INTERNATIONAL JOURNAL OF PURE AND APPLIED RESEARCH IN ENGINEERING AND TECHNOLOGY

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LITHIUM SALT DOPED POLYANILINE CONDUCTING POLYMER- CLADOPHORA BASED CO_2 GAS SENSOR

DR. SARIKA A. KHAPRE, S.P. YAWALE AND S. S. YAWALE, A.V. KOHALE.

Department Of Physics, Genba Sopanrao Moze College Of Engineering, Balewadi, Pune-45

Accepted Date: 15/03/2016; Published Date: 01/05/2016

Abstract: The polyaniline (PANI) has been subject of many studies due to its synthesis, environmental stability and simple doping /dedoping chemistry. The polyaniline conducting polymer is synthesized by chemical oxidation method using ammonium persulfate as oxidizing agent. The cladophora is used as substrate for preparation of thin film of Lithium salt doped polyaniline. Three samples were prepared by varying the Lithium salt such as Li_2SO_4, $LiClO_4$ and LiCl. The sensor so prepared was used for sensing the CO_2 gas at different ppm. It was observed that the sensitivity of the film increases with increase in CO_2 gas concentration. The static and dynamic response of the sensor gives ON and OFF time which are found to be different for different Lithium Salt.

Keywords: Polaniline, CO_2 gas, Li_2SO_4, $LiClO_4$, LiCl, Cladophora.

Corresponding Author: DR. SARIKA A. KHAPRE

Access Online On:

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How to Cite This Article:

Sarika A. Khapre, IJPRET, 2016; Volume 4 (9): 153-161

PAPER-QR CODE

INTRODUCTION

Chemical sensors are devices which are sensitive to changes in their environment, convert the changes into electrical signals and give quantitative or qualitative feedback of these changes. The definitions of chemical sensors are not

always consistent in the literature because there is ambiguity in the definition and distinction between a chemical sensor and a physical transducer. A chemical sensor can be defined as a device that responds to a particular analyte in a selective way through a chemical or physical reaction and that can be used for the qualitative or quantitative determination of the analyte [1]. The development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. It is well known that chemical gas sensor performance features such as sensitivity, selectivity, response time, stability, durability, reproducibility and reversibility are largely influenced by the properties of the sensing materials used [2-4].

In recent years, a great attention has been paid to the development and application of environment gas sensors. Many efforts have been made to develop chemical sensors based on solid state technology, exploiting either the surface characteristic or the bulk conduction properties of ceramics. Based on the surface characteristic, there are two types of sensors, capacitive and resistive (chemoresister). Carbon dioxide is an important gas in many industrial and biological processes, so numerous CO2 sensors have been developed for emissions monitoring and process control. The two most common approaches to CO2 detection are sensors based on electrochemical cells or sensors using Surface Acoustic Wave (SAW) devices. Electrochemical sensors for low temperatures are generally liquid-based, while solid electrolytes can be used in high temperature sensors. SAW-based sensors used for the measurement of mass changes associated with the interaction between CO2 and a CO2-absorbent layer. However, a recent report describes the use of a conducting polymer for development of a solid-state CO2 gas sensor. Gas- sensing materials can be typically classified into two kinds, which are organic and inorganic materials. However these sensors show low performance with respect to sensitivity and selectivity and require an elevated temperature ranging from 100 to 350 oC. On the other hand, gas-sensing devices based on organic materials, such as polyaniline (PANI), have high gas sensitivity at room temperature, whereas their long response time due to orderly structure hinders their usage [5-6]. Literature survey reveals that polyaniline is the oldest and potentially one of the most useful conducting polymers because of its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry [7]. Tin ions doped PANI hydrochloride was synthesized using the monomer of aniline hydrochloride and insitu varying concentration of $SnCl_4$ by chemically oxidative polymerization in presence of oxidant ammonium peroxides. Dan Li et al [8] demonstrated the use of flash-welded polyaniline films for monolithic actuators. In addition, the use of polyaniline nanofibers or their composites can significantly enhance the sensitivity, selectivity and response time of polyaniline-based chemical sensors. Tin dioxide (SnO_2) plays a dominant role in solid state gas sensor and exhibit sensitivity towards oxidizing and reducing gases by the variation of its electrical properties [9,10]. It is seen that semiconducting polyaniline (PANI) thin films have proven to be an optically sensitive element for detecting gaseous NH_3 and NO_2 at room temperature [10], although absorption of either of them on PANI films results in the color change of the films, from green to blue. The mechanism of the interaction of each gas with the polymer is different. The development of conductive PPy-Cladophora cellulose composite paper sheets obtained by combination of PPy and Cladophora cellulose [11] has been addressed for high-tech applications. The conducting polymer polypyrrole based CO_2 gas sensor was studied by Yawale et al [12, 13].

Conducting polymers such as polypyrrole, PANI, polythiophene and their derivatives are being explored as promising materials for micro sensors, because of their ability to form a good basis for chemical sensor either as a sensing element or as matrices to immobilize specific reagents [14]. The principle sensing mechanism in conducting polymer is generally based on the modification of doping level due to redox interaction of analyte molecules and thereby resulting in change in conductivity. Among conducting polymers, PANI has successfully been demonstrated as an efficient gas sensor for monitoring air borne organic and inorganic components especially alcohols, ethers, ammonia, nitrogen CO_2, H_2S, SO_2, etc [15], whereas the use of PANI as a sensing element for chlorinated hydrocarbons such as CCl_4, $CHCl_3$, CH_2Cl_2, etc is less investigated, probably due to their weak interaction with PANI.

It is seen that cladophora can be found in fibers having nanosize diameter and its cell wall consists of cellulose again having nanosize thickness. This material is easily available in the nature as a nano material. Therefore it can be used for various applications such as polymer batteries, sensors etc. The cladophora is one of the types of algae which available as plenty. Keeping this view in mind possibility of exploiting cladophora as a substrate material is tested.

2 Experimental

2.1 Synthesis of polyaniline (PANI)

Polyaniline was synthesized in conventional route in aqueous medium using mineral acid such as HCl as dopant ion and oxidizing agent, ammonium persulfate, $(NH_4)_2S_2O_8$, as initiator. The aniline monomer (AR grade) was obtained from M/S SD Fine Chemicals and acid dopant and oxidizing agent $(NH_4)_2S_2O_8$ were received from M/S Loba Chemie India, were taken in the molar ratio of 1:1:1.1. Hydrochloric acid was taken in distilled water in which aniline monomer was added and stirred to get aniline-acid complex and kept the freezing mixture to attain the reaction temperature 0–5 oC. In another beaker $(NH_4)_2S_2O_8$ was dissolved in distilled water and kept it at 0-5 oC. After both of these solutions attained the reaction temperature, they were mixed together and stirred well and kept for six hours for the completion of reaction. Polyaniline powder formed was filtered, washed thoroughly with water to remove excess salts and dried for 24 h to make it moisture free.

2.2 Preparation of Cladophora Based Sensor

The Cladophora (150 mg) was dispersed for 8 min in 100 ml deionized water at room temperature and wash it, and press for 10 min to remove water to form film or paper. Finally a Cladophora film is formed. This cladophora film is dipped into PANI-PEO-Li_2SO_4 blend containing Li_2SO_4, (7 wt %). Then PANI- PEO- Li_2SO_4 composite allowed soaking in to the film. The paper sheet was then dried in air. The electrodes of conducting silver paste were formed on adjacent sides of the film for good electrical contacts, and then the films were subjected to heating at 70-900C for 20-30 min for drying. Same procedure is repeated for 11wt % $LiClO_4$ for PANI- PEO- $LiClO_4$ and 9wt % of LiCl for PANI- PEO -LiCl composites.

2.3 Gas chamber

The gas chamber having dimensions 30 x 30x30 cm3 with an attached CO_2 gas flow meter (Flowtran make, India) was used for the sensor testing. The gas flow was adjusted to 2ml /min. The readings were carried out in a CO_2 gas environment at different ppm levels. The thickness of the film was measured by Digimatic outside micrometer (Japan) having resolution ± 0.001mm. The voltage drop method is used for the measurement of change in resistance of the sensor.

Conducting polymer has tremendous technological potential for the development of sensor. Polyaniline appears to be a good candidate to realize gas sensors because of its sensitivity at room temperature, its ease of synthesis by various methods and its low cost. At present, the trend seems as the use of composite with polyaniline. Parameters like response time and selectivity of resistive gas sensors remain to be improved. It is seen that cladophora can be found in nanosize and its cell wall consists of cellulose. If cladophlora is used as substrate better results can be obtained.

3 Results and discussion

3.1SEM pictures

Cladophora is a hair like freshwater plant and causes bad-looking, bad-smelling beaches. Cladophora is an alga characterized by producing a kind of cellulose with a very large surface area (of course, in its microscopic details). Scientists say it has 100 times the surface of the cellulose found in paper.

Cladophora, green algae prefer large solid substrate with a high roughness and porosity. Scanning electron microscopy (SEM) picture shows a typical web like structure with numerous intertwined fibers, which are about 20–30 nm in width. Figure 1 shows a typical SEM picture of Cladophora cellulose. The high surface area of Cladophora cellulose makes this material a suitable substrate for the manufacture of highly porous composite paper materials. Cellulose is generally considered to be a material with insulating properties. However, when the cellulose fibers are coated with a layer of a conductive polymer, for example, polypyrrole (PPy) or polyaniline, the cellulose can be rendered with conductive properties.

The surface morphology of 7wt%, 9wt% and 11wt% PANI -PEO- Li_2SO_4, PANI -PEO- LiCl and PANI -PEO- $LiClO_4$ composites respectively was examined by Scanning Electron Microscope (SEM). ‘‘sponge-like” appearance observed for the 7 wt% PANI -PEO- Li_2SO_4 film, indicative of a highly inhomogeneous microstructure within the composite (Fig 2). 9wt% PANI -PEO- LiCl image shows fumes like structure and the surface of that 11wt% PANI -PEO- $LiClO_4$ is quite rough. From the SEM pictures it is observed that the films are amorphous in nature.

3.2 Gas sensing

The sensitivity is defined as

$$S = (R_g - R_a) / R_a$$

$$S = \Delta R / R_a$$

Where Ra and Rg are the resistances of the sensor in air and the CO_2 gas respectively.

The relationship between sensitivity and CO_2 gas concentration for PANI -PEO- Li_2SO_4, PANI -PEO- LiCl and PANI -PEO- $LiClO_4$ sensors at room temperature (303 K) is displayed in Fig 3. It is observed that, the resistance of the sensor increases with CO_2 gas concentration. Figure 3 shows that the sensitivity increases linearly for the lower concentration but for higher concentration it deviates from linearity. PANI-PEO- Li_2SO_4 sensor shows high sensitivity to CO_2

gas, compared with PANI-PEO-LiClO4 and PANI-PEO- LiCl sensors. PANI -PEO- Li2SO4 sensor exhibits a good response with CO2 gas concentration up to 840 ppm.

3.3 Static and Dynamic Response

The static response of the sensor at 303K for 150 ppm of CO2 gas is shown in fig 4.The dynamic response of composite film for 150, 300 and 450 ppm CO2 gas concentration at room temperature is shown in fig 5. The response (τres) and recovery (τrec) time are two important parameters to characterize a sensor. The response time is defined as the time taken to reach 90% of the response when ppm of gas is changed. The recovery time is defined as the time taken to reach 90% of the recovery when gas is turned off. The (τres) and (τrec) are reported in table I.

Table I: The response and recovery time for the sensor.

Composition of film wt%	Response time (τ_{res}) (s)	Recovery time (τ_{rec}) (s)
7wt% of Li_2SO_4 for (PANI -PEO- Li_2SO_4)	252	165
11wt% of $LiClO_4$ for (PANI -PEO- $LiClO_4$)	324	162
9 wt% of LiCl of for (PANI -PEO- LiCl)	198	288

It is observed that the response is fast for PANI -PEO- LiCl (~ 198s) compared with PANI -PEO- Li2SO4 and PANI- PEO- LiClO4 sensors but the recovery time of the sensor takes longer time. The CO2 gas detection mechanism in PANI -PEO- LiClO4, PANI -PEO- LiCl and PANI -PEO- Li2SO4 is totally based on the surface reaction occurring in sensor. When ions adsorb to the surface of the material removes electrons from the bulk and creates a potential barrier that limits electron movement and resistivity. When it is exposed to the gas then it is a chemisorbed and bridging oxygen atom with the formation of surface subsequently increasing the barrier height and the resistivity.

4 Conclusions

From these studies the following conclusion can be drawn-

From the SEM it is observed that the films are amorphous in nature. Sensitivity increases as CO2 gas concentration increases. Preparation of Cladophora based sensor is a simplest. PANI-PEO-Li2SO4 sensor shows a high sensitivity to CO2 gas, compared with PANI -PEO- LiClO4 and PANI -PEO- LiCl sensors. Response is fast for PANI -PEO- LiCl (198 s) compared with PANI -PEO-Li2SO4 and PANI -PEO- LiClO4 sensors (252 &324 s respectively). Recovery of the sensor takes longer time for PANI -PEO- LiCl (288 s) compared with PANI -PEO- Li2SO4 and PANI -PEO- LiClO4 sensors (165 &162 s). The resistance of the film decreases by increasing concentration of CO2 gas at room temperature (303K).The sensitivity increases linearly for the lower concentration range but for higher concentration range it deviates from linearity.

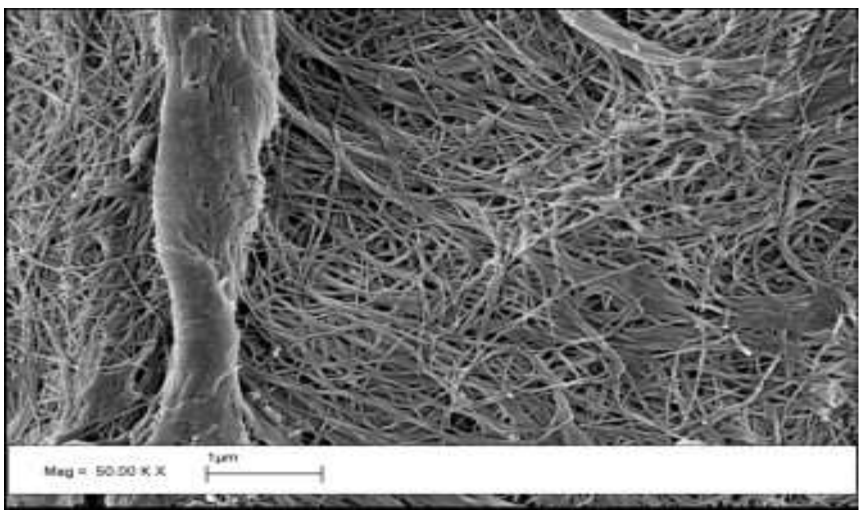

Fig 1: SEM picture of Cladophora cellulose at 50,000× magnification.

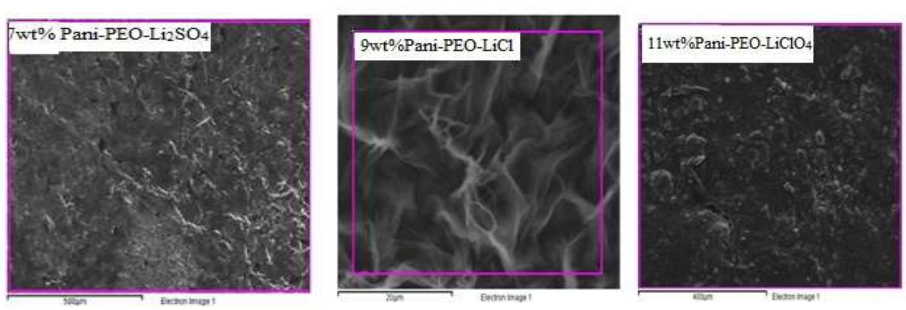

Fig 2 Scanning electron micrographs of 7wt%, 9wt% and 11wt% PANI-PEO-Li2SO4,PANI-PEO-LiCl and PANI-PEO- LiClO4 blends respectively.

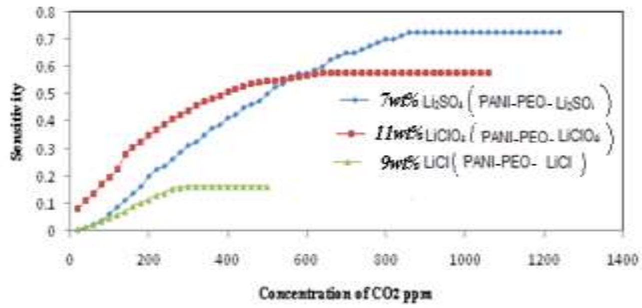

Fig.3 Variation of sensitivity with cshange in concentration of CO_2 gas at room temperature(303K).of PANI -PEO- Li_2SO_4, PANI -PEO- $LiClO_4$ and PANI -PEO- LiCl composite film.

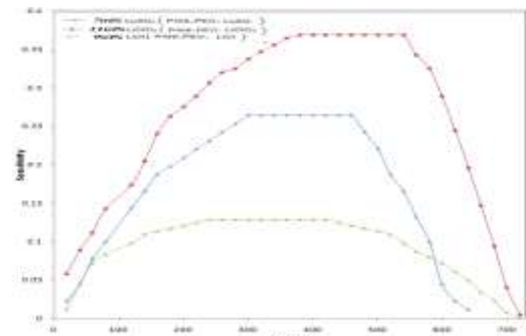

Fig.4 Response-recovery curves of PANI -PEO- Li_2SO_4, PANI -PEO- $LiClO_4$ and PANI -PEO- LiCl thin films to Concentration of CO_2 gas at room temperature (303K).

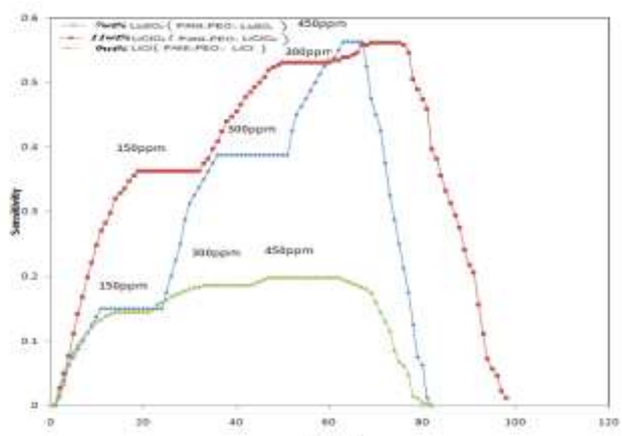

Fig.5 Dynamic response of PANI -PEO- Li_2SO_4, PANI -PEO- $LiClO_4$ and PANI -PEO- LiCl sensor for 150, 300, and 450 ppm CO_2 gas at room temperature (303K).

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