Studies on Copper Molybdate as Humidity Sensor

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Abstract : Monitoring and controlling environmental humidity is receiving wider attention mainly for physical comfort and for industrial processes. In this attempt copper molybdate is used as humidity sensor. It is synthesized by solution method. Using electronic sensor kit output voltages are measured for different output voltages are measured for different percentage of humidity. Standardization of the electronic sensor kit is done using known values of Rh. Resistive sensors measure the change of humidity. At low Rh levels the electronic conduction based on the electron donation from water molecule is the dominant mechanism. At medium Rh levels both electronic and ionic conduction are responsible with the dominant transition from electronic to ionic conduction mechanism. At high Rh levels ionic conduction based on proton hopping between water molecules is the dominant mechanism. Copper molybdate behaves as a good humidity sensor at all levels and the results of this compound as humidity sensor are presented and discussed in this paper.
Key words: Humidity sensor, Copper molybdate, Rh levels ionic conduction

Introduction

Humidity measurement is one of the most significant issues in various areas of applications such as agriculture, climatology. In recent years improvements in sensor manufacturing technologies have taken place in high-speed, low-power and low-cost microelectronic hybrid circuits [1–4], modern signal conditioning methods [5,6] and advances in miniaturization technologies [7–11]. Utilization in intelligent systems and networks as monitoring sensors to determine the soil moisture during irrigation in agriculture, or for diagnosis of corrosion and erosion in advanced batteries, like lithium batteries, are among the applications of humidity sensors [12]. Nanocomposites incorporating ceramics, ceramics/polymers and polymers/carbon nanotubes with nanoporous, nanofiber and nanowire forms are amongst the most promising materials for future applications.

Monitoring and controlling environmental humidity is receiving ever-wider attention mainly for physical comfort and for industrial processes [13]. The trend towards using automated control systems had recently gained importance in environmental control because of the declining cost of interface circuits and microprocessors, and their improved reliability and extensive applications [14]. For this purpose, humidity sensors making use of electrical parameters are preferable [15]. Particularly in recent years, the use of humidity control in production processes and products in a wide range of industries, like manufacturing electronic devices, precision instruments, textiles and processed food has gained momentum [16]. Further, in many domestic applications humidity sensors are used to maintain a comfortable humidity level [17]. Sometimes it is necessary to monitor the absolute humidity, or the dew point, but more often it is important to control the relative humidity (RH). The application of humidity sensors are presented in figure 1. The choice of the material was made on the basis of their humidity, temperature, low hysteresis and stability with respect to ageing and thermal cycling.

The materials used in humidity sensors exploiting variations of electrical parameters were roughly classified into three groups: electrolytes, organic polymers and ceramics [18]. The electrolyte-based humidity sensors employing LiCl, developed by Dunmore *et. al.* was used for over 40 years, which was the only electrical device then available for moisture sensing. However, this sensor showed rather low response time, and was unable to function in highly humid environment as well as those bearing ammonia or organic vapours. Other materials were thus studied for use in those environments where LiCl-sensor was not suitable [19]. At present the materials used in commercially developed humidity sensors are mainly organic polymer films and porous ceramics. However, all the available materials show some limitations Polymer films could not operate at higher temperature/humidity besides exhibiting hysteresis, slow response time, long-term drift, and degradation upon exposure either to solvent vapor or to electrical shocks. They also required independent temperature compensation. Nevertheless, recent developments in research on this subject have resulted in notable improvement in this characteristic [20, 21]. Amongst these, polymeric capacitive sensors had proved to be moderate commercial success [22].

The ceramic metal oxides had shown advantages in terms of their mechanical strength, resistance towards chemical attack and thermal as well as physical stability. Ceramic materials studied for use in humidity sensing were mainly porous sintered bodies, resulting from traditional ceramic processing methods in order to facilitate water vapour transpiration through their pores and capillary condensation in the grain interfaces. Quite a few ceramic materials in general possess a unique structure consisting of grains, grain boundaries, surfaces and pores, which make them amenable for chemical sensing [23]. The processing techniques had paved way to modify the stages of ceramic production such that the desired microstructure of the compacts could be tailor-made. The modification of the microstructure and the chemical composition of the ceramic materials permit both performance optimizations exploiting electrical properties) and catering to specific requirements [24]. The humidity sensing ceramics had to be heat cleaned to ensure reversibility. The prolonged exposure to humid environments lead to the gradual formation of stable chemisorbed OH^- on the surface, causing a progressive drift in the resistance of the ceramic humidity sensor.

The hydroxyl ions were removed by heating to temperatures higher than 673K [17]. Moreover, humidity sensors were usually exposed to atmospheres that contained a number of physical impurities, which destroyed the reversibility of the sensor material. These impurities get adsorbed like water molecules and are removed through heat cleaning. Various humidity-sensing mechanisms and operating principles had been identified for ceramics. Most of the currently used sensors were based on porous sintered bodies of ionic type humidity-sensitive ceramics [25]. Among the other sensors, the ones based on the solid-electrolyte type, employ the hetero-contacts between p- and n-type semi conducting oxides [26, 27].

Materials and Methods

All the reagents employed for the syntheses were of pure grade and in most cases the following chemicals are used:

Copper Sulphate (CuSO4), Copper Oxide (CuO), Ammonium Molybtate, acetone, Potassium acetate (CH3COOK), , Sodium Nitrite (NaNO$_2$), Barium Chloride (BaCl$_2$), and Copper Sulphate Pent hydrate (CuSO$_4$.5 H$_2$O) are the chemicals required. We used this pellet for the humidity studies.

Chemicals required for the pellet fabrication

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Preparation of copper molybdate (Solution Method)

The salts, Copper Sulphate Pentahydrate (mole wt=249.68g) and Ammonium Hepta Molybdate (mole wt=1235.86g) taken in equimolar ratio (1:1) are dissolved in water separately and these two solutions are mixed with constant stirring at room temperature. The mixture is digested on a water bath for 30 minutes and tested for complete precipitation. The precipitate is allowed to settle for an hour. The precipitate is then filtered through a

sintered glass crucible. It is washed with cold water until the washings are free from Chloride ions. It is then dried in the oven at 200° C for 3 hours.

Analysis of copper molybdate

Copper Molybdate is analyzed qualitatively and quantitatively for the presence of Copper and Molybdenum.

Qualitative analysis for copper and molybdenum

The Copper Molybdate was digested with a mixture of concentrated HNO_3 and concentrated HCl. This solution was treated as original solution.

Test for Copper

To the 5 drops of solution, 5 drops of Iodine is added and shaked well, white precipitate with blue supernatant was obtained. This confirms the presence of Copper.

Test for Molybdenum

To the solution 2 drops of conc. HCl and 3 drops of bromine water were added and heated to evaporate the excess bromine vapour. Then the solution was cooled. To the solution 2 drops of stannous chloride and 5 drops of Ammonium thiocyanate and 10 drops of amyl alcohol were added, then the solution was shaked well, red alcohol layer was appeared.

Quantitative analysis for copper and molybdenum (Volumetric method)

Test for copper

0.5 g of the $CuMoO_4$ was digested with aquaregia. To the digested sample few drops of NH_4OH was added till a blue precipitate was obtained. The precipitate was dissolved in minimum amount of dil. CH_3COOHfollowed by the addition of 100ml of 10% KI and titrated against standardized Sodium thiosulphate using starch as indicator. The end point is appearance of creamy white precipitate. This confirms the presence of copper.

Tests for Molybdenum

0.5 g of Copper Molybdate was dissolved in conc. HNO_3 and conc.HCl. To that 2ml Ammonium acetate was added to neutralize it. Then the neutralized solution was kept for boiling, to that hot solution 3% of 8-hydroxy quinoline was added in drop wise, yellow precipitate was obtained. This confirms the presence of Molybdenum.

By measuring output voltage using electronic sensor kit for different percentage of humidity

The voltage measurement of the composites was done using our kit for different humidity levels, which were generated using various buffers. These buffers are saturated solution of hydrated salt and can give rise to humidity levels in closed environment. Controlled humidity environment were achieved using an hydrous saturated aqueous solution of Potassium acetate (CH_3COOK), Sodium nitrite ($NaNO_2$), Barium Chloride ($BaCl_2$) and Copper Sulphate Pentahydrate ($CuSO_4.5 H_2O$) in a desiccator at an ambient temperature of 25^0C, which yielded approximately 22%, 51%,79%,98% relative humidity respectively.

The humidity levels were monitored using an independent hygrometer. Conductivity study of metal oxide composites ($CuMoO_4 – CuO$) is carried at in room temperature at different water vapour buffers by applying a voltage of from 200mV to 1200 mV increased in steps of 200 mV and the corresponding output voltage was measured for all the prepared samples CMCO-82,64,55,46,28, are listed in tables from Figure. 1. The plots of input voltage (V_{in}) v_s output voltage (V_o) is resistance are computed from the measured data.

The composite CMCO – 82 was kept at relative humidity for 22%, a known voltage is applied and the corresponding output voltage observed is tabulated in the above figure 1.
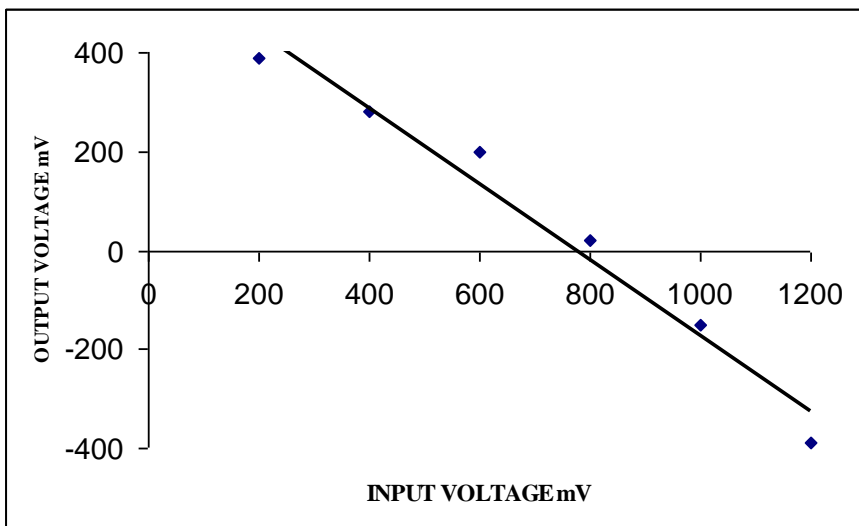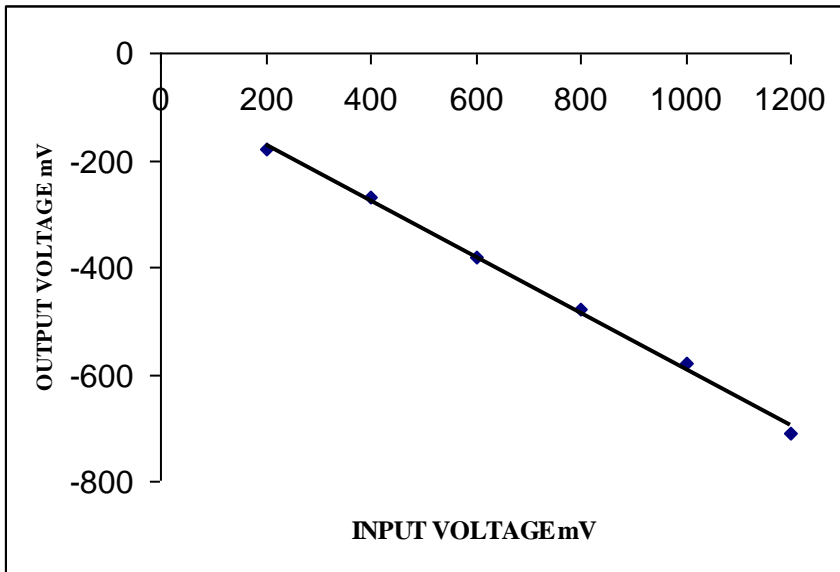
Figure 1. Sample, CMCO-82, Plot Of Input Voltage (V_{in}) Vs Output Voltage (V_o) At 22% RH

The composite CMCO – 82 was kept at relative humidity for 51%, a known voltage is applied and the corresponding output voltage observed and plots of Input voltage v_s output voltage shows the linear form in the figure 2.
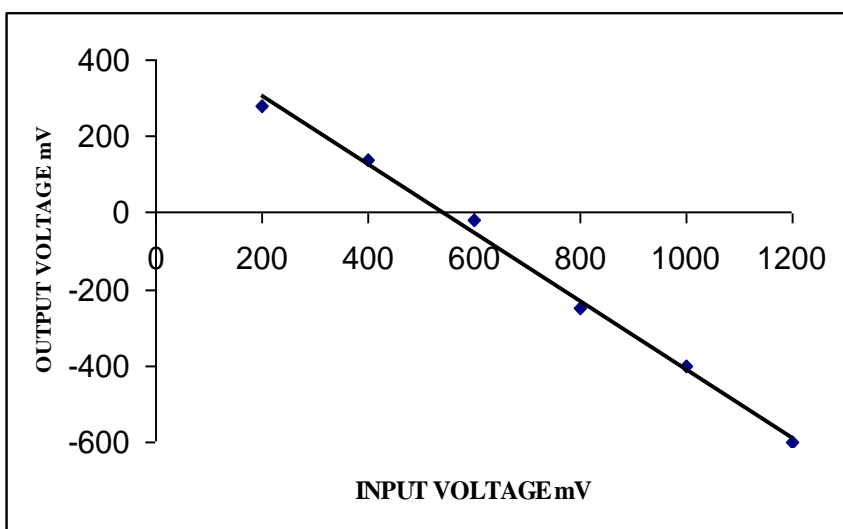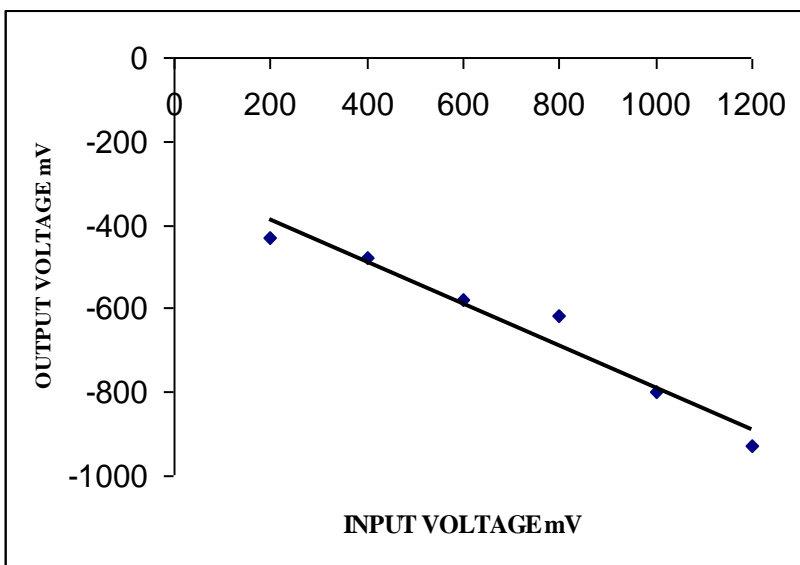

Figure 2. Sample, CMCO-82 Plot Of Input Voltage (V_{in}) Vs Output Voltage (V_o) At 51% RH

The composite CMCO – 82 was kept at relative humidity for 79%, a known voltage is applied and the corresponding output voltage observed and plots of Input voltage v_s output voltage shows the linear form in the figure 3.

Figure 3. Sample , CMCO – 82, Plot Of Input Voltage (V$_{in}$) Vs Output Voltage (V$_o$) At 79%RH

The composite CMCO – 82 was kept at relative humidity for 98%, a known voltage is applied and the corresponding output voltage observed and plots of Input voltage v$_s$ output voltage shows linear form in the figure 4.

Figure 4 Sample, CMCO – 82, Plot of Input Voltage (V$_{in}$) Vs Output Voltage (V$_o$) At 98% RH

The composite CMCO – 82 was kept at different relative humidity, output voltage was measured for given input voltage. The resistance of the pellet can be determined from the plot of V$_{in}$ (input voltage) v$_s$ V$_{out}$ (output voltage) for the composite at different Relative Humidity. A plot of Relative Humidity Vs Resistance using the above shows linear form in the figure 5.
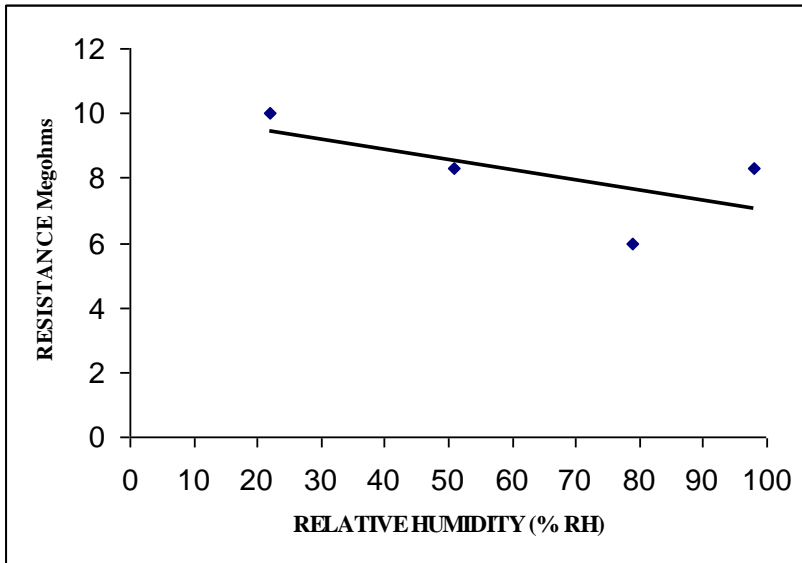
Figure 5. Sample , CMCO – 82 , Lot of Relative Humidity Vs Resistance

The Relative Humidity was varied and output voltage observed for six input voltages. The plot of Relative Humidity v_s Output Voltage using the figure 6 shows that variation of Output Voltage with percentage of Relative Humidity is in linear trend.
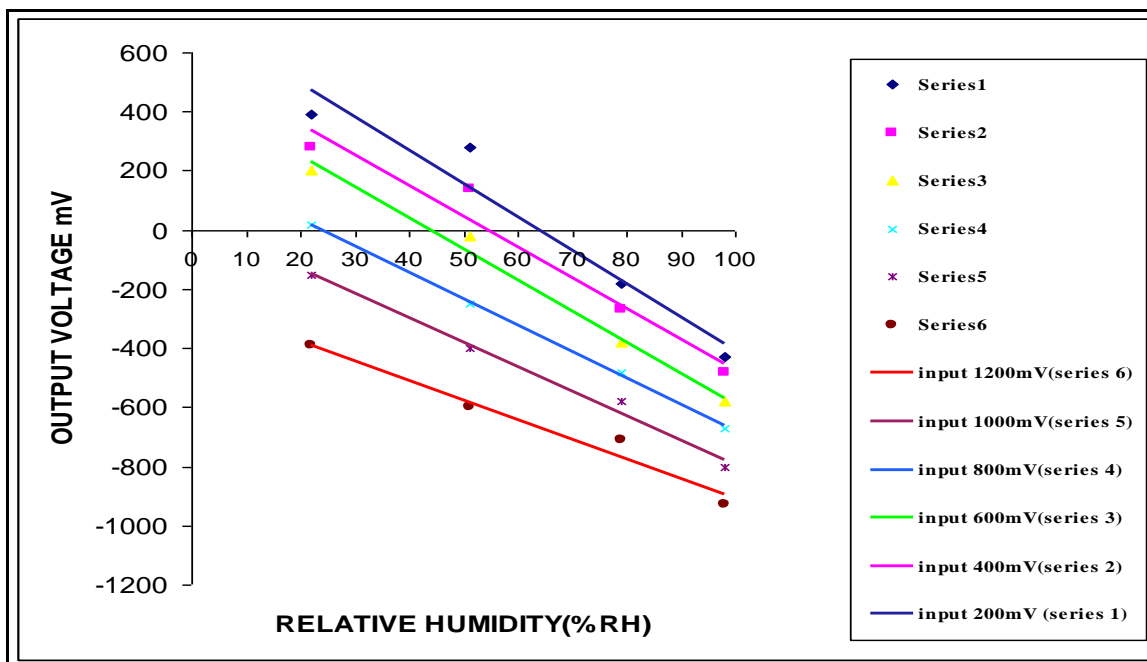

Figure 6. Sample , CMCO – 82, Relative Humidity Vs Output Voltage for Various Input Voltage

Discussion:

Resistive type humidity sensors generally contain noble precious metal electrodes. Resistive sensors measure the change of the humidity and translate it into a change in electrical impedance of the hygroscopic medium. As a principle, upon adsorption of water vapor its molecules are dissociated to ionic functional hydroxyl groups and these results in an increase of film electrical conductance.

The humidity sensing mechanism of perovskite type oxides with general formula of ABX3 was reported to be based on the electron donation from water vapour molecules. It was claimed that their activity can be attributed to the trapped electrons due to the presence of surface defects such as ionized oxygen

vacancies, and these trapped electrons may be liberated by adsorption of water vapour molecules on the defect sites [28]. Depending on the applied precursor for A or B sites of the complexes these sensors showed humidity sensitivity from 8%–20% to higher RH values of around 98% [29].

Viviani et al. have studied the humidity sensing behavior of porous barium molybdenum oxide (BaMO3) with compositions of M = Ti, Zr, Hf, or Sn prepared by wet chemical synthesis and different elevated temperatures ranging from 1,250 °C to 1,700 °C. The samples with lower sintering temperature and higher open porosities have shown an increase of both conductance and capacitance with an increment of the humidity range from 20% to 80% RH at room temperature (25 °C). In recent years there has been a growing contribution by the usage and evolution of composites prepared from organic/inorganic substances for humidity sensing applications. The preparation methods offer the possibility of preparing numerous potential compounds, which enable the synthesis and foundation for nanostructure sensitive films/condensed pellets [29]. Nanoparticles (NPs) have attracted much interest owing to their notable chemical, physical, magnetic, electronic and mechanical attributes, in addition of their bulk/surface catalytic activities and feasible utilization in electrochemical sensing applications, e.g., humidity and gas composite thin films showed the highest sensitivity, least hysteresis and greatest linearity. Therefore, at present, a commonly acknowledged sensing mechanism at room temperature is the electronic-ionic type. Humidity behaviours can be sequential in different regions:- At low RH levels, electronic conduction based on the electron donation from water molecules is the dominant responsible mechanism.

At medium RH levels, based on the number of physisorbed layers in different intervals, therefore electrostatic fields are due to first chemisorbed layer, both electronic and ionic conduction are responsible with the dominant transition being from electronic to ionic conduction mechanism. At high RH levels, ionic conduction based on proton hopping between water molecules is the dominant responsible mechanism. Thus the copper molybdate behaves as ahumidity sensor . In the light of the aforementioned discussion it may be construed that at lower RH levels the conduction may be elelctronic, and at medium RH levels it may be due to both electronic and ionic and at RH levels it may be due to proton hopping between water molecules.

Conclusion

A simple device is possible to construct with copper molybdate which will be useful as humidity sensor. At low RH levels, electronic conduction based on the electron donation from water molecules is the dominant mechanism. At medium RH levels, based on the number of physisorbed layers in different intervals, therefore electrostatic fields are due to first chemisorbed layer, both electronic and ionic conduction are responsible with the dominant transition being from electronic to ionic conduction mechanism. At high RH levels, ionic conduction based on proton hopping between water molecules is the dominant mechanism. Thus the copper molybdate behaves as a humidity sensor. In the light of the aforementioned discussion it may be construed that at lower RH levels the conduction may be electronic, and at medium RH levels it may be due to both electronic and ionic and at RH levels it may be due to proton hopping between water molecules. Thus copper molybdate behaves as a useful material in almost all the Rh levels.

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