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Effect of composition on electrical and humidity sensing properties of $NiO:MnO_2:CuO$ solid mixture

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The ternary solid mixture of transition metal oxides [nickel(II), manganese(IV) and copper(II)] NMC were prepared with different mole ratios of their component oxides and sintered at 850 K in the form of cylindrical disks. The humidity sensing is described by experimental results on NMC. The transition metal oxide mixtures were subjected to dc resistance measurement as a function of relative humidity in the range of 5–98% RH, achieved by different water vapour buffers thermo stated at room temperature. The sensitivity factor ($S_f = R_{5\%}/R_{98\%}$) measured at 298 K revealed that NMC-121 metal oxide mixture has the highest humidity sensitivity factor 2705. The sample having highest sensitivity factor NMC-121 is characterized by powder XRD and FT-IR data. The same has been subjected to dc conductance measurements in the temperature range from 318 K to 623 K and hence the activation energy is calculated. The activation energy value was found to be 0.327 eV. These ternary solid mixtures of transition metal oxides can be used as commercial thick film humidity sensor because of their humidity sensing factors.

Keywords: Sensor, humidity, transition metal oxides, dc resistance, sensitivity.

Introduction

Humidity in the environment is most important factor for physical comfort and industrial processes[5]. For controlling and monitoring humidity in environment, humidity sensors making use of electrical parameters are preferably suitable. Especially, humidity control is necessary in manufacturing of electronic devices, precision instruments, textiles, food processing gained attention in recent years[1(b)]. Here often it is important to control the relative humidity (RH). There are so many materials have been applied for humidity sensing of which transition metal has been widely investigated[1(e),6,1(a),4(a)]. Sensors based on changes in dc resistance and capacitance is preferred to the conventional ones owing to their small size and with electronic circuits[2(a)]. Transition metal oxides constitute one of the most fascinating variety of structures, the properties and phenomena due to the unique nature of the outer d electrons and the metal-oxygen bonding varying from nearly ionic to metallic[1(c),10,2(b)]. The most important aim of the work was to promote the electrical and humidity sensing properties of transition metal oxides[11–13]. The humidity dependent electrical resistance characteristics of transition metal oxides [NiO-MnO_2-CuO]-NMC ternary solid mixture have been reported.

Experimental

All the chemicals are used for the synthesis were AnalaR grade. The metal oxides NiO, MnO_2 and CuO were used as supplied. The ternary mixture of metal oxide sensors were synthesized from different mole ratio of NiO, MnO_2 and CuO. The mixture was vibromilled and ground mechanically for 5 h in the presence of acetone. The samples were compacted in a form of cylindrical disk of about 10 mm diameter and 2 mm thickness. These pellets were then heated at a rate of 10 K min^{-1} up to 850 K at this temperature for 12 h to facilitate sintering followed by furnace cooling of the samples. The phase presented in the sample is characterized by recording XRD. The surface functional groups were determined by scanning in the spectral range of 4000–400 cm^{-1} in infrared spectrometer. The electrical contacts were made on the surface of the sample by means of two thin copper wires affixed silver point. The sample was inserted in the middle of the Pyrex tube of 5 cm diameter on which the kanthal wire was wounded uniformly in external. The kanthal wire ends were connected to a Varian to vary the temperature and a Constantine thermocouple kept at the pellet was used to measure the temperature of the sample. The applied field (V/d), where V is the voltage and d is the distance between the electrodes, was varied and the corresponding current at room temperature was measured. A plot of current versus applied field was obtained. The dc resistance and its temperature dependence (318–623 K) were measured by a two-probe method[3(b),4(b)]. The controlled humidity level was achieved by using anhydrous P_2O_5 and saturated aqueous solutions of $CaCl_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, NH_4Cl and $CuSO_4.5H_2O$ in a closed glass vessel at an ambient temperature of 298 K, which approximately 5, 31, 51, 79 and 98% relative humidity respectively and was exactly measured with Barigo hygrometer. After heating the pellets of metal oxide mixture were placed inside the controlled humidity environment for 2 h. The change in current was measured by varying the voltage from 2 to 32 volts. The sensitivity factor was calculated from the ratio of the resistance of 5% to 98% of relative humidity

$$\text{Sensitivity factor, } S_f = R_{5\%}/R_{98\%} \quad (1)$$

Results and discussion

The results of resistance measurements as a function of RH at 298 K are presented in Fig. 1. It has been observed that a markable drop in resistance against the increasing MnO_2 contents. For a better appreciation of the material characteristics towards moisture, the ratio of resistance, $R_{5\%}$ and $R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the dc resistance at 5 and 98% RH, respectively are measured as presented in Table 1. If the sensitivity factor, S_f, value is higher means that the sensitivity of the material towards moisture[1(d)]. The sample NMC-121 (2705) shows maximum sensitivity among NMC metal oxide mixture in which the resistance drops by more than four orders of magnitude. The samples showed the linear current voltage curves and thus the electrical conductivity was calculated from the slope by curve fitting using least square method. The humidity measurement observed that the resistance of metal oxide mixtures ranges from 3.545 to 9.403×10^{-6} ohms. The mixture of metal oxides showed a decrease in the resistance as the humidity, increased indi-

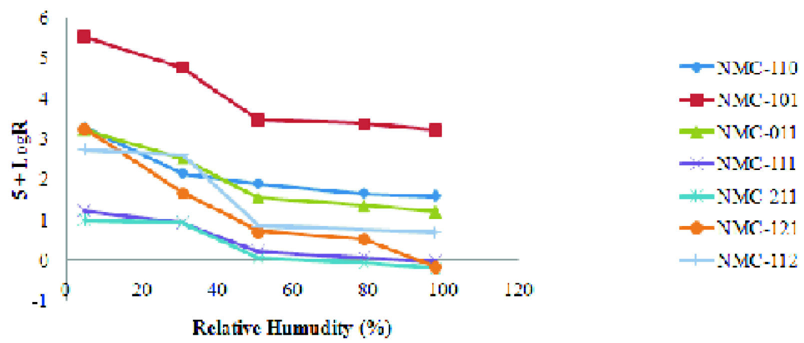

Fig. 1. Relative humidity versus log resistance plots at 298 K for NMC solid mixtures.

Table 1. Mole ratios, resistance, sensitivity factor and activation energy data for NMC transition metal oxide solid mixture

NiO (No. of moles)	MnO_2 (No. of moles)	CuO (No. of moles)	Sample code	Résistance[a] (Ω) $R_{5\%}$	$R_{98\%}$	S_f ($R_{5\%}/R_{98\%}$)	E_a (eV)
1	1	0	NMC-110	1.940×10^{-2}	3.902×10^{-4}	49.74	
1	0	1	NMC-101	3.545	1.725×10^{-2}	205.51	
0	1	1	NMC-011	1.691×10^{-2}	1.628×10^{-4}	103.87	
1	1	1	NMC-111	1.654×10^{-4}	9.403×10^{-6}	17.59	
2	1	1	NMC-211	9.756×10^{-5}	6.198×10^{-6}	15.74	
1	2	1	NMC-121	1.801×10^{-2}	6.657×10^{-6}	2705	0.326
1	1	2	NMC-112	5.436×10^{-3}	5.069×10^{-5}	107.24	

[a]$R_{5\%}$ and $R_{98\%}$ stand for dc resistances measured at 298 K corresponding to RH 5 and 98% respectively.

cating that the conduction is takes place at the grain surface. The conduction occurs due to physisorption and chemisorptions of water molecules which dissociated into hydroxyl and hydronium ion at low humidity level.

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (2)$$

The sintered samples create pores which enables electrolytic conduction to takes place in addition to the adsorbed layers. So that conduction increases at high humidity level[9,1(d)]. NMC-121 has been chosen for temperature dependence study. The activation energy of the sample was determined in the temperature range of 318–623 K using the Arrhenius equation (Table 1)

$$I = I_0\, e^{-E_a/kT} \quad (3)$$

where I is the current, E_a the activation energy, k the Boltzmann constant and T the temperature.

$$\ln I = \ln I_0 - E_a/kT \quad (4)$$

A linear curve is obtained by plotting the ln I versus $1/T$ as shown in the Fig. 2. The slope ($-E_a/k$) of linear curve the activation energy was calculated. The low value of activation energy (0.326 eV) shows small polaron mechanism is operating in this temperature range. It also indicate that lower energy is required to cross the energy band for conduction[3(a)]. The ternary mixture of transition metal oxides having highest sensitivity factor is NMC-121 having powder

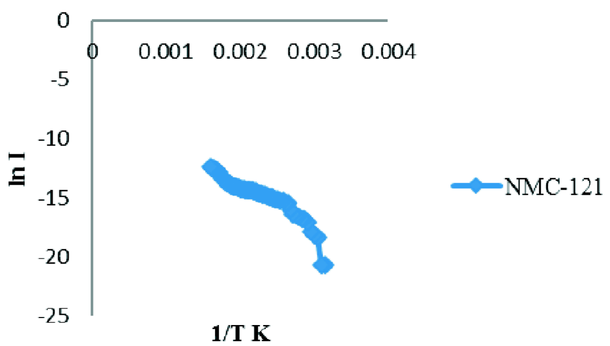

Fig. 2. Temperature dependent dc conductance plot of NMC-121.

XRD pattern as shown in the Fig. 3 corresponding to (400), (220), (222), (440) characteristic peaks of NiO of JCPDS-895881 were found. Similarly the characteristic peaks of MnO_2 (011), (111), (201), (311) corresponding to JCPDS-822169 were found. The peaks (111), (011), (200), (022) corresponding to CuO of JCPDS-895899 were found. This

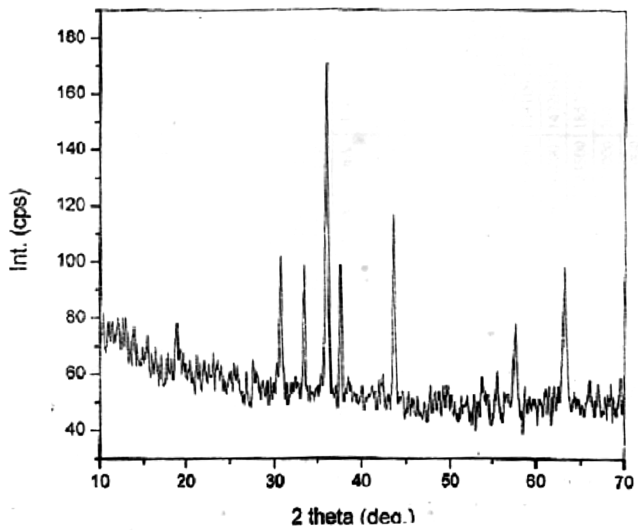

Fig. 3. X-Ray diffraction pattern of NMC-121.

shows that there are no impurity peaks. A common broad band near 3400 cm^{-1} was observed in the FT-IR spectrum of NMC-121 is attributed to OH^- stretching vibration of free and hydrogen bonded hydroxyl groups and at 1600 cm^{-1} is assigned to the deformative frequency of water molecules which is most probably due to water absorption during compaction of the powdered specimens with KBr[7,8]. The bands from 400 to 1000 cm^{-1} assigned to metal oxide adsorption and also indicate that these metal oxide mixture are not amorphous.

Conclusions

Ternary solid mixture of transition metal oxides with seven different mole ratios NMC (NiO-MnO_2-CuO) were fabricated and studied for humidity sensing properties. The X-ray diffraction study shows that no new phase has been formed and confirmed the presence of the individual metal oxides in the solid mixture. In all the systems a decrease in resistance with increase in humidity was observed, this was explained using Grotthuss chain mechanism. Comparing all the NMC systems the solid mixture NMC-121 has the highest sensitivity factor. These ternary solid mixtures of transition metal oxides can be used as commercial thick film humidity sensor because of their humidity sensing factors.

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