 , and 1000°C for $\text{Au-V}_2\text{O}_5$, Pt and $\text{Ni}_3\text{V}_2\text{O}_8$.

3. Results and Discussion

Figure 3 shows the responses of $\text{Ni}_3\text{V}_2\text{O}_8$ (Figure 3a) and $\text{Au-V}_2\text{O}_5$ (Figure 3b) sensors to different gases such as CO , NH_3 , NO_2 and NO in the base gas of $12\% \text{ O}_2$ and $1.5\% \text{ H}_2\text{O}$, balanced with N_2 . In each case, sensors A and B are two sensors which are fabricated and tested at the same conditions in order to take into account irreproducibility of system. It can be seen in Figure 3a, that sensors with $\text{Ni}_3\text{V}_2\text{O}_8$ working electrode show a response to NH_3 at 700°C but also to NO in lower ratio, while this sensor is weakly sensitive to CO and NO_2 . Regarding $\text{Au-V}_2\text{O}_5$ electrodes at 600°C (Figure 3b), it is evident that the sensor is selective to ammonia compared to CO , NO_2 and NO gases.

The operating temperature of 700°C was chosen for $\text{Ni}_3\text{V}_2\text{O}_8$ based sensor because no significant response was monitored for weaker temperature. In order to study the influence of temperature on selectivity and to emphasize the interest of V_2O_5 based electrodes, responses of Pt/YSZ/ $\text{Au-V}_2\text{O}_5$ sensors are compared in Table 1 to the ones of a Pt/YSZ/ Au sensor studied in a previous study [8]. By comparing these results, we can observe that the responses related to Au gas sensors decrease considerably by increasing temperature. However, regarding $\text{Au-V}_2\text{O}_5$ sensors, the cross sensitivity to other interfering gases can be completely eliminated at 600°C and selective ammonia sensor is achieved.



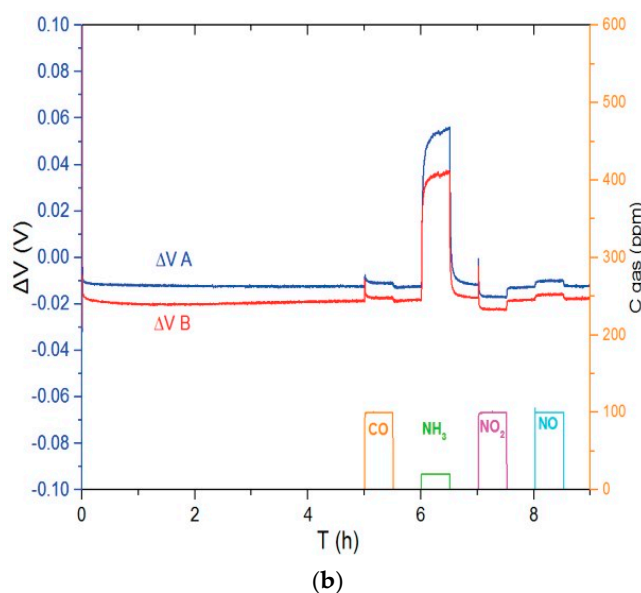


Figure 3. Response of the (a) $\text{Ni}_3\text{V}_2\text{O}_8$ sensors at 700 °C and (b) $\text{Au-V}_2\text{O}_5$ sensors at 600 °C for pulses of CO (100 ppm), NH_3 (20 ppm), NO_2 (100 ppm) and NO (100 ppm) in base gas.

Table 1. Comparison of Au and $\text{Au-V}_2\text{O}_5$ sensor responses (ΔV in mV) at different temperatures to pulses of CO (100 ppm), NH_3 (20 ppm), NO_2 (100 ppm) and NO (100 ppm) in base gas (ΔV experimental uncertainties around 5 mV).

Temperature (°C)	Sensor	CO	NH_3	NO_2	NO
475	Au	58	66	89	30
	Au-V_2O_5	40	85	116	46
550	Au	14	25	26	8
	Au-V_2O_5	13	83	28	16
600	Au	2	6	4	2
	Au-V_2O_5	2	60	4	2

4. Conclusions

Two vanadium-based working electrodes were tested in order to find a sensitive ammonia sensor at high temperature. By comparing all these results, we can conclude that although both $\text{Ni}_3\text{V}_2\text{O}_8$ and $\text{Au-V}_2\text{O}_5$ sensors are sensitive to ammonia, $\text{Au-V}_2\text{O}_5$ sensors show better sensitivity and selectivity toward NH_3 at operating temperature of 600 °C.

Further characterizations of electrode materials is yet to be done in order to better understand the specific interaction with ammonia, leading to higher selectivity.

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