Study of Metal Doped Polymeric Membrane for Hydrogen Purification

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Abstract: The Pd-ceramic composite membrane has good permeability and selectivity for hydrogen, very much depends upon the thickness, size and operating conditions. The solubility and diffusivity of the penetrant in the polymer matrix control the transport through nonporous dense membrane. An additional mode of sorption that is available in glassy polymers, the filling of Langmuir type micro voids or regions of localized free volume by suitable moieties. In present work, the La Ni Si and Al doped polymer membrane has been characterized by gas permeation measurements. The effect of swift heavy ion and microwave irradiation on metal doped polymer membrane has been studied.

1.Introduction

Various methods have been employed to purify the hydrogen i.e solid, liquid and gas contaminated methods. The common methods used in research and industry are scrubbers for particulate and KOH removal [1] Zeolites can act as molecular sieves and can be used for separating gas mixtures. Zeolites membranes can withstand wide temperature and pressure ranges and challenging chemical resistance to environment thus being used as catalytic membranes in reactor applications related to coal conversion and gasification[2].

Hydrogen storage alloys having importance in versatile technical application. The La Ni, is used as a potential material of hydrogen storage. The substitution of Ni by some other metals i.e. Al, Si, Pd, Co, Fe, Ag, Cu leads to alter its properties [3-5]. For an example of Ni is to develop the polymer filters especially for hydrogen using La Ni Si as dopant in polymers keeping in mind that this material is very sensitive to hydrogen.

The metal doped polymer membrane can used for removing the undesirable contamination present in the impure hydrogen. The palladium and titanium are extremely sensitive for hydrogen. The Ti coated and doped polymer membrane shows the remarkable reduction in hydrogen permeability, but the perm selectivity of hydrogen over carbon dioxide increases for these membrane as reported by Vijay et al[7].

To develop a new class of polymer membrane of high permeability for hydrogen. We introduce hydrogen active material to fill the micro voids of glassy polymers and compare the results with hydrogen inactive material. In present study the composite membrane of polycarbonate (PC) doped with Al and La289 Ni675 Si36 in various concentration 2% , 5% and 10% are prepared by solution east technique. The permeation of hydrogen through these membranes has been studid.

2. Experimental

2.1 Preparation of samples

The polycarbonate (PC) membranes of various thicknesses 25-30um has been prepared using solution cast method [1]. The Al and La Ni Si in different concentration of 2.5 and 10% as added in polycarbonate during solvent preparation and made a viscous solution. The LaNiSi was changed in its hydrogenated form by employed some pressure of the order of 2.06 X 106 Pa at a particular temperature. The details. The details of method used for activation of La Ni Si are discussed by Jain and Dakka[6].

2.2 Swift Heavy Ion irradiation

The metal powder of size less than 1um have been used for doping. The particles are expected to discribute to non-uniformly over the thickness 25um of polymer while solution casting. The microwave and swift heavy ion (SHI) irradiation has been used for homogenization of these moieties in polymer matrix. The SHI irradiation was carried out whit 35Cl9+ 120 MeV in General purpose Scattering Chamber (GPSC) under vacuum of the order of 10-6 torr. At nuclear Science Centre. New Delhi. The microwave irradiation has been done in a oven of 700 watts power at 2.6 GHz for five minutes. The excess exposure physically distort the membrane.

2.3 Gas permeability measurement

The polymer membranes were characterized by hydrogen gas permeability. The permeability is calculated by Fick's formula as discussed by Remmert et al [8]. The permeability of hydrogen for various polymer membranes was measured using permeability setup [7]. The pressure was kept constant (30 psi.) for measuring permeability.

2.4 Optical absorption measurements

In order to examine uniform doping of metal powder in polymers films optical absorption has been compared in the visible range using spectrophotometer Hitachi-330. The metal doped polymer films have distinct properties over virgin films. The transmission spectra of these membranes have been shown in Figure 1. The transmission of a virgin sample was found above 95% in the wavelength range 840-340nm. In this wavelength range, the 10% hydrogenated LaNisi doped in polycarbonate shows results have been observed in case of 10% A1 doped polycarbonate 90% transmission recorded and it reduces to 70% after irradiation. Wheras in case of 10% nonhydrogenated LaNisi doped in polycarbonate the transmission was 65% and it was increased to 75% after irradiation.

3.Results and Discussion

3.1 Effect of doping

The 10% non hydrogenated La Ni Si doped polycarbonate membrane shows different characteristic to 10% non hydrogenated La Ni Si doped in polycarbonate and 10% A1 doped membrane. These results can be confirmed by hydrogen gas permeability.

The permeation occurs by solution diffusion process. Initially the penetrate sorption takes place at high pressure sid, than diffuse in the polymer matrix and finally desorbed at lower pressure side. In, 10% hydrogenated La Ni Si doped in polycarbonate and 10% A1 doped polycarbonate membrane shows that the permeability of hydrogen decrease as concentration of doping increases. But 10% non hydrogenated La Ni Si doped polycarbonate membrane shows increasing permeability as concentration of doping increases. The systematic behavior of hydrogen gas permeability with various doping in polycarbonate is shown in Table 1.

The irradiated La Ni Si doped samples show higher permeation rates. While Al doped exhibits slight increment in permeability. Also, microwave treated samples have higher permeation rate.

The Al doped membrane exhibits the lower permeation with increasing concentration due to the filling of micro voids present in the polymer matrix by Al consequently the available free volume reduces, where as non-hydrogen Hydrogenate $La_{28.9}$ $Ni_{67.5}$ $Si_{3.6}$ doped membrane shows higher permeability with increasing doping percentage and at 10% doping the remarkable change in permeability was observed. In Hydrogenate $La_{28.9}$ $Ni_{67.5}$ $Si_{3.6}$ the permeability reduces as concentration increases.

Since $La_{28.9}Ni_{67.5}Si_{3.6}$, is hydrogen active material so the energy require to sorption and diffusion process is less and consequently the permeability of the membrane having 10% doping of non hydrogenated $La_{28.9}Ni_{67.5}Si_{3.6}$, is increases. The results are shown in Table.

3.2 Effect of microwave irradiation

The microwave irradiation of doped polymer membrane exhibits remarkable change in hydrogen permeability. The Al doped microwave irradiated polycarbonate membrane shows permeability 395 barrer whereas the non hydrogenated La Ni Si doped microwave irradiated polycarbonate shows permeability near 11000 barrer. The tremendous change in permeability after microwave irradiation of metal doped polymer membrane attributed to displacement of metal particles in polymer matrix results the drastic change in available free space to pass molecules.

3.3 Effect of SHI irradiation

The SHI irradiated metal doped polymer membrane also shows the sweeping change in permeability.

Conclusion:

It is concluded from the above study that metal doped polymer membrane alter the permeation properties. The Al and hydrogenated La Ni Si doped membrane has less permeability with doping increasing percentage, whereas non hydrogenated La Ni Si doped polycarbonate membrane has greater permeability with increasing doping percentage Also, the effect of SHI and microwave irradiation leads to expand the available free volume properties.

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Table 1

S.NO.	Sample PC doped with	Permeability (in barrer*)		
		2%	5%	10%
1	Al	11.07	10.6	9.44
2	Hydrogenate $La_{28.9} Ni_{67.5} Si_{3.6}$	11.52	9.58	9.22
3	Non Hydrogenate $La_{28.9} Ni_{67.5} Si_{3.6}$	9.75	10.34	20.54

*1 barrer = 10^{-10} {cm^3(STP) cm/cm^2.s.cm.-Hg}

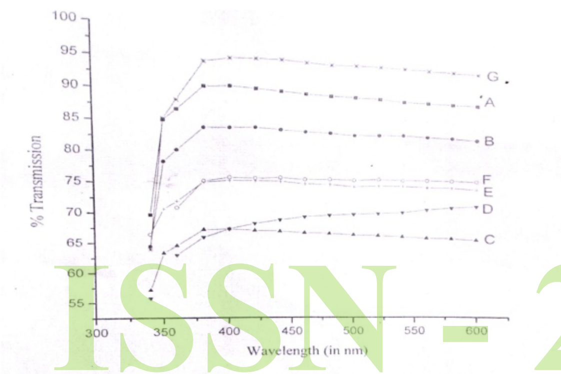

Figure 1

Figure Caption

Table 1: Permeability for hydrogen for various dopants at different concentration

Figure 1 : Graph of transmission versus wavelength of polycarbonate for (i) without irradiation (A) 10% Al doped (B) 10% hydrogenated La Ni Si (C) 10% non hydrogenated La Ni Si, (ii) Irradiated by 120 MeV35 Cl9+ ions (D) 10%Al (E) 10% Hydrogenated La Ni Si (F) 10% Non hydrogenated La Ni Si, (iii) For (G) Without doping and without irradiation.