Investigation of Molybdenum and Tungsten Binary and Ternary Oxides for High Temperature Detection of Environmentally Hazardous Sulfur Species

Engin Çiftyürek^a, Katarzyna Sabolsky^a and Edward M. Sabolsky^a

^a Department of Mechanical and Aerospace Engineering, West Virginia University (WVU), Morgantown, WV, 26505, USA

1. INTRODUCTION

Sulfur dioxide (SO₂) is known to a major air pollutant since it is a precursor to acid rain and acidic particulates, which are dangerous not only for human health but also a major contributor to green-house 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 SO₂ (and hydrogen sulfide, H₂S) [4, 5]. Modern desulphurization methods can eliminate 98% of the SO₂ from the emission gases by applying multiple levels of filtering, where the prime means is through passing the exhaust gas through lime. However, SO₂ emissions 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 SO₂/H₂S from these energy and industrial systems. The key factor is to develop sensors that are capable of withstanding harsh environmental conditions that exist in the 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 SO₂/H₂S, and display low cross-sensitivity towards other reducing gases, and this must be simultaneously achieved at high temperatures.

A great number of the SO₂ 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°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 (SMO) compositions to sense SO_2 . The number of these publications is limited in comparison to the sensing of other gasses using SMOs. Semi-conducting metal oxides that were investigated for SO_2 sensing include CeO_2 , WO_3 , $\text{V}_2\text{O}_5\text{-TiO}_2$, $\text{MoO}_3\text{-SnO}_2$ and NiO [10-16]. Generally, the SMOs used for SO_2 sensing were only applicable at low temperature ($<500^\circ\text{C}$) due to stability problems in the highly reducing atmospheres [8]. There are only a few instances of materials that were tested at higher temperatures ($>300^\circ\text{C}$) for sulfur species; four studies deserve to be mentioned in detail due to their unique strategies employed in order to increase the sensitivity 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 (sodium superionic conductor) membrane with a vanadium (V)-doped TiO_2 composition acting as the SO_2 sensing material [11, 12]. The sensor showed excellent sensitivity 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 sensitivity 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 sensitivity and eventually the sensitivity diminished down to only -10% at $\sim 600^\circ\text{C}$ [11]. The negative designation for the sensitivity 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 SMOs for detecting SO_2 at high temperature. Regrettably, the sensitivity diminishes as the temperature increases beyond 600°C . CeO_2 is the last example of a SMO tested and tailored for SO_2 sensor applications at high temperature within 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 $300\text{-}800^\circ\text{C}$) due to fact that physi/chemi-adsorption does not occur due to stoichiometric perfection 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 SMOs 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 $\text{Cr}_{2-y}\text{Ti}_y\text{O}_{3+x}$ sensing composition for a resistive-type sensor design [18]. The material demonstrated a p-type characteristic at elevated temperatures ($>250^\circ\text{C}$) 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 sensitivity 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 ($\geq 600^\circ\text{C}$). 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 use of 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 O₃, NO, NO₂, NO_x, H₂, DMA, NH₃, C₂H₅OH, and O₂ species. WO₃ is a d⁰ compound in a 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 metal oxide with the band gap 2.7 eV. Among those wide range of reducing and oxidizing agents tested, it was observed that NO_x, H₂S and SO₂ were detected with high sensitivity compared to the other gasses. In the case of the binary MoO₃ composition, it is structurally similar to that of WO₃ 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. MoO₃ was first tested for sensing NH₃, CO, CH₄, NO₂ and SO₂ by Azad *et al.* They used the composition alone and as a composite with ZrO₂ [44-46]. The composition showed adequate sensitivity to all gasses; unfortunately, it displayed a high cross-sensitivity to H₂. Imawan *et al.* was one of the few other researchers that investigated gas sensing properties of MoO₃ (modified with V₂O₅) for SO₂ gas, where the sputtered films were 500 times higher in sensitivity to H₂ over that of NH₃ and SO₂. Furthermore, the response to H₂ was 12 times that of SO₂ [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 SO₂ and H₂S in the range of 5 to 2000 ppm. As known by many researchers, the selective detection of SO₂ and H₂S in the presence of reducing gasses, such as H₂ 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 SO₂ and H₂S in this case). The SO₂ sensing tests were initially completed for all sensing materials; the most sensitive compositions towards SO₂ were then further tested for 50-100 ppm H₂S within N₂ and coal syngas gas streams. After this evaluation process, H₂ and CO cross-sensitivity tests were completed in the range of 1000 to 4000 ppm in order to evaluate the level of

interference to the SO₂ and H₂S 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: WO₃, MoO₃, SrMoO₄, NiMoO₄, Sr₂MgMoO_{6-δ} (SMM), Sr₂MgWO_{6-δ} (SMW), NiWO₄, and SrWO₄.

1. 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 1-10 μm) were initially screened for their sulfur sensitivity using 2000 ppm SO₂ (balanced with N₂) at temperatures of 600-1000°C. The following materials were initially tested: MoO₃ (molybdenum oxide, 99.5%, Alfa Aesar), WO₃ (tungsten oxide, Alfa Aesar, 99.8%), SrMoO₄ (Alfa Aesar, strontium molybdenum oxide, 99.9%), NiWO₄ (nickel tungsten oxide, 99.9%), SrWO₄ (strontium tungsten oxide, 99.9%) and NiMoO₄ (nickel molybdenum oxide, 99%, Alfa Aesar). The MoO₃ and WO₃ compositions were included in this work in order to provide a baseline performance and stability level to compare to the ternary and quaternary compositions tested at the higher temperatures and lower oxygen partial pressures. These conditions were not reported by other researchers in literature. For the Sr₂MgMoO_{6-δ} (SMM) and Sr₂MgWO_{6-δ} (SMW) compositions, commercial powders were not available, so a basic solid-state method was employed to synthesize the powders. The precursor materials used were SrCO₃, MgO, and MoO₃ (Alfa Aesar, 99.9% purity for each). The powders were ball-milled in ethanol and then calcined at 1000°C for 4 h in air within a high-form alumina crucible. The powder was then attrition-milled for 4 h to the specified particle size range. The material was re-fired at 1200°C for 4 h in 5 % H₂/N₂ to insure full dissolution of the residual SrMoO₄, which is typically found to remain as a second phase within the powder after the first firing [47, 48].

2.2 Synthesis of Molybdate Sensing Nanomaterials

The best performing sensor material from the initial 2000 ppm SO₂ screening tests was re-synthesized to the nano-scale using a hydrothermal method in order to increase the active sensing surface area. The best performer was the SrMoO₄ composition. The sensor testing protocol for this nanomaterial will be discussed further in the next subsection. To control the particle size and morphology of the nanomaterial, the hydrothermal solution variables were altered, such as pH, ion concentration, and the processing temperature and time. The method was based upon the previous works discussed in literature for SrMoO₄, which produced varying nano-particle morphologies [49-53]. The general procedure includes the dissolution of 1.48 g of strontium nitrate (Sr(NO₃)₂ (99.0%,) and 1.23g of ammonium molybdate (((NH₄)₆Mo₇O₂₄)·4H₂O, 99%, Alfa Aesar) into de-ionized (and de-carbonized) water in separate beakers. A clear solution was obtained after magnetic stirring the two solutions for 15 min. The pH of the final solution ranged from 4.5 to 5.5. The final product was transferred into a 300 ml PTFE lined autoclave and processed at 180°C, 120°C and 80°C for 12 and 8 h, respectively, with a 3°C heating and cooling rate in all cases. After mixing the two solutions, the final pH of the solution was adjusted to the corresponding values through the addition of ammonia hydroxide. The effect of altering the chemistry and thermal processing on the morphology and size will be further discussed in the “Results and Discussion” section. The as-synthesized SrMoO₄ powder was washed with de-ionized (and de-carbonized) water in order to remove remaining salts. The washing procedure was repeated until the conductivity (σ) of the solution measured less than 10 mS·cm⁻¹.

2.3 Sensor Fabrication and Testing Protocol

The sensor platform was composed of alumina (Al₂O₃) substrates which were fabricated by a tape-casting/lamination process. The green laminates were fired to 1400°C for 2 h, and were diamond polished to a 1 μ m finish. The platinum (Pt) interdigitized electrodes (IDEs) were screen-printed through 100 μ m mesh screen and annealed at 1200°C for stabilization. The Pt ink was made from Pt powder (Technic Engineered Powders) with average particle size of around 1 μ m. The electrodes displayed a total length of

10 mm with finger widths and finger spacing of 0.25 mm. The sensor materials were dispersed within an ink vehicle (J2M, 63/2, Johnson-Matthey, UK) and then stenciled over the IDEs. The sensing material was printed to a thickness of ~300 μm and sintered at 1200°C in order to promote the adhesion between the substrate and printed sensing material. The sensors were placed on a hotplate at 90°C for half an hour to dry and then heat treated in a box-furnace with a heating rate of 2°C·min⁻¹ to 600°C, and then 4 °C·min⁻¹ to 1200°C, and held for 1 h. A tube furnace was used as the testing chamber, where the Pt electrode wires from the sensor were connected to the sample in the center of the tube through a sealed two-bore holed alumina rod. The sensor face was placed horizontal to the testing gas flow. The testing gas composition was controlled by mass flow controllers (Sierra Instruments, MFCs) (for each gas) and the 2-point resistance signal was measured with a Keithley 2700 Multimeter/Data Acquisition System which supplied a 5-10 μA DC current to obtain the measurement. A LabView® program controlled the testing and data acquisition in order to simultaneously read gas flow rate, temperature and resistance of the sensor during testing. Parameters such as sensitivity, cross-sensitivity, and response and recovery times were characterized. There are many different ways to characterize the variation in resistance and present it as a sensor signal. As it is common in sensor literature, the normalized response (R) is defined as a change in the resistance of a SMO upon exposure to target gas. It is calculated with the formula presented in Eq. 1 for an n-type material. R represents change in resistance as a percentage, in where R_{Base} is the resistance in 1% O₂ balanced with pure N₂ and R_g is the resistance in the target gas.

$$R (\%) = \left[\left(\frac{R_g - R_{Base}}{R_{Base}} \right) \times 100 \right] \quad [\text{Eq. 1}]$$

The response time was defined by the time for the sensor to reach 90% of the total resistance variation due to the change in concentration of the target gas [54-59]. If the relative change in R is a negative value, then response will be termed in this paper as an “n-type response”. In the case that the R is a positive value, then the response will be termed as a “p-type response”. The maximum change in the normalized response (R_{max}) will be termed as the “*sensitivity*” and will be denoted as S throughout the

work. The gas exposure cycle used throughout the work are presented as insets within the figures, which includes the concentration of the target gas and time of exposure during holds at the designated temperatures. In all tests, the total flow was adjusted to 50 sccm by adjusting the flow of H₂, CO, SO₂, N₂ and O₂ via the mass flow controllers (MFCs). Three different concentration levels of target gas, balanced with nitrogen (N₂, 99.99%, Matheson Ultra High Purity grade), were tested at three different exposure times. During these tests, the sensors were heated and held at 600°C, 800°C, and 1000°C for 8.5 h, and then the sensors were cooled to room temperature under atmospheric conditions, unless otherwise indicated. In a few situations, the sensor was cooled under N₂ flow in order to conduct chemical analysis of the final sensing material. Three different ultra-high purity O₂ concentrations (1, 5 and 20%) were further tested for the selected compounds in order to understand the effect of possible oxygen partial pressure variations. Matheson research Grade 99.998% O₂ was used in this work. As seen in the inset plots for SO₂ testing, the exposure cycle increased the ppm level of SO₂ from 500 to 1000, and then to 2000 ppm, and then decreased back down to 500 ppm. Each of these gas concentrations were held for 20 min and then the pyramid was repeated with a hold time of 5 min. A final pulse of the maximum concentration was placed on the sensors for 30, 15, and 5 sec in order to test the response and recovery time. Each of these pulses was balanced with pure N₂ with 1% O₂ background during the entire isothermal hold. A 30 min holding time in the 1% O₂+N₂ mixture was placed on the sensors between each pulse in order to allow the sensors to recover before further exposure testing. As previously discussed, the sensing materials showing the highest sensitivity to SO₂ were selected and tested in the presence of 1000, 2000 and 4000 ppm for H₂ and CO. The material that showed the highest sensitivity towards SO₂ was further tested for 50-100 ppm H₂S and also tested within a coal syngas composition. The coal syngas composition selected was 32% H₂, 40% CO, 20% CO₂, 1% O₂, 1% steam (H₂O), 5% N₂ and 1% H₂S. The latter two testing practices differ from the initial SO₂ tests, and those differences will be explained in details in the related subsections [60, 61].

2.4 Sensing Material Characterization

The crystallinity of all synthesized powders were characterized by X-ray diffraction (XRD) at room temperature using a Panalytical X-Pert Pro diffractometer (PW 3040 Pro) with Cu K α radiation with a scan rate of 2° min⁻¹. Transmission electron microscope (JEM-2100 TEM) was utilized to confirm crystallinity and lattice parameter. Their morphologies were examined using a scanning electron microscope (JSM-7600F SEM). The energy dispersive spectroscopy (EDS) was completed using an Oxford INCA 350 connected to JEOL 7600F SEM. X-ray photoelectron spectroscopy (XPS PHI 5000 Versaprobe) was also conducted to further analyze the secondary phase formation and/or chemical state of the ions within the structures. The X-ray source was operated at 15 kV and 25 watts using Al K α (1486.6 eV) radiation. The powders were analyzed by a combination of 117.40 eV survey scan and 23.50 eV detailed scans of the relevant peaks. A 0.5 eV step was used for the survey scan and a 0.05 eV step for the detailed scan. Prior to spectral analysis, all coating surfaces were cleaned to remove atmospheric and post-depositional contamination with Ar ion sputter cleaning at 2 kV accelerating voltage for 30 seconds. During the measurement, the analysis chamber pressure was maintained at ($\sim 10^{-11}$ Torr). Gold (Au) was used as a reference with the binding value of 84.5 eV when possible; otherwise, carbon (C) was used as the reference at a value of 284.5 eV. In addition to this characterization, the nano-SrMoO₄ material was subjected to further UV-Vis (ultraviolet-visible spectroscopy) in order to measure the band-gap (E_g).

3. RESULTS AND DISCUSSION

3.1 Initial Screening of SO₂ Sensing of the Molybdates and Tungstates

In this subsection, the initial screen testing of the molybdate and tungstate systems will briefly be discussed. Again, the compositions tested were WO₃, MoO₃, SMM, SMW, NiMoO₄, NiWO₄, SrWO₄ and SrMoO₄, where the particles were in the micron-size range (1-10 μ m for all compositions). Fig.1 shows the comparison of the sensitivities (S) of the different sensing materials at three different temperatures against 2000 ppm of SO₂ for 20 min pulses balanced with N₂-1% O₂. WO₃ showed an n-type response towards SO₂ at 600°C with a sensitivity of -15%; however, at elevated temperatures (800°C and 1000°C), the sensitivity

decreased and eventually diminished. A chemical reduction of the oxide semiconductor was suspected to be the reason behind the decrease in sensitivity. Therefore, XPS analysis (not included) was conducted in order to clarify the final chemical state of the WO_3 after the complete sensor test. Cooling the WO_3 material post-testing in a N_2 atmosphere further clarified the final phase state by showing that the WO_3 reduced to metallic tungsten (W) during testing. The main photoelectron spectra of the W in this case showed a large portion of the surface is reduced to the metallic state, where the W metallic phase 4f peaks were observed at 31.6 and 33.7 eV with 2.1 eV spin-orbital splitting. Molybdenum trioxide (MoO_3) has previously not been studied to a large extent for gas sensing applications. As seen in Fig.1, the sensor initially showed a large p-type response, which is unusual for the n-type semiconductor MoO_3 . The sensitivity was 14% in this case. It should be noted that after the full test, it was observed that the MoO_3 sensing material was almost fully evaporated due to its high vapor pressure. The reason is not clear for the p-type response, and no literature information could be found in order to further clarify the response. However, it is well-known for WO_3 that a change in response behavior (from n-type to p-type or opposite) has occurred upon exposure to different levels of target gasses at different temperatures and oxygen partial pressures [39]. The same characteristic can also be attributed to MoO_3 in order to explain the unexpected p-type response. The $\text{Sr}_2\text{MgMoO}_6$ (SMM) and Sr_2MgWO_6 (SMW) compositions did not sense SO_2 at 600°C . The sensitivities for 2000 ppm of SO_2 were -21% and -20% at 800°C , and similarly, -20.5% and -21.5% at 1000°C for SMM and SMW, respectively. The SO_2 sensitivity of the SMM and SMW were comparable to each other. Both compositions were inaccurate at distinguishing different levels of the target gas. SMM and SMW were not further investigated due to its lack of repeatability and lower sensitivity; moreover, it showed cross-sensitivity against H_2 at 1000°C (not included). Although the performance was not optimal, the SMM and SMW showed superior high temperature sensitivity compared to binary oxides of tungsten and molybdenum due to their high temperature stability.

NiMoO_4 was the fifth material to be tested for SO_2 sensing on a resistive-type sensing platform. As can be seen from Fig.1, the material showed a p-type response with a sensitivity value of 20% at 600°C upon

the exposure to 2000 ppm SO₂; however, repeatability was very poor at this temperature. At 800°C, the sensing material experienced a large reduction event. At 1000°C, the recorded resistance value was comparable to the metallic state of Ni. Due to this complete reduction event, the material was not further subjected to the investigation and experiments were not completed. The XPS analysis proved that the tested sensor surface was composed of Ni metal and different suboxides of Ni, such as Ni₂O₃, NiO, and metallic Ni over the sensor surface which dictated the response behavior. The metallic nature of the sensor material eliminated the desired electrocatalytic reaction which allows for sensing of the target gas.

NiWO₄ was the sixth sensor composition tested for SO₂. As can be seen from Fig. 1, an n-type response was seen with a sensitivity of -5% at 600°C for 2000 ppm of SO₂. The sensing composition displayed -16% at 800°C. Interestingly, the sensitivity did not further increase above 800°C; the sensitivity decreased to -2.5% at 1000°C. At this temperature for the 2000 ppm of SO₂, the sensor output was not smooth as observed at 800°C; moreover, at 1000°C the signal was not reliable and diminished towards the end of testing. The SEM micrographs of the material after testing showed small grains coating over the larger NiWO₄ (not included). The XPS characterization of the sensor surface was again completed after SO₂ testing (and cooled down in N₂) (not included). The XPS spectra showed the presence of metallic Ni on the surface. The detailed spectra taken from the sensor showed Ni 2p_{3/2} and 2p_{1/2} doublets, in which the main photoelectron lines are positioned at 852.8 and 870.1 eV, respectively. The binding energy values agree well with chemical state values for metallic Ni at 852.7±0.1 and 869.9±0.1 eV. Also, NiO (Ni²⁺) was also identified within the material, but the amount was lower compared to metallic Ni. As in the case of NiMoO₄, the NiWO₄ structure was shown to reduce at 1000°C, even though the atmosphere was not strongly reducing. Ni migrated and subsequently agglomerated on the surface of the grains. This fact was clearly observed from the XPS data of the Ni and W. This accumulation of Ni grains on the surface was also observed by Sabolsky *et al.* [62], where the same composition was used within a solid-oxide fuel cell anode. Basically it can be summarized, NiWO₄ showed SO₂ sensitivity up to 800°C and showed a lower reduction rate compared to the WO₃ baseline composition in the same atmosphere. Above 800°C, metallic

phases were formed which drastically decreased the sensor response. The inclusion of Ni within the molybdate and tungstate compounds is a good choice for SO₂ adsorption, but it is not good for redox stability, especially beyond 800°C under an insufficient oxygen background concentration.

The SrWO₄ was the seventh composition tested for SO₂ sensitivity within the resistive-type sensor platform. The SrWO₄ composition has a scheelite structure and was recently utilized within photocatalysis processes [63]. The total sensitivity data at three different temperatures for this composition is again reported in Fig. 1. At 600°C, the sensor response was p-type upon exposure to SO₂. The SrWO₄ sensitivity toward SO₂ was 110%. At 800°C, the sensing behavior of SrWO₄ changed to an n-type response, where the sensitivity was -18%. The response also showed great variance and began to drift over time. Moreover, the sensor did not recover after removal of the SO₂ before moving to the 1000°C test temperature. The change in the sensing response mechanism has been seen before for WO₃-based sensors, but p-type to n-type (or opposite) was only reported for a change in oxygen content and/or temperature. XPS analysis of the SrWO₄ sensor after SO₂ testing (and cooled down in N₂) was also completed (not included in this work). Broad W, O and Sr peaks indicated that the SrWO₄ structure reduced during testing; however, W⁰ was not detected which is important to note. Moreover, the Sr was also found to be in two different chemical states (but both of them oxides). This occurrence may be due to the partial reduction of the SrWO₄ and the formation of WS₂, which is a p-type semiconductor. The broad XPS peak, which is supposed to be a doublet with the clear electron orbital splitting, may correspond to the presence of O in different oxidation states coordinated with the W and Sr. Even with the alternation in sensing compound chemistry, the functionality of the material survived, and no adsorbed sulfur species was detected. At 1000°C, the SrWO₄ showed repeatable and smooth responses to SO₂ characterized by an n-type behavior with a sensitivity of -20%. SrMoO₄ was the final compound tested for high temperature SO₂ sensing. Fig. 1 provides the sensitivity values of the material against 2000 ppm of SO₂ at the three different temperatures. The SrMoO₄ showed n-type sensing response at all temperatures. It showed the highest sensitivity toward SO₂ among all of the initial micron-size oxides tested, and interestingly, the sensitivities did not vary too

much for the same 2000 ppm level at the three different temperatures. The sensitivities were -31%, -38% and -28% at 600°C, 800°C and 1000°C, respectively. The response was repeatable. Due to this promising performance, the SrMoO₄ composition was synthesized by a hydrothermal process (described in the “Experimental Section”) at a finer, nano-scale for further testing. The nano-flower morphology for the nano-SrMoO₄ was tested to the 2000 ppm SO₂, similar to the previously described compositions. As shown in Fig. 1, the sensitivities of the nano-SrMoO₄ were -17.2%, -50.2%, and -40.5% at 600°C, 800°C and 1000°C, respectively. Nano-SrMoO₄ showed the highest sensitivity toward SO₂ at 800°C and 1000°C compared to all other compounds tested. Therefore, in the rest of the present work, further testing and characterization was completed on the nano-SrMoO₄ composition to better understand the sensing mechanism, as well as, the compound’s physical and chemical characteristics in the synthesized and post-mortem testing state.

3.2 Characterization of nano-SrMoO₄

In this section, the characterization results for the nano-SrMoO₄ powders fabricated by various hydrothermal routes will be presented. As discussed in subsection 2.2, the thermal conditions, pH and solids loading were all altered in order to control the morphology of the nanomaterials. Table 1 shows the conditions used for the synthesis of the nano-SrMoO₄ compositions. Fig. 2 displays the micrographs of the as-synthesized nanomaterials, where various morphologies, termed as nano-teeth, -sheet, -flowers and micro-rice throughout the paper, were fabricated. The decrease in the temperature and increase in the ion concentration affected the growth rate of the nano-particulates, and this decreased the feature size as expected [53]. As can be seen from Fig. 2-c and -d, at the same pH and higher solute concentration with lower processing time and temperature, particles with a higher anisotropic morphology were synthesized. Decreasing the hydrothermal processing temperature and doubling the anion and cation concentration lead to more isotropic growth. The morphology changed from nano-teeth to nano-sheets with symmetrical spatial growth. It should be noted that the same processing time and temperature were used, but the different pH levels caused changes in the growth mechanism and rate. The morphology of the powder

evolved from a nano-flower-like morphology (with a loosely packed anisotropic structure) to a densely packed, isotropic rice-shaped morphology. The SrMoO₄-nanoflower morphology was chosen for future sensing experiments due to its loosely packed structure with increased surface area (and thus, potential sensing efficiency). The SrMoO₄ nanoflowers will be termed as nano-SrMoO₄ within the rest of the paper.

All of the as-synthesized nano-structures for the SrMoO₄ material were subjected to XRD analysis to investigate the crystal structure of each powder. Fig. 3 displays the XRD spectra of the as-synthesized nano-SrMoO₄. All of the diffraction peaks can be indexed with the JCPDS card number 01-085-0586. The sharp and high intensity diffraction peaks of the as-synthesized nano-flower powder showed very good crystallinity with no secondary phases such as MoO₃ and/or SrO present; therefore, further calcination steps were not needed after the hydrothermal technique to form the full phase materials. The nano-sheets, nano-teeth and nano-rice morphologies also showed an excellent match between the measured and reference XRD data (not included). The XRD spectra showed that the anisotropic tetragonal structure was synthesized for all SrMoO₄ morphologies. This form of SrMoO₄ displays the scheelite structure which contains four formula units per unit cell. A unit cell contains 4 Sr²⁺ and four (MoO₄)²⁻. In the scheelite structure, Mo is surrounded by 4 O²⁻ and the Sr is surrounded by 8 O²⁻. Investigating the nano-flower morphology specifically, the XRD pattern matched well with the JCPDS 01-085-0586 data, with the lattice parameters $a=b=5.3236$ and $c=12.1230$ Å. Using the plane spacing and Bragg's law for diffraction, the lattice parameters were calculated and presented in Table 2. As compared to the position given in the JCPDS 01-085-0586, the calculated a -, b - and c -parameters of the as-synthesized nano-SrMoO₄ nanomaterial showed residual strain, which is shown by the constriction of the a - and b -lattice parameters and the expansion in the c - lattice parameter. The strain may be attributed to oxygen vacancies (V_O) in addition to charge compensation and cation/anion columbic interactions. The strain is further supported by HRTEM (High Resolution Transmission Electron Microscopy) imaging of the (112) plane of the as-synthesized powder. As seen in this micrograph, the measured d-spacing for (112) via HRTEM was 3.20 Å.

A detailed XPS analysis was also conducted in order to quantify the chemical state of the Mo and Sr in nano-SrMoO₄, in addition to the defect concentration within the structure (such as oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) and oxygen interstitials ($\text{O}_i^{\bullet}$)). Fig. 4 presents the deconvolution of the O, Sr and Mo main photoelectron lines that were used to quantify the relative amount of the different chemical states. Oxygen peaks were consistently fitted to a nearly Gaussian distribution, which assisted in assigning the relative contribution of the different chemical states of the oxygen. After deconvolution of the O 1s spectrum, three main chemical states of the oxygen were determined. Those are located at 530.34, 531.15 and 532.85 eV. The former is in a good match with the values presented in literature for lattice O^{2-} ion in SrMoO₄, while the latter corresponds to that reported for interstitial oxygen ions; the last photoelectron energy aligns with the values reported for chemisorbed oxygen (surface adsorbed oxygen) [64-70]. The corresponding full width at half maximum (FWHM) values for lattice, interstitial and adsorbed oxygen ions are 1.2, 1.9 and 1.8 eV, respectively. The broad nature of the interstitial component can be interpreted as the contribution of the oxygen deficient regions [69]. In this work, 50 at% of O^{2-} ions were located at regular lattice sites, while 37 at% of O^{2-} ions was positioned at interstitials, with the remaining 13 at% was detected as chemi/physi adsorbed.

The Mo 3d doublet consisted of two distinct chemical states, Mo^{6+} and Mo^{5+} . For Mo^{6+} , the main photoelectron lines were positioned at 233.86 and 237.01 eV. The convolution of the Mo doublets proved that the Mo^{5+} chemical state existed in the as-synthesized material and they were located at 232.64 and 235.79 eV. These measured values are in a good agreement with the literature values. The narrow feature of the Mo^{6+} and Mo^{5+} with the 1.3 and 1.2 FWHM values suggested that Mo^{4+} and other possible Mo chemical oxidation states did not exist. It was proven from the deconvolution that the as-synthesized material contained ~86.8 at% Mo^{5+} , while the remaining contained 13.2 at% Mo^{6+} . Sr^{2+} had well resolved spin-orbit components with the value of 1.76 eV for 3d_{5/2} and 3d_{3/2}, as is the usual in its stable compounds. However, in addition to the well-defined 3d doublet, the shoulder formation was observed at the high energy side, which was not possible to be fitted into another doublet; therefore, this formation could be

attributed to the low level electrostatic interaction with surface adsorbed oxygen. This discussion supports the formation of a pure SrMoO_4 phase without any secondary SrO or SrCO_3 . The relative amounts of cations were found to be 50.5% and 49.5% for Sr and Mo, respectively, which is close to the nominal stoichiometry of the as-synthesized compound.

3.3 SO_2 Sensor Testing of the nano- SrMoO_4 and Post-mortem Analysis

All four morphologies of the SrMoO_4 nanomaterials were tested using the same protocol described in the experimental section. In comparison to other morphologies of SrMoO_4 , the nano-flowers showed the highest sensitivity at all three temperatures. The time dependent normalized response curves (R) of the nano- SrMoO_4 at 600°C , 800°C and 1000°C are shown in Fig. 5(a-c). Nano- SrMoO_4 showed a regular SMO sensing behavior, where the normalized response gain was in accordance to the level of the target gas it was exposed. In this case, it can be assumed that the conduction band charge carrier concentration in the SrMoO_4 was proportional to the partial pressure of the reducing gas in the sensor environment [71-73]. Another significant point is that the nano- SrMoO_4 showed an n-type sensing response to the target gas at all concentration levels and testing temperatures. It was not observed that sensor signal output switched from n-type to p-type (or opposite), as was previously observed for WO_3 , MoO_3 and NiMoO_4 . The result revealed that nano- SrMoO_4 showed an n-type response with the sensitivity values of -6.7%, -11.8% and -17.2% upon exposure to the 20 min pulse of 500, 1000 and 2000 ppm of SO_2 at 600°C . The nano- SrMoO_4 showed a smooth and repeatable response to the 5 min pulses of SO_2 as well. At this temperature, the sensitivities for the 5 min pulses of 500, 1000, 2000 ppm of SO_2 were -6.3%, -11.6%, -17.1%, respectively. Despite the detection at the 30 s pulse for the 2000 ppm SO_2 (showing a sensitivity of -3.7%), the sensor could not detect the SO_2 at the 5 s and 15 s pulses. At 800°C , the nano- SrMoO_4 showed the highest sensitivity towards 2000 ppm SO_2 among all other oxides tested. As can be seen from Fig. 5-b, the sensor signal was smooth and a signal drift was not observed. In other words, the material recovered to its initial resistance once the target gas was removed from the testing chamber. The sensitivities were -6%, -18% and -50.2% for the 20 min exposure of 500, 1000 and 2000 ppm SO_2 at 800°C , respectively. At this

temperature, the nano-SrMoO₄ detected the 30 and 15 s exposures of 2000 ppm SO₂ with the sensitivity values of -6.6% and -3.9%, respectively. Unfortunately, the sensor could not detect the 5 s pulse. The normalized response curve of the nano-SrMoO₄ at 1000°C is presented in the Fig. 5-c. The sensor material not only demonstrated very good repeatability, but also the sensing material permitted the ability to distinguish between the different concentrations levels of the target gas. The sensitivities were -23.5%, -27.0%, and -40.1% for the 20 min pulses of 500, 1000 and 2000 ppm SO₂, respectively. The same trend was valid for the 5 min pulses. At this temperature, the sensitivity values for 30 and 15 s pulses were -15.0% and -11.3%, respectively. In this case, the sensitivities are -17.9%, -21.7%, and -26.8% for 500, 1000 and 2000 ppm SO₂, respectively. The material showed very high sensitivity and excellent repeatability (especially at 1000°C). The recorded response times for the nano-SrMoO₄ against 2000 ppm of SO₂ were 15.6, 12.0 and 13.2 min at 600°C, 800°C and 1000°C, respectively. These values were found to be lower than that measured in this work for the NiWO₄ and SrWO₄ compositions at 800°C and 1000°C. The only comparable work in literature to these results was completed by Morris *et al.* [11]. They reported a 16.5 min response time at 375°C to SO₂ with a sensitivity value of -60%.

Post-mortem assessment after SO₂ testing included SEM and XPS analysis. Fig. 6 shows the overall microstructure and tortuosity of the nano-SrMoO₄ powder after SO₂ testing, while the inset figure provides a higher magnification SEM image revealing the nature of the intergranular connection. The micrograph shows that the nanomaterial succumbed to coarsening/sintering, and the nano-features were lost. The average grain size ranged from 1 to 5 µm. XPS analysis was completed on the nano-SrMoO₄ after SO₂ testing and the measured data is presented in Fig. 7. The sensor was cooled down in N₂ atmosphere without any O₂ background in order to preserve the final chemical composition. The Mo⁴⁺ oxidation state was detected at 231.9 eV in addition to Mo⁵⁺ and Mo⁶⁺. The amount of each oxidation state was determined by deconvolution of the main Mo photoelectron position. The amount of Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺ were 38.6, 32.8 and 28.6 at%, respectively. The significant increase in Mo⁴⁺ was observed; this phase was not detected in the as-synthesized state. The increase in Mo⁴⁺ was accompanied by a decrease in Mo⁵⁺ concentration.

The increase in FWHM values also suggested that non-stoichiometric sub-oxides formed in the nano-SrMoO₄, which were not present in the as-synthesized state. No metallic state for Mo was detected. It is important to confirm the overall stability of the composition, since many of the other W- and Mo-based compositions displayed significant chemical reduction after SO₂ testing.

Although it is still debatable about the exact mechanism that dictates the sensing for semi-conducting metal oxides toward SO₂ and H₂S [54], it is widely accepted in literature that the interaction of these semi-conducting oxides and gas leads to a redox (reduction-oxidation) reaction that results in the release of electrons to the conduction band of the semiconductor. This reaction causes an increase in carrier concentration and a macroscopic decrease of the sensor resistance. The mechanism described above is valid for an n-type semi-conducting metal oxide with the grain size larger than that of the space charge layer depth [74]. This is a more holistic view of the electrical response; there is still minimal understanding of the redox reaction at the surface. The redox reaction depends upon the sulfur species adsorption, dissociation, surface diffusion, charge-transfer, and product desorption; this is to name just a few of the steps related to the sulfur species. Similar reaction steps associated with the oxygen are just as important for the sensing mechanism, especially when source of the oxygen may vary due to the atmospheric conditions. The oxygen may originate from the atmosphere, and/or surface, bulk lattice, and interstitial sites within the sensing semi-conducting metal oxide. For the testing completed in this work, it is believed that the oxygen source is of prime importance in defining the steps for the sensing mechanism. Therefore, the concentration and state of the oxygen was quantified in detail in the previous section for the as-synthesized powder. A few of the more probable reactions defining the sensing mechanism are listed in Eq. 2 through Eq. 12. The overall redox reaction(s) that define the sensing mechanism include the reduction reaction of the oxygen species followed by the transformation of oxygen ions into regular lattice and/or interstitials sites (displayed in Eq. 2-8), and the subsequent oxidation of SO₂ (and similarly for oxidation of H₂S, which will later be discussed) and release of SO₃ from the surface (displayed in Eq. 9-12).

Before discussing the interrelation of each of the reaction steps in the sensing mechanism, the oxygen reduction must first be focused upon due to the nature of the testing conditions used in this work. The reduction reactions are believed to be of prime importance due to the high temperature and low oxygen content used in the current study (and related to the potential application discussed in the “introduction section”). The oxygen source described in Eq. 2-8 may originate from surface ($O_{2(ads)}^-$, $O_{(ads)}^-$), bulk lattice (O_o^{2-}) and interstitial (O_i^{2-} , O_i^-) sites within the nano-SrMoO₄. It is important to note that the functionality of typical low and room temperature semi-conducting metal oxide-based resistive-type sensors are highly dependent on the high concentration of adsorbed oxygen surface species, and the ability of regeneration of these species (and associated defect states) after steady state operation is achieved (or alteration of the reactant concentration). This dependence is drastically altered in the current work at high temperature, where the concentration of adsorbed oxygen would be insignificant. Hirschwald *et al.* indicated that the $O_{2(ads)}^-$ to $O_{(ads)}^-$ transformation occurs at about 200°C, and desorption of the latter occurs beyond 250°C [73-77]. Based on this fact, the functionality of the semi-conducting metal oxides theoretically should be terminated beyond 300°C; therefore, the number of semi-conducting oxide sensors discussed in literature that function beyond that temperature are limited. Many of the semi-conducting oxide sensors described in literature lose sensitivity due to the desorption of the chemi/physi adsorbed oxygen along with reduction of the sensing material at elevated temperature. Thus, for the functionality of the given nano-SrMoO₄ sensing material used at high temperature, oxygen diffusion from lattice and interstitial sites are required for the redox reaction. It is known that scheelite oxides have the ability to include high concentrations of stable

interstitial oxygen ions within its structure , and previous research has shown that this leads to a compensating mechanism to enhance structural stability under low oxygen partial pressure environments at high temperature [78, 81] [82].

In the current work, the concentration of $V_{\text{O}}^{\bullet\bullet}$ and O_i as well as Mo^{5+} and Mo^{6+} were calculated by means of deconvolution of corresponding photoelectron positions and this data is presented in the Fig. 4(for the as-synthesized sensing material) and Fig. 7(for the post-testing sensing material). From this data (and the previous discussion), it has been shown that the nano- SrMoO_4 defect structure contains both a high concentration of $V_{\text{O}}^{\bullet\bullet}$ and O_i , which assist in the overall redox reaction at elevated temperatures. This is especially important since the adsorption of O_2 to the stoichiometric oxide surface would be very difficult compared to the non-stoichiometric counterpart [17]. The oxygen vacancies play a very important role as oxygen sinks for atmospheric oxygen (expressed as Eq. 2-8) to replenish oxygen surface sites in order to retain the oxidation reactions (Eq. 9-12). The atmospheric oxygen may also be transferred into the interstitial and regular lattice sites (Eq. 5-8) within the structure to sustain the oxygen reaction (where the scheelite nano- SrMoO_4 was shown to have a percentage of interstitial oxygen as characterized by the XPS data). It has been shown that these oxygen vacancies not only facilitate adsorption of molecular oxygen, but also SO_2 gas at high temperature. This aspect is important since thermal desorption of the SO_2 from metal oxide surfaces has been shown to increase at temperatures $>500^\circ\text{C}$ and most oxide surfaces are typically free of O^{2-} and SO_2 by 1000°C [18, 83, 84].

The redox reaction is initiated with the SO_2 interaction with the surface. As discussed above, it is assumed that the nano- SrMoO_4 surface vacancy sites assist in trapping the sulfur species. Again, the O^- and O^{2-} is supplied to the surface reaction sites, as described above, where the SO_2 (and similarly for H_2S) undergo an oxidation process as described by Eq. 9-12. The release of the electrons (e^-) to the impurity level conduction band leads to the subsequent decrease in resistance. The sites that are exposed to SO_2 do not form any compound with the cations, and thus, the possibility of further oxidation of SO_3 to SO_4^{2-} may

be ruled out. It is assumed that the final product (SO_3) is released from the surface immediately at these testing temperatures, in accordance with that discussed in previous literature and the post-mortem XPS analysis completed in this work [18, 71, 73, 83-87]. It may be noticed in Fig. 5 that all the responses show a quick change in resistance followed by a slower exponential decrease in the response to the equilibrium level, which is representative of a diffusion-controlled process. These two distinct responses indicate that the overall SO_2 oxidation reactions (Eq. 9-10) are limited at the surface by the availability of the surface oxygen. The initial rapid response represents the reaction of the sulfur species with the available surface oxygen (such as the interstitial oxygen ions), and the second slower portion of the response is aligned with the change in kinetic rate due to the diffusion of oxygen to the surface reaction sites from the bulk and/or interstitial pathways within the scheelite structure. This diffusional limitation can be boldly seen in the difference in final response for the 5 and 20 min exposure times, where the diffusional time is too short for full oxygen diffusion from the bulk and interstitial pathways to complete the full oxidation of the surface sulfur species concentration. Therefore, the sensor response for the 5 min exposure never reaches full signal saturation due to the diffusional limitation.

3.5 Electrical Characterization of micro- and nano- SrMoO_4 Sensing Materials

As shown in this work, the nano- SrMoO_4 showed a high sensitivity to SO_2 , and this performance was quite repeatable. Interestingly, the sensing performance was even higher than that of its micron-size SrMoO_4 counterpart. The micron- and nano- SrMoO_4 shared the same nominal stoichiometry, and after testing at high temperature, the grain size/morphology of the nano- SrMoO_4 was similar to that of its micron-size counterpart. In order to provide a better understanding of the difference in sensing characteristics between the micron- and nano- SrMoO_4 , the band gap and electrical resistivity (as a function of temperature) of each material was further measured and compared. The electronic contribution for the n-type sensor mechanism was studied using UV-Vis on the SrMoO_4 materials. The formula proposed by Wood *et al.* [88] was used to estimate the bandgap of the nano- SrMoO_4 (and micron-size SrMoO_4 as a baseline) by extrapolating the linear portion of the UV-Vis curve. The UV-Vis absorption spectrum of the

nano-SrMoO₄ is presented in Fig. 8. The measured values for the band-gap were 3.7 and 3.9 eV for the nano-SrMoO₄ and micron-SrMoO₄, respectively. The band-gap value for the nano-sized powder is a good match with literature [52, 89-91]. The decrease in the bandgap value can be attributed to the oxygen deficiency in the nano-SrMoO₄ as compared to the micron-size counterpart. The absorption spectrum of nano-SrMoO₄ displays the typical behavior for a wide bandgap semiconductor; however, it also should be noted that the distortion, which was not observed for micron-SrMoO₄ in the curvature of the higher energy section, is due to the Mo⁵⁺ defect states that create a continuous adsorption instead of a smooth cut-off.

The total electronic resistance in the SrMoO₄ is assumed to be governed by the resistivity of the bulk grain core and the grain boundary region (which includes the grain boundary Schottky barrier and double-layers near the grain boundaries). In this case, the large grains are thought to be separated by grain boundaries with a large neck formation. Therefore, the intergrain electrical conduction would be governed by bulk trap limitations, while the absolute sensor resistance would be governed by the grain boundaries. The average grain size of nano-SrMoO₄, which is in the micron range (as can be seen in Fig. 6) is larger than that of the electron depletion layer which is in the range of a nanometer. Due to the coarsened grain structure of the nano-SrMoO₄ at the temperature of interest, the conductance is assumed to be primarily limited by the Schottky barrier electronic conductance [74]. The magnitude of the Schottky barrier (E_A) can be estimated from the formula presented in Eq. 13.

$$G = P\sigma_0 e^{\frac{-(E_A)}{2k_B T}} \Rightarrow R = G^{-1} \Rightarrow R \propto e^{\frac{(E_A)}{2k_B T}} \quad \text{Eq. 13}$$

The formula presented by Schierbaum *et al.* extended from conductance (G) to resistance (R), where a linear fit was applied to represent the temperature dependence of resistance [74]. Fig. 9 shows the natural logarithm of the resistance data based on data acquisition for every other second versus $(k_B T)^{-1}$ for nano- and micro-SrMoO₄. The resistances of both porous SrMoO₄ materials were measured in air on the same sensor platform; a current of 5-10 μ A DC current was applied to measure the resistance. Again, the plot shows the logarithmic fit of the actual data. By taking the slope of the $\ln(R)$ vs $(k_B T)^{-1}$ plot, it was possible

to quantify the E_A values for both materials. In Eq.13, the E_A represents the energy to form and move the charge carrier (e^-) through the Schottky barriers and grain boundary resistance, T represents absolute temperature, and k_B is the Boltzmann constant, while P and σ are the proportionality constant and bulk conductivity, respectively. The E_A values calculated for nano-SrMoO₄ and micro-SrMoO₄ were 1.63 and 1.98 eV, respectively. Both values are higher than the values previously reported in the literature [92]. In this work, it is assumed that the Schottky barrier was formed due to the existence of interstitial oxygen ions and the trapping of electrons from the conduction band [93]. Nano-SrMoO₄ undergoes significant coarsening/sintering starting at ~600°C; it may be assumed that the grain size (or number of grain boundaries) did not significantly influence the sensing performance difference between the micro- and nano-SrMoO₄. The nano-SrMoO₄ exhibited the lower band-gap and E_A in comparison to the micro-SrMoO₄ material. In addition, there was a slight difference in stoichiometry between the powders, where the micron-SrMoO₄ showed a slight residual SrO phase which may have influenced the grain boundary state (and thus resistance).

3.4 SO₂ Sensor Testing of nano-SrMoO₄ at Various Oxygen Levels

Nano-SrMoO₄ was tested for SO₂ at 1000°C with the same testing protocol used throughout the current work at three different O₂ concentrations (1, 5 and 20%). These experiments were completed in order to resolve the possible effect of fluctuations in oxygen partial pressure on the sensing mechanism under targeted operation environments (such as in the more highly oxygen-deficient areas within coal-fired power plants and gasifiers). It was concluded from the results (not included) that a change in the oxygen concentration from 1% to 5% did not affect the sensitivity (S) more than 2%; however, a further increase from 1% to 20% in O₂ concentration resulted in a 7.5% change in sensitivity at the same temperature. The relatively low effect of oxygen partial pressure on the sensor signal is important to note. The possible fluctuations in the oxygen concentration could alter the oxygen vacancy concentration, which would alter the sensing mechanism significantly. Further surface chemistry studies will be required to better understand

the compensating mechanism for the altering localized oxygen concentration, and how this effects (or in this case, limits the effect) of the surface oxygen vacancy concentration.

3.5 H₂S Sensor Testing of the nano-SrMoO₄

As previously discussed, semi-conducting metal oxide sensors for hydrogen sulfide (H₂S) detection have received much more attention than that for SO₂ sensing. The main focus of these works related to safety sensors for low temperature (<500°C) applications. The human threshold exposure limit for H₂S is 10 ppm, with concentrations above 250 ppm H₂S causing instantaneous death [19]. As discussed above, the nano-SrMoO₄ showed high sensitivity toward SO₂; the same sensors were tested against H₂S. The following testing approach was employed, which was slightly altered from the protocol used for SO₂ testing. This change was completed to better understand the sensing mechanism and to evaluate the sensor material under practical service environment, as well as, for potential use in fuel cell applications. The sensors were heated to 800°C at 5°C/min in pure N₂ and then held at 800°C overnight without any oxygen background with data collection over the entire time. The total flow of all gases into the testing chamber was set at 100 sccm. The H₂S exposure was completed within a fuel gas blend containing 200 ppm of H₂S and balanced with H₂. The sensing material was tested for 5, 50 and 100 ppm of H₂S. A 1% O₂ content was maintained during the H₂S exposure, as was the case for the SO₂ testing. Fig. 10 shows the time dependent normalized response (*R*) of the nano-SrMoO₄ against H₂S at 1000°C. The Nano-SrMoO₄ showed a highly reliable sensor response toward H₂S under the exposure of H₂. The compound showed an n-type sensing response to the target gas at all concentration levels and testing temperatures. The response at 800°C (not included) showed a difference between the exposure to 5, 50 and 100 ppm concentration levels of the target gas. Moreover, the difference in the gain of the normalized response increased at 1000°C. The material detected 5 ppm of H₂S with a sensitivity value of -5%. For the 20 min pulses for 50 and 100 ppm of H₂S, the sensitivity values were -65% and -95%, respectively. The nano-SrMoO₄ showed a similar normalized response characteristic for 5 min pulses with a decrease in sensitivity. The high sensitivity and accurate results were obtained from the nano-SrMoO₄ for the low H₂S impurities in H₂ gas.

Fig.11 displays the XPS analysis of the nano-SrMoO₄ sensor after H₂S testing. Fig. 11 also includes the XPS spectrum of the nano-SrMoO₄ as-synthesized and post-testing in SO₂ for comparison purposes. The sensor was cooled down in N₂ without any oxygen background in order to preserve the final chemical state after testing. The Mo main peak positions and shapes suggested that there was a reduction of Mo⁶⁺ to Mo⁵⁺ and Mo⁴⁺; however, metallic Mo was not detected. There was no shift in core peak positions for Mo⁴⁺ and Mo⁵⁺, but there was a 0.4 eV shift towards the low binding energy position observed for Mo⁶⁺. The further broadening of the Mo⁴⁺ and Mo⁵⁺ peaks (exhibited by an increase in the FWHM values) suggests that additional suboxides were formed as was the seen in the SO₂ testing. The relative measured concentration of Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺ was 38.8, 48.5 and 14.2 at%, respectively. The relative amount of Mo⁴⁺ remained constant; however there was a further reduction in the quantity of Mo⁶⁺, which accompanied by an increase in the amount of Mo⁵⁺. During the 20 min exposure to 100 ppm H₂S, the measured low resistance value suggested that the composition was reduced to the metallic state which governed the electrical conductance [94-96]. It should be noted that the reduction of the scheelite SrMoO₄ to a perovskite SrMoO₃ has been reported by other researchers; therefore, we postulate that at 1000°C under the reducing atmosphere, the scheelite nano-SrMoO₄ partially reduced to the perovskite SrMoO₃. The suggested reduction was proven by the detection of the Mo⁴⁺, which corresponds to the oxidation state of the Mo in SrMoO₃. Interestingly, as soon as the H₂S/H₂ gas mixture was removed from the testing environment, the nano-SrMoO₄ recovered to its initial resistance value (indicating a reversible transformation) under 1% O₂ balanced with N₂ in 20 min. The 5 min pulses were also detected with full precision and sensitivity by the nano-SrMoO₄. Different researchers indicated that SrMoO₄ could be reduced under high partial pressure of H₂ at temperatures as high as 1200°C with oxygen background as low as (log P(O₂)=-12.45). In these works, the SrMoO₃ phase was found to be not stable and highly prone to oxidize back to SrMoO₄. The oxidation starts around 200°C [94-97].

3.6 H₂S Testing of the nano-SrMoO₄ in Coal Syngas

The high sensitivity and accurate results obtained from the nano-SrMoO₄ for H₂S prompted further testing in other operational conditions, such as the testing within coal syngas for sulfur impurities. The coal syngas simulant used in this test was composed of 32% H₂, 40% CO, 20% CO₂, 1% O₂, 1% steam (H₂O) and 5% N₂ with different levels of H₂S at 800 and 1000°C for 5 and 20 min pulses. The time dependent sensor response for the syngas composition is presented in the Fig. 12-a and -b for 800 and 1000°C, respectively. During steady state exposure to the above-mentioned syngas composition, 4, 34 and 68 ppm of H₂S was introduced into the testing chamber. The nano-SrMoO₄ unexpectedly showed a p-type sensing behavior. This is the first time nano-SrMoO₄ showed n/p-type switch. The calculated sensitivities were up to 52% and 63% upon exposure to 64 ppm of H₂S for 20 min at 800°C and 1000°C, respectively. The sensor detected 4 ppm H₂S at 800°C, as well as, at 1000°C for the 5 min and 20 min pulses. In addition to the 20 min exposure, the compound managed to distinguish between the 4, 34 and 68 ppm H₂S concentrations in the syngas flow for the 5 min exposure time at both 800°C and 1000°C. The sensitivity was reduced from 63% to 45% as the exposure time was changed from 20 min to 5 min at 1000°C.

At this time, it is not possible to provide an explanation for this response switch in sensing behavior; however, it may be related to the complexity imposed by the CO and steam in addition to continuous presence of H₂ in the testing chamber. As previously discussed, a p-type and n-type switch has been shown for various tungstate and molybdate compositions for certain temperature changes and reducing gas exposures. The bulk of the literature related to this anomaly was shown for the WO₃ composition. Shimizu *et al.* observed the temperature dependent n/p-type switch upon exposure to SO₂; however, the authors did not elaborate over the mechanism [39]. Fruhberger *et al.* indicated that the sensing mechanism was totally dependent on the H₂S and lattice oxygen interaction, and the subsequent desorption of the product (SO₂). The work did not include a discussion on the chemical reaction between the surface adsorbed oxygen (interstitials as well) and H₂S. Barret *et al.* also reported the same characteristics for very

low H₂S partial pressures [98, 99, 100, 27, 101]. Further work is planned to further investigate this change in response behavior.

3.7 Cross-sensitivity testing of nano-SrMoO₄ to H₂ and CO

Nano-SrMoO₄ showed sensing to both SO₂ and H₂S at the ppm level (1% O₂) at $\geq 600^{\circ}\text{C}$. The altered sensing response of the nano-SrMoO₄ within the coal syngas simulant instigated further study of H₂ and CO sensing. The cross-sensitivity tests towards H₂ and CO were completed in accordance with the testing procedure described previously for SO₂. The sensitivity results for a 20 min exposure to 4000 ppm of H₂ and CO balanced with N₂ (with 1% O₂) at 600, 800 and 1000°C are presented in Fig. 13. It should be noted that the concentration levels were doubled for CO and H₂ in comparison to SO₂ (where these tests were conducted for ≤ 2000 ppm level). As seen in the sensitivity graph, the material showed the typical n-type response. In addition, the sensitivity was very low towards H₂. The sensitivity to the 4000 ppm H₂ was approximately -10% and -5% at 800 and 1000°C, respectively. This level of sensitivity is far below the SO₂ sensitivity at the same temperature; this may indicate that cross-sensitivity issues may not be a significant issue. The sensitivity against CO at 1000°C was -2.5%, which was half of the sensitivity against H₂ at the same temperature. The sensor showed no sensitivity to CO at 600°C. At 800°C and 1000°C, the nano-SrMoO₄ sensitivity for SO₂ was 50 and 16 times higher than that of CO. The sensitivity values for the 20 min exposure of 2000 ppm of SO₂ are presented for comparison purposes.

4. CONCLUSION

An array of micron-size tungstate and molybdate compositions were initially screened for SO₂ sensitivity on a chemi-resistive platform at 600-1000°C. For many of these compositions, the testing performance presented in this work was the first time it has been reported in literature. Most of the compositions showed intermittent response to the 2000 ppm SO₂ (N₂ balanced) exposure at 600-800°C, but then the compositions reduced to various sub-oxide or metallic states as the temperature was increased. After the initial screening, the SrMoO₄ composition showed the highest sensitivity and stability within the

entire temperature range. The SrMoO_4 composition was then synthesized to the nanoscale using a hydrothermal method; depending upon the hydrothermal processing conditions, pH and precursor concentration, various morphologies of the composition were synthesized. In the end, a nano-flower SrMoO_4 particle morphology was chosen for further SO_2 and H_2S testing and characterization (which included chemical, microstructural, and electrical measurements). The nano-flower SrMoO_4 (termed nano- SrMoO_4 throughout the paper) showed high sensitivity for the 500-2000 ppm SO_2 exposure (over the same high-temperature testing range), and the sensing response was found to be very reliable and repeatable. The promising response for this material remained consistent regardless of the change in morphology due to coarsening and sintering over the testing protocol. The nano- SrMoO_4 was further tested up to 100 ppm of H_2S diluted in H_2 , as well as, in a coal syngas composition. The material again showed very promising sensing capabilities and low cross-sensitivity under the extremely reducing atmosphere and high temperatures. The stable response characteristics were attributed to the high concentration of oxygen vacancies and oxygen interstitials, which were characterized by XPS. The presence of these two defect states were presented as possible structural characteristics that helped maintain sulfur specie adsorption and oxidation at the elevated temperatures. This was further supported by the difference in response kinetics between the micron- SrMoO_4 and nano- SrMoO_4 , where the final microstructure of each were similar after testing. The sensing performance of the nano- SrMoO_4 was still enhanced over that of its micron counterpart, where the defect characteristics were shown to be the main difference in the final sensing state. Further work is planned to alter the micron-size SrMoO_4 stoichiometry to produce similar defect states as the nano- SrMoO_4 in order to better correlate the influence. In addition, further work is required to better understand the change in the sensing mechanism (n/p-type switch) for the SrMoO_4 when testing H_2S at various O_2 concentrations.

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Figure 1

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Table 1: Process parameters for hydrothermal synthesis of nano-SrMoO₄ with different morphologies.

Morphology	Processing Time (h) and Temperature (C°)	Precursor ion concentration (M)		pH
		Anion (MO ₄ ²⁻)	Cation (Sr ²⁺)	
Nano-teeth	12 & 180	0.0134	0.0934	8
Nano-sheet	12 & 120	0.025	0.175	8
Nano-flowers	8 & 80	0.05	0.35	8
Micro-rice	8 & 80	0.05	0.35	10

Table 2 : Comparison of calculated cell parameters and reference data (01-085-0586).

In this study	In JCPDS no. 00-085-0586
Crystal system: Tetragonal unit cell, a=b≠c, α=β=γ=90°, Space group: I41/a, Space Group number: 88, Scheelite	
(112) plane at 27.892°, d ₍₁₁₂₎ = 3.1988 Å	(112) plane at 27.667°, d ₍₁₁₂₎ = 3.2205 Å
(204) plane at 45.302°, d ₍₂₀₄₎ = 2.0008 Å	(204) plane at 45.134°, d ₍₂₀₄₎ = 2.0072 Å
(004) plane at 29.907°, d ₍₀₀₄₎ = 2.9989 Å	(004) plane at 29.706°, d ₍₀₀₄₎ = 3.0050 Å
a=b=5.3236 Å, c= 12.123 Å, a/c= 0.4391, c/a=2.2774	a=b=5.3944 Å, c= 12.020, a/c= 0.4487, c/a=2.2286
Crystalline Size with Scherrer formula: 35 nm	NA