Synthetic Metals 220 (2016) 410–420

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Vapor phase sensing response of doped polyaniline-poly (vinyl alcohol) composite membrane to different aliphatic alcohols

Manmatha Mahato, Basudam Adhikari*

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

ARTICLE INFO

Article history:
Received 12 April 2016
Received in revised form 9 June 2016
Accepted 24 June 2016
Available online 19 July 2016

Keywords:
Doped polyaniline
Sodium dodecyl sulfate
Polymer membrane
Sensor set up
Alcohol sensing

ABSTRACT

Conductive polymers in the form of pellet and coating on a suitable substrate have been extensively used in recent years as sensor materials for the vapor phase sensing of aliphatic alcohols. But due to lack of mechanical stability and reversible adsorption/desorption of alcohol molecules the use of conducting polymers in the above forms suffers from limited repeatability of sensing response. Here, we have developed some mechanically stable free standing doped polyaniline-poly (vinyl alcohol) (PVA-PANI) composite membranes as efficient materials for sensing of aliphatic alcohols in vapor phase. Camphor sulphonic acid (CSA), L-aspartic acid (ASP) and *p*-toluene sulphonic acid (PTSA) were used as dopants at the time of synthesis of polyaniline in presence of sodium dodecyl sulfate (SDS) by oxidative polymerization of aniline using 1 (M) ferric chloride solution at 0 °C under nitrogen atmosphere. Membranes of thickness 0.15–0.18 mm were prepared with PVA in dimethyl sulphoxide (DMSO) by solution casting. Doped polymer membranes were spectroscopically characterized. It has been observed that dopant has significant effect on the formation of polyaniline morphology in presence of SDS as seen in SEM images. Conductivities of doped membranes, viz., CSA-PANI-PVA, PTSA-PANI-PVA and ASP-PANI-PVA, are 9.30×10^{-3}, 3.86×10^{-4} and 4.83×10^{-4} S/cm respectively. Membranes have shown good sensing responses and repeatability of response patterns towards aliphatic alcohols with lower response time.

1. Introduction

Synthesis and preparation of free standing film/membrane of conducting organic polymer have considerable practical importance for the development of ideal sensor and sensing system in various fields, viz., in electrochromic devices, display, capacitors, and chemical sensors, etc. Beside these applications, sensing of hazardous gases based on these conducting polymers [1–7] have received much more attention in today's research and development. The sensing characteristics of these gases have been studied by measuring the change of resistivity/conductivity of the sensor arising out of the interaction of the gas molecules with the sensor surface. The changes of electrical properties of those sensors have been further improved by incorporating organic/inorganic dopants as well as surface stabilizing materials to the conducting polymers. Several polyaniline and polypyrrole-based composites [8–15] have been reported as alcohol sensor materials. Conducting polymer based composites can be prepared either by blending with graphene/carbon nanotubes [16,17] or by electrochemical deposition [18,19] on graphite sheet or conducting material and/or by electrochemical codeposition [20] of carbon nanotubes along with the monomer of a conducting polymer on a substrate.

It is difficult to get a permanent and uniform deposition of conducting polymers on a substrate without surface stabilizing material. The surface stabilizing material should possess some kind of physical or chemical affinity between the deposited conducting polymer and the substrate surface. Although resistivity increases to some extent as the density of conducting polymer decreases due to the presence of surface stabilizing agent but uniform surface morphology is obtained, which is required for good alcohol vapor sensing ability. Uniform surface morphology of the deposited conducting polymer provides better sensing repeatability/reproducibility of the sensor since absorption/desorption phenomenon of alcohol vapor molecules occurs reversibly with respect to time. On the other hand, selectivity of the sensor is important when a series of analytes are subjected to gas sensing measurements. To reach optimum selectivity for the sensing of aliphatic alcohols one can (a) modify the conducting

* Corresponding author.
E-mail address: ba@matsc.iitkgp.ernet.in (B. Adhikari).

http://dx.doi.org/10.1016/j.synthmet.2016.06.020
0379-6779/

polymer by using various dopants; (b) synthesize highly selective material; (c) use multi-sensor array with suitable pattern recognition algorithm; (d) measure more than one sensing parameters simultaneously, such as, resistance and mass change [21], resistance and frequency change [22], etc.

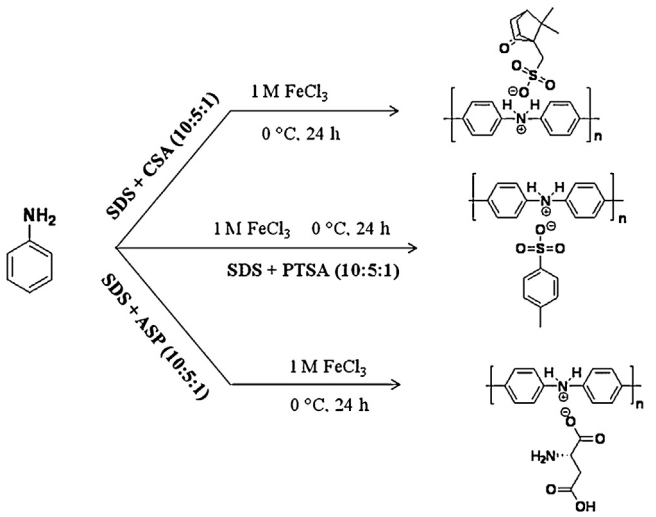
Selectivity of a conducting polymer based sensor mainly depends on the magnitude of interaction between the alcohol vapor molecules and conducting polymer surface. If different alcohol molecules in vapor phase have different magnitudes of interactions with the sensor material, selectivity of that sensor towards different aliphatic alcohols is increased. It also depends on the sensitivity as highly sensitive material can recognize a minute change of chemical or physical properties of the gas molecules under study. It is a challenging task to develop a sensor having both high sensitivity and selectivity as well as good repeatability for sensing alcohol molecules in vapor phase. It is reported that majority of sensors lack in either selectivity or repeatability [8–15] towards different alcohol vapors, as the pellet forms of the materials used for sensing are mechanically less stable.

This investigation reports the alcohol vapor sensing characteristics of doped conducting polyanilines in the form of membranes. We have synthesized polyaniline in presence of a structure directing agent, SDS along with organic dopants, viz., CSA, ASP and PTSA by oxidative polymerization technique using aqueous solution of 1 (M) $FeCl_3$ as oxidant at 0 °C temperature. At the end of polymerization, SDS and iron salts were removed by washing with hot water and then normal distilled water for several times. Although the synthesized doped polymers are soluble in DMSO but they are unable to form freestanding film/membrane. To prepare freestanding membrane these doped conducting polymers were blended with 5 wt% PVA in DMSO solution followed by casting on a clean petridish. Membranes were obtained by evaporation of the solvent at reduced pressure and then by slow evaporation of DMSO at 90 °C for 16 h in a vacuum oven. These *in situ* doped membranes, viz., CSA-PANI-PVA, PTSA-PANI-PVA and ASP-PANI-PVA, were then used as sensor materials for sensing measurements of short chain aliphatic alcohols in the vapor phase, viz., methanol, ethanol, propanol and iso-propanol at room temperature (30 °C) as they have high vapor pressure at this temperature by measuring the change of resistivity of the sensor with the change of concentration of alcohol. Due to high boiling points and low vapor pressures, butanol and pentanol were difficult to detect at room temperature.

2. Materials and methods

2.1. Materials

Aniline for synthesis and six aliphatic alcohols, viz., methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, and *n*-amyl alcohol were taken from Merck (India) Limited. $FeCl_3$, SDS, DMSO were purchased from Merck (India) Limited. PVA was purchased from S d fine chemicals Ltd. CSA and ASP were purchased from LOBA CHEMIE Pvt. Ltd. PTSA was procured from Spectrochem Pvt Ltd., Mumbai (India).



Scheme 1. Synthesis of CSA-PANI, PTSA-PANI and ASP-PANI polymer materials.

2.2. Preparation of CSA, PTSA and ASP doped PANI-PVA composite membrane

2.2.1. Synthesis of CSA, PTSA and ASP doped polyaniline in presence of SDS

In this typical synthetic method, 4.05 g (1 M) $FeCl_3$ was taken in a 250 mL three neck round bottom flask with distilled water (25 mL). It was kept for 30 min under magnetic stirring at 27 °C. 1.857 g (6.44 mmol) SDS in distilled water (25 mL) was added to it under stirring condition for 1 h. It was then cooled by putting the round bottom flask on an ice-bath at a temperature of 0 °C and made inert atmosphere inside the flask by continuous N_2 bubbling. 1.20 g (12.88 mmol) aniline and 0.323 g (1.288 mmol) CSA in distilled water (10 mL) were added simultaneously to the above solution drop-wise under continuous stirring. The reaction mixture was continued to stir under N_2 atmosphere at 0 °C for 24 h. A greenish-black colored precipitate was formed indicating the polymerization of aniline so as to obtain CSA-PANI material. The precipitate was filtered by Whatman-41 filter paper and washed several times by hot distilled water. Finally, it was washed with normal distilled water until the complete removal of unreacted reagents and kept in an oven at 90 °C for 6 h.

PTSA-PANI and ASP-PANI polymer materials have been synthesized by following the same method as described above. The only difference is the use of PTSA (0.25 g, 1.288 mmol) in distilled water (10 mL) instead of CSA for the synthesis of PTSA-PANI. ASP (0.171 g, 1.288 mmol) in distilled water (50 mL) has been used for ASP-PANI material. Scheme 1 shows the synthesis of CSA-PANI, PTSA-PANI and ASP-PANI polymer materials. Designations of all the synthesized doped polyaniline materials along with their solubility in DMSO are shown in Table 1.

2.2.2. Preparation of PANI-PVA composite membrane

Solutions of doped polyanilines in DMSO were used to prepare membranes with PVA. Each of the individual polymer membrane

Table 1
Identification codes of the doped polyaniline materials and their solubility in DMSO.

Sample ID	Polymer/base material	Surfactant	Dopant	Solubility in DMSO (mg/100 mL)
CSA-PANI	Polyaniline	SDS	CSA	965
PTSA-PANI	Polyaniline	SDS	PTSA	875
ASP-PANI	Polyaniline	SDS	ASP	910