

Humidity sensing behaviour of polyaniline/magnesium chromate (MgCrO₄) composite

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Abstract. ‘*In situ*’ polymerization of polyaniline (PANI) was carried out in the presence of magnesium chromate (MgCrO₄) to synthesize PANI/ceramic (MgCrO₄) composite. These prepared composites were characterized by XRD, FTIR and SEM, which confirm the presence of MgCrO₄ in polyaniline matrix. The temperature dependent conductivity measurement shows the thermally activated exponential behaviour of PANI / MgCrO₄ composites. The decrease in electrical resistance was observed when the polymer composites were exposed to the broad range of relative humidity (ranging between 20 and 95% RH). This decrease is due to increase in surface electrical conductivity resulting from moisture absorption and due to capillary condensation of water causing change in conductivity within the sensing materials. PANI / MgCrO₄ composites are found to be sensitive to low humidity ranging from 20 to 50 % RH.

Keywords. Polyaniline; ceramic; magnesium chromate; humidity sensor.

1. Introduction

Humidity sensors are of increasing interest in electronic control systems (Kulwicki 1991). Many different materials have been studied and used as sensing elements in humidity measurement devices. Amongst them, ceramic oxides have shown advantages in terms of thermal, physical and chemical stability, and mechanical strength. For humidity sensing, ceramic materials have mainly been used in the form of porous sintered bodies. Thus, controlling porosity and surface activity is of great importance in determining the humidity-sensitive electrical properties of ceramic products (Traversa 1995). During the last two decades, numerous humidity sensors based on different transduction techniques have been studied extensively at both room and elevated temperatures (Delannoy *et al* 2000; Sakai *et al* 2000; Ren *et al* 2001; Gu *et al* 2004). Generally, a humidity sensor has to match stringent working requirements, possess fast response, high sensitivity, negligible hysteresis over periods of usage and possibly a large operating range for both humidity and temperature. And all these issues are not yet fully satisfied by a single commercially available sensor. Ceramic materials used for detection of humidity are represented by metal oxides, for which different mechanisms of conduction in a humid environment have been reported, each corresponding to a class of sensors, i.e. ionic, electronic, solid electrolytes and hetero-contacts (Traversa 1995; Nenov and Yordanov 1996). Ceramic-type humidity sensors are based on sintered oxides via solid state reactions and in general possess superior performance to electrolytic and polymeric

sensors, due to their high thermal stability with respect to a variety of chemical species, wide range of operating temperatures, fast response to changes in humidity (Viviani *et al* 2001; Cosentino *et al* 2003) and the ease with which it may be produced in thin film form. However, they are to a certain extent, not fully satisfactory in terms of the need for periodic thermal cycling to recover their humidity-sensitive properties. In recent years, thin film ceramic sensors possessing nanometer-scale grain size and porous structure have drawn particular interest because of their potential applications in micro sensors (Tai and Oh 2002). Three basic phenomena lie behind the operational principles of both polymeric and ceramic humidity sensors: the formation of a chemically adsorbed layer of hydroxyl ions bonded to metal ions at the grain surface; the successive growth of multi-layer, physisorbed water molecules; and further condensation of liquid water into capillary pores. Contribution to surface conductance can be expected from both protons hopping between adjacent hydrogen bonded water molecules (Toshko *et al* 1996) and the electrolysis of the condensed liquid. In addition, reorientation of the molecules in the second physisorbed layer under an applied field produces a variation in the dielectric constant with air moisture.

As conducting polymers, polyaniline (PANI) and its derivatives have been found to be humidity sensitive for a long time (Chiang and MacDiarmid 1986; Nechtschein *et al* 1987). Due to polymerization by some strong oxidant (e.g. (NH₄)₂S₂O₈), PANI synthesized in this manner may be regarded as *p*-type doping. Due to the un-bonded electron pair on the nitrogen atom, both forms can be protonated, according to a buildup model (Chen and Lu 2005; Parvatikar *et al* 2006, 2007), the electron transferring (hopping) from

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the 'protonated reduced form' to the 'protonated oxidized form' is the dominant conduction process of PANI. Absorbed water molecules play an important role in the conductivity. The humidity-sensing property of PANI to water vapour can be regarded as electron hopping assisted by proton exchange. The ionic conduction is favourable as long as mobile counter ions (for example, Cl^-) exist in the polymer (Angelopoulos *et al* 1987). Many polyaniline and metal oxide composites have been studied, for example, polyaniline–molybdenum trisulfide composite (Fusalba and Belanger 1999), conducting polyaniline/inorganic salt composite (Krivka *et al* 1999), and polyaniline V_2O_5 composite (Lira-Gautu and Gomez-Romero 1999). Many oxide ceramic materials have been successfully tested, based for example on $\text{TiO}_2\text{-SnO}_2$ (Arai and Seiyama 1991), SiO_2 (Uchikawa and Shimamoto 1985), MgFe_2O_4 (Montesperelli *et al* 1995), $\text{MgCr}_2\text{O}_4\text{-TiO}_2$ (Kim

et al 1992). These promising ceramic materials and conducting polyaniline has motivated the authors to study humidity sensing properties of organic and inorganic composites.

In this communication we report data on the preparation, characterization, electrical and humidity-sensing properties of polyaniline and polyaniline/ceramic (MgCrO_4) composites.

2. Experimental

All chemicals used were of analytical grade (AR). The monomer aniline was doubly distilled prior to use. Ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), hydrochloric acid (HCl) and magnesium chromate (MgCrO_4) were procured and used as received. Synthesis of polyaniline–magnesium chromate

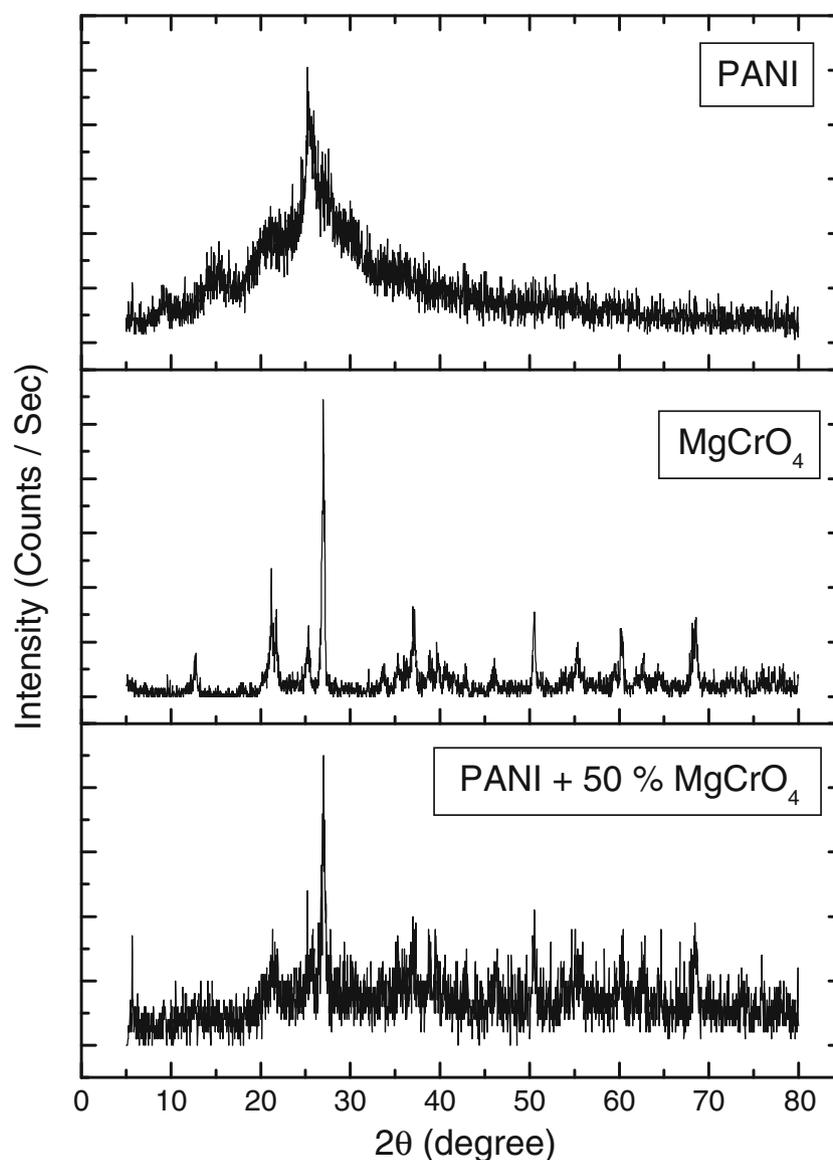


Figure 1. X-ray diffraction pattern of pure PANI, MgCrO_4 and polyaniline MgCrO_4 composite with 50 wt% of MgCrO_4 in polyaniline.

($MgCrO_4$) composites was carried out by *in situ* polymerization. 0.1 mol of aniline was dissolved in 1 M HCl to form aniline hydrochloride. Magnesium chromate ($MgCrO_4$) in weight percentages of 10, 20, 30, 40 and 50 was added to the above solution with vigorous stirring in order to keep magnesium chromate suspended in the solution. To this reaction mixture, 0.1 M of ammonium persulphate $[(NH_4)_2S_2O_8]$ which acts as the oxidant was added slowly with continuous stirring for 4–6 h at 0–5 °C to polymerize. The precipitated powder recovered was vacuum filtered and washed with deionized water. Finally the resultant precipitate was dried in an oven for 24 h to achieve a constant weight. In this way 5 different polyaniline / $MgCrO_4$ composites with different wt% of $MgCrO_4$ in polyaniline were synthesized (Parvatikar *et al* 2006, 2007). The pellets of 10 mm diameter were formed with a thickness varying up to 2 mm by applying pressure of 10 tons in a UTM – 40 (40 Ton Universal testing machine). For temperature dependent conductivity and sensor studies, the pellets were coated with silver paste on either side of the surfaces. The copper elec-

trodes were placed on each of the surface to obtain better contacts.

The characterization technique like X-ray diffraction studies were performed on Phillips X-ray diffractometer (PW3710) with Cu $K\alpha$ as source of radiation. FTIR spectra of samples were recorded on a Perkin – Elmer 1600 spectrophotometer in KBr medium and SEM has been carried out for polyaniline / $MgCrO_4$ composites, on Phillips XL 30 ESEM.

The specific electrical conductivity of a solid ' σ ' $S\ cm^{-1}$, was defined as the current, in amps, flowing through a centimeter cube of the material under unit electrical potential. Measurement of temperature dependence of electrical conductivity was carried out using Keithley - 2000 multimeter, USA.

The samples in the pellet form were used for humidity sensing. The planar resistance of the sensor was recorded by controlling the humidity in a closed glass chamber at room temperature. The humidity was first lowered by keeping $CaCl_2$ in a chamber. Controlled water vapours at room

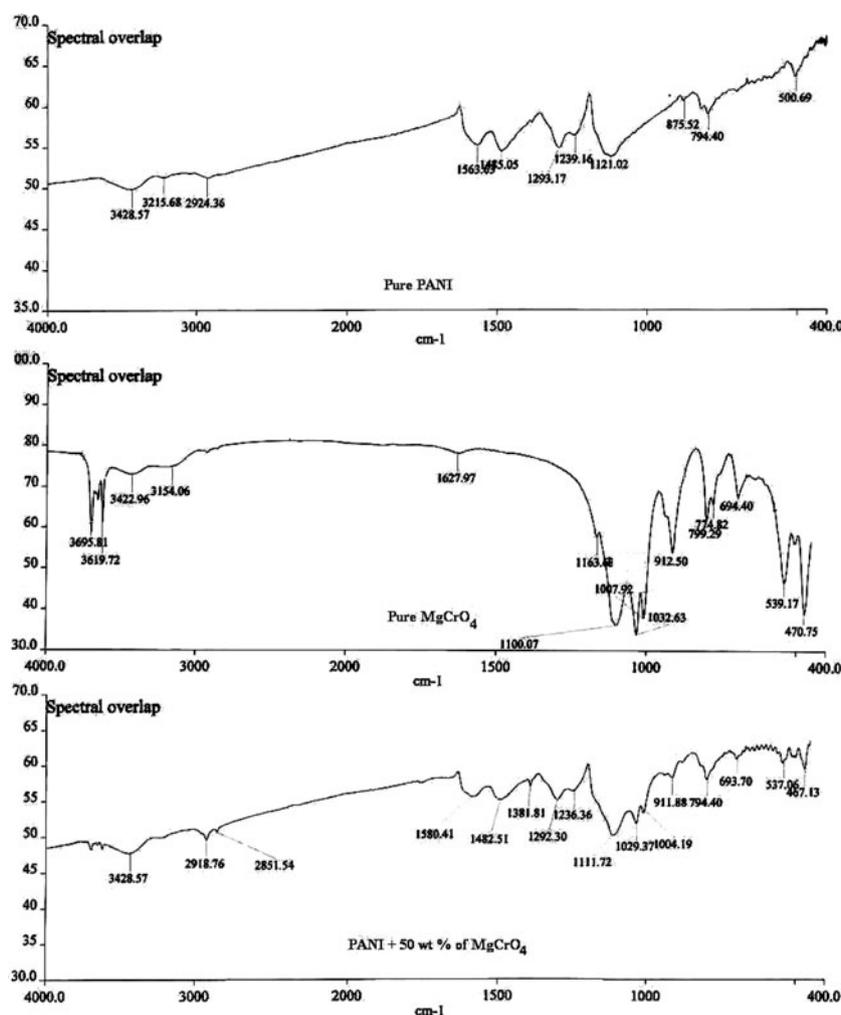


Figure 2. FTIR spectra of pure PANI, $MgCrO_4$ and polyaniline $MgCrO_4$ composite with 50 wt% of $MgCrO_4$ in polyaniline.

temperature were then introduced steadily for increasing the humidity inside the chamber which was maintained from 20 to 95 %RH. Relative humidity inside the chamber was monitored by a standard pre-calibrated humidity meter (Mextech-DT-615).

3. Results and discussion

The results thus obtained from the experimental technique are discussed as follows. Figure 1 shows X-ray diffraction pattern of pure PANI, MgCrO_4 and polyaniline- MgCrO_4 composite with 50 wt% of MgCrO_4 in polyaniline. It is seen from the figure that the orthorhombic peak of MgCrO_4 indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of MgCrO_4 , prominent peaks correspond to $2\theta = 21.85^\circ, 35.32^\circ, 39.75^\circ, 41.51^\circ$ and 48.75° and are due to (111), (112), (220), (221) and (113) planes (JCPDS 72-1606) of MgCrO_4 . By comparing XRD patterns of the composite and MgCrO_4 , it is confirmed that MgCrO_4 has retained its structure even though

dispersed in PANI during polymerization reaction (Parvatikar *et al* 2006, 2007).

FTIR spectra of pure PANI, MgCrO_4 and PANI + 50 wt% of MgCrO_4 is shown in figure 2. The important peaks observed in MgCrO_4 are at 467 cm^{-1} and 537 cm^{-1} which are due to the presence of metal oxygen stretching frequencies. The characteristic stretching frequencies are observed at 3428 cm^{-1} for NH stretching, 1627 cm^{-1} for benzenoid ring stretching, 1580 cm^{-1} for quinoid ring stretching, 1482 cm^{-1} for $\text{C}=\text{N} + \text{C}-\text{C}$ stretching, 1381 cm^{-1} for $\text{C}-\text{N}$ stretching + CH bending, 1292 cm^{-1} for $\text{C}-\text{N}$ stretching + $\text{C}-\text{C}$ stretching, and 794 cm^{-1} for metal oxygen stretching. By comparing IR spectra of polyaniline and polyaniline- MgCrO_4 composite, it is observed that in the composite the characteristic stretching frequencies are shifted toward higher frequency side which may be attributed due to the van der Waals kind of interaction between MgCrO_4 and polyaniline chain (Lu *et al* 1986; Sun *et al* 1990; Parvatikar *et al* 2006, 2007).

Figure 3 shows the scanning electron micrograph (SEM) of pure PANI and polyaniline- MgCrO_4 composite (50 wt% of MgCrO_4 in polyaniline). Among five composites that were synthesized using MgCrO_4 with different wt% (10, 20, 30, 40 and 50), a composite of polyaniline- MgCrO_4 with 50 wt% of MgCrO_4 in polyaniline is selected to obtain

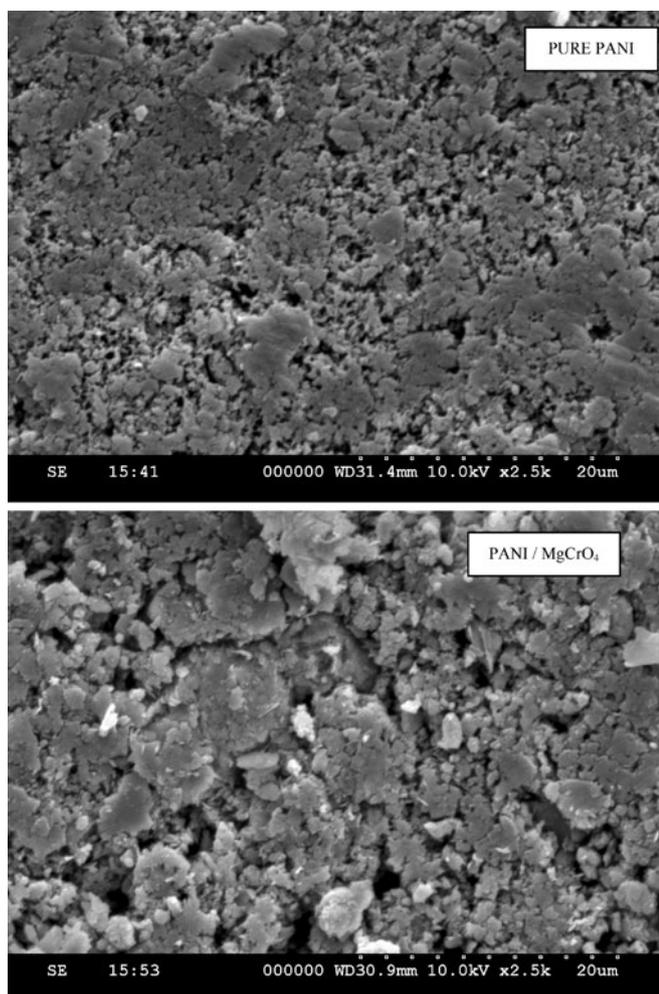


Figure 3. SEM of pure PANI and polyaniline MgCrO_4 composite with 50 wt% of MgCrO_4 in polyaniline.

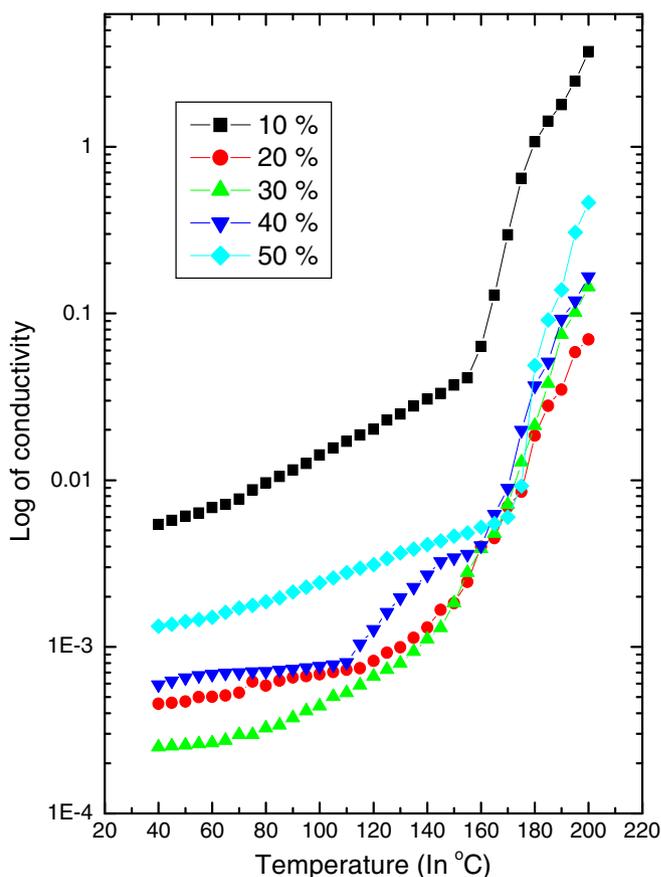


Figure 4. Variation of $\log \sigma_{dc}$ as a function of temperature of PANI / MgCrO_4 composites.

SEM micrograph. A very high magnification reveals the presence of MgCrO₄ in polyaniline which is homogeneously distributed throughout the polymer sample. From SEM micrograph it clearly indicates highly branched chain structure (or branched morphology) (Parvatikar *et al* 2006, 2007). The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and MgCrO₄.

Figure 4 shows variation of log of d.c. conductivity as a function of temperature which suggests that as temperature increases conductivity also increases, hence thermally activated exponential behaviour of conductivity has been observed. Also, there had to be molecular rearrangement on heating, which made the molecular conformation favourable for electron delocalization (Kobayashi *et al* 1993). The conductivity varies directly with temperature, obeying an expression of the following form:

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/4}],$$

where σ is the conductivity, T the temperature, and σ_0 the conductivity at characteristic temperature T_0 . Conductivity varies with various values of the exponent (e.g. $T^{-1/4}$, $T^{-1/3}$, $T^{-1/2}$, and T^{-1}) which have been reported, and different models have been used to interpret the data. Also, for the first time, an allometric scaling law for a conductive polymer

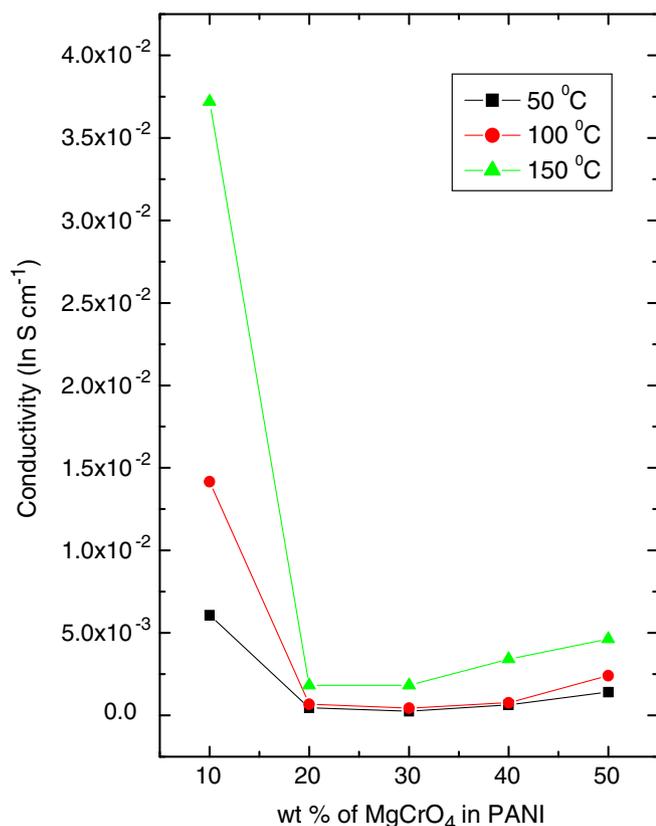


Figure 5. Conductivity vs wt% of MgCrO₄ in polyaniline at three fixed temperatures.

between the resistance and the section area was proposed (He 2004). Figure 5 shows the conductivity vs wt% MgCrO₄ in PANI at three fixed temperatures viz. at 50°, 100° and 150°C. Through the graph it has been observed that the values of d.c. conductivity of these composites decreases till 20 wt% of MgCrO₄ in polyaniline and for excess wt% of MgCrO₄ in polyaniline, d.c. conductivity increases up to 50 wt% of MgCrO₄ in polyaniline.

The initial increment in conductivity for 10 wt% of MgCrO₄ in polyaniline may be due to extended chain length of polyaniline in which the charge carriers possess sufficient energy to hop between various favourable localized sites. For 20, 30, 40 and 50 wt% of MgCrO₄ in polyaniline, because of blocking of charge carrier, charge carriers are unable to hop between favourable localized sites and hence conductivity decreases (Parvatikar *et al* 2006, 2007).

Figure 6a shows the variations in resistance as a function of relative humidity (RH) value for pure PANI (0 wt% of MgCrO₄). Under dry conditions the polymer chains would tend to curl up into compact coil form. On the contrary, at high humidity, the polymer absorbs water molecules, followed by the uncurling of the compact coil into straight chains, those which are aligned with respect to each other

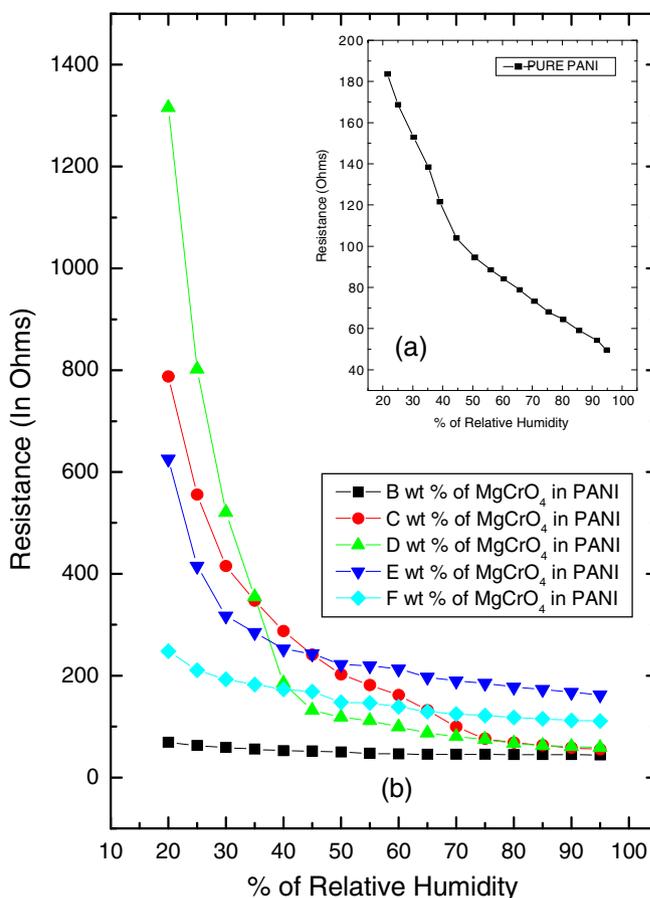


Figure 6. Variations of resistance as a function of relative humidity (%RH) value for (a) pure polyaniline and (b) PANI / MgCrO₄ composites.

is responsible for variation in resistance. Figure 6b shows the variations in resistance as a function of relative humidity (RH) value for PANI/MgCrO₄ composites in the form of pellets as shown in figure 7. The decrease in resistance or increase in conductivity with increasing relative humidity can be attributed to the conversion of polymer complex into more *p*-type in nature due to absorption of water molecules, i.e. the hole concentration is increased by donation of the lone pair from the conducting complex towards the MgCrO₄ water molecules. Thus, the partial charge transfer process of conducting species with that of water molecules results into the decrease in sheet resistivity. Further the presence of MgCrO₄ in PANI increases absorption of water molecules, hence the variation of resistance in PANI / MgCrO₄ composite is observed in comparison with pure PANI (Parvatikar *et al* 2006, 2007). The conductivity depends on capillary

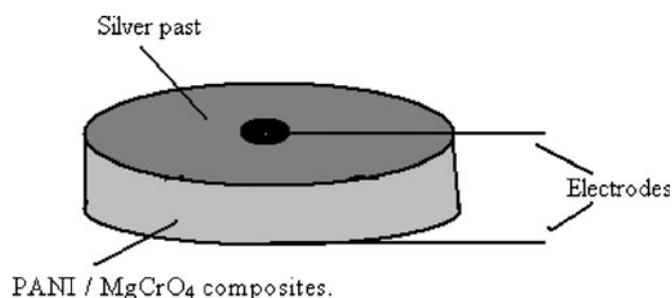


Figure 7. Sample in pellet form used for humidity sensing.

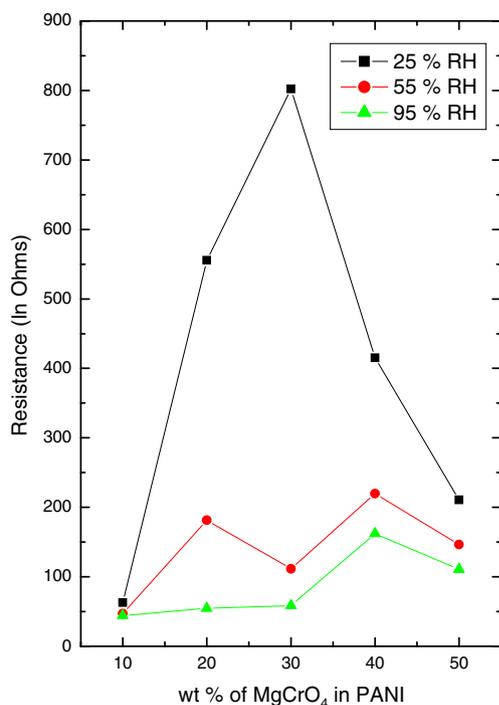


Figure 8. Resistance vs wt% MgCrO₄ in polyaniline at three fixed percentages of relative humidity (25, 55, 95 %RH).

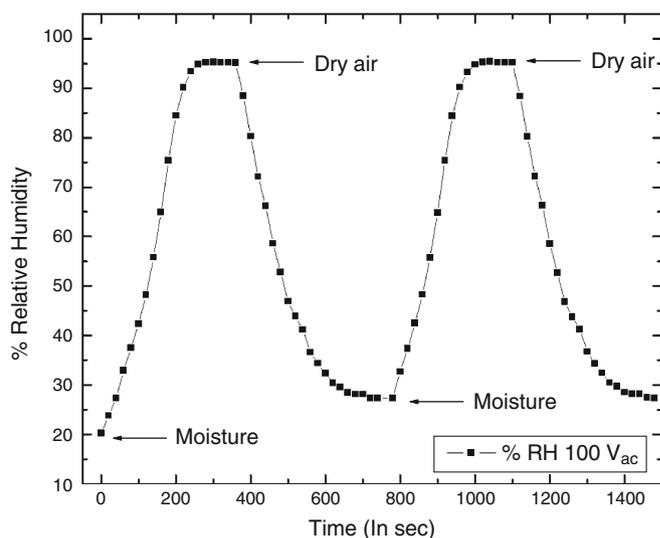


Figure 9. Response and recovery behaviour of humidity sensor obtained at room temperature.

condensation of water causing ionic conductivity within the sensing materials (Yamazoe and Shimizu 1986). The resultant surface conductivity increases with increase in humidity due to combined effect of the proton type hopping and the ionic conduction (Pingale *et al* 1996). The performance characteristics of humidity sensor, such as sensitivity, reproducibility, and response time are correlated to its microstructure. The specific surface area is the principle microstructure for sensing humidity under low RH conditions, while mesopore volume dominates under high RH conditions. Definite correlation was obtained between resistance quantities of water taken up by porous of the materials (Chou *et al* 1999). Figure 8 shows the variation of conductivity with weight percent of MgCrO₄ in PANI for six different wt% of MgCrO₄ (0, 10, 20, 30, 40 and 50 wt%) in PANI, where it is observed that the addition of MgCrO₄ in PANI matrix has increased the resistance and facilitates the absorption of water molecules. Further it is observed that as weight percent of MgCrO₄ increases, the resistance increases up to 30 wt% and with further increase in wt%, the resistance decreases. It is reported that 30 wt% of MgCrO₄ in PANI is very sensitive to humidity.

Response and recovery behaviour is one of the significant features for the estimation of humidity sensors. Constant humidity is used for the measurement of response time. Figure 9 shows response and recovery times of the humidity sensor, in which the relative humidity is plotted against time in seconds. For the 20 and 95 % RH environment, there is a steady increase and saturates after 95 % RH and by the introduction of dry air there is a steady decrease. The sensor is occasionally dewed during the measurements at high humidity. In general, humidity sensors tend to drift significantly when used at high humidity. The humidity response and recovery times are found to be 6.6 min and one cycle of increasing and decreasing humidity is found to be 13.3 min.

4. Conclusions

In this communication, we have presented a humidity sensor based on polyaniline/magnesium chromate (PANI/MgCrO₄) composites synthesized by 'in situ' polymerization. This is the novel polymerization process for direct synthesis of emeraldine phase of the polymer and its composites. Formation of mixed phases of polymer together with conducting emeraldine salt phase is conformed for the spectroscopic techniques. High temperature conductivity measurements show thermally activated exponential behaviour. The decrease in the resistance or increase in the conductivity with increasing humidity can be attributed to the mobility of MgCrO₄ ion which is loosely attached to the polymer chain by weak van der Waals forces of attraction, mobility of ions may be due to principle microstructure of specific surface area exposed and capillary condensation of water molecules within the sensing material. These composites are sensitive to low humidity ranging from 20–50 % of RH, high sensitivity is observed for PANI/30 wt% of MgCrO₄ composite. The response and recovery times for increasing and one cycle times being 6.6 and 13.3 min, respectively. Polyaniline / magnesium chromate (MgCrO₄) proves to be a competent material for low humidity sensing.

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References

- Angelopoulos M, Ray A, MacDiarmid A G and Epstein A J 1987 *Synth. Metals* **21** 21
- Arai H and Seiyama T 1991 *Humidity sensors*, in: *Sensors: A comprehensive survey* (eds) W Göpel *et al* (VCH) 1990 **3** pp 982–1012
- Chen Zhi and Lu Chi 2005 *Sens. Letts* **3** 274
- Chiang J C and MacDiarmid A G 1986 *Synth. Metals* **13** 193
- Chou Kan-Sen, Lee Tzy-Kuang and Liu Feng-Jiin 1999 *Sens. Actuators* **B56** 106
- Cosentino I C, Muccillo E N S and Muccillo R 2003 *Sens. Actuators* **B96** 677
- Delannoy F P, Sorli B and Boyer A 2000 *Sens. Actuators* **A84** 285
- Fusalba F and Belanger D J 1999 *Mater. Res.* **14** 1805
- Gu Lei, Huang Qing-An and Qin Ming 2004 *Sens. Actuators* **B99** 491
- He J-H 2004 *Polymer* **45** 9067
- Kim T Y, Lee D H, Shim Y C, Bu J U and Kim S T 1992 *Sens. Actuators* **B9** 221
- Kobayashi A, Ishikawa H, Amano K, Satoh M and Hasegawa E 1993 *J. Appl. Phys.* **74** 296
- Krivka I, Prokes J, Tobolkova E and Stejskal J J 1999 *Mater. Chem.* **9** 2425
- Kulwicki B 1991 *J. Am. Ceram. Soc.* **74** 697
- Lira-Gautu M and Gomez-Romero P J 1999 *Solid State Chem.* **147** 601
- Lu F L, Wudl F, Nowak M and Heeger A J 1986 *J. Am. Chem. Soc.* **108** 8311
- Montesperelli G, Bianco A, Morten B, Prudenziati M, Traversa E, Gusmano G and Traversa E (eds) 1995 *Proceedings of the 4th Euro-Ceramics, Gruppo Editoriale Faenza Editrice S.p.A. (Italy: Riccione)* **Vol. 5**, pp 467–474
- Nechtschein M, Santier C, Travers J P, Chroboczek J, Alix A and Ripert M 1987 *Synth. Metals* **18** 311
- Nenov T G and Yordanov S P 1996 *Ceramic sensors* (Basel: Technomic) pp 74–75
- Parvatikar Narsimha, Khasim Syed, Revansiddappa M, Jain Shilpa, Bhoraskar S V and Ambika Prasad M V N 2006 *Sens. Actuators* **B114** 599
- Parvatikar Narsimha, Jain Shilpa, Kanamadi C M, Chougule B K, Bhoraskar S V and Ambika Prasad M V N 2007 *J. Appl. Polym. Sci.* **103** 653
- Pingale S S, Patil S F, Vinod M P, Pathak G and Vijayamohan K 1996 *Mater. Chem. Phys.* **46** 72
- Ren Y, Mormile P, Petti L and Cross G H 2001 *Sens. Actuators* **B75** 76
- Sakai Y, Matsuguchi M and Hurukawa T 2000 *Sens. Actuators* **B66** 135
- Sun Y, MacDiarmid A G and Epstein A J 1990 *J. Chem. Soc. Chem. Commun.* **7** 529
- Tai W P and Oh J H 2002 *Thin Solid Films* **422** 220
- Toshko G, Nenov P, Stefcho D and Yordanov P 1996 *Ceramic sensors, technology and applications* (Pennsylvania: Technomic Publishing Company) p. 87
- Traversa E 1995 *Sens. Actuators* **B23** 135
- Uchikawa F and Shimamoto K 1985 *Am. Ceram. Soc. Bull.* **64** 1137
- Viviani M, Buscaglia M T, Buscaglia V, Leoni M and Nanni P 2001 *J. Eur. Ceram. Soc.* **21** 1981
- Yamazoe N and Shimizu Y 1986 *Sens. Actuators* **B10** 379