

Investigation Of Hydrogen Production By Using Composite Membrane (Nafion/ZrO₂)-Based Solid Polymer Electrolyte Water Electrolyser

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ABSTRACT

In the present study, Composite materials based on perfluorinated cation-exchange membrane incorporating particles of Zirconium and Nafion is synthesized. With this membrane the performance of the electrolysis cell improved considerably at room temperature and atmospheric pressure. In addition, by using catalysts and membranes, the performance of this Composite membrane is studied by varying voltage range with respect to hydrogen yield and at current density 0.1, 0.2, 0.3, 0.4, and 0.5(A cm⁻²), With a Nafion 115 membrane as a reference electrolyte. Experiments have shown that 99.9% purity of hydrogen Gas is evolved. The physicochemical properties of the composite membranes such as thermogravimetric analyzer (TGA), Scanning Electron Microscope (SEM), XRD (X-ray powder diffraction), Fourier transform infrared spectroscopy and Ion Exchange Capacity is determined. The fabricated composite membranes have shown the significant improvement of all tested properties compared to that of pure Nafion membrane.

Keywords: catalysts, Composite membrane, Hydrogen, PEM water Electrolyser, ZrO₂.

I. Introduction

Hydrogen is considered as a clean and efficient energy source for the future [1], because it is efficiently converted to electricity with no CO₂ emissions by a fuel cell system [2]. Hydrogen as an energy carrier is an attractive option, because of its flexible, ecofriendly, affordable, used in all sectors of the economy. At present, however hydrogen is mainly produced by steam reforming of fossil fuels such as coal, oil, and natural gas, in which a large amount of pollutants are inevitably released into the atmosphere. Thus, there has been increasing attention given to water decomposition as a clean method for hydrogen production. Today hydrogen is commonly used in industrial applications to manufacture petrochemicals and fertilizers. The current hydrogen industry does not produce hydrogen as an energy carrier or as a fuel for energy generation, except for pilot scale R&D projects.

Therefore the electrolysis of water using proton exchange membrane (PEM) can be a novel approach for developing a technology for hydrogen production. Recently, the research interest in polymer electrolyte water electrolysis (PEWEC), the proton exchange membrane (PEM) is expected to be an alternative electrolyte for a water electrolysis cell, because its solid form ensures a higher current density and safer operation compared to the

conventional alkaline water electrolysis. The key component of the so-called solid polymer electrolyte water electrolysis is said to be this PEM, which transports protons from the anode to the cathode and prevents the produced gases from mixing. Currently, the most widely used PEM material is Nafion (Dupont Co.) due to its moderate proton conductivity and chemical stability [3]. The conventional proton conducting polymer electrolyte membrane is mechanically unstable at temperatures above 100°C [4]. Nafion-like have a few drawbacks such as high cost, water dragging during operation. One of the promising techniques for the preparation of Nafion-alternative PEMs is composite membranes

The effort to develop these higher temperature membranes includes modification of the conventional host polymers, via incorporation of various hygroscopic inorganic particles or by developing alternate new polymer system [5-8]. One of the inorganic membranes is Nafion/ZrO₂ [9-11]. The membrane having good electrochemical stability satisfactory mechanical strength and high proton conductivity [12-14]. Hence, research and development is needed to improve the performance and lower costs of hydrogen production. So, far less amount of work has been reported on inorganic membrane to produce hydrogen. Hence in the present study an attempt has been made to evaluate the

performance of composite membrane in water electrolysis process for the production of hydrogen. The conductivity of the PEM is measured at 30°C. The characterisation studies of the Composite membrane is done by ion exchange capacity (IEC) and FT-IR.

II. Materials and methods

2.1. Materials

ZrO₂, NaCl, NaOH, and 10 wt% Pd on Activated carbon, RuO₂, N, N-Dimethylacetamide are purchased from SRL Chemicals India and Nafion 115 membrane, 5 wt% Nafion solution is procured from M/s. Ion power Inc, USA.

2.2 Membrane preparation

For the preparation of the ZrO₂ Composite membrane [15,16], A known amount of ZrO₂ is dissolved in DMAC solution and added to 5wt% Nafion solution and then sonicated in an ultrasonic water bath to get fine dispersion of ZrO₂ in the Nafion solution. Clear solution obtained at RT is then cast on a petri dish and the solvent was evaporated at 100°C without vacuum. The solvent when completely evaporated, The Nafion/ ZrO₂ was pulled off from the Petri dish by adding a small amount of water [18]. For Obtaining a transparent Composite membrane, the Composite membrane (Nafion/ZrO₂) and Nafion membrane 115 is pretreated with a standard treatment procedure described below [17-18].

- Boiling in 3% hydrogen peroxide (H₂O₂) for 1h to oxidize organic impurities.
- Rinsing with boiling water for 2h.
- Boiling in H₂SO₄ for 1h to remove ionic impurities.
- And finally the composite membrane is washed with deionized water to remove any excess acid and then dried.

2.3 Preparation of Membrane Electrode Assemblies (MEAs)

The membranes [Figure: 1] is assembled by hot-pressing between home-made electrodes to obtain the membrane-electrode-assemblies (MEAs) [Figure: 2]. The electrodes preparation procedure based on a spraying technique is described elsewhere [18].



Figure: 1 Nafion-ZrO₂



Figure .2 Pneumatic hotpress

10 wt% Pd on Activated carbon is mixed with 5 wt % Nafion solution and coated on a composite membrane on one side as hydrogen electrode (Cathode) and RuO₂ is mixed with 5 wt% Nafion solution is coated on another side as oxygen electrode (Anode) [Figure: 1]. Similarly the same procedure has been used to Nafion 115 membrane. The prepared MEAs are tested in-house single cell PEM water electrolyser.

2.4 Description of single cell PEM water electrolyser

The PEM water electrolyser is fabricated with SS316 material of 10 cm² single cell. Current collectors used are perforated titanium sheets. The thickness of each end plate is 20 mm, with a provision for inlet/outlet for water/gases for the respective electrodes. Each end plate has horizontal and vertical flow fields so as to hold water and for the free flow of produced gases during electrolysis operation [19]. The testing of the prepared MEA (fixed in single cell) is operated in electrolysis mode at 1 atm pressure and at room temperature. The water used for this experiment is purified by reverse osmosis (Millipore Milli Q equipment). Thus obtained pure water is supplied from water reservoir atop and supplied on the both sides of the single cell. The produced hydrogen and oxygen gases are evolved from top of the cell at respective electrodes. Thus evolved water, gases are lifted by circulating water on both sides of the single cell and collected in vessels atop of the electrolyser.

2.5 Performance of the Membrane electrode assembly (MEA)

The performance of prepared MEA is evaluated using in-house fabricated single cell assembly. A DC voltage of 1.8 to 2.32V is applied during water electrolysis operation. The cell is kept under experimental condition for 2 hrs. The performances is evaluated by current and voltage (I-V) characteristics curves generated during water electrolysis operation [20].

Membrane characterization

2.6 Water uptake

The water uptake is calculated by the difference between wet and dry samples weight [21]. The wet weight (W_w) was determined after immersion of the sample in de-ionized water at room temperature for 24 h while, for the dry weight (W_d), the sample was kept in an oven at 60 °C under vacuum for 4 h. The percentage of absorbed water is given as follows equation1:

$$\text{Water - uptake} = \frac{(W_w - W_d) \times 100}{W_d} \quad \dots 1$$

Where, W_w and W_d are the weight of wet and dry membranes, respectively.

2.7 Ion Exchange Capacity Measurement

The ion exchange capacity (IEC) was determined through an acid –base titration method[22]. The sample is placed in 1M aqueous NaCl and kept still for 1 day. The solution was then back titrated with 0.01M NaOH to neutralize exchanged H^+ , using phenolphthalein as an indicator. The titrant volume at the equivalent point was determined. IEC was calculated by the following equation 2.

$$\text{IEC} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{Sample}}} \quad \dots \dots 2$$

Where V_{NaOH} is the added titrant volume at the equivalent point (ml). C_{NaOH} is the molar concentration of the titrant, W_{sample} is the dry mass of the sample (g).

2.8 FT-IR spectrum analysis

FT-IR spectrum of the Nafion/ ZrO₂ was recorded on a Perkin FT-IR spectrometer to further verify the structure of Nafion/ZrO₂ particles. FT-IR spectrum was measured for the pellet with KBr.

2.9 XRD analysis

To gather information on the Nafion/ZrO₂ catalyst, the X-ray powder diffraction (XRD) analysis was performed using a Broker D8 advanced. The X-ray diffractogram was obtained for 2θ varying between 20 and 100

2.10 SEM– analysis of composite membrane

The cross-sectional morphology of the Nafion/ZrO₂ composite membrane was investigated by using SEM (Phillips XL 30 series). The distribution of silicon, sulfur and fluorine elements along the membrane cross-section is detected by EDX (Energy dispersive X-ray) technique (Microanalysis 1350).

2.11 Thermo-Mechanical analysis

Thermal stability of the membrane was investigated by using thermo gravimetric analyser (TGA) (Mettler Toledo TGA/STDA 851) with a heating rate of 50⁰c per minute in nitrogen atmosphere from 30 to 500⁰c.

2.12 Gas chromatography

Hydrogen gas purity, investigated by using Gas chromatography.

III. Results and discussion:

3.1 Water uptake

It shows that the Nafion/ZrO₂ has a higher water uptake than the unmodified Nafion at the considering temperature, the water uptake of the Nafion is 35%, while Nafion/ZrO₂ has water up ke of 60%, much higher than that of the unmodified Nafion. That should attribute to the hydrophilicity of the ZrO₂ nano particles, of which the surface –OH groups have excellent capability of water maintenance region.

3.2 Ion Exchange Capacity Measurement

The important property of PEM is Ion exchange capacity (IEC). It can be seen that Composite membrane exhibited IEC value (0.97 meq g⁻¹) in comparison to that of Nafion membrane 115 (0.84 meq g⁻¹), indicating an active contribution of the synthesized fillers in providing free acid groups to the membrane, as expected from the proton conductivity features of the sulfated oxides itself. However Composite membrane was found to higher than Nafion membrane.

3.3 FT-IR

The FT-IR spectrum of Composite membrane is exhibited in [Figure 3].

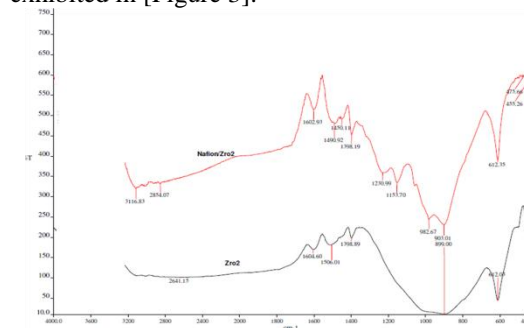


Figure:3 FT-IR Spectra for Nafion-ZrO₂ and ZrO₂ powder

The two signals at 1230 cm⁻¹ and 1153 cm⁻¹ that are related to the CF₂ stretching vibration of the PTFE backbone. The peaks observed at 982 and 903 cm⁻¹ are attributed to the stretching vibration moieties of SO₃⁻ and C-O-C, respectively [23]. The peak at 1100cm⁻¹ and 1200cm⁻¹ represent symmetric and asymmetric stretching of the CF₂ bonds. The peak at 1602.93 cm⁻¹ was due to the formation of

CF=CF bonds in the polymer. These spectra also exhibit O-H stretching vibration around 3431, O-H bending vibration and C-H stretching vibration 2854 cm^{-1} . The zirconium oxide bands in the composite membrane are observed in the region between 820 – 520 cm^{-1} [26, 34], 612 cm^{-1} to the vibrations feature of ZrO_2 , show the various stretching frequencies around 612 cm^{-1} , 455 cm^{-1} , 475 cm^{-1} . The features particularly at 612 cm^{-1} and 475 cm^{-1} , due to Zr-O₂-Zr asymmetric and Zr-O stretching modes respectively, confirm the formation of ZrO_2 phases [24, 25].

3.4 XRD analysis

Figure.4a Illustrates the XRD patterns of pure ZrO_2 characteristic peaks 2θ at 20.04°, 27.00°, 35.63° 53.49° (2θ), as reported in the literature [26]. crystal peak is observed for ZrO_2 particles .

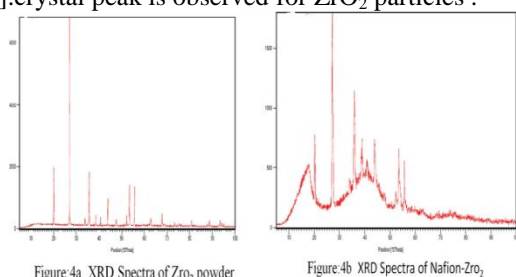


Figure 4b. shows the X-ray diffraction pattern of Nafion / ZrO_2 . The analysis of the broad peak at 17.7° (2θ) is related to the crystalline scattering of the polyfluorocarbon chains in Nafion membranes [27], the inorganic materials ZrO_2 is subjected to X-ray diffraction. The diffraction patterns of the ZrO_2 powder (Figure 4a) shows Several peaks located at 20.04°, 27.00°, 35.63° 53.49° (2θ) corresponding to the crystalline Zirconium , and several others that are attributed to the presence of ZrO_2 . The peaks of ZrO_2 in the composite membrane are slightly shifted to the right compared to the peaks of ZrO_2 powder.

X-ray spectra related to the developed composite membrane show the peaks of the considered ZrO_2 Powder confirming the presence of the inorganic compound within the Nafion polymeric matrix.

3.5 SEM analysis

The morphologies of membrane surface and cross-section is investigated by SEM analysis. Figure. 5a shows the SEM images of the Nafion/ ZrO_2 Membrane inorganic (ZrO_2) additives is incorporated into the Membrane.

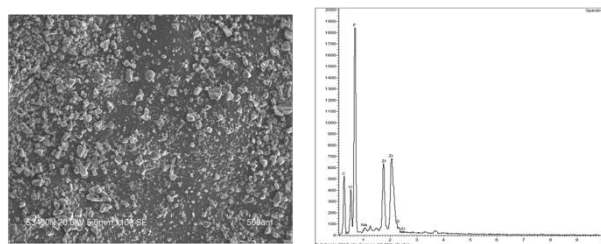


Figure:5a Nafion-Zr₂ SEM image

Figure:5b Nafion-Zr₂EDX Spectra

The atom composition analysis by EDX analysis on the composite membranes in Fig. 5a, there is a particle layer located on the surface of Nafion/ ZrO_2 membrane .Figure. 5b. EDX indicates that Zr element is well formed inside the modified membrane while there is no Zr element in the original Nafion membrane. The coexistence of the atom peaks for Zr, C, F, O and S suggests the coverage of Nafion molecules on the formed metal oxide particles. These results confirm that ZrO_2 particles are successfully fabricated in the surface of the fabricated membrane.

3.4 Thermo-Mechanical analysis.

The TGA [Figure:6] thermo grams of the inorganic additive incorporated membranes are shown in Fig. Initially, the weight loss 100°C corresponding to the water desorption is observable, at 320°C ,the de-sulfonation process beings and after 390°C there is a complete decomposition of the membrane. which is attributed to the loss of residual water in the membrane. It is seen that the decomposition temperature of the composite membranes shifts with the nature of inorganic content [28].

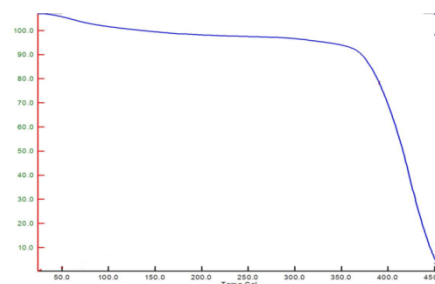


Figure:6 TGA for Nafion-Zr₂

3.5 Performance of Single cell with respect to hydrogen yield.

The polarization curves for the electrolysis cells based on bare Nafion and composite membrane Nafion/ ZrO_2 at 30°C under atmospheric pressure are reported in Figure 1. Hydrogen yield is calculated by using Faradays law where the experimental yields of hydrogen with respect to current densities at different voltages at room temperature (30°C) are studied[Figures 7&8] and [Tables 1&2].

Experimental Hydrogen Yield(ccmin ⁻¹)	Current Density (A cm ⁻²)	Voltage (V)	Theoretical Hydrogen yield (ccmin ⁻¹ at STP)
6.43	0.1	1.8	6.9
12.32	0.2	1.89	13.8
19.95	0.3	2.0	20.7
24.10	0.4	2.12	27.7
30.20	0.5	2.24	34.2

Table: 1 Experiments carried out for 10wt% Pd/AC for Composite membrane (Nafion/ZrO₂).

Experimental Hydrogen Yield (ccmin ⁻¹)	Current Density (A cm ⁻²)	Voltage (V)	Theoretical Hydrogen yield (ccmin ⁻¹ at STP)
6.43	0.1	1.85	6.9
12.32	0.2	1.9	13.8
19.95	0.3	2.15	20.7
24.10	0.4	2.25	27.7
30.20	0.5	2.32	34.2

Table: 2 Experiments carried out for 10wt% Pd/AC for Nafion membrane 115.

The performance of Composite membrane shows [Figure 7] the decrease in voltage from 2.32 to 2.24 at current density 0.5 Acm⁻². The composite membrane is performing better than the Nafion 115 membrane. The hydrogen yields are 6.43, 12.32, 19.95, 24.1, 30.2 cc/min respectively at current densities 0.1, 0.2, 0.3, 0.4, 0.5 A/cm² at temperature 30°C.

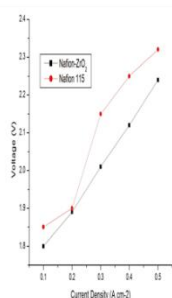


Figure:7 Current density Vs Cell voltage for Composite membrane (Nafion/ZrO₂) and Nafion membrane 115.

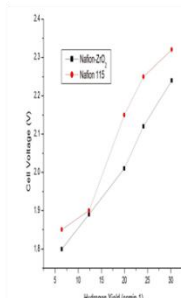


Figure:8 Hydrogen Yield with respect to Cell voltage for Composite Membrane (Nafion/ZrO₂) and Nafion Membrane 115.

3.6 Gas chromatography

The purity of evolved hydrogen gas is 99.99% and is detected by Gas chromatography.

IV. Conclusions

Composite membranes with inorganic compound contents was investigated and characterised in terms of IEC, water uptake, SEM, XRD measurements and thermo-gravimetric analysis. The membrane was prepared by mixing the inorganic compound with a Nafion solution in DMAc as a solvent. The presence and amount of ZrO₂ was confirmed through SEM, TG and X-ray analysis.

Nafion-ZrO₂ composite membrane for SPE electrolyser has shown promising properties at room temperature operation allowing to achieve significantly higher performances with respect to a bare commercial Nafion. This effect is mainly due to a significantly better Stability than the bare perfluorosulfonic membrane and it is also observed that during the electrolysis operation the overvoltages are reduced. A promising increase of electrical efficiency was recorded at low current densities at room temperature compared to conventional membrane-based devices. The lower over potential

saves the energy (current) consumption in electrolysis process which is important for Industrial application. Further improvements of the MEA are necessary to ameliorate the electrochemical stability at high temperatures.

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