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Study of Cerium Doped Polyaniline Composites for Resistive Type CO_2 Gas Detection

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Abstract

Polyaniline (PANi) has been regarded as a good sensing material due to its advantages of gas sensing ability and optimum performance at room temperature. The thick films of chemically synthesized cerium (Ce) doped polyaniline (PANi) were prepared by screen-printing on a glass substrate. The 5 samples of Ce doped PANi were synthesized by varying $CeCl_3$ concentration from 0.1 to 0.5 M in constant 1 M aniline monomer with ammonium persulfate as an oxidant at room temperature. The sensitivity of films was measured for different concentration of CO_2 gas (injection) at room temperature. The film of the 0.1 M concentration shows the highest sensing response. The O_2^- ions may form weak bonds with free electrons in the conduction band. This may lead to formation of surface carbonates. This causes an increase in the resistance of the material in the presence of CO_2 gas. The material (0.1 M) in powder form was characterized by FTIR analysis for the confirmation of polymerization of aniline.

Keywords: Cerium, polyaniline, screen-printing technique, CO_2 gas

Introduction

Conducting polymers and their composites with metal oxides have a large spectrum of applications due to their low cost, relative simplicity and easy surface modification. The polymer composites may constitute the key for the development of semiconducting gas sensors with improved gas-sensing properties. Not only in chemo-resistive gas sensors, but also in general in solid state gas sensors, composite materials play a fundamental and determinant role in the new generation of gas sensors. The conducting polymer composites are, in fact, devoting great efforts to the development of novel materials for gas sensor applications. Ozkazanc *et al.* [1] reported the investigation of morphological, thermal and dielectric properties of chemically synthesized polyaniline and its cerium (III)-nitrate-hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) doped composites with various doping levels. Kosalge *et al*. [2] investigated the CeO_2 thick film resistors and their sensitivity to CO_2 gas. Cerium chloride can be used as a precursor material rather than cerium nitrate [3,4]. Cerium chloride is a better material to use in biological applications due to the fact that leftover chloride should not harm a biological system, as it is likely to already have chlorine in its environment [5]. PANi, a kind of conductive conjugated polymer, has been regarded as a good sensing material due to its advantages of gas sensing ability and optimum performance at room temperature. It has been exploited in thin films sensors for several gas molecules as well as volatile organic compounds. In spite of the various advantages of PANi based gas sensors, some fundamental problems, such as long-time instability and irreversibility and low selectivity, still persist [6-11]. During the past 2 decades, both fundamental and applied research in conducting polymers has grown enormously [12]. PANi owing to its ease of synthesis, remarkable environmental stability, and high conductivity in the doped form, has remained one of the most thoroughly studied conducting polymers. While it is long known that proton doping can make PANi conducting, the possibility of using non-protonic dopants such as electron-decent Lewis acids was demonstrated only about 10 years ago [13-16].

In the present study, the thick films of Ce doped PANi materials were prepared by screen-printing on a glass substrate. The sensing response of sensor films was investigated for CO_2 gas at different concentrations at room temperature. The material was characterized by FTIR analysis to determine the extent of polymerization of aniline.

Materials and methods

AR grade chemicals (SD Fine, India) were used in the present work. Ce doped PANi under investigation was prepared in the laboratory for different concentration of $CeCl_3$ (0.1 - 0.5 M). A solution of 1 M ammonium persulfate in 20 ml distilled water was first prepared in a round bottom flask. The aniline monomer (1 M) was added to the ammonium persulfate solution with constant stirring. During polymerization of the aniline monomer, $CeCl_3$ (0.1 M) was added into the solution. As the polymerization is a low temperature favored process, the polymerization was left for 12 h at room temperature. A powder material formed after complete evaporation of water. In the same way, material samples were synthesized for 0.2 - 0.5M $CeCl_3$.

The sensor films were prepared by screen-printing. The binder was prepared by thoroughly mixing 8 wt. % butyl carbitol with 92 wt. % ethyl cellulose. The paste for screen-printing was prepared by taking 60 wt. % $CeCl_3$ powder with 40 wt. % binder in an agate mortar and thoroughly mixed. Cleaned and dried glassware was used in this study to maintain purity and reproducibility of results. The paste thus prepared was screen printed onto a chemically cleaned glass substrate of size 25 × 25 mm and then dried at room temperature (303 K) for 24 h. The prepared film was heated at 323K for 3 h. During this stage, the volatile organic solvent was removed via decomposition and the prints adhered to the substrate. For surface resistance measurements the electrodes of conducting silver paint were formed on adjacent sides of the film and then the film was subjected to heating at 80 °C for 15 min to dry the silver paint. The resistance of films was determined using a voltage divider. The film was characterized by FTIR spectroscopy for confirmation of polyaniline peaks as well as spectral data of synthesized materials.

Results and discussion

Figure 1 shows the FTIR analysis of the 0.1 M sample. Prominent peaks were observed in the FTIR and confirm polymerization of the aniline monomer. The FTIR spectra of the Ce doped PANi powder samples were recorded in the range 4000 - 400 cm^{-1} to confirm polymerization. The IR spectrum of the Ce doped PANi shows six principal absorptions at 1590, 1508, 1304, 1210, 1145 and 831 cm^{-1}. The peaks at 1590 and 1508 cm^{-1} are assigned to C-C ring stretching vibrations. The peaks at 1304 - 1310 cm^{-1} correspond to N-H bending. The bands at 1145 and 831 cm^{-1} can be attributed to the in plane and out-of-plane C-H bending modes, respectively. The band at 1145 cm^{-1} does not appear prominently due to the high scan rate. The corresponding peaks for the PANi salt appear at 1560, 1482, 1306, 1245.9, 1148 and 814 cm^{-1} respectively. In addition to the above peaks, the spectrum of the polyaniline exhibits new peaks around 3220, 1653 and 684 cm^{-1}. The peak at 2390 cm^{-1} could be attributed as due to NH stretching mode and the 1653 cm^{-1} band to the NH bending vibration. The band characteristic of the conducting protonated form is observed at 1246 cm^{-1}. It has been interpreted as originating from a bi-polaron structure, related to C-N stretching vibration [17].

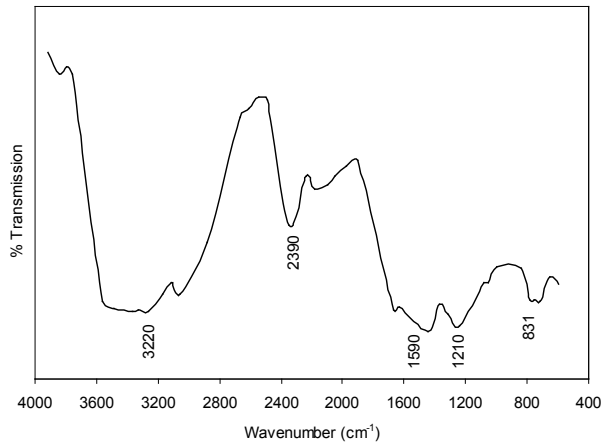

Figure 1 FTIR spectrum of 0.1M Ce doped PANi.

The sensor response is defined as in Eq. (1) [18].

$$S = (Rg - Ra)/Ra \quad (1)$$

where, Ra is the resistance of the sensor in air and Rg is the resistance in CO_2 gas, respectively.

The resistance of the films was found to increase with increasing concentration of CO_2 gas. The sensing response of the films was measured for different concentration of CO_2 gas at room temperature (**Figure 2**). The gas chamber has a volume of 5 L attached to the sensing system for sensor testing. Gas was introduced into the chamber by injection. Each injection introduced 0.38 mg of CO_2 gas. The experiment was carried out 10 times to confirm the reproducibility of the sensor. The results were found to be almost reproducible.

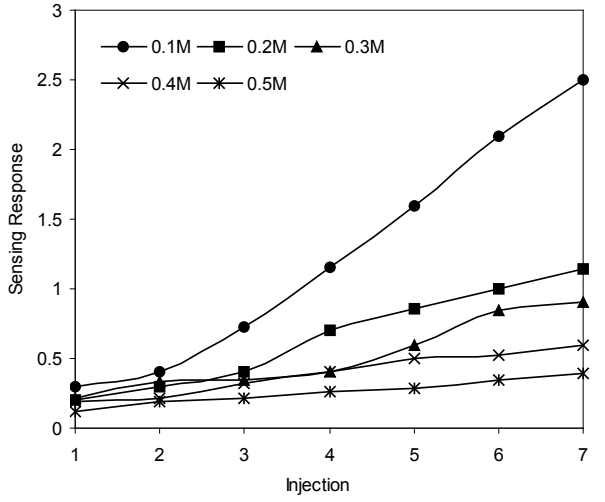

Figure 2 CO_2 gas sensing response of Ce doped PANi films at room temperature.

It is directly notable from the plot that the sensing response decreases with an increase in molar concentration of CeO_2. This shows that lower concentrations of CeO_2 result in improved sensing response. The differences observed in sensing response with 5 Ce (0.1 - 0.5 M) doped PANi films, suggest that a possible mechanism for CO_2 gas detection with the material is based on reactions that occur at the sensor surface, resulting in a change in concentration of adsorbed oxygen. As CO_2 is an oxidizing species, it has high power to withdraw electrons from the sensing surface by forming surface carbonates on the sensing surface. Therefore, the electron density in the conduction band of the film decreases rapidly. This decrease in electron density results in an increase in resistance. The CO_2 molecule may form a weak bond with the π-electron cloud of the polyaniline surface, oxygen ions adsorb onto the surface of the material which removes electrons from the bulk, subsequently increasing the barrier height and the resistively. The mobility of π-electrons of Ce doped PANi may be interrupted by Ce ions. This results in a decrease in sensing response with an increase in molar concentration of Ce in PANi.

Conclusions

The resistance of all Ce doped PANi films increased with an increase CO_2 gas concentration. The decrease in sensing response was observed with increasing concentration of Ce in PANi. O_2^- ions readily form weak bonds with π-electron clouds of PANi. The O_2^- ions adsorb onto the surface of the material which removes electrons from the bulk, subsequently increasing the barrier height and the resistively.

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