Physics and Technology of Humidity Sensing Through a Solid State Pellet of Cerium Oxide

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Abstract: This paper reports the physics and technology of cerium oxide as solid state humidity sensor. Pellet of cerium oxide powder having diameter 9 mm and thickness 3 mm was made by hydraulic pressing machine under a load of 616 MPa and annealed at 200, 400, 600, 800 °C for 2 hrs in an electric furnace successively. After each step of annealing, this pellet was exposed to humidity in a specially designed humidity chamber. It was observed that as relative humidity (%RH) increases, there is a decrease in the resistance for the entire range of humidity i.e. from 15 to 95 %. The sensitivity of the humidity sensor was found 26 MΩ/%RH at room temperature. The proposed method in this study provides a simple, reliable and sensitive humidity sensor. The gross structural/phase identification of the pellets/powder was done using X-ray diffraction (XRD) and the surface morphology by scanning electron microscopy (SEM).

Keywords: Humidity, Pellet, Sensitivity, Cerium oxide, SEM, XRD.

1. Introduction

Humidity sensors are of increasing interest in electronic control system [1-3]. A wide variety of ceramic, polymeric and composite sensors are presently being made. Commercial sensors are generally based on organic thin films, but have limitations in the temperature and humidity range in which they can function accurately. Bulk ceramic sensors based on porous materials show higher mechanical and chemical resistance [4-5]. The response mechanism has been related to the adsorption of water molecules inside the pores and at the grain boundaries of the porous material which causes an increase of the surface conduction. Percent relative humidity (%RH) is the most well known and perhaps the most widely used method for expressing the water vapour content in air. It is defined as the ratio of the prevailing water vapour pressure to the water vapour pressure if the air is saturated at a given temperature. In general, a good humidity sensor should have a good sensitivity with wide humidity range, quick response, good reproducibility, easily interface ability, tough durability with long life, resistance to contaminants, insignificant dependence on temperature and simple structure and low cost. A wide range of humidity sensors have been developed in recent years in response to these needs. In spite of these developments, however the reliable and repeatable application of these elements for the control of humidity has been found to be difficult. For these humidity sensors; ceramics, metal oxides, polymeric films are used as the humidity sensing element.
Depending upon the environmental conditions, various materials for humidity sensing have been studied so for [6-7]. Among all the materials, ceramics are found to be better choice in terms of stability, cost and performance in a wide operating range [8]. Among resistive-type humidity sensors, the electrical response of a cerium oxide ceramic sensor was investigated by Jyoti Shah, et al. [9]. A different type of ceramic sensor based on kaolin and sodium salt of carboxymethyl cellulose in deionised water has been investigated, confirming the correlation between pore size volume and conductivity of the sample [10]. But sensitivity and sensor response reported by these investigators were not adoptable for device fabrication. A good adsorbing material should have a large surface area so that it can attach more molecules on its surface. So, by increasing the porosity, the surface area can effectively be increased by many folds. In cerium oxide, predominant ionic defects are the electron trapped by cerium and oxygen vacancy and it has large diffusion coefficient [11-20]. In addition it has some advantages e.g. large oxygen concentration dependence on its resistance in lean burn region, good corrosion-resistance etc. In view of these we thoroughly investigated cerium oxide as humidity sensor.

Our group has already investigated solid state humidity sensor using nanostructured tin oxide synthesized via mechanochemical method [21], nanostructured ZnO (oxalate route) [22] and nanostructured ZnO (hydroxide route) [23] having sensitivities 5.2, 7 and 8 MΩ/%RH respectively. Further humidity sensor using ZnO-TiO₂ nanocomposite has sensitivity 18 MΩ/%RH [24]. Also our group has worked on Nd₂O₃ system and ZnO-Nb₂O₅ as solid state humidity sensors and got sensitivity 19 MΩ/%RH [25-26] with least hysteresis, therefore this work was a next step in devising a resistive type humidity sensor.

In this paper, we studied the surface morphology of the material under investigations through SEM images and their phase identification by XRD. Further the electrical responses of this material to relative humidity were studied. In the humidity range 15-95 %RH, it showed good response. The correlation between resistance and relative humidity was studied on the basis of microstructure of porous ceramic and crystallite size. The sensor was found to be sensitive for entire range of %RH having sensitivity 26 MΩ/%RH.

2. Principle of Operation

Humidity sensors based on water-phase protonic ceramic materials are used widely in industry and research laboratories. The adsorbed water condensed on the surface of the materials and protons will be conducted in the formed aquatic layers. For ionic sensing materials, if the humidity increases, the conductivity decreases and the dielectric constant increases [2-3]. In bulk water, proton is the dominant carrier responsible for the electrical conductivity. The conduction is due to the Grotthuss chain reaction mechanism, through which protons tunnel from one water molecule to the next via hydrogen bonding that universally exists in liquid-phase water (Fig. 1).

![Fig. 1. Brief illustration of the Grotthuss chain reaction mechanism.](image)

This mechanism was reported about 200 years ago [27]. The mechanism of protonic conduction inside the adsorbed water layers on the surface of the sensing materials was discovered in study of TiO₂ and α-Fe₂O₃ [28]. As shown in Fig. 2, at the first stage of adsorption, a water molecule is chemically adsorbed on an activated site (a) to form an adsorption complex (b), which subsequently transfers to surface hydroxyl groups (c). Then, another water molecule comes to be adsorbed through hydrogen bonding on the two neighboring hydroxyl groups as shown in (d). The top water molecule condensed cannot move freely due to the restriction from the two hydrogen bonding (Fig. 2(d)). Thus this layer or the first physically-adsorbed layer is immobile and there are not hydrogen bonds formed between the water molecules in this layer. Therefore, no proton could be conducted in this stage. As water continues to condense on the surface of the ceramic, an extra layer on top of the first physically adsorbed layer forms (Fig. 3). This layer is less adsorbed than the first physically-adsorbed. For example, there may be only one hydrogen bond locally. If more layers condense, the ordering from the initial surface may gradually disappear and protons may have more and more freedom to move inside the condensed water through the Grotthuss chain reaction mechanism. In other words, from the second physisorbed layer, water molecules become mobile and finally almost identical to the bulk liquid water, and the Grotthuss mechanism becomes dominant. This mechanism indicates that sensors based purely on water-phase protonic conduction would not be quite sensitive to low humidity, at which the water vapor could rarely form continuous mobile layers on the sensor surface. The two immobile layers, the chemisorbed and the first physisorbed ones, while cannot contribute to proton conducting activity, could provide electron tunneling between donor water sites [29-30]. The tunneling effect, along with the energy induced by the surface anions, facilitates electrons to hop along the surface that is covered by the immobile layers and therefore contributes to the conductivity. This
mechanism is quite helpful for detecting low humidity levels, at which there is no effective protonic conduction.

\[
\begin{align*}
\text{Me} & \quad \text{O} \quad \text{Me}^- + \text{H}_2\text{O} \\
\rightarrow & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \\
\text{Me}^- & \quad \text{O} \quad \text{Me}
\end{align*}
\]

Fig. 2. Four stages of the adsorption.

\[
\begin{align*}
\text{Me} & \quad \text{O} \quad \text{Me}^- + \text{H}_2\text{O} \\
\rightarrow & \quad \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \\
\text{Me}^- & \quad \text{O} \quad \text{Me}
\end{align*}
\]

Fig. 3. Multi-layer structure of condensed water.

3. Experimental Procedure

3.1. Preparation of Sensing Element

The starting material was cerium oxide powder (Loba Chemie, India). On vigorous grinding the material in mortar with pestle for 6 hrs, it gave very fine powder. There are a number of workable methods of mixing the powders. The recommended procedure for modestly equipped laboratories is to first use a mortar and pestle to grind down any lumps or large particles in the chemical powders, then to shake the mix or stopped flask for several minutes vigorously in a capped jar. Use a dust mask and avoid breathing any of the chemical powders. Pellets of this material were made using hydraulic pressing machine by applying uniaxial pressure of 616 MPa at room temperature. These pellets were annealed at 200, 400, 600 and 800 °C for 2 hrs inside a tubular electric furnace (Ambassador, India). Each pellet was kept within an electrode holder and has been exposed to humidity in the self-designed humidity chamber. Variations in resistance with humidity were recorded. Relative humidity is measured using digital hygrometer. Variations in resistance were recorded by using a digital multimeter (VC 9808, Aplab, Thane, India). The least count of Hygrometer used here is 1 %RH.

3.2. Study of Surface Morphology and Crystal Structure

3.2.1. Scanning Electron Microscopy

Surface morphology was studied using Scanning Electron Microscope Unit (SEM, LEO-0430, Cambridge). Fig. 4 shows the SEM image of CeO₂ at room temperature. The annealing effects on the morphologies of material were investigated at different temperatures. Fig. 5 shows the SEM image of sensing material annealed at 200 °C, having pores size of 170 nm. Fig. 6 shows SEM image of CeO₂ prepared after annealing at 400 °C. It shows that as annealing temperature increases grains contracted with each other and form cluster like structure, voids are decreased. Fig. 7 shows SEM image of CeO₂ prepared after annealing at 600°C having average pore size 113 nm. Fig. 8(a) and Fig. 8(b) show SEM images of sensing material prepared at 800 °C at microscale and nanoscale respectively and it is found that at 800 °C, pore size became 98 nm. Thus pore size varied from 240 nm to 98 nm and as a result material has become less porous with increasing annealing temperature.

Fig. 4. Scanning Electron Micrograph of CeO₂ pellet prepared at room temperature.

Fig. 5. Scanning Electron Micrograph of CeO₂ pellet prepared at 200 °C.
3.2.2. Powder X-Ray Diffraction

The X-ray Diffraction characterization was carried out through wide-angle X-Pert PRO XRD system (Netherland) with CuKα radiation. The diffractograms were recorded with scan speed 2°/minute (0.03°/s) and in range 0-75°. The typical X-ray diffractogram of sensing element at room temperature is shown in Fig. 9. The recorded peaks were analyzed and indexed with standard data of ‘Joint Committee on Powder Diffraction Standards/File’ (JCPDS/F). The analysis of diffractogram revealed that the crystal system of the sensing material correspond to cubic phase and having chemical formula CeO₂. Lattice parameters determined from the XRD peaks in the high angle range (2θ = 60-80°), where a = b = c = 5.4113 Å for CeO₂. Analysis shows that CeO₂ exists in excess amount (96 %). Its peaks occur at 2θ values 28.6, 33.0, 47.6, 56.5, 59.0 and 69.4° respectively. These peaks have the ‘d’ values 3.12, 2.705, 1.912, 1.631, 1.562 and 1.352 Å with corresponding planes (111), (200), (220), (311), (222) and (400) respectively.

Using Debye-Scherrer formula the crystallite size has been calculated and it is found that the minimum crystallite size is 92 nm corresponding to the plane (400) and maximum size of the particle is 223 nm corresponding to plane (111). The average size of particle corresponding to all peaks is 133 nm.
4. Device Assembly

The experimental setup [23] in this study consists of a controlled humidity chamber, a hygrometer, a thermometer and a digital multimeter. The Cu-Pellet-Cu electrode arrangement is fixed on a non-conducting base inside the chamber such that connecting wires remain outside the chamber. Saturated aqueous solution of potassium sulphate in a small container has been placed inside the steel chamber. It yielded more OH- ions in the chamber and consequently humidity increases inside the chamber. The percentage relative humidity (%RH) inside the chamber was varied from 15 % to 95 %. The sequential changes in resistance of the pellet with variation in %RH were recorded. The chamber was then dehumidified up to 15 %RH by putting saturated salt solution of potassium hydroxide in a dish inside it. %RH is measured by using standard digital hygrometer. A thermometer having an accuracy of ±1 °C is allowed to hang in the chamber. Variations in the resistance were noted by using digital multimeter of MΩ order (VC 9808).

5. Results and Discussion

Fig. 10 (a) and Fig. 10 (b) show the physical models which illustrates the change in barrier height of junction before and after the exposure of humidity. The barrier height ΦB is a function of moisture content. From the figure, it can be seen that, the carrier concentration starts to increase near the interface of heterojunction upon exposure of humidity. This increase in carrier concentration reduces the potential barrier at heterojunction interface as shown in Fig. 10(b). As the width of potential barrier decreases current flowing through the heterojunction increases.

Variations in resistance with humidity have been recorded for sensing element at room temperature and other annealing temperatures. For sensing element CeO2 prepared at room temperature, 200, 400, 600 and 800 °C curves are shown in Fig. 11 by ‘a’, ‘b’, ‘c’, ‘d’ and ‘e’ respectively. Curve ‘a’ shows that as humidity increases the resistance decreases slowly from 15 % to 50 %RH and then decreases gradually up to 95 %RH. At 200 °C resistance decreases gradually up to 40 % and then decrease sharply up to 95 %RH as shown in Fig. 11 by curve ‘b’. Curve ‘c’ shows the variations in resistance with %RH for sensing element annealed at 400 °C. It reveals that nature of curve is linear; hence resistance decreases linearly with the variation of humidity. For sensing element annealed at 600 °C, resistance decreases gradually with humidity in the range 15 to 55 %RH. After this curve shows linear behavior as shown by curve ‘d’. Curve ‘e’ describes the variation of resistance with %RH for sensing element annealed at 800 °C. It shows that as humidity increases, resistance of sensing element decreases drastically up to 35 %RH then slightly increases up to 45 %RH and further decreases markedly up to 75 %RH after that it becomes linear up to 95 %RH.
it is seen that as annealing temperature increases, sensitivity of sensing element decreases up to 800 °C. Highest sensitivity achieved in this case is 26 MΩ/%RH at room temperature which is enough for device fabrication and minimum sensitivity is 15 MΩ/%RH at 800 °C for sensing element CeO₂. Variations in average pore size with annealing temperature have been also plotted in Fig. 13. From curve it can be seen that sensing material at room temperature was more porous than the material prepared at different annealing temperatures. At room temperature average pore size is highest which is 240 nm.

We have studied the hysteresis behavior of sensing element CeO₂ at room temperature and other annealing temperature 200, 400, 600 and 800 °C. Sensing element prepared at 400 °C showed minimum hysteresis behavior which is 0.81 % as shown in Fig. 14.

For sensing element CeO₂ we have also studied the aging effect. After humidity treatment, samples were kept in desiccator in the laboratory ambient for 6 months and their characteristics were regularly monitored. The characteristics of the fresh samples, just after humidity treatment and those after 6 months of exposure are shown in Fig. 15. Here curve ‘a’ depicted the nature of sensing element before 6 months and curve ‘b’ showed the nature of sensing element after 6 months. It is found that the sensor became less sensitive and it has been deteriorated by 31 %.

6. Conclusions

Here we investigated CeO₂ for its humidity sensing characteristics at room temperature and annealing temperatures 200, 400, 600 and 800 °C. As annealing temperature increases sensitivity decreases up to 800 °C. It yielded maximum sensitivity 26 MΩ/%RH at room temperature which is maximum till the date for sensor fabrication. Surface morphology shows that pore size decreases with increasing annealing temperature. The pores sizes are varied from 240 nm to 98 nm and material has become less porous with increasing annealing temperature. Crystallinity and phase identification were done by X-ray diffraction and the minimum size of the crystallite was found 92 nm and phase was cubic.
Thus humidity sensor reported here based on electrical resistance is highly sensitive, cost effective and user friendly. It can be used for both indoor and outdoor applications. Hence, CeO$_2$ proved to be the sensor with excellent properties showing very high sensitivity and the characteristic is stable over the entire range of humidity.

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References

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