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Novel Non-Stoichiometric Manganese – Cobalt – Nickel – Oxide Composite as Humidity Sensor Through Solid-State Electrical Conductivity Measurements

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Abstract: Equimolar amounts of manganese(II) chloride, cobalt(III) nitrate and nickel(II) chloride in aqueous solution were reacted with ammonia and the resulting precipitate of hydroxides was heated to 750^0 C in 6h to yield a non stoichiometric oxides having a composition of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$ as analyzed by atomic absorption spectroscopy to a pellet and sintered at 600°C. Characterization of the material has been made with AAS, Far-IR, TG-DTA, XRD, SEM, VSM and electrical conductance measurement. The far-IR spectra indicated the presence of metal-oxygen bonds and the discrete nature of the oxide was established from power X-ray diffraction pattern recorded at room temperature. The thermogravimetric data indicated the successive loss and gain of fraction of oxygen atoms, a specific feature of non-stoichiometric metal oxides. It was subjected to solid-state DC electrical conductivity measurements at room temperature. The current increases linearly with applied field and exponentially with increase in temperature showing conformance to ohmic law and semiconducting nature. The scanning electron microscopy (SEM) studies were carried out to study the surface and pores structure of the sensor materials. The Brunauer-Emmett-Teller (BET) surface adsorption studies showed that the radiuses of the pore sizes were found to be distributed from 10-45 Å with the pore specific volume being 0.01 cm^3 g^{-1}. As the composites having micropores are preferred for humidity sensing properties, the material was subjected to water vapour of different humidity achieved by various water buffers at room temperature and the electrical conductivity was measured as a function of relative humidity (RH). The electrical resistivity drastically decreases with increase in humidity, proving the material to be a good water vapour sensor. The sensitivity factor (S_f) was 55000 in the range 5–98% RH, meaning the resistivity falls by a factor of 5.5×10^4 when the atmospheric RH increases from 5-98%. Such a high value of sensitivity for water vapour has seldom been reported in literature, making the composite possibly the most sensitive water vapour sensor. The response and recovery time for this humidity-sensing composite was also studied.

Keywords: Electrical conductivity, Humidity sensors, Manganese oxide, Nickel oxide, Cobalt oxide, Non-stoichiometric tri-metallic oxides.

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1. Introduction

Stoichiometric nickel-copper manganites have already been reported [1] as negative temperature coefficient (NTC) thermistors since they possess interesting electrical properties such as low resistivity and electrical stability [2]. The non-stoichiometric nickel manganites are very reactive towards CO total oxidation. However, these nickel manganites are relatively unstable when heated in air. Growing interest has been devoted to transition metal mixed – oxides for matrices of intercalation / deintercalation reversible processes and for molten carbonate sensor materials [3]. LiM_2 – type (M = Mn, Co and Ni), constituted by a two dimensional array of LiO_6 octahedral have been studied for such applications. A non-stoichiometric mixed metal oxide has attracted much attention because of their enormous application [4]. Various methods are employed for the measurement of humidity [5] of which the measurement of relative humidity seems to be very convenient. The possible applications of humidity sensors in automated systems for environmental control in many industrial and domestic fields [6]. However, our earlier investigations indicated that materials that posses metastable coexistence can have excellent sensitivity towards moisture [7, 8]. The aim of this paper is to humidity sensing features of non-stoichiometric Mn-Co-Ni oxides. The main results were obtained by scanning electron microscope, surface measurements and reversibility studies. As a result, oxides turned out to be the best sensing material for detecting humidity at room temperature.

2. Experimental

$MnCl_2.H_2O$ (2.49g), $NiCl_2.H_2O$ (2.28g), $Co(NO_3)_2.6H_2O$ (2.31g) were weighed and dissolved separately in 20cm^3 water. These solutions were then mixed together followed by addition of ammonia drop wise and stirred in a magnetic stirrer for more than an hour. The green colored precipitate obtained was filtered and washed with water several times. It was then dried, ground well, pressed into pellets under a pressure of 0.5 tons and sintered to 750^{o}C in 6 h under controlled heating rate. The sintered pellets were ground well and compacted into pellets using cetyl alcohol as the binder, of diameter 10 mm and thickness 2 mm, which were then heated to 600^{o}C.

The percentage composition of the metals can be studied by atomic absorption spectroscopy. Nature of the sample was studied, using X-ray diffraction recorded in powder form by a Rigaku Rotofles diffractometer using Cu-K_α radiation. The thermogravimetric studies were carried out to monitor the thermal stability of the sample and to determine its decomposition temperatures against the phases formed in air ambient at a heating rate of 10^{o}C/min. A recording Seiko SII thermal analyzer was employed. The far-IR spectrum of the sample was recorded in a Bruker IFS66V spectrophotometer model in the region of 450–100 cm^{-1} using polyethylene film. Magnetic susceptibility measurements were done on an EG & G Princeton research model–155 vibrating sample magnetometer at room temperature. The corrected magnetic moment was obtained after incorporating the necessary diamagnetic corrections for oxygen [9]. The sample was coated with gold (60 u thickness) for 5 min. by using EIKO IB ion coater. The gold-coated specimens were then observed on a HITACHI scanning electron microscope S415A operating at an accelerating voltage of 25 kV. The surface area of the composite was determined employing BET equations in a Carlo Erba Sorptometer using N_2 adsorption at 77 K. The sample was preheated at 473 K at 20 μ vacuums before measurements.

The experimental samples were made in to cylindrical disks of 10 mm diameter and 2 mm thickness in a hydraulic press at a pressure of 100 Mpa. The sample was electrically connected to a DC power supply and a picoammeter (Keithley 485) in series. The applied field was increased from 1 to 300 V/cm in steps and the corresponding current was measured. The electrical conductivity was measured, as above using a two-probe method [10]. In order to study the temperature dependence of conductivity, the sample was kept inside a Pyres cylinder of 5 cm diameter and 75 cm length kanthal aluminum wire uniformly wound around it. The ends of the kanthal wires were connected to a variac for heating. A copper–constantine thermocouple was calibrated for temperature measurements by making use of a standard platinum thermocouple that in turn was calibrated at the freezing points of Sn, Bi, Sb and Ag as per IPTS 68.

The controlled humidity environments were achieved [11] using anhydrous P_2O_5 powder and saturated aqueous solutions of potassium acetate, $CaCl_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, $NaNO_2$, NH_4Cl, $BaCl_2.2H_2O$ and $CuSO_4.5H_2O$ in a closed glass vessel at an ambient temperature of 25^oC, which yielded approximately 5, 20, 31, 42, 51, 66, 79, 88 and 98 % relative humidity respectively, which are independently monitored by using a Barigo hygrometer. Heat cleaning of the samples was done at 200^oC, followed by cooling in a humidity-free atmosphere before and after the sensitivity measurements especially when the sensors were operated at higher RH.

A degassed glass chamber of about 200 cm^3 volume was made use for evaluating the response and recovery characteristics. This chamber has a provision for a two-way inlet, one for transpiring dry air and the other for transpiring moist air from a wet candle. The air-drying was accomplished by transpiring the air stream through drying columns packed with anhydrous $CaCl_2$ and dry P_2O_5 connected in series. The resistance measurements in dry air as well as in moist air alternatively helped to establish the recovery and response characteristics for moisture sensing. The response and recovery characteristics were assessed as described earlier [12].

3. Results and Discussion

The mixed metal non-stoichiometric oxide was precipitated as hydroxide and heated to 750^oC in 6h to convert in to the oxide. The green colour of the hydroxide changed into black after sintering. The chemical composition of the mixed metal oxide arrived from the AAS data, Mn (3.54%), Co (34.99%) and Ni (36.65%). Based on the AAS percentage composition and considering the fact that the starting materials were precipitated as hydroxides in the mole ratio of 1:1:1, the chemical composition of the mixed metal oxide is proposed to be as $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$. It is well known [13] that manganese hydroxide on heating gets converted to MnO_2, which on further heating get converted to Mn_2O_3 and subsequently to Mn_3O_4. Manganese oxide on further heating to temperatures above 475^oC suffers loss of both manganese and oxygen. The target temperature for the preparation of the mixed metal oxide is fixed at 750^oC and at this temperature considerable loss of manganese has occurred, as evidenced from the AAS data.

It is important to prove that the mixed metal oxides is not a simple mixture of the oxides of manganese, cobalt and nickel but discrete in nature, the d-values from the X-ray patterns (Fig. 1) along with their intensities are 2.5425 (49), 2.5286 (56), 2.1646 (82), 2.1176 (100), 1.5185 (89), 1.5138 (86), 1.5076 (62), 1.4646 (48) and 1.4592 (57). The d-values are compared with the JCPDS-ICD data cards against the various oxides of manganese, cobalt and nickel such as MnO_2, Mn_2O_3, Mn_3O_4, NiO, and Co_3O_4. The XRD indicated the absence of any of the above oxides and further evidenced the formation of non-stoichiometric mixed metal oxide. However, it should be mentioned that none of peak could be matched with any of the non-stoichiometric oxides of Mn, Co and Ni available in the JCPDX database.

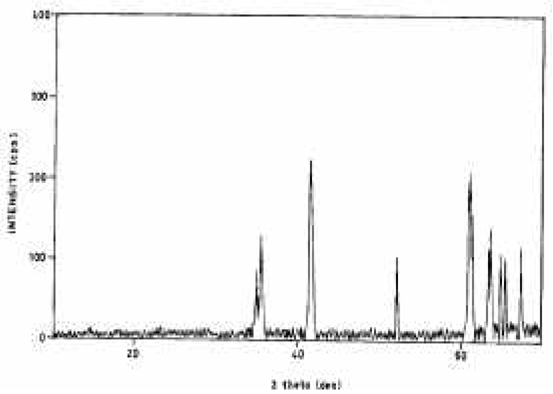

Fig. 1. Powder XRD patterns of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

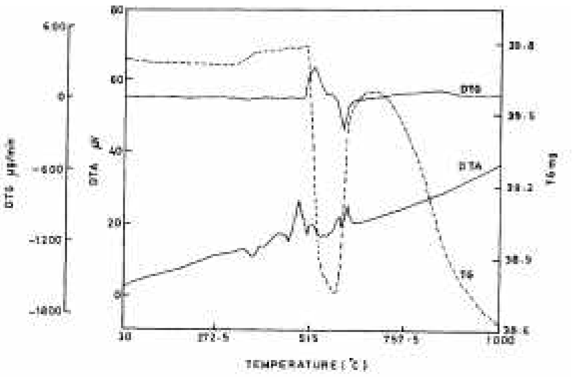

Fig. 2. TG/DTA studies of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

The temperature varied from 30–1000°C at a heating rate of the 10°C/min. The metal oxide TC-DTA (Fig. 2) showed an increase in weight in the temperature range of 140–505°C, due to oxygen gain amounting to 0.8% corroborated by a DTA endothermic peak at 458°C. Subsequent weight loss was observed in the temperature range of 505–587°C amounting to 2.44% loss of oxygen. Further weight gain was observed in the temperature range 590–664°C amounting to 2.1%, supporting by an exotherm at 591°C. The oxide showed further continuous decrease in the weight from 690°C onwards till 1000°C recording a 2.39% loss. In all the steps involving weight loss and gain could be attributed only to fraction of oxygen, a common feature of the non-stoichiometric oxides.

The far infrared spectral bands at 405 and 340 cm^{-1} could be attributed to the (Co-O) and (Ni-O). The band at 160 cm^{-1} suggested [14] the presence of Mn-Mn bond and the band at 360 cm^{-1} could be attributed to Mn-O multiple bonding. The band at 446 cm^{-1} is due to ν(Co–O). These assignments further evidence the formation of an integrated Mn-Co-Ni-oxides system. The applied magnetic field (Kilo Gauss) and the magnetic moment (emu) observed are 2 (0.0134×10^{-1}), 4 (0.025×10^{-1}), 6 (0.032×10^{-1}), 8 (0.044×10^{-1}) and 10 (0.054×10^{-1}). The magnetic moment was calculated to be 1.34 BM after incorporating the necessary diamagnetic correction. The analytical data suggested the probable chemical composition as $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$. The oxidation states of the metal atoms have been suggested based on the magnetic moment value. If manganese(II) and cobalt(II) were oxidized to manganese(III) and cobalt(III) and with nickel(II) being stable, the theoretical magnetic value of Mn(II) gives to 2.84 BM per manganese atom. For 0.06 manganese atom the contribution is 0.17 BM. Co(III) with d^6 configuration is diamagnetic. Ni(II) with d^8 configuration has the magnetic moment of 2.84 BM per nickel atom. For 0.6 Ni atom of nickel the contribution is 1.704 BM. Thus the total expected theoretical magnetic moment of the non-stoichiometric compound should be 1.874 BM. This observed value is much less than the calculated magnetic moment, which could be attributed to the extensive spin-spin interaction between the two paramagnetic metal centers that are very close to each other.

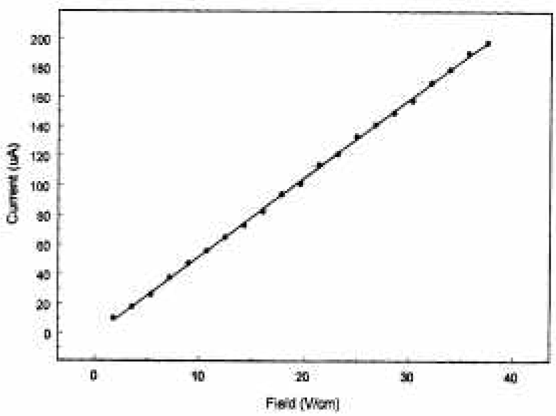

Fig. 3. Field vs current studies of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

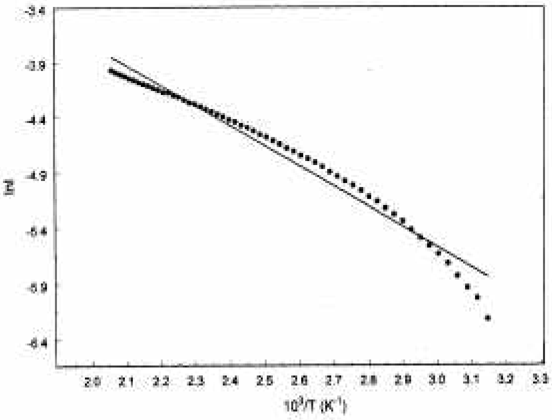

Fig. 4. lnI vs 1000/T plots of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

The electrical field was varied from 1.75 to 38 V/cm and the corresponding current was recorded. The current was found to vary linearly (Fig. 3) with the applied field suggesting the ohmic nature of the sample. The resistance of the material and the conductance at the ambient temperature were calculated using the Ohms law. The resistance at 30°C was found to be 2.115×10^4 ohm from which the conductance was calculated to be 4.7×10^{-5} ohm^{-1}. The temperature dependence of electrical conductivity was carried out in the temperature range of 350–600 K (Fig. 4). From the temperature dependence conductivity data, a lnI vs 1/T plot was drawn to determine the activation energy. The activation energy calculated for $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$ composite was 0.24 eV respectively.

The results of resistance measured as a function of relative humidity at a fixed ambient temperature of 298 K are presented in Fig. 5. The resistance of the composites is in order of 10^9 ohms under dry conditions (RH5%). The plot of logR vs RH (%) shows that sensitivity towards moisture of the composites. As the humidity is increased, the logR value drops and the sensitivity of the elements towards humidity increase. The composite is found to have the highest sensitivity factor $S_f = 5\times10^4$ as inferred from the ratio $R_{5\%}/R_{98\%}$, where $R_{5\%}$ and $R_{98\%}$ are the dc resistances at 5% and 98% RH respectively. The variation in logR with RH(%) is almost linear in the entire range of humidity, a prerequisite for commercial humidity sensors.

The Brunauer–Emmett–Teller (BET) surface adsorption studies revealed that the pore size of the samples were distributed (Fig. 6) between 10 and 45 Å in radius, and the specific volume of the pore was 0.01 cm^3 gm^{-1} which can easily trap the water molecules to it. The sensitivity factor of the composition should be indicative of the extent of moisture condensation in the pores. The pore size, grain size of the two phases, and the distribution of the pores should in turn govern the extent of moisture sorption. The scanning electron microscopy (SEM) photograph of the sensor materials sintered at 973 K for 5 h indicated that the porosity and grain size of the materials significantly increases. SEM photographs revealed (Fig. 7) qualitatively that $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$ has greater and larger number of pores.

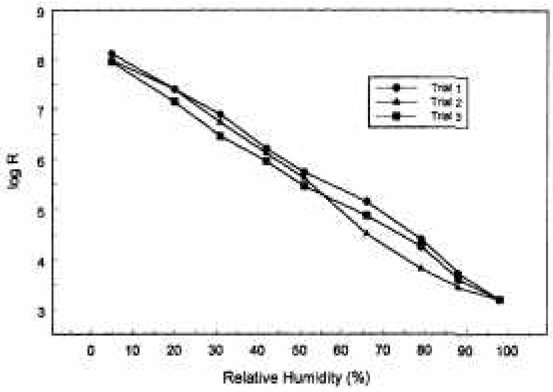

Fig. 5. log R vs RH (%) plot of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

Fig. 6. SEM photograph of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

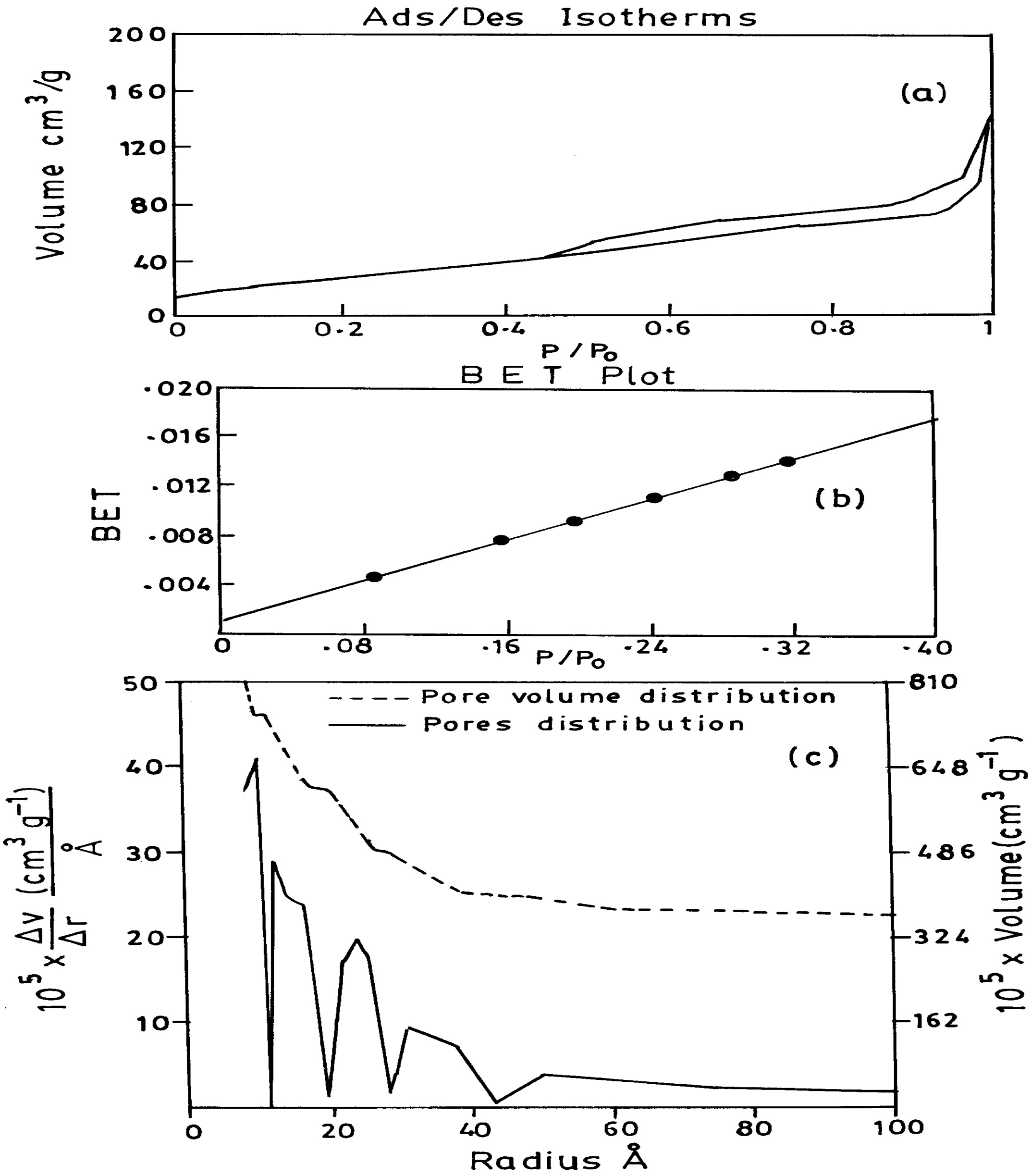

Fig. 7. Pore size and pore volume distribution of $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{3-\delta}$ composite.

The evaluation of the response and recovery characteristics has been carried out. The DC resistance in dry air as well as in moist air alternatively helped to establish the response and recovery characteristics. The results (Fig. 8) show that the invariant resistance in dry air is in the order of 10^9 ohms. Within about 3 min of purging with moist air, the resistance drops by three orders of magnitude to reach a constant value of approximately 10^3 ohms. However, when dry air was again introduced to monitor the recovery characteristics, the recovery time was around 6 min. Hence for better response and recovery characteristics, the sensors were repeatedly heat-refreshed at 353 K before and after the measurements.

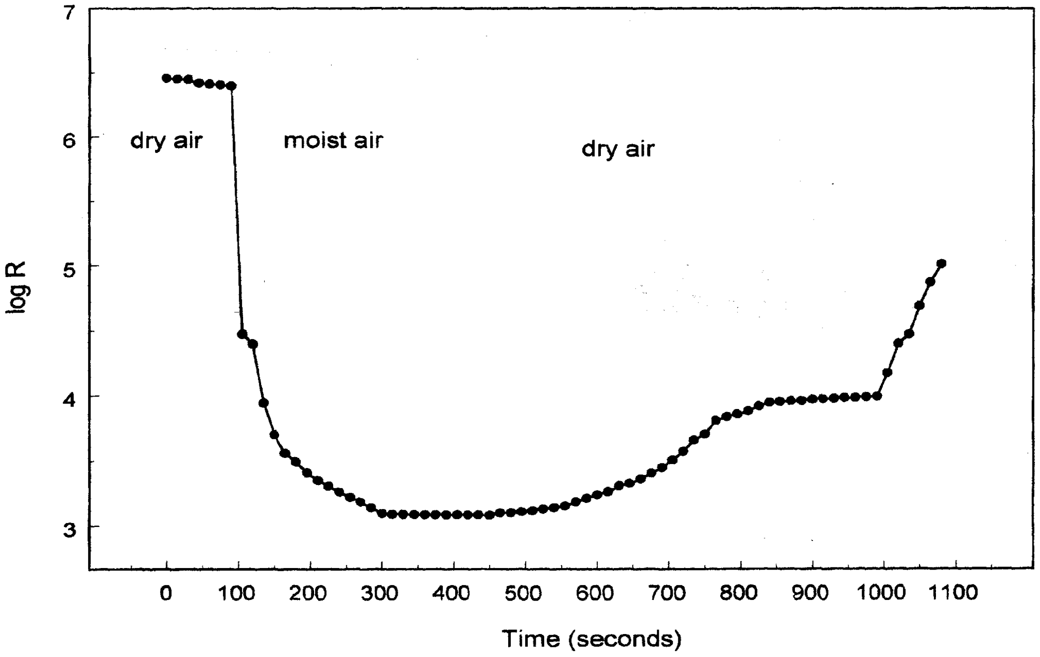

Fig. 8. Invariant resistance in dry air.

4. Conclusions

A novel mixed oxide of Mn, Ni and Co was synthesized by a combined solution route and solid-state high temperature route. The chemical composition was suggested to be $Mn_{0.06}Co_{0.6}Ni_{0.6}O_{2.5}$ based on the AAS data. The scanning electron microscope revealed that the Mn-Co-Ni oxide has larger and greater number of microscopic pores hence is a good candidate for humidity sensor, which was further evidenced by the surface studies and its sensitivity factor higher than 5.5×10^4. The good response and recovery characteristics even at 298K were another proof for a good humidity sensor and could be used either *in situ* or on line applications.

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