Ag$_6$Mo$_{10}$O$_{33}$ – A New Silver Ion Conducting Ammonia Sensor Material

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Abstract. Electrical and gas sensing properties of Ag$_6$Mo$_{10}$O$_{33}$ are investigated for the first time. Wagner’s polarization experiment carried out on this material shows that it is a good silver ion conductor in the temperature range of 533 to 657 K. Studies show that it possesses good selectivity and sensitivity towards ammonia with fast response and retrace times indicating its potential as a sensor material for this gas below its TLV value. Morphological changes associated with this compound when exposed to ammonia are studied by using SEM and the corresponding compositional changes associated with each grain is studied by using EDAX. The results indicate that the compound breaks down when exposed to ammonia. When equilibrated with air the reaction products recombine fast to form the original compound.

1. Introduction
Molybdenum trioxide has been well known for its application as catalyst in oxidation of hydrocarbons and reduction of NO$_x$ [1,2]. The sensor properties of MoO$_3$ has been studied by various authors [3-5]. Efforts also have been made in author’s laboratory to examine the sensor properties of MoO$_3$ [6,7]. MoO$_3$ has shown cross sensitivities to LPG and H$_2$ while operating them above 548 K and the sensitivity values obtained for 500 ppm of ammonia at this temperature was low [6]. Our studies also pointed out the need to enhance the sensitivity to enable detection of ammonia at TLV (threshold limit values) levels. We have undertaken two different approaches in order to enhance the selectivity and sensitivity of MoO$_3$ towards ammonia. In the first approach, thin film sensors of this compound were made using pulsed laser deposition (PLD) technique, which yielded selectivity towards ammonia in presence of hydrogen and LPG [7]. In the second approach, additives such as TiO$_2$, V$_2$O$_5$, Ag, etc. are added to MoO$_3$ in a variety of concentration ranges to improve the sensor properties. In this paper, the results obtained when silver is added to MoO$_3$ are discussed in detail.

2. Experimental Details
Molybdenum trioxide was prepared by heating ammonium heptamolybdate tetrahydrate at 673 K for 30 h in air. Complete decomposition of ammonium heptamolybdate to MoO$_3$ under these conditions was previously confirmed by thermogravimetric and differential thermal analysis (model STA 1500, Rheometric Scientific, UK). MoO$_3$ prepared was mixed with three different concentrations of silver powder (99.9 %) viz. 10, 20 and 31.02 wt.% under acetone and pelletised. The compacted pellets were heated in air at 773 K for 24 h with intermittent grinding and recompaction. The final products were analyzed by X-ray powder diffraction (D 500 model of M/s Siemens, Germany) using Cu Kα radiation. With a view to identify any phase transitions in the sample with 31.02 wt.% of silver in MoO$_3$, differential scanning calorimetric experiments (821E700 model of M/s Mettler Toledo, USA) were carried out in static air up to
773 K with a sample size of ~ 50 mg. Electrical conductivity of the sample with 31.02 wt.% of silver was measured by impedance spectroscopy. Samples for this measurement were made in the form of pellets of 10 mm diameter and 2 - 3 mm thickness prepared by compacting the powders with addition of polyvinyl alcohol as binder followed by sintering at 773 K for 5 h. The densities of the pellets were measured by Pycnometry before the measurements. During the electrical conductivity measurements the pellet was mounted between two spring-loaded platinum foils of identical dimensions placed inside a quartz chamber which in turn was heated by a furnace. Conductivity in air (~ 50 % relative humidity) was determined in the temperature range of 300 – 773 K using a frequency response analyser (Model SI 1255 of Solartron, M/s Schlumberger, UK) coupled with an electrochemical interface (Model 1286 of Solartron, M/s Schlumberger, UK) in the frequency range of 1 Hz - 1 MHz. Transport number of silver ion in the sample with 31.02 wt.% Ag was also determined using Wagner’s polarization technique [8] in the temperature range of 533 – 683 K. For this purpose a cell with following configuration was constructed and used:

\[
\text{Pt} | \text{AgI} | 31.02 \text{ wt.\% Ag} - 68.98 \text{ wt.\% MoO}_3 | \text{Pt} \quad (1)
\]

Typically between 100 and 150 mV was applied across the sample using a source meter, (model SMU 236 of M/s Keithley Instruments, USA) and the current was measured as a function of time. The initial current \(I_o\), i.e. the total current contributed by ionic and electronic species and the current at the infinite time \(I_\infty\), i.e. current due to the electronic species alone were obtained from these experiments. The transport number due to the ionic species was deduced from the equation given below:

\[
t_{\text{ion}} = \frac{(I_\infty - I_o)}{I_o} \quad (2)
\]

For sensor studies, a pellet sample was sandwiched between two platinum electrodes and housed in a glass test chamber. Sensor was heated by a resistance furnace and the temperature was controlled to ± 1 K at a chosen temperature. Resistance of the sensor was measured using an electrometer (Model 616, M/s Keithley Instruments, USA). At each temperature, the sensor was equilibrated till a steady baseline resistance in air was observed. In order to optimize the suitable temperature for sensor operation, tests were carried out for 500 ppm \(\text{NH}_3\) in the temperature range of 498 – 628 K as per the detailed procedure given in reference [9]. Appropriate amount of the analyte gas was injected into the test chamber of known volume through an injection port and the resistance was measured as a function of time till a steady final resistance was reached. The chamber was then purged with air for about 2 minutes, and then allowed to reach the initial resistance value before the next experiment was carried out. The sensitivity for a given concentration of analyte gas was calculated as follows:

\[
\% \text{ Sensitivity} = \frac{(R_s - R_g)}{R_s} \times 100 \quad (3)
\]

where \(R_s\) = resistance of the sensor in air and \(R_g\) = resistance of the sensor in containing the analyte gas. Cross-sensitivity studies were carried out for 500 ppm each of \(\text{H}_2\) and LPG. Minimum three tests were made using each of these gases at all sensor operating temperatures. This cycle of testing which lasted for ca. 24 h was followed by two more cycles to check the reproducibility and stability of the sensors. Sensitivity for a given concentration of an analyte gas was calculated by taking the arithmetic mean of the values (which were with in ± 5 %) obtained from individual tests made at each temperature in these cycles. In order to check the reproducibility of the data, experiments were repeated with two to three pellets. These experiments were carried out with pellets of samples having 10, 20 and 31.02 wt.% Ag in \(\text{MoO}_3\). Sensitivities of the pellet samples with 31.02 wt.% Ag were also measured for different concentrations of \(\text{NH}_3\) (10 to 500 ppm) at operating temperatures of 598, 623 and 673 K.

Probable sensing mechanism exhibited by the silver incorporated compositions was also elucidated. For this purpose detailed experiments were carried out and the results obtained from these studies are presented elsewhere [10]. The results concerning the morphological changes of the sample with 31.02 wt.% Ag in \(\text{MoO}_3\) on its exposure to ammonia are presented here. These experiments were carried out by heating a chamber containing the pellet of this sample sandwiched between two spring-loaded platinum electrodes to 673 K and injecting about 6.66 % of ammonia gas into the chamber and equilibrated it for 2 minutes. The chamber was then allowed to cool at the rate of 10 – 15 °C/min to room temperature under the same ambient. Morphologies of the samples before and after exposure to ammonia were investigated by scanning electron microscopy (Philips Scanning Electron Microscope, model No. XL 30). Morphological changes exhibited by grains were subsequently investigated for possible variation in composition by energy dispersive analysis of X-rays (EDAX -