

EFFECT OF Pd AND Pt CATALYSTS ON THE PERFORMANCE OF ELECTROLYTE MEMBRANE IN HYDROGEN SENSOR

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Abstract: Hydrogen is a promising potential fuel for vehicles and can be converted into electricity in fuel cells. According to this trend, the hydrogen sensor is becoming more important because hydrogen should be treated with stringent caution. An electrochemical gas sensor is one of the candidates for a room-temperature operated and low cost hydrogen sensor. In this study a sulphonated polystyrene ethylene butylene polystyrene electrolyte membrane are prepared and characterized for hydrogen sensor application. The impedance result shows the conductivity of 10^{-3} S/cm. The effect of catalyst on the performance of the membranes in hydrogen sensor was evaluated. Three different combinations of catalyst were tried, anode and cathode coated with a) Pt catalyst, b) Pt/Pd & Pt, and c) Pd & Pt catalyst. Among these three, the third type coated membranes sensed more effectively than the other two due to the fact that Pd has more hydrogen affinity than platinum.

Key words: hydrogen sensor, electrolyte membrane, impedance, effect of catalyst.

1. INTRODUCTION

The future economy is projected as hydrogen economy and fuel cells may become the energy source either replacing or augmenting the present oil based technology ([1], [2]). Hydrogen is expected to replace conventional energy sources as a pollution-free alternative. Hydrogen is the most attractive and ultimate candidate for a future fuel and an energy carrier, because it burns cleanly. In fuel cells hydrogen rich gases are used either directly or via a reformer. For successful utility of any technology the same should be user friendly and safe. For safe usage of fuel cell technology hydrogen used as a fuel in fuel cells has to be monitored continuously. It is known that hydrogen forms an explosive mixture with air once its concentration exceeds beyond the explosion limit of four percent hydrogen in air. Hydrogen is no more dangerous than current transportation fuels, but it is different. One key

difference is that hydrogen is colorless and odorless and its flames are virtually invisible in daylight. When hydrogen is used as fuel in futuristic automobiles, there is need for hydrogen sensor to monitor the fuel leak. Hydrogen detectors will therefore be a key part of safe design for hydrogen fueling stations and other hydrogen facilities.

Hence the development of hydrogen sensors has gained importance these days for application in fuel cells. Safety is an important issue when using hydrogen. A common need in this technology area is the ability to detect and monitor gaseous hydrogen, but hydrogen gas sensors that can quickly and reliably detect hydrogen over a wide range of oxygen and moisture concentrations are not currently available.

Commercially available sensors can detect the presence of hydrogen and then close valves, shut down equipment, or trigger alarms. A variety of sensors has been developed, including electrochemical, catalytic, semiconductor and resistivity sensors. Electrochemical sensors include both potentiometric ([3], [4]) and amperometric ([5], [6]) devices. However, current technologies typically have limitations related to cost, speed of operation, susceptibility to interference from other gases, and temperature range. Research and development on hydrogen sensors is necessary for development of reliable sensors with good sensitivity, selectivity, response time and long-term stability. Detection and measurement of hydrogen at low concentration has always been a technological challenge.

Electrochemical hydrogen sensors may use both solid and liquid proton-conducting electrolytes. Solid electrolytes have an advantage against the possibility of spillage when compared to liquid electrolytes, but most of them need humidification of the sample gas. Nafion has already been used as an electrolyte for sensor applications [7]. Membranes are materials, which allow the selective permeation of at least one of the species of a mixture to which they are exposed. Membrane reactors consist mainly of a membrane, which plays the role of the reactor wall.

Formerly, gas sensors were fabricated using metal oxide based ceramic semiconductors. However, in recent researches metal oxides were substituted by conducting polymers because of their high sensitivity, room temperature application, low cost, ease of fabrication and doping capability (to increase selectivity). Also, polymer thin films are much easier to fabricate, as the base of gas sensors.

This paper describes the hydrogen sensor performance of the new sulphonated polystyrene ethylene butylene polystyrene (SPSEBS) electrolyte membrane. The prepared SPSEBS membrane is permeable to protons. Hydrogen sensing behavior of the membrane was detected with various catalyst combinations. Platinum and Palladium catalysts were used for the study.

2. EXPERIMENTAL

2.1. Materials

Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene (PSEBS) ($M_w = 89,000$; 29% styrene) was obtained from Aldrich (Germany). Chlorosulphonic acid (CSA) was purchased from Spectro-Chem, India and used without further purification. Tri - butyl phosphate (TBP) (Lancaster) and Methanol (SRL) were purchased and used as received. The tetrahydro furan (THF) solvent was purchased from Merck. The electrolyte polymer used for this work was synthesized from commercially available PSEBS. The polymer PSEBS was modified with chlorosulphonic acid by sulphonation reaction according to the literature method [8]. In this paper, sulphonated PSEBS has been used for membrane formation.

2.2. Membrane preparation

Sulphonated polymer electrolyte membranes can be easily obtained by casting the polymer dispersion in a proper solvent. The sulphonated polymer was dissolved in THF solvent. Then the clear solution was poured in to a clean Petri dish and dried at room temperature until the complete evaporation of the solvent has taken place. The obtained uniform dry membrane was washed with deionized water and then dried at 50 °C for 1 day.

The prepared electrolyte membrane was purified to remove the impurities from the membranes before feeding into the sensors. The prepared polymer electrolyte membranes were allowed to boil in 3% H_2O_2 for half an hour, then allowed in boiling water for 15 minutes and then for half an hour in 10% H_2SO_4 . Finally, it was washed with boiling water and dried at 60 °C for one day. The purified membranes were used for further studies.

2.3. Membrane properties

Ion exchange membranes are suitable for electro membrane process [9]. The electrolyte membrane should have the high ion conductivity, which is accomplished by a high ion-exchange group content named as ion exchange capacity. The ion exchange capacity of the membrane was determined by titration method as described [10].

Swelling of the membrane facilitates the hopping mechanism of the proton in the membrane. It needs moderate swelling because, too much swelling leads to a poor mechanical stability of the membrane which is disadvantages for the application in electro membrane processes and sensors. The weight gained by dried membranes was monitored over a period of 24 hours with distilled water. After 24 hours the external liquid was wiped off and the samples were weighed. The water absorption was obtained using the equation

$$\text{Absorption} = \{(M_w - M_d) / M_d\} \times 100 \% \quad (1)$$

Where, M_w and M_d are the mass of membranes before and after absorption respectively.

Ageing test helps to know about the life cycle of the membrane, which undergoes degradation normally under operating conditions. The test involves fastening of the degradation potential, there by indicating the mechanical and chemical stability of the membrane over a period of time. The membranes were subjected to a solution of 3% hydrogen peroxide accelerated by 4ppm of ammonium iron II sulphate hexahydrate for 8 hours at 80 °C.

2.4. Characterization

FTIR spectra were recorded in absorbance mode on a Perkin – Elmer FTIR spectrometer. The spectra were obtained for both PSEBS and SPSEBS membranes. The TGA was carried out using a thermo balance SDT Q600 US analyzer at a heating rate of 20 °C/min under nitrogen atmosphere. The catalyst coated samples of the sulphonated membrane was subjected to optical polarizing microscopy to study the distribution of catalyst on the surface of the membrane. Optical polarizing microscopy is the study of the morphology of objects with the use of microscope, which resolves details at the micrometer level.

2.5. Proton conductivity

Proton conductivity of the each polymer composite membranes was determined by AC impedance spectroscopy ([11], [12]). The measurements were taken using Volta lab dynamic-EIS voltametry model PGZ 301. Studies were carried out by using the O-ring joint between the compartments, using platinum foil electrodes and 1M H₂SO₄ solution as the electrolyte. From the difference between the resistance of the blank cell and the one membrane separating the working and the counter electrode compartments, the resistance of the membrane was calculated and converted to conductivity values using the formula,

$$C = \frac{t}{R \times A} \quad (2)$$

Where, C- conductivity (S/cm), R- sample resistance (ohm), t- wet sample thickness (cm), A- sample area (cm²)

2.6. Catalyst coating and sensor performance

Metals are chosen to function as catalysts in electro membrane process due to their multifaceted molecular orientations. These facets serve as active sites for rapid and efficient oxidation and reduction reactions. Each metal has its own unique structure and chemical properties. This gives metals some aspects of selectivity for certain fuels. Most of the optical fiber sensors use palladium (Pd) film as transducer to detect the concentration of hydrogen as the palladium sensors provides good hydrogen sensitivity.

In this study both palladium and platinum were attempted on the sensing side as electrode material. Pt paste was prepared by dissolving the platinum chloride in alcohol. 0.025 g/cm² platinum chloride was dissolved in few drops of propanol and then the mixture was pasted onto the membrane sheets. Next to that, the catalyst was reduced with hydrogen gas for 5–10 minutes. Similarly the Pd catalyst was prepared from palladium chloride and reduced with hydrogen. The hydrogen sensing effect of catalyst was studied with different combination of Pt and Pd catalysts in anode and cathode sides. (i) The anode and cathode was modified with multiple layers of Pt particles. (ii) The anode was modified with 80% Pt and 20% Pd catalyst and the cathode with Pt. (iii) anode and cathode was coated with Pd and Pt catalysts. The catalyst coated membranes were hot pressed and the temperature used for the

hot pressing is 50 °C with pressure 5 tones. The goal of hot pressing is to provide better contact between the catalyst and the membrane. After their preparation, the sensor performance for hydrogen gas was investigated.

3. Results and discussion

Sulphonation of PSEBS was carried out using CSA and the degree of sulphonation was controlled by varying the concentration of CSA and reaction time. The membranes were prepared by solvent evaporation method. The IEC (0.416 meq/g) of the sulphonated polystyrene ethylene butylene polystyrene (SPSEBS) membranes was measured at room temperature. The IEC is usually defined as the moles of fixed $-\text{SO}_3\text{H}$ sites per gram of polymer.

The water absorption of the membranes was 209%. The water sorption of the membranes was usually defined in weight percentage with respect to the weight of the dry membrane. The absorption of water depends on the degree of sulphonation (DS). Higher the DS, greater is the absorption of the solvents due to the increase in the number of sulphonic acid groups. PEMFCs use a proton conducting polymer membrane as an electrolyte, which is typically a poor proton conductor unless water is present. Therefore the hydration of a PEM is very important to the performance of the sensor. During the durability test, the samples were subjected to 80 °C in a solution containing 3% hydrogen peroxide and 4ppm ferrous ammonium sulphate. All the membranes were found to be dimensionally stable beyond 8 hr.

3.1. FTIR

The FTIR spectra of both PSEBS and SPSEBS membranes are shown in Fig.1. The hydrogen bond seems to play an important role in the proton conductivity. The appearance of broad envelope around 2924 cm^{-1} and 2854 cm^{-1} depends on CH_2 stretching, $3000\text{--}3600\text{ cm}^{-1}$ was assigned to $-\text{OH}$ stretch of the sulfonic acid group. Appearance of peak around 1175 , 1071 cm^{-1} was assigned to the $\text{O}=\text{S}=\text{O}$ (asymmetric stretch), which is due to the presence of SO_2 stretching. This confirms that the polymer PSEBS has been sulphonated. Disappearance of peak at the frequency of 720 cm^{-1} and 693 cm^{-1} shows that sulphonic acid group is substituted in the aromatic ring, when compared to the unsulphonated PSEBS. Appearance of peak at around 869 cm^{-1} shows that sulphonic acid group is substituted at para position.

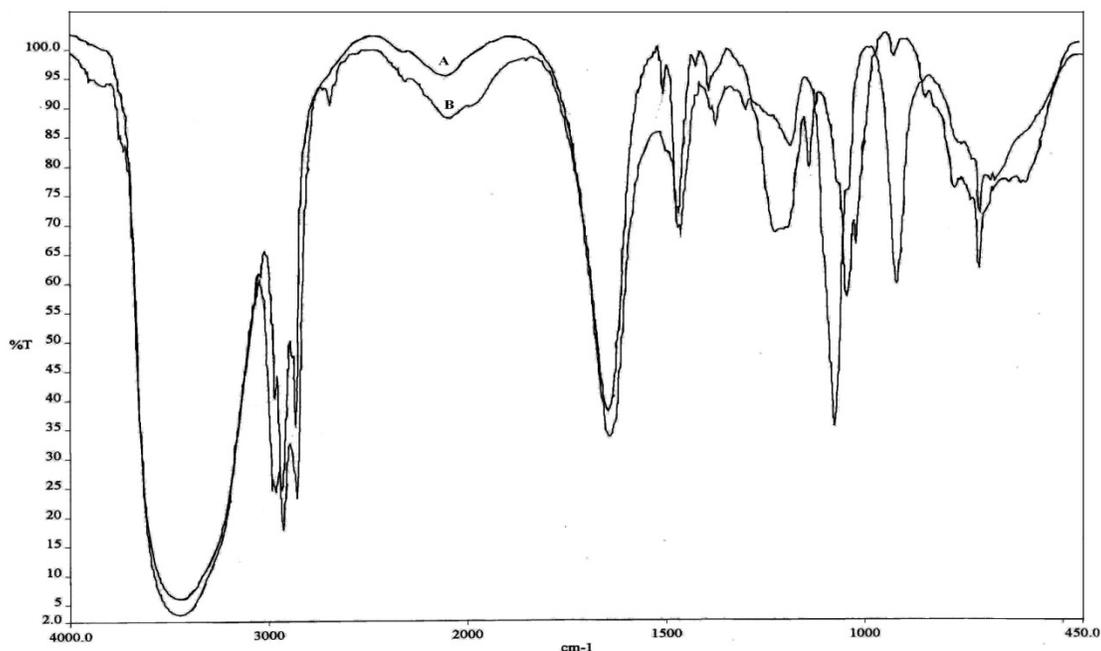


Fig. 1. FTIR spectrum of (A) unsulphonated PSEBS and (B) sulphonated PSEBS

3.2. Thermogravimetric analysis

The TGA curves of membranes are shown in Fig. 2. The thermal decomposition temperature of the membrane is a function of sulphonation degree. The unsulphonated sample display thermal stability up to 380 °C but the sulphonated membrane loses its stability beyond 200 °C. These curves can be divided in to regions corresponding to different weight loss. The transition around 250 °C may be due to the thermal degradation of sulphonic acid groups. The second decomposition was found to be around 400 °C. This weight loss is assigned to the final thermal decomposition of polymeric network. The small weight loss observed at low temperature and the position of the lower temperature exothermic peak between 200 and 220 °C indicate that the thermal stability of these membranes is quite sufficient and will be stable enough within temperature range of sensor application.

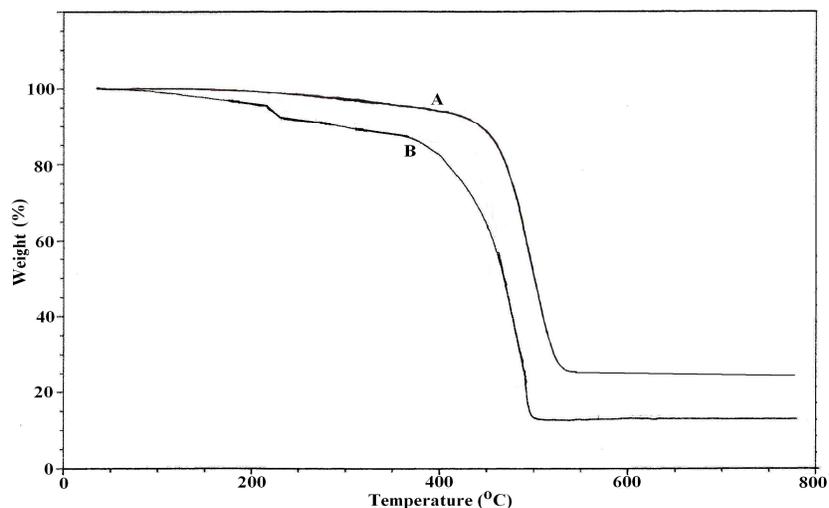


Fig. 2. TGA curves of (A) PSEBS and (B) SPSEBS

3.3. Membrane morphology

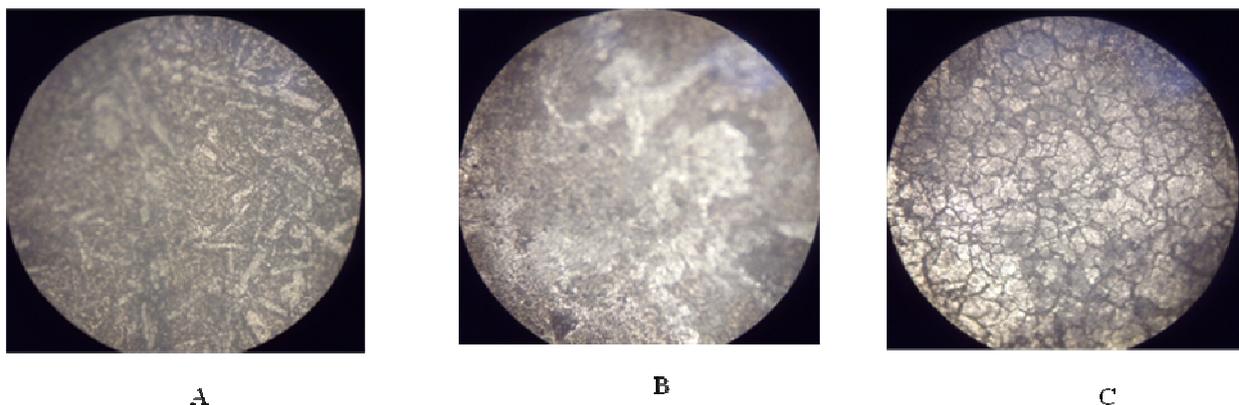


Fig. 3. OPM images of (A) Pt coating, (B) Pt/Pd coating and (C) Pd coating

The physical and electrochemical behavior of membranes depends on their internal structure [13]. The sulphonated groups might aggregate into hydrophilic cluster in the polymeric membrane, which would provide cation transport pathways or ionic transport channels. The OPM images investigate the distribution of sulphonated groups in membranes. The morphology of the sulphonated PSEBS membranes is shown in Fig.3. This image reveals that the membranes are uniform and homogeneous without any pores and cracks. Figures 3A, 3B and 3C show the morphology of catalyst coated membranes. All the images indicated the

uniform distribution of catalyst throughout the membrane. It ensures the good adhesion of the catalyst to the polymer matrix.

3.4. Proton conductivity

IEC provides an indication of the content of acid groups present in a polymer matrix, which are responsible for the conduction of protons and thus is an indirect and reliable approximation of the proton conductivity. Sulphonation is commonly used to modify the polymers to increase their hydrophilicity. The PSEBS polymer is hydrophobic in nature and when sulphonated, it becomes hydrophilic in nature. The sulphonated groups might aggregate into hydrophilic cluster in the polymeric membrane, which could provide cation transport pathways or ionic transport channels. The conductivity was determined using impedance spectroscopy. The proton conductivity of the membranes was found to be in the order of 10^{-3} S/cm. The conductivity was measured at 100% relative humidity and at room temperature.

3.5. Measurements of hydrogen

Sensor uses SPSEBS membrane as the proton conducting polymer electrolyte membrane. The catalyst was coated on both the side of the membrane by hydrogen reduction method. The sample gas is passed over the sensing electrode. Sensor testing was performed at ambient pressure and room temperature at a gas flow rate of 0.0116 ml/sec to 0.0694 ml/sec, and pure hydrogen was used for the investigation. Hydrogen gas detection in different measuring environments has recently become a very important problem, lots of efforts have been made to develop high-performance hydrogen sensors with safety and longer life. The sensor operates in amperometric mode and the limiting current is linearly dependent on hydrogen concentration in sample gas. Fig. 4 shows the response curve of the sensor for hydrogen in ppm range.

In the first case: hydrogen sensor uses a polymer electrolyte membrane, with platinum as the catalyst at both anode and cathode. The maximum output current of the sensor versus the hydrogen gas concentration at room temperature are given in Fig. 4. The maximum sensitivity of the sensor is 25 mA for 1ppm concentration of hydrogen.

However, the use of pure platinum poses a problem for the efficacy of its operation. Although platinum is effective as a catalyst, its affinity for poisoning reduces efficiency.

Additionally, a platinum oxide layer forms on the electrode surface, dramatically slowing the reaction rate, the transfiguration of precious metals with other metals as alloys can customize the electrode interface for synergistic results and improved reactions. These catalysts have the potential to lessen the effects of poisoning through oxidation and material loss. Also, the introduction of other transition metals as a blend reduces the cost of electrodes.

Recent advances in the electrochemical devices include a platinum alloy catalyst. By using an alloy, it is possible to develop smaller electrodes, thereby reducing cost and increasing efficiency. Platinum-based catalysts are utilized in current electrochemical technology to facilitate oxidation of fuels (hydrogen gas) in the electrochemical cell.

In the second case the anode was coated with 80% Pt and 20% Pd and cathode with Pt catalyst and in the third case anode was coated with Pd and cathode was coated with Pt catalyst. Palladium particles are chosen because, when exposed to hydrogen, they adsorb the gas and swell slightly to form palladium hydride. In fact, some available sensors rely on the different conductivity of palladium and palladium hydride to indicate hydrogen concentration. The combination of high lattice hydrogen solubility and high values of the hydrogen diffusion coefficient and retention of metallic elasticity makes palladium the best choice for the sensor anode at low hydrogen partial pressures.

From the results, it is observed that the Pd catalyst sensitivity is higher (75 mA at 1 ppm) than Pt/Pd alloy catalyst (12 mA at 1 ppm), the results are shown in Fig. 4. It is because; the palladium has high hydrogen sensitivity and affinity to hydrogen. Platinum is used as cathode owing to its lower activation energy for reduction of oxygen than palladium [14,15]. Palladium is used as anode and the earlier report also confirmed that palladium is not a suitable material for cathode side of the sensor. Because, there is a decrease in catalytic activity of the Pd cathode owing to oxide formation on the air side [16]. The anode was retained as a Pd film since the high solubility; sticking coefficient and diffusion coefficient for hydrogen in Pd are advantageous for sensing low concentration of hydrogen. Changes in hydrogen concentration in the palladium matrix lead to corresponding changes in the electrical resistance of the palladium that is easily measured. It was observed that palladium is more suitable as anode when hydrogen concentration is very low. When compared to Pt – Pt catalyst, in the first case which shows 63 mA at 6 ppm of hydrogen feed, the case of Pd – Pt

catalyst shows a better result of 75 mA at 1 ppm. From the results, it is evidenced that palladium catalyst is found to be more suitable than platinum catalyst for sensing hydrogen at low concentrations using 48% degree of sulphonated PSEBS membrane.

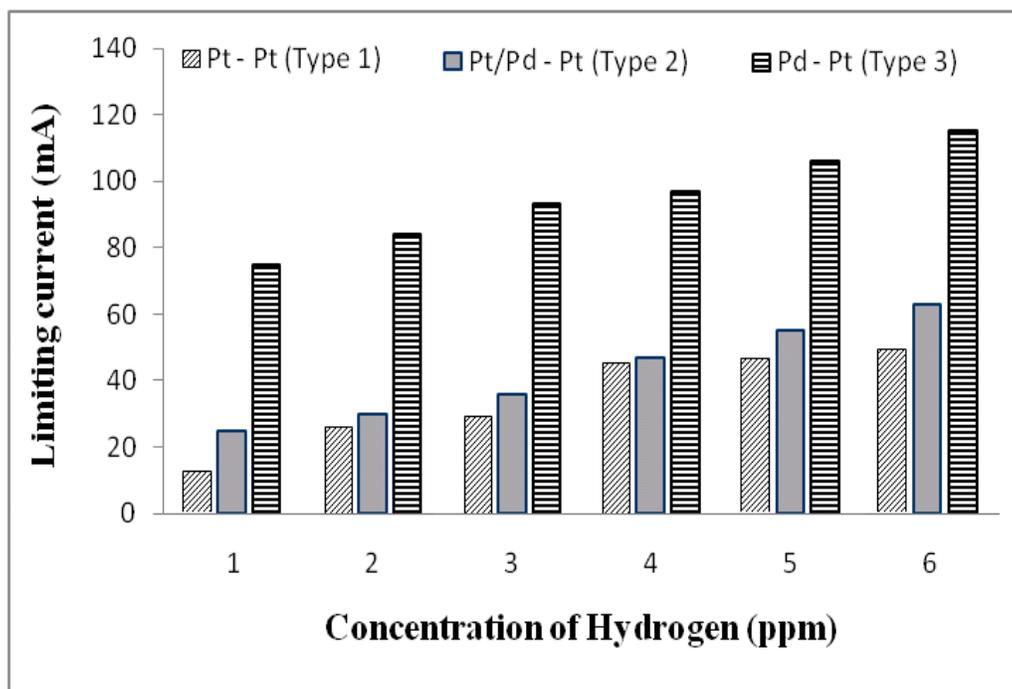


Fig. 4. Effect of various catalysts in hydrogen sensor performance of SPSEBS membrane at ambient temperature with varying the H₂ flow rate

4. CONCLUSION

In this study, the sulphonated membranes have been prepared for hydrogen sensor application. The membrane exhibited the conductivity of 10^{-3} S/cm. FTIR band confirms the sulphonation of PSEBS. The TGA studies reveal the thermal stability of these membranes is quite sufficient and are thermally stable up to 220°C. The morphology study of the catalyst coated polymer membranes confirmed the uniform distribution of the catalyst on the membrane. The sensor was developed with Pt, Pt/Pd and Pd catalyst based electrodes and its performance was investigated. The electrodes were prepared using impregnation reduction method. The hydrogen sensor prepared shows good performance along with good sensitivity.

The sensor can be used to monitor concentration of hydrogen even at low level (1ppm) at ambient temperature and pressure. The sensor showed a fast and stable maximum current output of 25 mA for Pt – Pt coating, 12 mA for Pt/Pd – Pt catalyst and 75 mA for Pd – Pt catalyst at 1ppm hydrogen input. The simple construction of the sensor and its performance characteristics make the investigated device very promising for practical applications.

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