Production of hydrogen using composite membrane in PEM water electrolysis

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Abstract
Electrolysis of water is the best known technology till today to produce hydrogen. The only practical way to produce hydrogen using renewable energy sources is by proton exchange membrane (PEM) water electrolysis. The most commonly used PEM membrane is Nafion. Composite membrane of TiO_2 is synthesized by casting method using Nafion 5wt% solution. RuO_2 is used as anode and 10 wt% Pd on activated carbon is used as cathode in the water electrolyser system. The performance of this Composite membrane is studied by varying voltage range 1.8 to 2.6V with respect to hydrogen yield and at current density 0.1, 0.2, 0.3, 0.4, and 0.5(A cm^{-2}). This Composite membrane has been tested using in-house fabricated single cell PEM water electrolysis cell with $10cm^2$ active area at temperatures ranging from 30,45,65 85^0c and at 1 atmosphere pressure.

Keywords: TiO_2; Nafion; Pd on activated carbon; Composite membrane; PEM water electrolyser; Hydrogen.

1. Introduction
Energy is the most essential and vital entity to survive on this Planet. From past few decades majority of the mankind depend on fossil fuels for transportation, power, etc., due to this a drastic increase in usage of fossil fuels has led to tremendous demand of energy. As the fossil fuels are limited, there is a need for an alternative source which is efficient, reproducible, applicable, recyclable and byproduct shall be free from CO_2 emissions. Hydrogen is considered as a clean and efficient energy source for the future [1]. Hydrogen as an energy carrier is an attractive option, because of its flexible, ecofriendly, affordable, used in all sectors of the economy. 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. In water electrolysis the main components are PEM and electrocatalysts, the most commonly used PEM is Nafion and Composite membrane like Nafion/TiO_2, Nafion/ZnO_2 etc.
Perfluorosulfonate ionomer membranes such as Nafion are specifically used in several industrial applications that require an ion-conducting polymer membrane with good thermal and chemical stability [2-3]. 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. 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/TiO$_2$ [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 characterization studies of the Composite membrane are done by ion exchange capacity (IEC) and FT-IR.

2. Materials and methods

2.1 Materials
TiO$_2$, NaCl, NaOH, and 10 wt% Pd on Activated carbon, RuO$_2$, 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 TiO$_2$ Composite membrane, 3gm of TiO$_2$ is dissolved in DMAC solution and added to 5wt% Nafion solution by stirring vigorously After Obtaining a clear solution at temperature, the mixture was then cast on a Petri dish and the solvent was evaporated at 100°C without vacuum once the solvents was completely evaporated, then Composite membrane was annealed at 120° C for 1 hour [15]. For Obtaining a transparent Composite membrane, the Composite membrane (Nafion/TiO$_2$) and Nafion membrane115 is pretreated with a standard treatment procedure described below [16, 17].

- Boiling in 3% hydrogen peroxide (H$_2$O$_2$) for 1h to oxidize organic impurities.
- Rinsing with boiling water for 2h.
- Boiling in H$_2$SO$_4$ 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)
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 RuO$_2$ 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.

Figure 1. Composite membrane (Nafion/TiO$_2$)

2.4 Description of single cell PEM water electrolyser
The PEM water electrolyser is fabricated with SS316 material of 10 cm^2 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 [18]. The testing of the prepared MEA (fixed in single cell) is operated in electrolysis mode at 1 atm pressure and temperatures 27°C, 45°C, 65°C. 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 2.6V 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 [1, 19].

2.6 Ion exchange capacity
The ion exchange capacity (IEC) is determined by an acid –base titration method .The sample is dried over night at 80°c and then immersed in an amount of 0.1 M NaCl solution overnight at 65°c under continuous stirring, so that H$^+$ ion of the polymer acid side chains could be replaced by Na$^+$ ion. The solution is then titrated with 0.1M NaOH by using indicator phenolphthalein .IEC is calculated by the following equation

$$IEC = \frac{V_{NaOH}XC_{NaOH}}{W_{Sample}}$$

(1)

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).

2.7 Hydrogen production
The hydrogen produced during the electrolysis operation is collected in vessels provided at the top of the single cell electrolyser .The theoretical yield of hydrogen is calculated using Faraday laws equation(Eq:2) as given below [20]

$$W_{H_2} = \frac{I\,t\,M}{F\,N_e}$$

(2)

where w is the weight of the hydrogen produced at the cathode, I the applied current intensity (A),t the time (s),M the molecular weight of hydrogen (g mol^{-1}),F the faraday's constant (96485 C mol^{-1}) and N$_e$ the number of electrons involved in the reaction. The experimental yields of the hydrogen with composite membrane and10 wt% of Pd on activated carbon is calculated. Both the experiments (composite membrane and Nafion 115 membrane) are run for 10min at current densities 0.1, 0.2, 0.3, 0.4, 0.5 A/cm^2 at temperature 27°C,45°C,65°C and the produced hydrogen and oxygen gases are collected in respective vessels. The yield of hydrogen is calculated by taking the volume of the vessel and length of the vessel and length of the hydrogen gas occupied in the vessel at 1 atm pressure.

3. Results and discussion
3.1 Ion exchange capacity measurement
The one of the important characterization of PEM is Ion exchange capacity (IEC) .It can be seen that Composite membrane exhibited relatively better IEC value (0.96 meq g^{-1}) in comparison to that of Nafion 115 Membrane (0.84meq g^{-1}) by using (Eq: 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 is higher than Nafion membrane.

3.2 FT-IR

The FT-IR spectrum of Composite membrane is exhibited in (Figure 2). The strong and wide peak at 3414.19 cm^{-1} and peak at 1628 cm^{-1} are due to the hydroxyl groups of
Ti-OH with which physisorbed water molecule are bound by weak hydrogen bonds. The strong absorption centered at 710.55 cm-1 is the typical Ti-O-Ti vibration [21-23]. The characteristic peak of –SO$_3$- group of Nafion of 1240 and 1132 cm^{-1}.Moreover the adsorption band of Nafion at 1240cm^{-1}, attributed to –SO$_3$- asymmetric stretch, shifted to 1235.54 cm-1 and that at 1135cm^{-1} attributed to –SO$_3$- symmetric stretch shifted to 1152.98cm-1. The peak at 1100cm^{-1} and 1200cm-1 represent symmetric and asymmetric stretching of the CF$_2$ bonds. The peak at 1628.15 cm-1 is due to the formation of CF=CF bonds in the polymer. Other common peaks that can be identified in this spectrum are symmetric S-O stretching at 1058.19 cm^{-1}.
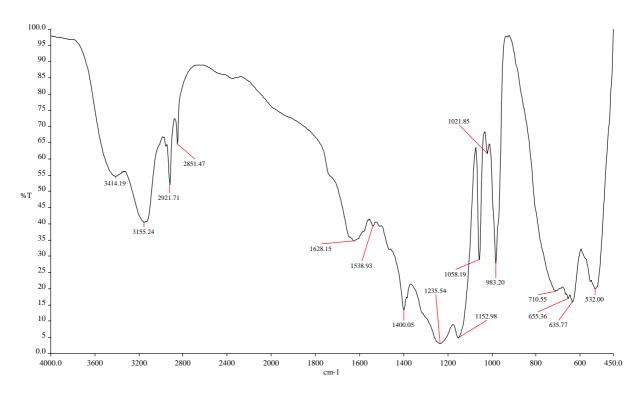

Figure 2. FT-IR spectra for composite membrane (Nafion/TiO$_2$)

3.3 Performance of single cell with respect to hydrogen yield

The current-voltage (I-V) characteristics curves for the prepared TiO$_2$ composite membrane (Figure 1) and Nafion 115 is studied in single cell water electrolysis system using 10 wt% palladium on activated carbon as cathode and ruthenium oxide (RuO$_2$) as anode electrode. Hydrogen yield is calculated by using Faradays law, the experimental yields of hydrogen with respect to current densities at different voltages at temperature 27°C, 45°C, 65°C are studied (Figures 3, 4) and Table 1, shows that The performance of Nafion membrane 115 (Figure 3) shows the decrease in voltage from 2.8 to 2.0 V when temperatures increased from 27 to 65°C at current density 0.4 Acm^{-2}. (Figures 5, 6) and Table 2, Similarly the performance of composite membrane (Figure 5) is better than the former as it shows the decrease in voltage from 2.2 to1.8 V at current density of 0.4 Acm^{-2}, the decrease in overvoltages are because of the The decrease in temperatures from 27 to65^o respectively during single cell. The prepared MEA with Pd on carbon support demonstrates better performance during the electrolysis operation.
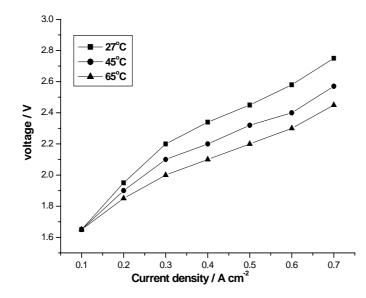
Figure 3. Polarization curves for 10 wt% Pd on activated carbon at 27°C, 45°C, 65°C for Nafion membrane 115
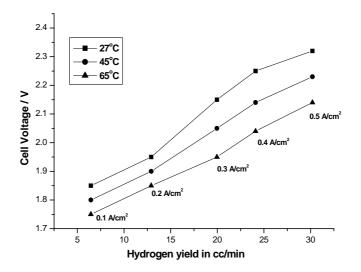

Figure 4. Hydrogen yield with respect to cell voltages at different temperatures and current densities for Nafion membrane 115

Table 1. Experiments carried out for 10 wt% Pd on activated carbon for Nafion Membrane 115: Cathode: Pd on activated carbon; Anode: RuO_2

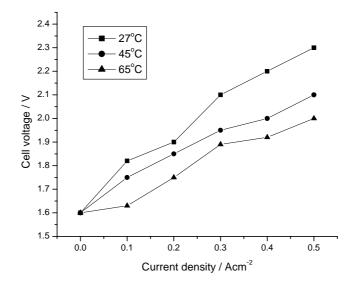| Experimental Hydrogen yield (cc/min)	Current density (A/cm^2)	Time (min)	Voltage during electrolysis process (V)			Theoretical Hydrogen yield (cc/min at STP)
			27°C	45°C	65°C	
6.45	0.1	10	1.85	1.80	1.75	6.9
12.29	0.2	10	1.95	1.90	1.85	13.8
19.92	0.3	10	2.15	2.05	1.95	20.7
24.10	0.4	10	2.25	2.14	2.04	27.7
30.20	0.5	10	2.32	2.23	2.14	34.2

Figure 5. Polarization curves for 10 wt% Pd on activated carbon at 27°C, 45°C, 65°C for composite membrane
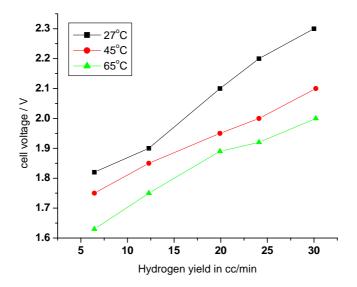

Figure 6. Hydrogen yield with respect to cell voltages at different temperatures and current densities for composite membrane

Table 2. Experiments carried out for 10 wt% Pd on activated carbon for Composite Membrane (Nafion/TiO$_2$): Cathode: Pd on activated carbon; Anode: RuO$_2$

Experimental Hydrogen yield (cc/min)	Current density (A/cm^2)	Time (min)	Voltage during electrolysis process (V)			Theoretical Hydrogen yield (cc/min at STP)
			27°C	45°C	65°C	
6.45	0.1	10	1.82	1.75	1.63	6.9
12.29	0.2	10	1.9	1.85	1.75	13.8
19.92	0.3	10	2.1	1.95	1.89	20.7
24.10	0.4	10	2.2	2.0	1.92	27.7
30.20	0.5	10	2.3	2.1	2.0	34.2

4. Conclusion

A novel modified Composite membrane is prepared by casting method is having good proton conductivity. The experiments reveal that the composite membrane is slightly performed better than

Nafion membrane115 and it is also observed that during the electrolysis operation the over voltages are reduced with increase in temperatures, the hydrogen yield are 6.45,12.29,19.92,24.10,30.20cc/min respectively at current densities 0.1, 0.2, 0.3, 0.4, 0.5 A/cm2 at temperatures 27^oc, 45^oc, 65^oc. The lower over potential saves the energy (current) consumption in electrolysis process which is important for industrial application. This results in an improvement in cell performance as well as hydrogen yield. That the composite membrane shows a good electrical conductivity and also shows sustainability hydrogen yields with respect to cell voltage and current density.

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