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DEVELOPMENT OF POLYANILINE GRAFTED CHITOSAN SENSOR FOR DETECTION OF AMMONIA & ETHANOL VAPOUR

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Abstract - *The use of conducting polymers as sensing elements in electrochemical or chemical sensors is a center of attraction due to their good sensitivity in changing electrical and optical properties when exposed to different types of gases and liquids. The demand for gas sensor is increasing day by day due to requirements in air quality monitoring, safety of processes & medical applications. Polyaniline is one of the most commonly used polymer and its characteristics as sensor can be enhanced by adding other material to form composite. Chitosan has promising characteristics to be used as biosensor, vapor sensor, electrochemical sensor etc. The present work explores the possibility of development of electrochemical gas sensor by using conducting polyaniline and chitosan base composite film using cloth and paper substrates. Six electrodes, three each of cloth and paper base using PANi powder and PANi–gf-Ch film as sensing elements have been developed. These electrodes are evaluated for their sensitivity for ammonia and ethanol vapor using electrochemical cell. Based on the result & discussion, it can be said that the sensitivity of PANI-gf-Ch composite film electrode showed higher current output than using only PANI powder coated electrode. The best response in ammonia sensing, is obtained by the filter paper based substrate electrode PPCh1 of the magnitude of 0.15 mA, followed by cloth based film electrode CPCh1 as 0.04. Similarly CPCh1 and PPCh1 are observed to be effective in sensing ethanol with good current output when compared with electrodes like CP1, C1, P1 and PP1 which do not contain chitosan*.

Key Words: *Polyaniline grafted Chitosan film Electrodes, Electrochemical sensor, filter paper, cloth strips.*

1. INTRODUCTION

Today, the use of conducting polymers as sensing elements in electrochemical or chemical sensor is a centre of attention due to their good sensitivity in changing electrical and optical properties when exposed to different types of gases and liquids. The demand for gas sensors is increasing day by day due to requirements in air quality monitoring, safety of processes and medical applications. These conducting polymers can be synthesised easily by means of chemical or electrochemical methods. The sensitivity at room temperature adds to the sensor's advantage and is importance particularly as ammonia or alcoholic compounds are used in different applications in process industries. Polyaniline is one of the most commonly used conducting polymers due to its unique electrical properties, atmospheric stability and intrinsic redox reaction. Polyaniline is also used in different applications such as light emitting diodes, rechargeable batteries and photovoltaic cells, anticorrosive coating material etc. However the disadvantages of these conducting polymers are their low processing ability, poor chemical stability and mechanical strength due to its thinness. There is an approach for improving the mechanical strength and characteristics of sensors by adding organic or inorganic material to form composites.

Chitosan can be synthesized by using seafood waste like crab & shrimp. Chitosan has promising characteristics to be used as biosensor, vapour sensor, volatile organic compound sensor, electrochemical sensors and many more. Chitosan has been used as a biosensor due to its excellent film forming properties and ability to retain its original properties. Apart from that, chitosan is low cost because it is synthesized from waste and is a natural reproducible polymer. Another important feature is that, chitosan can be effective in sensing vapour at room temperature.

1.1 Literature Survey

Sadanand Pandeya et al studied and reported in review paper some of the current breakthrough developments in the area of gas sensors based on polyaniline (PANI) nanocomposite. PANI-based sensor experiences some important disadvantage of poor reproducibility, selectivity & stability. In order to overcome this restriction PANI was functionalised or incorporated with nanoparticles (NPs), carbon compounds and shows outstanding properties for gas sensing. Herein, author summarize recent advantages in PANI nanocomposite preparation, sensor construction, and sensing properties of various PANI nanocomposites based gas/vapor sensors, such as NH_3, H_2, HCl, NO_2, H_2S, CO, CO_2, SO_2 & LPG.[1]

Li Huixia, et al investigated the gas sensing properties of hydroxyapatite based composites which were prepared by mixing different contents of conductive polymers: polypyrrole and polyaniline (PAni). The compositions, microstructures and phase constitutions of polymer/HAp composites were characterized, and the sensing properties

were studied using a chemical gas sensing (CGS-8) system. 5%PPy/HAp and 20%PAni/HAp composites exhibited the best sensitivities to ammonia, and the sensitivities at 500 ppm were 86.72% and 86.18%, respectively. Besides, the sensitivity of 5%PPy/HAp at 1000 ppm was up to 90.7%. Compared to pure PPy and PAni, the response and the recovery time of 5%PPy/HAp and 20%PAni/HAp at 200 ppm were shortened several times, and they were 24 s/245 s and 15 s/54 s, respectively. In addition, the composites showed a very high selectivity to ammonia. [2]

S. L. Patil & M. A. Chougule, investigated the performance of a room temperature ammonia gas sensor based on Polyaniline-ZnO nanocomposite. The nanocomposite film was fabricated using spin coating method on glass substrate. Polyaniline-ZnO nanocomposites were characterized for their structural as well as surface morphologies and ammonia response was studied. The structural (XRD) analysis showed formation of nanocrystalline ZnO while polyaniline exhibited amorphous nature. The nanocomposite showed the maximum response of 14 % upon exposure to 100 ppm NH_3 at room temperature. [3]

Sandra C. Hernandez et al reported the synthesis, characterization and ammonia gas sensing with single nanowire of conducting polypyrrole. Three hundred nanometer in diameter and 50 to 60 mm long polypyrrole nanowires were synthesized by chemical polymerization inside SiO_2 coated alumina membranes. Temperature dependent electrical resistance studies established that the chemically synthesized nanowires were more ordered compared to electrochemically synthesized nanowires. It is further demonstrated that gas sensors based on single polypyrrole nanowire exhibited good sensitivity towards ammonia, and provided a reliable detection at concentration as low as approximately 40 ppm. [4]

A. Z. Sadek1 et al investigated that a polyaniline/In_2O_3 nanofibre composite based layered surface acoustic wave (SAW) sensor has been developed and investigated for different gases. Chemical oxidative polymerization of aniline in the presence of finely divided In_2O_3 was employed to synthesize a polyaniline nanofibre/ In_2O_3 nanoparticle composite. The nanocomposite was deposited onto a layered ZnO/64◦ YX $LiNbO_3$ SAW transducer. The novel sensor was exposed to H_2, NO_2 and CO gases. Fast response and recovery times with good repeatability were observed at room temperature. [5]

Devi Shantini Chandrasakaran et.al. reported that Ammonia classified as one of the hazardous chemical to environment and human & therefore, monitoring the ammonia in air is vital. Chitosan film was selected as a sensing material for ammonia detection in this study. Chitosan powder was dissolved in 2% of acetic acid to form chitosan solution gel. It was subsequently deposited on patterned electrode by using electrochemical deposition technique. The response of the chitosan sensor towards ammonia was tested via electrical testing by exposing different ammonia concentration ranging from 20 ppm, 100 ppm, 200 ppm, and 300 ppm using air exposure technique. The response of the chitosan sensor towards ammonia was recorded as output voltage. Sensor properties which include sensitivity, stability, recovery, and repeatability were studied. The electrical result showed that the response of chitosan sensor increases as the ammonia concentration increases. All the sensing properties were achieved. [6]

Manju Gerard mentioned in her review paper conducting polymers have attracted much interest in the development of biosensors. The electrically conducting polymers are known to possess numerous features, which allow them to act as excellent materials for immobilization of biomolecules and rapid electron transfer for the fabrication of efficient biosensors. In the present review an attempt has been made to describe the salient features of conducting polymers and their wide applications in health care, food industries, environmental monitoring etc. [7]

Devi Shantini and Irwana Nainggolan investigated Hexanal which is identified as one of the major volatile gases & produced in degraded dairy products and wood industries. Electrical testing with chitosan as a sensing material to sense hexanal gas in low concentration was carried out at room temperature. Chitosan sensor was fabricated by using electrochemical deposition technique to form active sensing layer. The response of the chitosan film sensor (CFS) towards hexanal was tested via electrical testing by exposing different hexanal concentrations ranging between 20 ppm, 100 ppm, 200 ppm, and 300 ppm using air as a carrier gas. Sensing properties of the CFS toward hexanal exposure including responsibility, recovery, repeatability, stability, and selectively were studied. Overall, the result suggested that hexanal sensor based on chitosan was able to perform well at room temperature demonstrated by good response, good recovery, good repeatability, good stability, and good selectively. [8]

2. PRESENT WORK

2.1 Objective of Present Work

The main objective of the present work is to explore the possibility of development of electrochemical gas sensor by using conducting polyaniline and chitosan base composite film using cloth and paper substrates.

The present work is divided in following parts:

Part 1: Preparation of composite film of polyanline and chitosan on cloth and paper substrate.

Part 2: Electrochemical sensitivity study of electrodes made up of composite films prepared in part 1.

2.2 Methodology

The methodology adopted in present work is depicted schematically in fig no. 1.

2.3 Materials and equipment:

Laboratory grade conducting polyaniline, lab grade chitosan, commercial grade cloth, ordinary filter paper, lab grade acetic acid, distilled water, lab grade hydrochloric acid, plastic air tight container, digital multimeter, power supply battery 9 (Volts)[9].

2.4 Experimental procedure

2.4.1 Part 1: Electrode preparation

The following procedure is adapted in the preparation of various electrodes used in present work:

(i). Two types of substrates ordinary filter paper and cloth strips having various dimensions are used.
(ii). Known quantity and proportion of Polyaninline(PANI) and Polyaniline grafted chitosan (PANI-gf–Ch) as composite are used.
(iii). Appropriate quantity of enamel i.e commercial grade aluminum base paint is used as a binder to attach sensing element i.e composite film as mentioned in part (ii) to substrate mentioned in part (i).
(iv). The details of the electrodes dimensions are given in table number 2.

The actual photographs of process steps are given in fig no. 2[9].

2.4.2 Part 2: Electrochemical sensitivity studies

2.4.2.1 Procedure:

- Known quantity of electrolyte, acetic acid or hydrochloric acid in aqueous solution is taken in a container.
- One of the electrodes mentioned in part 1 is dipped in electrolytic solution
- Second electrode is made from aluminum foil as mentioned in table 2 and dipped in the same electrolytic solution.
- The electrode assembly is put in an air tight container having arrangement for voltage supply of 9 volts using a DC battery.
- In vapor generation chamber, known quantity of ammonia or ethanol solution is taken.
- The variation in current is measured in micro ampere till the steady state is reached.[9]

Table 1: Electrode details and specifications

Type of electrode base		Cloth base			Filter paper base		
Type of sensing electrode with description		C1 Cloth base strip is coated with enamel	CP1 Crushed PANI powder coated with enamel paint to cloth base	CPCh1 PANI/Chitosan composite film attached to cloth base by using enamel paint coat	P1 Filter paper strip base is coated with enamel	PP1 PANI crushed powder is coated with enamel base paint	PPCh1 PANI /Chitosan Film stick by using enamel paint coat
Dimensions of electrode base (cm)		11*1.5	11*1.5	11*1.5	11*1.8	11*1.8	11*1.8
Weight of electrode base strip (gm)	Before Coating	0.56	0.65	0.68	0.22	0.23	0.22
	After Coating	0.87	1.42	2	0.46	0.52	0.6
	Wt of Enamel coat	0.31	0.37	0.44	0.18	0.19	0.38

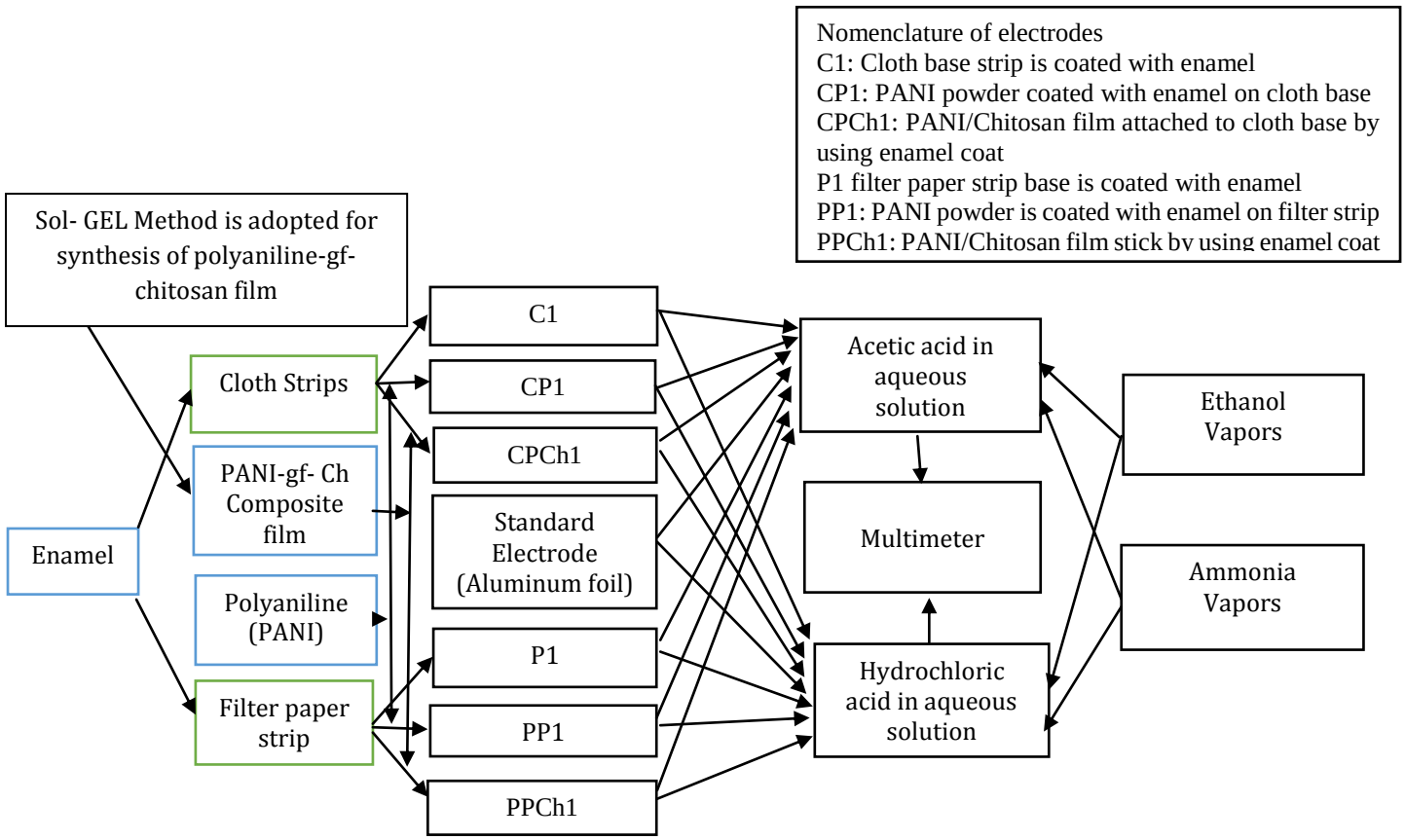

Fig. 1 The Methodology of present work

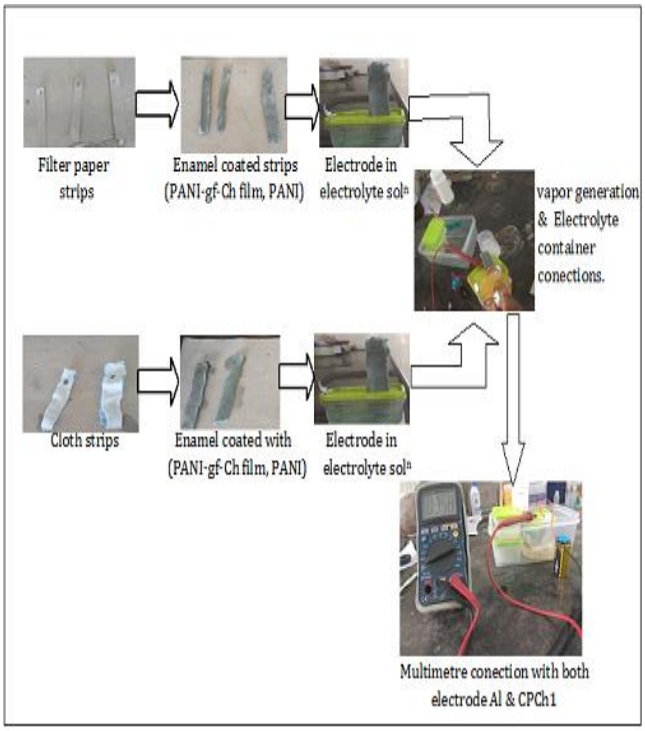

Fig. 2 Actual photographic of process steps

3. RESULT AND DISCUSSION:

Graphs have been plotted between current and time for sensing of ammonia (NH_3) from aqueous ammonia solution using acetic acid as electrolyte. Figure No. 3 shows the response curve of the gas sensor using different electrodes. As can be seen from these graphs, the electrical current generated is varying with time for electrodes namely PPCh1, PP1 and CPCh1. No change is observed for P1, C1 and CP1. The maximum deviation of around 0.2 mA is seen in PPCh1 followed by 0.13 mA for electrode CPCh1 and PP1 over a time period of 15 minutes.

The electrode CP1 is coated with polyaniline(PANI) powder by using enamel paint, electrode C1 is made of cloth strip coated with enamel and P1 ordinary filter paper coated with enamel have shown no change in current when exposed to 25% ammonia solution. These results show the successful development of electrochemical cell using electrodes PPCH1, PP1 and CPCh1 that can be incorporated into Gas Sensor.

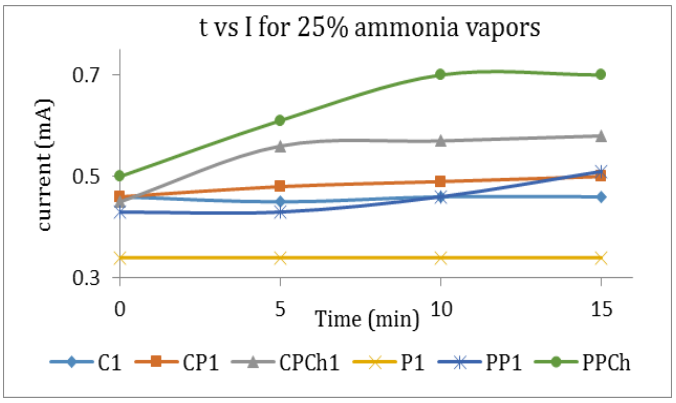

Fig. 3 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to ammonia (25%)

Figure No. 4 shows the response of various electrodes in sensing ammonia vapour from 25% ammonia in water solution using aqueous hydrochloric acid as electrolytic solution. As can be seen from this figure, electrodes CPCh1, CP1, PPCh1 and PP1 have shown sensitivity for ammonia. C1 and P1 have shown no sensitivity for ammonia. The best response is observed for PPCh1 of the magnitude 0.15 mA, followed by 0.04 CPCh1 and 0.08 mA for CP1. Thus it can be said that electrode synthesized in present work, PPCh1 and CPCh1 have shown measurable variance in current generation highlighting the successful development of gas sensor.

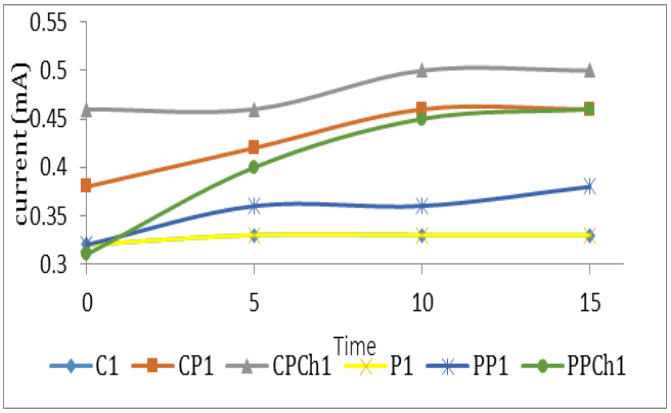

Fig. 4 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to ammonia (25%)

The present work also addresses to reuse of electrode strips. For this process, sensitivity studies of used electrode strips have been carried out. The electrolyte concentration of hydrochloric acid is doubled for this study. Fig 5 shows the graph plotted depicting the sensitivity for ammonia vapour from 25% ammonia in aqueous solution. The magnitude of variation in current is measured as 0.03 mA and 0.028 mA respectively for PPCh1 and CPCh1.

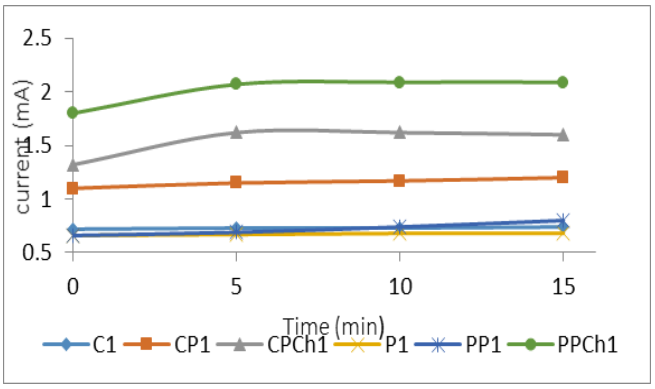

Fig. 5 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to ammonia (25%).

Figures 6, 7 and 8 show the graphs plotted between time and current response for various electrodes in sensing of ethanol vapor from 25, 75 & 100% ethanol respectively. It can be seen from these graphs that electrodes developed, CPCh1 and PPCh1 have successfully sensed ethanol irrespective of concentration. The variation in current using electrode CPCh1 is ranged between 0.02 to 0.2 mA depending upon ethanol concentration, For PPCh1 these values ranged from 0.05 to 0.08 mA depending upon concentration.

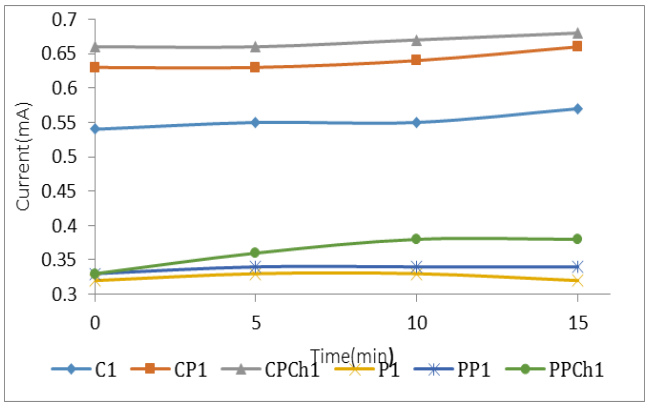

Fig. 6 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to ethanol (25%).

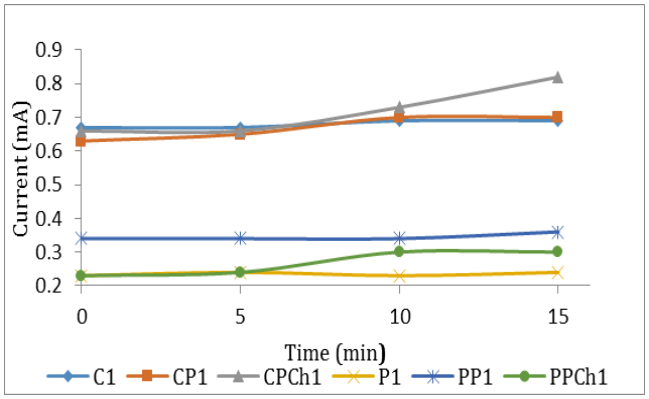

Fig. 7 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to ammonia (75%)

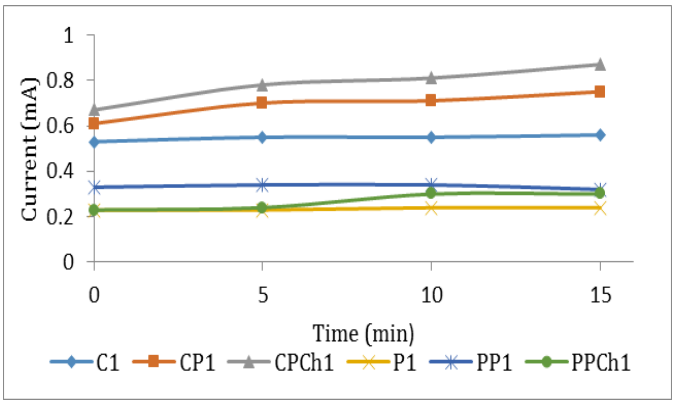

Fig. 8 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to pure Ethanol

Similarly figures 9, 10 and 11 show the graphs plotted between time and current response for sensing ethanol but using aqueous hydrochloric acid as electrolytic solution. The variation in current for electrode CPCh1 ranged between 0.08 to 0.11 mA, depending upon the concentration of ethanol whereas for electrodes PPCh1 it ranged between 0.02 to 0.08 mA. However some of the readings are not consistent with respect to magnitude and current.

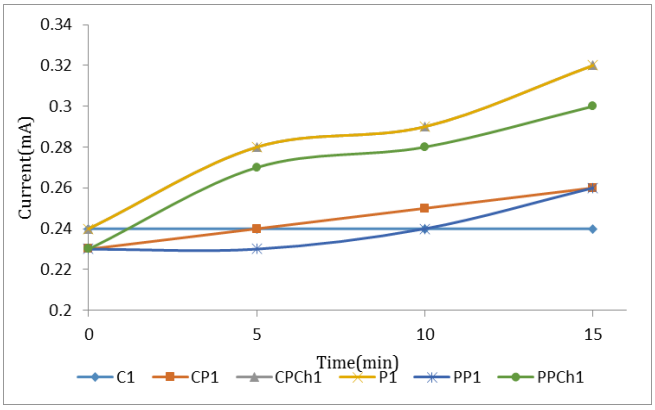

Fig. 9 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to Ethanol (25%)

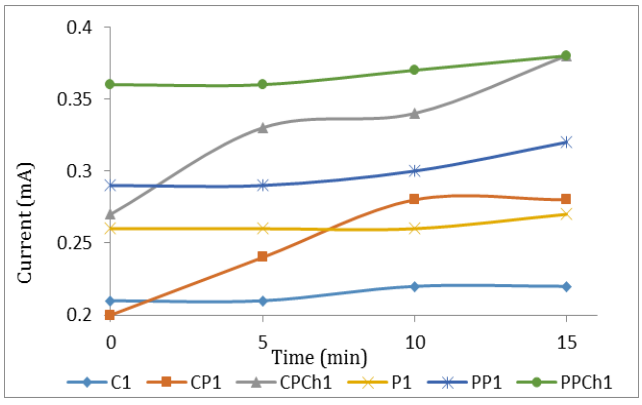

Fig. 10 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to Ethanol (75%)

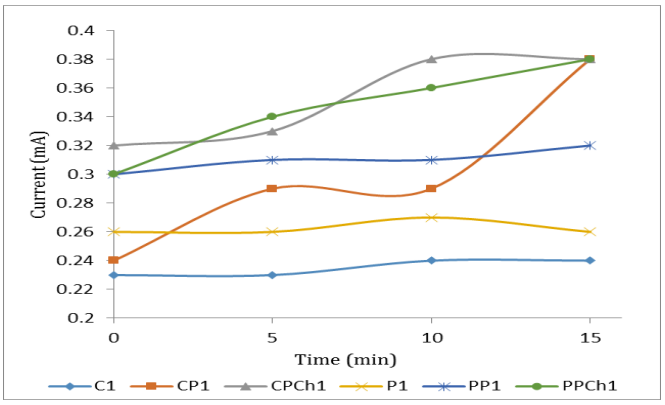

Fig. 11 Gas response of electrodes C1, CP1, CPCh1, P1, PP1and PPCh1to 100%Ethanol

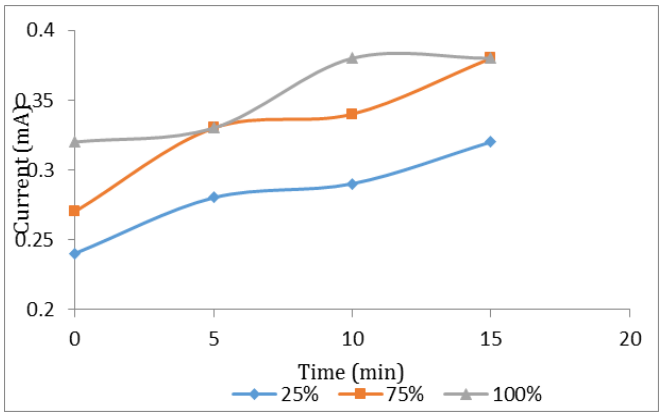

Fig. 12 Gas response of PANI-gf-Ch film to Ethanol (25-100 %)

Figure 12 shows a graph plotted between current and time for sensing of ethanol using electrode CPCh1. The change in current with respect to time is observed with varying concentration, with some discrepancy.

4. CONCLUSIONS

The present work addresses to development of bio-composite films prepared by using PANI & chitosan on paper & cloth sheets as substrate and enamel as adhesive agent. These strips are used as electrodes and are employed in sensitivity study in the detection of ammonia & ethanol vapors originating from respective aqueous solutions. The concentration of ethanol water solution is varied as 25, 50 and 100 vol%. Similarly 25% of ammonia aqueous solution is used. Two types of electrolytic solutions are used, aqueous hydrochloric acid and acetic acid. Based on the result & discussion, it can be said that the sensitivity of PANI-gf-Ch composite film electrode showed higher current output than using only PANI powder coated electrode. The best response in ammonia sensing, is obtained by the filter paper based substrate electrode PPCh1 of the magnitude of 0.15 mA, followed by cloth based film electrode CPCh1 as 0.04. Similarly CPCh1 and PPCh1 are observed to be effective in sensing ethanol with good current output when compared

with electrodes like CP1, C1, P1 and PP1 which do not contain chitosan. This also highlights the success of present work.

It can be concluded that the present work has successfully developed PANI-gf-Ch based electrodes with paper and cloth substrate that can sense ammonia and ethanol vapor.

The work is demonstrative and it is felt necessary to explore possibilities of sensing other gas components by conducting more experimental studies. Similarly there is need for downstream current interpretation mechanism that can model the input signal with gas component and its composition.

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