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Zinc oxide based Sodium alginate Nanocomposite Membranes for Fuel cell Applications

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Abstract

Proton exchange membrane (PEM) fuel cells operate at comparatively low temperatures (<80ºC or <175ºF), offer quick start-up times, and require only hydrogen and oxygen to operate. PEM systems provide significant technical and cost advantages compared to competing solutions. Proton exchange membranes (PEMs) are the key components in fuel cell system. The researchers have focused to reach the proton exchange membrane with high proton conductivity, low electronic conductivity, low permeability to fuel, low electro osmotic drag coefficient, good chemical/thermal stability, good mechanical properties and low cost. These are classified into the “iron triangle” of performance, durability, and cost. Current PEMFC technology is based on expensive perfluorinated proton-exchange membranes (PEMs) that operate effectively only under fully hydrated conditions. In requirement of the energy generation, small steps have been attempted by means of synthesizing the proton exchange membranes. Sodium alginate and ZnO mixed matrix membranes were prepared in laboratory and measured for fuel cell applications.

Keywords: proton exchange fuel cell, sodium alginate, metal oxide nanoparticles, nanocomposite

1. Introduction

In recent years, global energy shortage and ecological pollution problems have created opportunities for fuel cells to replace the existing technologies in a variety of applications. Some common areas of application of fuel cells embody power for stationary, portable and transport applications. They are used to provide electricity and heat in large stationary applications [1-3]. They are also used to provide power in areas that are difficult to serve by the national grid. In sectors such as telecom, they find use in providing backup power. Another promising space of application is their use in transportable devices like mobile phones. Due to their light weight and higher operating times, they are seen as a good alternative to solid batteries. Their application in transport finds its roots in their ability to satisfy the rigorous emission norms. As far as the world fuel cell industry is concerned, most of the activities are concentrated in regions of North America, Europe, Japan and Korea. The areas of experience vary from R&D to element manufacture and system integration. Fundamental and applied R&D is carried out in universities as well as by commercial players. A large variety of companies are concerned in element producing and system integration. The governments in these regions offer robust funding for the event of the electric cell sector India’s electric cell business isn't quite developed as compared to the on top of mentioned regions. Even then, it can be considered a very important and emerging market. An economy growing at a fast pace and a country in need of energy to sustain the growth are the factors that strengthen India’s position as a prospective market for fuel cells. New national energy policies of the country that promote the growth of hydrogen and fuel cell technologies add to the market potential of fuel cells in India [4-7].

India – A Growing Economy

India is the second most populous country in the world and the fourth largest economy by purchasing power parity. India has seen dramatic economic growth over the last decade with GDP growth rates going as high as 9% in 2007-08 (Fig. 1). Although due to the global economic slowdown, Indian economy has also slowed (GDP growth rate of about 6.1 %) down from its high performance; it was one of the few economies where impact of this downturn was minimum. India’s growth rate was among the highest in the world along with China [8-10].

This high growth rate essentially signifies upliftment of large number of population from poverty to India’s growing middle class. This growing middle class is causing a consumer boom in Indian market which is contributing to India’s growth.

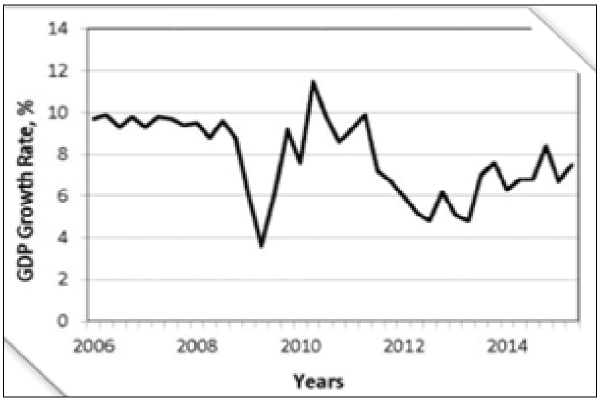


Fig. 1: India’s GDP growth rate over the years

Agricultural sector still employs about 60% of the population. A growing service industry is the largest contributor to India's GDP followed by industrial and agricultural sectors. Despite robust economic growth, India continues to face many major problems. One of the major challenges that India is facing to sustain its high levels of economic growth is lack of an effective infrastructure that can support its large population. A provision for reliable power supply and a network for energy supply to India's industrial and transportation sectors are the two key issues that need to be addressed [11-12].

Energy Landscape

India is the world's sixth largest energy consumer, accounting for almost 3.4% of the global energy consumption. Due to continuous high growth rates seen over the last few years, the demand for energy has been constantly growing in the economy. To sustain the growth rate for the next 20 years, India needs to increase its primary energy supply to 3-4 times. By 2030, the power generation capacity must increase to about 8, 00,000 W from the current levels of about 1, 60,000 MW (Planning Commission Report, 2006). A look at the current energy landscape shows India's dependence on fossil fuels for its energy needs [13-15].

About 76% of the electricity produced in India is generated by thermal power plants, 21% by hydroelectric power plants and almost 2-3% by nuclear power plants. India's fuel mix is heavily dependent on hydrocarbons. Fig. 2 shows the contribution of various fuels in the supply of energy. This heavily fossil fuel dependent fuel mix of India raises concerns over the energy security of India, particularly regarding imported oil. The main challenge facing India's energy sector is to increase and improve the delivery of energy services to various sections of the economy. A problem of disparity in demand and supply of energy is another big issue that needs to be addressed [16].

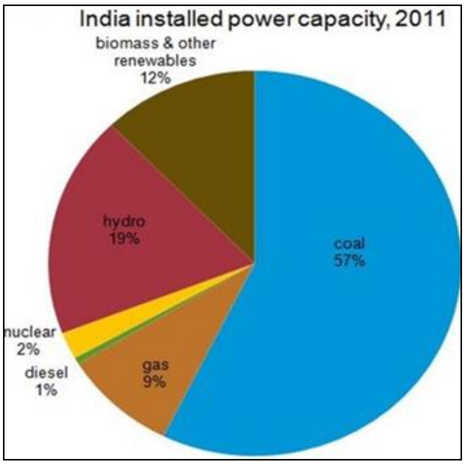


Fig. 2: India's fuel utilization for electricity generation

Policy Landscape

The Ministry of New and Renewable Energy (MNRE) largely govern India's policy regarding fuel cells and hydrogen technology development. The authority being quite active has set up a National Hydrogen Energy Board and a roadmap in 2006. The board set up five expert groups on hydrogen production, storage, power, transport and systems integration. It provided an integrated blueprint for the long-term public and private efforts required for hydrogen energy development inside the country. This roadmap was one of the measures taken in a series to improve the energy supply situation in India. The 2003 Electricity Act was responsible for developing an overall framework for renewable energy. The 2005 National Electricity Policy recognized renewable energy as a key option for areas where national grid is not feasible or cost effective [17-20].

The broad objectives of India's National Hydrogen Energy Program are as follows:

1. Reduce dependence on imported petroleum products
2. Promote use of diverse, domestic and sustainable new and renewable energy sources
3. Provide electricity to remote, rural and far flung areas
4. Promote hydrogen as a fuel for transport and power generation
5. Reduce carbon emissions from energy production and consumption
6. Increase reliability and efficiency of electricity generation

The National Hydrogen Energy Roadmap proposed two major initiatives in its Vision 2020– Prioritized Action Plan (Table 1). The Green Initiative for Future Transport (GIFT) aims to develop hydrogen-powered IC engine and fuel cell vehicles ranging from small (cars, 3-wheelers) to big vehicles through different phases of development and demonstration. The Green Initiative for Power generation (GIP) was to develop hydrogen-powered turbine and fuel cell based decentralized power generating systems.

What is a Fuel Cell?

Before going into details of fuel cell technology development in India and its further scope, let us first discuss the science of fuel cell technology. The fuel cell is an electrochemical device that converts the chemical energy of the reactants directly into electrical energy. The free energy of the chemical reaction is converted into electrical energy by redox reaction. The essential difference between a fuel cell and a battery is that the fuel cell can continuously generate power as long as the fuel is supplied. Further, the electrode material in fuel cell works as catalyst to facilitate redox reaction and the electrodes do not take part in the reaction or they do not get exhausted. Fuel cell has two electrodes, cathode and anode, which act as current collector as well as catalyst and thus they are also called electro-catalyst. Every fuel cell has an electrolyte in between the electrode, which carries ions from one electrode to the other. Electrons are produced at anode through fuel oxidation reaction [21-22]. These electrons take the least electrical resistive path and move from anode to outer circuit to do useful work such as powering an electric motor or illuminating a light bulb. The electron after traversing through the load or outer circuit reaches the cathode and participates in the reduction reaction to complete the process. Similarly, ions produced at the anode takes the least ionic resistive path for the ion and move from anode to cathode via electrolyte and participate in the reduction process to complete the reaction (Basu 2007). To make it clear, if we assume that hydrogen gas is fed at the anode and oxygen gas at the cathode of a fuel cell, with an acidic electrolyte in between the anode and cathode, the following individual and overall reaction would occur:

$$\begin{aligned} &Anode: H_2 \rightarrow 2H^+ + 2e^- \\ &Cathode: \tfrac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \\ &Overall: H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \end{aligned}$$

In this article, low temperature fuel cell, namely, polymer electrolyte or proton exchange membrane fuel cell based on hydrogen and alcohol fuels (methanol and ethanol) are discussed in detail in subsequent sections.

2. Experimental

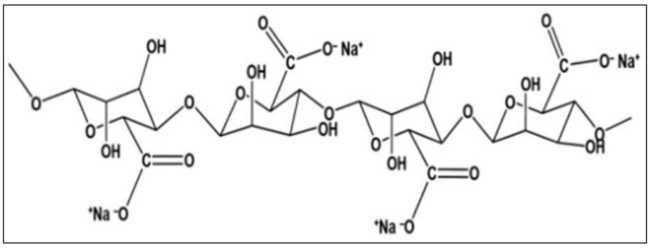
2.1 Zinc oxide nanoparticles

Nanotechnology research has gained momentum in the recent years by providing innovative solutions in the field of biomolecules materials of smart materials robotics optics and electronics. Nanoparticles are essentially a varied form of basic element derived by altering their atomic and molecular properties of elements. This article elaborates on the properties and application of zinc oxide nanoparticles.

Zinc oxide (ZnO) nanoparticles are available as nanopowders are available as powders and dispersions. These nanoparticles exhibit antibacterial anticorrosive Antifungal and UV filtering properties. Zinc comes under D-Block elements in periodic table. While oxygen is a P-block element in periodic table 2 element, some of these synonyms of the Zinc oxide nanoparticles are oxydatum zincioxium, permanent white ketozinc and oxyzinc.

2.2 Sodium Alginate

1. Sodium alginate is the sodium salt form of alginate acid and gum mainly extracted from the cell walls of brown algae with chelating activity. Upon oral administration sodium alginate binds to and blocks the intestinal absorption of various radioactive isotopes, such as radium 226 and strontium 90.
2. Sodium alginate (E401) is extracted from brown seaweed also and it is used as a stabiliser for ice creams and cheese it acts as thicker and emulsifier
3. It is highly viscous and is often used as on gelling agent these properties give sodium alginate to variety of uses in many industries.



Structure 1: Structure of Sodium alginate

2.3 Synthesis of Zinc Oxide Nanoparticles

Zinc chloride as the precursor, NaOH as a precipitating agent to synthesize ZnO nanoparticles were purchased from Sigma-Aldrich.

Preparation ZnO nanoparticles were synthesized by direct precipitation method using zinc chloride and NaOH as precursors. In this work, the aqueous solution (0.2 M) of zinc chloride ($ZnCl_2.6H_2O$) and the solution (0.4 M) of NaOH were prepared with deionized water, respectively. The NaOH solution was slowly added into zinc chloride solution at room temperature under vigorous stirring, which resulted in the formation of a white suspension. The white product was centrifuged at 3000 rpm for 30 min and washed three times with distilled water, and washed with absolute alcohol at last. The obtained product was calcined at 500 °C in air atmosphere for 3 hr.

2.4 Membrane characterization

2.5 Fourier Transmission Infrared (FTIR) spectral studies

FTIR spectra were taken for NaAlg before and after loading of NP's. Samples were scanned to confirm the crosslinking of NaAlg with ZnO in NaAlg matrix using Nicolet-740 and Perkin-Elmer-283B FTIR spectrophotometers. Membrane samples were ground well with KBr to make pellets under a hydraulic pressure of 400-450 kg/cm^2.

2.6 Differential Scanning Calorimetry (DSC)

DSC spectra of the plain and ZnO loaded NaAlg composite membranes were obtained using Rheometric Scientific (Model DSC-SP, UK). Measurements were done over the temperature range of 30° to 400°C at the heating rate of 10°C/min in hermetically sealed aluminum pans.

2.7 Electron Microscopic (SEM) Studies

SEM photograph of the ZnO loaded NaAlg membrane crosslinked with GA was taken. Membrane was sputtered with gold to make it conducting and placed on a copper stub. Scanning was done using Leica 400, Cambridge, UK.

2.8 Particle Size Measurement of Activated Charcoal Filler Particles

Particle size was measured by Zetasizer (Model 3000HS, Malvern, U.K). Sizes of the completely dried activated charcoal particles were measured by wet sample technique using a wet sample adapter. Particles were dispersed in water and placed on the sample couvette. The zeta average diameter was recorded. After measurement of particle size, the sample couvette was cleaned thoroughly to avoid any cross contamination. Triplicate measurements were taken and the average value was considered in data analysis and graphical display.

2.9 Mechanical Properties

Mechanical properties of the plain NaAlg and ZnO loaded NaAlg membrane strips were evaluated using the universal testing machine (UTM) (Hounsfield, UK), model H 25 KS, with an operating head load of 5 kN, following the procedure outlined in ASTM D-638 test method. Cross sectional area of the sample of known width and thickness was calculated. Membrane strips were placed between grips of the testing machine. The grip length was 5 cm; while the speed of testing was set at 5 mm/min. Tensile strength was calculated using the equation:

$$TensileStrength = \frac{Max\ Load}{Cross\ Sectional\ Area}$$

2.10 Preparation of Plain Sodium alginate Self Supportive Membrane

Sodium Alginate (E401) is extracted from brown seaweed. It is used as a stabilizer for ice cream, yogurt, cream, and cheese. It acts as a thickener and emulsifier for salad, pudding, jam, tomato juice, and canned products. It is a hydration agent for noodles, bread, cool and frozen products. In the presence of calcium and acid mediums, it forms resilient gels, *is a* natural polymer that is soluble in water. It is effective in film forming, semi-transparent quality. It has no odor and is not toxic. It is ductile but strong, flexible, and functions as a high oxygen and aroma barrier.

2.11 Preparation of Mixed Matrix Membrane

Sodium alginate (6 g) taken in 80 mL of water was stirred vigorously until the solution became homogeneous. Known weights of ZnO nanoparticles (i.e., 2.5, 5, 7.5 and 10 wt.% with respect to weight of NaAlg) were dispersed in 10 mL of water, sonicated for 120 min and added to the above prepared NaAlg solution. The whole mixture was stirred for about 24 h to obtain a homogeneous solution, which was poured on a completely cleaned dry glass plate with the help of doctor's knife to form membranes of uniform thickness. The caste membranes were kept at ambient temperature for drying; the dried membranes were peeled off from the glass plate. The hybrid composite membranes are designated as NaAlg-ZnO (2.5 wt.%), NaAlg-ZnO (5 wt.%), NaAlg-ZnO (7.5 wt.%), NaAlg-ZnO (10 wt.%), respectively that contained 2.5, 5, 7.5 and 10 wt.% of ZnO.

3. Results and Discussion

3.1 Fourier transform infrared spectroscopy Study

FTIR (Fourier transform infrared spectroscopy) spectra of Ammonium molybdate, sodium alginate, Blend with Ammonium molybdate hybrid membranes were taken in the range between 4000 and 400 cm^{-1} to confirm the crosslinking of NA-Alg with using Shimadzu IR Affinity-I FTIR spectrometer. Membrane samples were grounded well with KBr and pellets were formed by pressing under the hydraulic pressure of 400–450 kg/cm^2. FTIR spectral curves are displayed. All membranes used here are crosslinked with glutaraldehyde.. Abroad peak at 3200 cm^{-1} for plain NaAlg represents NH_2 stretching vibrations of the NH_2 group. In the region of 1000–1100 cm^{-1}, multiple bands have appeared for plain alginate due to C-O stretching vibrations. In case of hybrid matrix membrane, the intensity of this peak was increased, indicating the formation of C-O-C bonds between linear alkyl chains (-CH_2-CH-). However, -C-O- stretching is also observed in the same region as that of C-O stretching. The FTIR tracings are shown in Fig. 3 and Fig 4

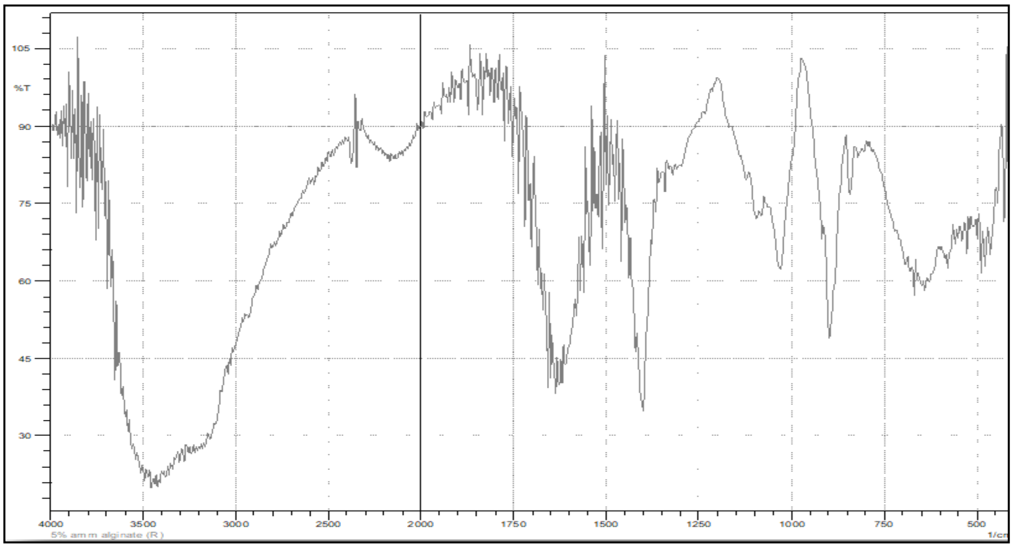


Fig 3: FTIR spectrum of Plain Na-Alginate

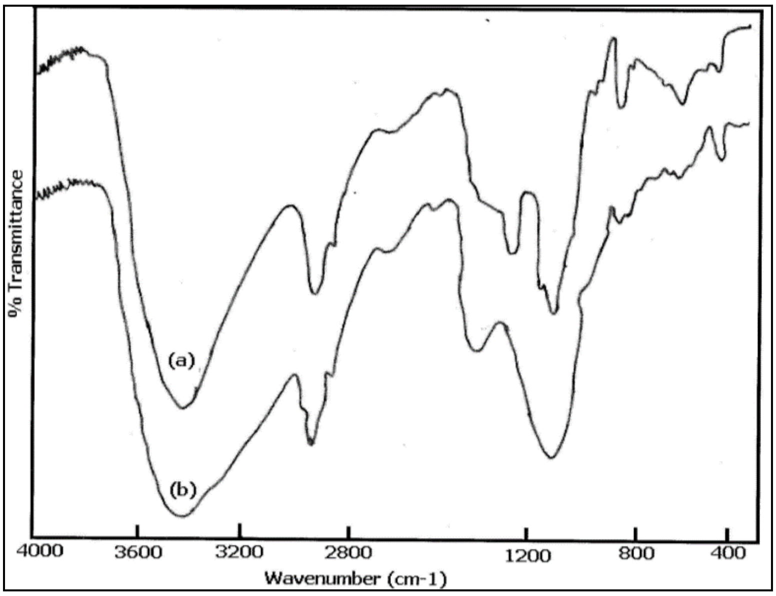


Fig 4: FTIR tracings of (a) Plain and (b) Na-Alg-ZnO membranes

3.2 X-ray diffraction studies

A Siemens D 5000 powder X-ray diffract meter was used to study the solid-state morphology ZnO nanoparticles. The XRD pattern of ZnO Nanoparticles was displayed in figure 5. X-rays of 1.5406 Å wavelength was generated by Cu Kα source. X-ray diffract grams of the ZnO nanoparticles. The angle of diffraction, 2θ was varied from 0° to 65° to identify any changes in the crystal structure and intermolecular distances between the inter-segmental chains. ZnO exhibits a typical peak at 2θ =32-37°, which corresponds to (1 0 0) and (1 0 1) mixed planes. Diffraction patterns of the particles show that intensity of the peak decreased around 2θ =47.

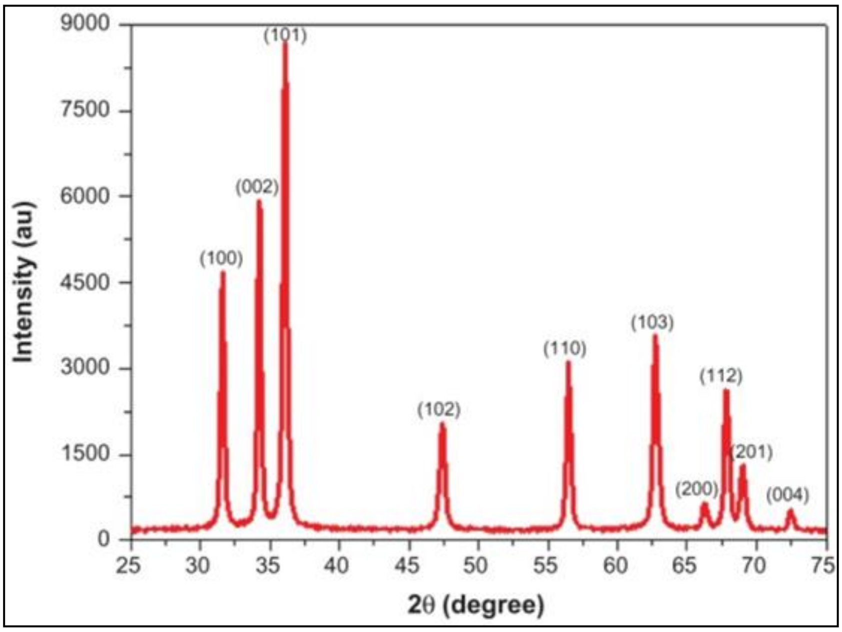


Fig 5: X-RD patterns of ZnO Nanoparticles.

3.3 Optical Microscopy Study

The optical microscopic study with the magnification X60 shown in the figure 6. According to the study one can observe the surface of the all membranes are found to be rough in nature. Which are the key point to start diffusion of the molecules and facilitate to attract the like molecules.

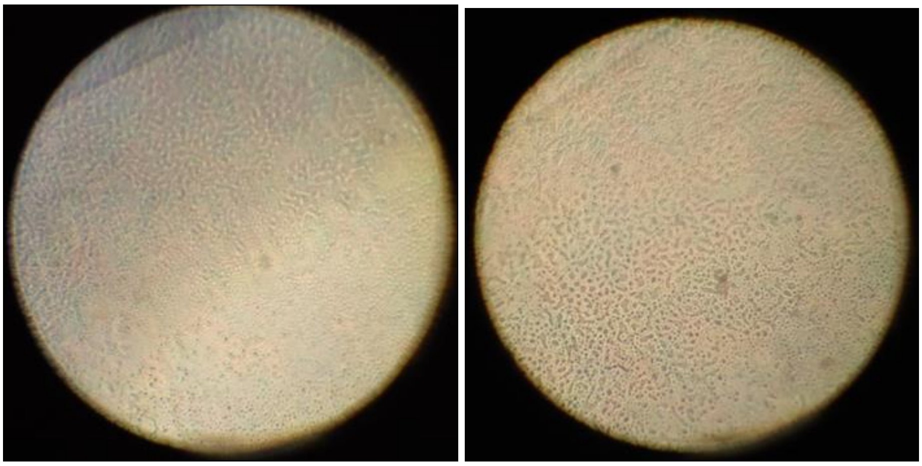


Fig 6: Optical microscopy of (a) plain Na-Alg and (b) Na-Alg loaded with ZnO (2.5 wt. %).

3.4 Scanning Electron Microscopy (SEM) Studies

Surface SEM micrographs of, blend NaAlg, Ammonium Molybdate composite membranes were obtained under high resolution (Mag. 300X 5 kV) using JOEL MODEL JSM 840A, scanning electron microscope (SEM), equipped with Phoenix energy dispersive analysis of x-rays (EDAX). SEM micrographs were taken. Micrographs of NaAlg-g-AAm-ZSM-5 mixed matrix membranes (MMM's) were obtained under similar resolutions (Mag. 2KX) using Leica Stereoscan-440 SEM equipped with Phoenix energy dispersive analysis of x-rays (EDAX). Since all these films were nonconductive, gold coating (15 nm thicknesses) was done on samples.

The Figure (a) represents the plain NaAlg blend membrane and found uniform and the figure (b) hybrid membrane of NaAlg-ZnO nanoparticles was distributed uniformly across the membrane matrix. The SEM images were displayed in figure 7.

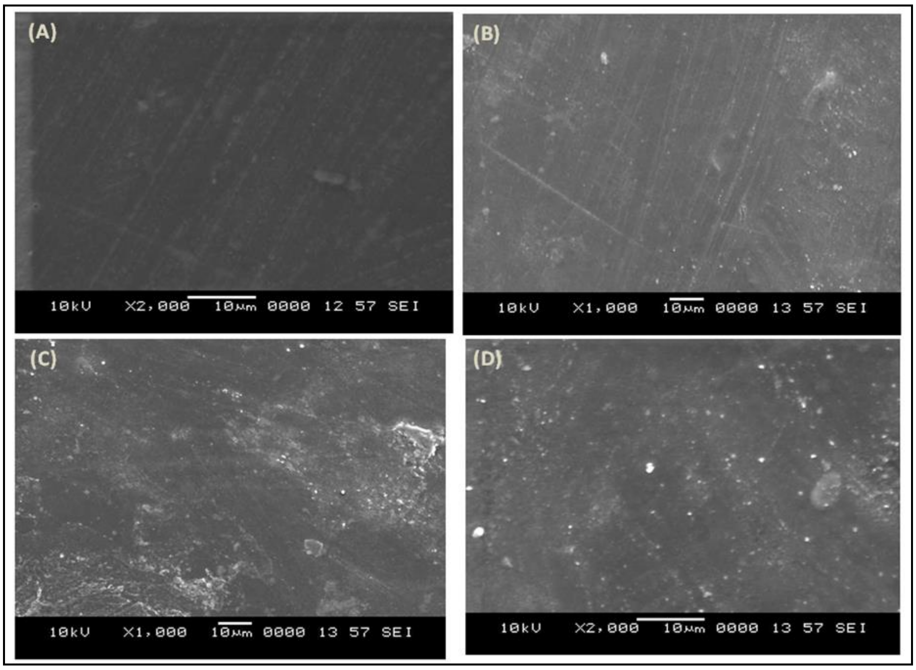


Fig 7: SEM images of (a) Plain Na-Alg, (b) NaAlg-ZnO-2.5 %, (C) NaAlg-ZnO-5 and (d) NaAlg-ZnO-7.5 % membranes

3.5 Differential Scanning Calorimetry

Noting the DSC curves of the composite membranes displayed in Figure 8, one can observe that the curve for plain NaAlg exhibits an endotherm with an onset at 60°C witha peak around 50°C due to melting. This endotherm has shifted to higher temperature in case of NaAlg–ZnO-2.5 % loaded membranes to about 100 °C, indicating that ordered association of NaAlg chains has increased due to crosslinking in the presence of ZnO particles.

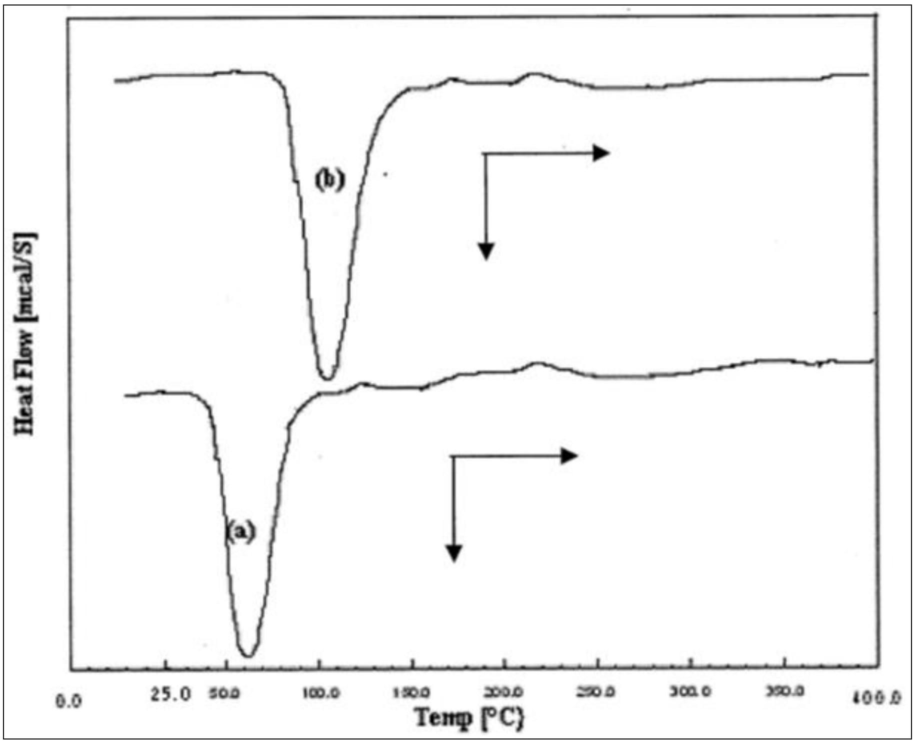


Fig 8: DSC Patterns of (a) Plain Na-Alg and (b) (C) NaAlg-ZnO-5 loaded Membranes.

3.6 Particle Size Analysis

By measuring the particle size of ZnO in nonsolvent media, size of the particles was around 100 nm as can be observed from the histogram plot of figure 9.

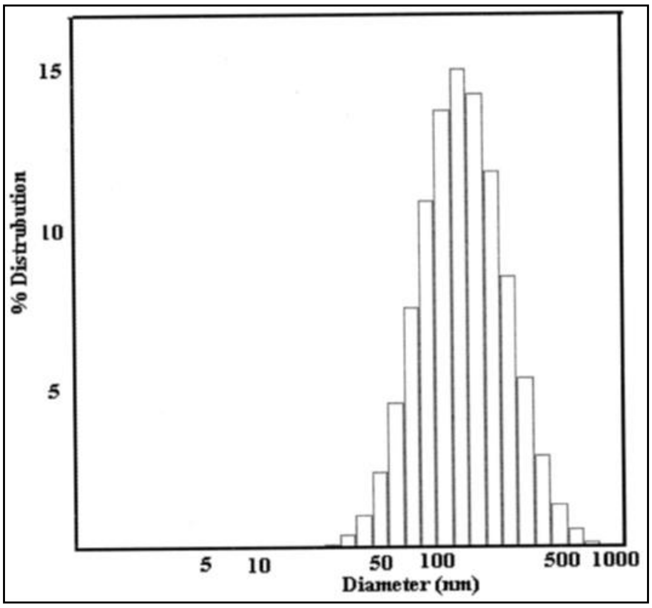


Fig 9: Histogram of activated ZnO Nanoparticles.

3.7 Mechanical Propertiess

Tensile strength data of plain NaAlg, Na-Alg-ZnO-2.5 % loaded NaAlg-ZnO-5%, NaAlg-ZnO-7.5 % and NaAlg-ZnO-10 % composite membranes were are presented in Table I. Among the four membranes tested NaAlg-ZnO-10 % exhibited highest tensile strength of 10.30 MPa. Consequently, tensile strength of NaAlg-ZnO-5 % was smaller than NaAlg-ZnO-10 % membrane, but that of plain NaAlg showed the least tensile strength of 3.83 MPa. These data suggest that after addition of ZnO nanoparticles to NaAlg, the mechanical strengths of the composite NaAlg membranes were improved due to crosslinking between NaAlg chains. The tensile strengths of the membranes followed the trend: NaAlg-ZnO-10 % > NaAlg-ZnO-7.5 % > NaAlg-ZnO-5 % > NaAlg-ZnO-2.5 % > plain NaAlg. Increased mechanical strength of the ZnO-reinforced NaAlg is the result of favorable physicochemical interactions between ZnO nanoparticles and the NaAlg matrix.

Table-I Mechanical Strength of the various prepared membranes

Membrane Type	Tensile Strength MPa
Plain Na Alg	3.83
NaAlg-2.5 %	4.41
NaAlg-5 %	5.34
NaAlg-7.5 %	7.97
NaAlg-10 %	10.30

4. Scope of the Future Work

A fuel cell is one of the recently identified electrical energy resources which undergoes certain chemical reactions to produce electrical power using hydrogen as fuel and oxygen as an oxidizing agent. The classification of fuel cells based on the types of fuel used is explained. This research mainly focuses on comparative performance analysis of emulating behaviour of well-known fuel cells systems such as Proton Exchange Membrane Fuel Cell and Solid Oxide Fuel Cell for grid applications and standalone systems. Both PEMFC and SOFC have valuable attractive properties like high efficiency and hence the impacts of these fuel cells on the distribution network are determined and compared by using computational simulations.

5. Conclusion

To improve membrane performance, one can generally follow two distinct strategies, i.e., either to synthesize new polymers with specific chemical architectures or to modify the existing polymers by incorporating suitable fillers. This paper reports results obtained according to the latter route. It is realized from the literature that fillers like molecular organic framework (MOF) can improve separation properties of membranes, provided that appropriate zeolite and polymer combinations are chosen. The ZnO types of MOF filled NaAlg hybrid nanocomposite membranes of this study had not been previously reported in the literature. The mixed matrix nanocomposite membranes studied here were effective in fuel cell applications 2.5 to 10 wt. % with respect to the polymer matrix. The addition of even a small amount of ZnO nanoparticles into NaAlg membranes has improved both flux and selectivity to water over that of the plain NaAlg membrane. The prepared mixed matrix membranes were shown moderate response to the measured fuel cell.

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