Molybdenum and tungsten oxide based gas sensors for high temperature detection of environmentally hazardous sulfur species

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ABSTRACT

There is an increasing desire to control and monitor gas emissions from coal-fired power plants and other industrial systems. With this desire, there is a growing need for distributed gas sensors to monitor these emissions at high temperature ($>600 ^\circ C$), especially for pollutants such as SO_2 and H_2S. The objective of this work was to investigate molybdenum and tungsten binary and ternary oxide thick films on a chemiresistive sensor platform for monitoring of gas sulfur species. The work evaluated the SO_2 sensitivity of WO_3, MoO_3, $SrMoO_4$, $NiMoO_4$, $Sr_2MgMoO_{6-\delta}$ (SMM), $Sr_2MgWO_{6-\delta}$ (SMW), $NiWO_4$, and $SrWO_4$ compositions at 600–1000 $^\circ C$. The $SrMoO_4$ composition at both the micro- and nano-particulate scale showed the most promise in sensitivity, stability and selectivity to SO_2 up to 1000 $^\circ C$. Hydrothermally-synthesized nano-$SrMoO_4$ showed the highest sensor response with the R_{max} values of −17.2, −50.2 and −40.5 upon exposure to a 20 min pulse of 2000 ppm of SO_2 at 600 $^\circ C$, 800 $^\circ C$ and 1000 $^\circ C$, respectively. Similar sensitivity trends were distinguished down to 1–5 min SO_2 pulses. The nano-$SrMoO_4$ showed low cross-selectivity to H_2 and CO. Finally, the nano-$SrMoO_4$ sensor was also tested with H_2 and coal syngas containing 5–100 ppm H_2S, where high sensitivities were realized for both, but the sensing mechanism was altered in the latter (n-type to p-type semiconducting behavior). In order to better understand the sensing mechanism, extensive microstructural, electronic and chemical property characterizations were completed in this work.

1. Introduction

Sulfur dioxide (SO_2) is known to be a major air pollutant contributing to acid rain and acidic particulates, which are dangerous not only for human health but also a major contributor to greenhouse effects [1]. Coal contains a significant level of sulfur species, and with the increased burning of this fossil fuel for energy by developing countries, the release of sulfur species into the atmosphere is expected to increase dramatically over the next decade [2,3] Coal-fired power plants are the main emitter of sulfur in the form of SO_2 (and hydrogen sulfide, H_2S) [4,5] Modern desulphurization methods can eliminate 98% of the SO_2 from the emission gases by applying multiple levels of filtering, where the prime is through passing the exhaust gas through lime. However, SO_2 emission control has become a significant challenge for scientists and engineers [6] With this in mind, it is very important to develop and deploy sulfur sensor systems to monitor and quantify the level of SO_2/H_2S from these energy and industrial systems. The key factor is to develop sensors that are capable of withstanding harsh environmental conditions that exist in coal processing, which would enable the sensors to be placed at any location within the exhaust stream. For this to occur, the sensors must be robust, catalytically active to SO_2/H_2S, and display low cross-selectivity towards other reducing gases, and this must be simultaneously achieved at high temperatures.

Many SO_2 sensors base their functionality on the use of a liquid electrolyte or a polymeric material [7–10]. These sensing technologies are generally limited to low temperatures. The measurement efficiency and accuracy would be increased if sensing could be completed near the combustion or reforming event at high temperatures (>800 $^\circ C$). The use of solid-state sensors has also been discussed in literature, and these primarily focus on the use of semi-conducting metal oxide compositions to sense SO_2. The number of these publications is limited in comparison to the sensing of other gasses using these oxides. Semi-conducting metal oxides that were investigated for SO_2 sensing include CeO_2, WO_3, V_2O_5-TiO_2, MoO_3-SnO_2 and NiO [10–16]. Generally, the semi-conducting metal oxides used for SO_2 sensing were only applicable at low temperature (<500 $^\circ C$) due to stability issues in the highly reducing atmospheres [8] There are only a few instances of materials

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that were tested at higher temperatures (>300°C) for sulfur species; four studies deserve to be mentioned in detail due to their unique strategies employed in order to increase the sensor response and selectivity. Liang et al. modified a compact tubular sensor used in a potentiometric sensor design, where they used a V_2O_5-modified NASICON membrane with a vanadium (V)-doped TiO_2 composition acting as the SO_2 sensing material [11,12] The sensor showed excellent sensor response to SO_2 at 300°C. Beyond this temperature, the sensing capabilities decreased and diminished drastically beyond 500°C. Morris et al. similarly investigated the sensing capabilities of various level V-doped TiO_2 against different levels of SO_2 balanced with dry air (with nearly 20% O_2) in a resistive-type sensor design. The maximum sensor response for a 0.5% V-doped TiO_2 composition was −60% at 375°C upon exposure to 1000 ppm SO_2 with a 16.5 min response time. An increase in the temperature decreased the sensor response and eventually the response diminished down to only −10% at ~600°C [11] The negative designation for the sensor response indicates that the response was n-type in behavior, where the resistance decreased on exposure to the sulfur species. It is noteworthy to indicate that TiO_2 is the most successful semi-conducting metal oxide for detecting SO_2 at high temperature. Regrettably, the response diminishes as the temperature increases beyond 600°C. CeO_2 is the last example of a semi-conducting oxides tested and tailored for SO_2 sensor applications at high temperature within a resistive-type sensor architecture. Varhegyi et al. concluded that the resistance of the CeO_2 is not affected by the presence of SO_2 up to 500 ppm, unless the O_2 partial pressure is low (between 300 and 800°C) due to fact that physi/chemi-adsorption does not occur due to the defect state of the CeO_2 surface [17] In other words, the presence of chemically or physically adsorbed oxygen reduces electron exchange reactions with SO_2 on the CeO_2 surface. These authors basically developed a better understanding of the SO_2−CeO_2 surface and bulk interactions, and proposed several mechanisms regarding surface CeO_2 and SO_2 reactions.

In the case of H_2S sensing, the volume of compositions tested is much larger than that of SO_2. Although the volume of the literature is remarkable, most of the works are devoted to semi-conducting oxides and the operation temperatures of these sensors have been reported from only room temperature to 300°C. One of the few papers describing sensing H_2S at higher temperatures was completed by Dawson et al.; they utilized a $Cr_{2-y}Ti_yO_{3+x}$ sensing composition for a resistive-type sensor design [18] The material demonstrated a p-type characteristic at elevated temperatures (>250°C) and showed an increase in resistance upon exposure to H_2S (50 ppm) within a testing range of 250–500°C. It is the sole paper, at least to our knowledge in literature, that provided temperature desorption curves for both SO_2 and H_2S. It was seen that H_2S exhibited two maxima at about 150°C and 470°C; however, the loss of SO_2 from the surface occurred at 470°C. It was concluded that a sensor that operates at 350°C can be cleaned by heat treatment, and a pre-treatment will increase the sensor response of the sensor [18] Some of the other transition metal oxides demonstrated for H_2S sensing are as follows: PdO_x, WO_3, MoO_3, In_2O_3, CeO_2, SnO_2, TiO_2, ZnO, CuO, CdO, and various ferrites [10,15,19–26] A majority of these reports are based on WO_3 compositions [8,10,15,19–21,22–34]

In the current work, tungstate and molybdate compositions were investigated as alternative sensing materials to the typical binary compositions for sulfur gas species at higher testing temperatures (≥600°C). Tungstates and molybdates are known to be wide band gap oxide semiconductors (3–5 eV). These compositions also demonstrate sulfur activity and present adequate stability at higher temperatures (especially compared to that of WO_3 and MoO_3). There are currently no publications focusing on these compositional families for sulfur species. As stated above, there are examples of the use of binary tungsten and molybdenum oxide

compositions for sulfur sensing. In the case of SO_2 sensing, the WO_3 composition was tested by many researchers with various morphologies as well as deposition techniques [7,10,35–42] Unfortunately, the same composition was shown to also be sensitive to O_3, NO, NO_2, NO_x, H_2, DMA, NH_3, C_2H_5OH, and O_2 species. WO_3 is a d^0 compound in its stoichiometric form [43]; therefore, it exhibits an insulator behavior. However, the non-stoichiometric forms of tungsten oxides (WO_{3-x}) show an n-type semi-conducting behavior with a band gap of 2.7 eV. Among the wide range of reducing and oxidizing agents tested, it was observed that NO_x, H_2S and SO_2 were detected with high response compared to the other gasses. In the case of the binary MoO_3 composition, it is structurally similar to that of WO_3 with similar electronic characteristics. The material is an n-type semi-conductor with a band gap of 3.2 eV, but it possesses a low melting point (795°C). The low melting temperature restricts use of this composition at high temperature. MoO_3 was first tested for sensing NH_3, CO, CH_4, NO_2 and SO_2 by Azad et al. They used the composition alone and as a composite with ZrO_2 [44–46]. The composition showed adequate response to all gasses; unfortunately, it displayed a high cross-selectivity to H_2. Imawan et al. was one of the few other researchers that investigated gas sensing properties of MoO_3 (modified with V_2O_5) for SO_2 gas, where the sputtered films showed 500 times higher response to H_2 over that of NH_3 and SO_2. Furthermore, the response to H_2 was 12 times that of SO_2 [45,46]

The ternary and quaternary tungsten and molybdenum oxides used in this work were tested initially within a resistive-type sensor platform (also termed as chemi-resistive platform) for impurity levels of SO_2 and H_2S in the range of 5–2000 ppm. As known by many researchers, the selective detection of SO_2 and H_2S in the presence of reducing gasses, such as H_2 and CO, is a formidable task, because the working mechanism of the resistive-type sensor is based primarily on surface redox (reduction-oxidation) reactions. These reducing gasses have an affinity for oxidation on oxide surfaces, which usually alters the surface defect state and carrier concentration, and thus overshadows any electrochemical reactions occurring with other interested species (such as SO_2 and H_2S in this case). The SO_2 sensing tests were initially completed for all sensing materials; the most sensitive compositions towards SO_2 were then further tested for 50–100 ppm H_2S within N_2 and coal syngas gas streams. After this evaluation process, H_2 and CO cross-selectivity tests were completed in the range of 1000–4000 ppm in order to evaluate the level of interference to the SO_2 and H_2S sensing for only the down-selected sensing materials. Within the work, multiple compositions were initially tested for comparison purposes in the micron-size range (either synthesized by solid-state method or commercially purchased). The best performing composition was then synthesized to the nano-scale by a hydrothermal route. The compositions of interest were: WO_3, MoO_3, $SrMoO_4$, $NiMoO_4$, $Sr_2MgMoO_{6-\delta}$ (SMM), $Sr_2MgWO_{6-\delta}$ (SMW), $NiWO_4$, and $SrWO_4$.

2. Experimental

2.1. Material source for initial sulfur sensing evaluation

As will be discussed in the "Results and Discussion" section, commercially available and solid-state powders (which all displayed an average particle size between 1 and 10 μm) were initially screened for their sulfur sensing capabilities using 2000 ppm SO_2 (balanced with N_2) at temperatures of 600–1000°C. The following materials were initially tested: MoO_3 (molybdenum oxide, 99.5%, Alfa Aesar), WO_3 (tungsten oxide, Alfa Aesar, 99.8%), $SrMoO_4$ (Alfa Aesar, strontium molybdenum oxide, 99.9%), $NiWO_4$ (nickel tungsten oxide, 99.9%), $SrWO_4$ (strontium tungsten oxide, 99.9%) and