

# Composite Membrane for Hydrogen Production as a Clean Fuel Using Pem Water Electrolyser

C. Mahender<sup>1\*</sup>, D. Venkat Ramulu<sup>1</sup>, T. Ramesh<sup>1</sup>

<sup>1</sup>Department of Chemistry, Malla Reddy Engineering College (Autonomous), Secunderabad 500 100, Telangana, India

Corresponding Author

Dr. C. Mahender

Associate Professor, Department of Chemistry  
Malla Reddy Engineering College (Autonomous), Secunderabad 500 100  
E-Mail: mahendercheva[a]gmail.com  
Tel: +91-9908127749, 91-7702296082

**Abstract:** Composite membrane of TiO<sub>2</sub> is synthesized by casting method using Nafion 5wt% solution. RuO<sub>2</sub> is used as anode and 10 wt% Pd on activated carbon is used as cathode in the water electrolyser cell. 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<sup>-2</sup>). This Composite membrane has been tested using in-house fabricated single cell PEM water electrolysis cell with 10cm<sup>2</sup> active area at temperature 27, 45 and 65°C and at 1 atmosphere pressure.

**Keywords:** TiO<sub>2</sub>, Nafion, Pd on activated carbon, Composite membrane, PEM water electrolyser, Hydrogen

## 1. Introduction

Hydrogen is considered as a clean and efficient energy source for the future [1-2]. 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 [3]. In water electrolysis the main components are PEM and electrocatalysts, the most commonly used PEM is Nafion and Composite membrane like Nafion/TiO<sub>2</sub>, Nafion/ZnO<sub>2</sub> 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 [4-5]. The conventional proton conducting polymer electrolyte membrane is mechanically unstable at temperatures above 100°C [6] 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 [7-10]. One of the inorganic membranes is Nafion/TiO<sub>2</sub> [11-13]. The membrane having good electrochemical stability satisfactory mechanical strength and high proton conductivity [14-16]. 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

### Materials

TiO<sub>2</sub>, NaCl, NaOH, and 10 wt% Pd on Activated carbon, RuO<sub>2</sub>, 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.

### Membrane preparation

For the preparation of the TiO<sub>2</sub> Composite membrane, 3gm of TiO<sub>2</sub> 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 [17]. For Obtaining a transparent Composite membrane, the Composite membrane (Nafion/TiO<sub>2</sub>) and Nafion membrane115 is pretreated with a standard treatment procedure described below [18-19].

- Boiling in 3% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for 1h to oxidize organic impurities.
- Rinsing with boiling water for 2h.
- Boiling in H<sub>2</sub>SO<sub>4</sub> for 1h to remove ionic impurities.
- And finally the composite membrane is washed with deionized water to remove any excess acid and then dried.

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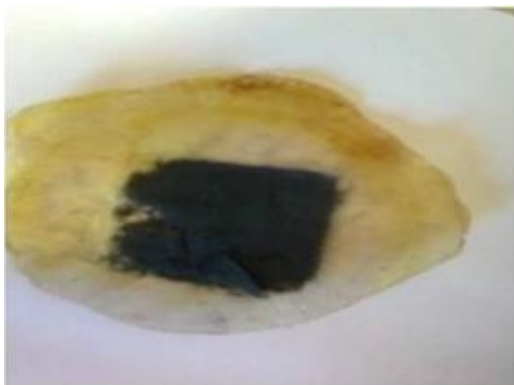
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**Preparation of Membrane Electrode Assemblies (MEAs)**

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<sub>2</sub> 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<sub>2</sub>)

**Description of single cell PEM water electrolyser**

The PEM water electrolyser is fabricated with SS316 material of 10 cm<sup>2</sup> 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 [20]. 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.

**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 are evaluated by current and voltage (I-V) characteristics curves generated during water electrolysis operation [2, 21].

**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 [22]

$$W_{H_2} = \frac{ItM}{FN_e} \dots\dots\dots (2)$$

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<sup>-1</sup>), F the faraday's constant (96485 C mol<sup>-1</sup>) and N<sub>e</sub> the number of electrons involved in the reaction. The experimental yield of the hydrogen with composite membrane and 10 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<sup>2</sup> 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****FT-IR**

The FT-IR spectrum of Composite membrane is exhibited in (Figure 2). The strong and wide peak at 3414.19 cm<sup>-1</sup> and peak at 1628 cm<sup>-1</sup> 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<sup>-1</sup> is the typical Ti-O-Ti vibration [23, 24, 25]. The characteristic peak of -SO<sub>3</sub><sup>-</sup> group of Nafion of 1240 and 1132 cm<sup>-1</sup>. Moreover the adsorption band of Nafion at 1240cm<sup>-1</sup>, attributed to -SO<sub>3</sub><sup>-</sup> asymmetric stretch, shifted to 1235.54 cm<sup>-1</sup> and that at 1135cm<sup>-1</sup> attributed to -SO<sub>3</sub><sup>-</sup> symmetric stretch shifted to 1152.98cm<sup>-1</sup>. The peak at 1100cm<sup>-1</sup> and 1200cm<sup>-1</sup> represent symmetric and asymmetric stretching of the CF<sub>2</sub> bonds. The peak at 1628.15 cm<sup>-1</sup> 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 1058.19cm<sup>-1</sup>.

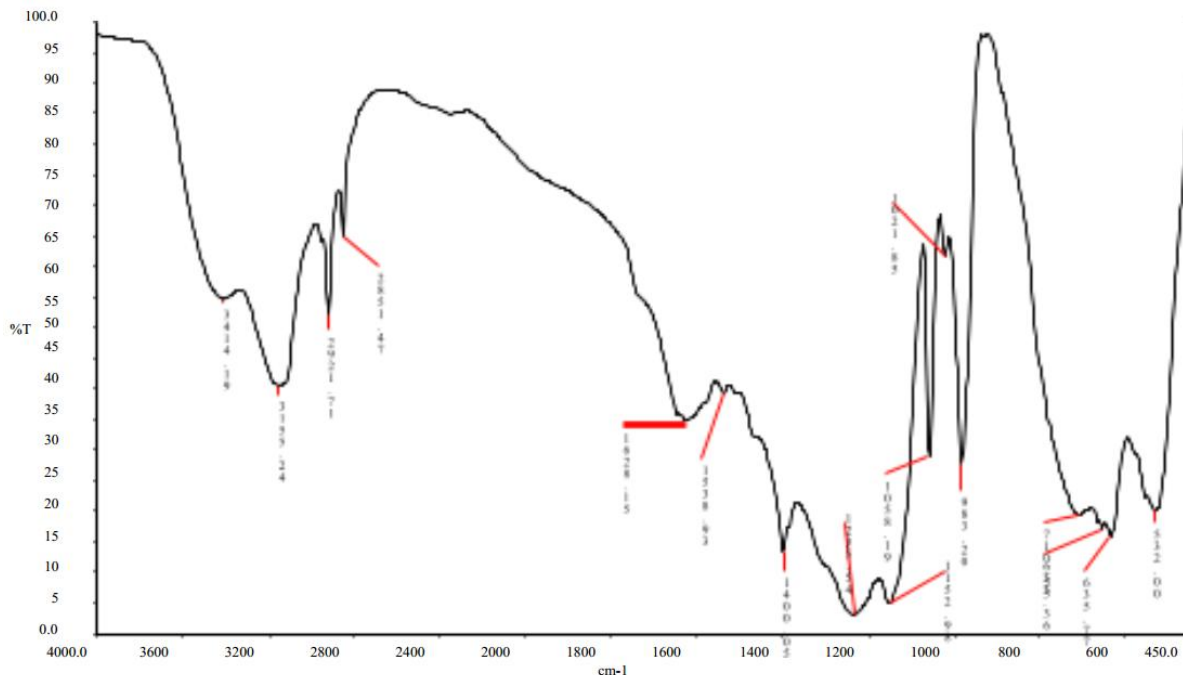


Figure 2: FT-IR spectra for composite membrane (Nafion/TiO<sub>2</sub>)

**Performance of Single cell with respect to hydrogen yield**

The current-voltage (I-V) characteristics curves for the prepared TiO<sub>2</sub> 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<sub>2</sub>) 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 room temperature are studied (Figure 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<sup>o</sup>C at current density 0.4 Acm<sup>-2</sup>. (Figure 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 to 1.8 V at current density of 0.4 Acm<sup>-2</sup>, the decrease in overvoltage are because of the decrease in temperatures from 27 to 65<sup>o</sup> respectively during single cell. The prepared MEA with Pd on carbon support demonstrates better performance during the electrolysis operation.

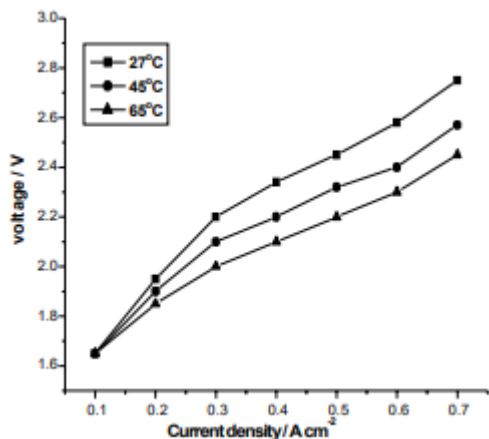


Figure 3: Polarization curves for 10 wt% Pd on activated carbon at 27<sup>o</sup>C, 45<sup>o</sup>C, 65<sup>o</sup>C for Nafion Membrane 115

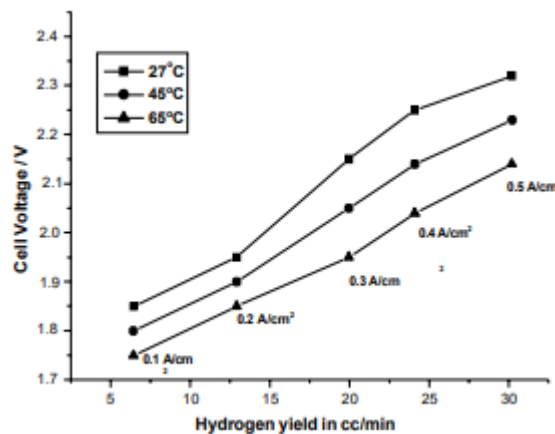


Figure 4: Hydrogen yield with respect to cell voltages at different temperatures and current densities for Nafion membrane 115

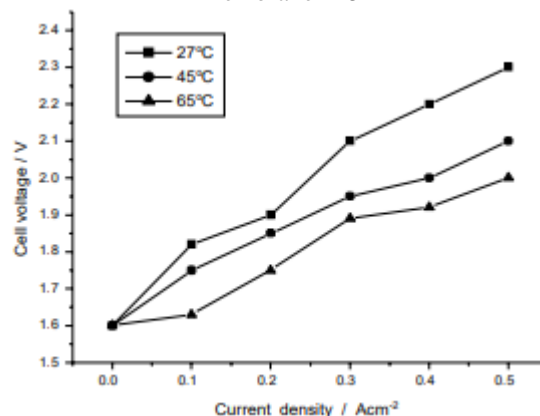
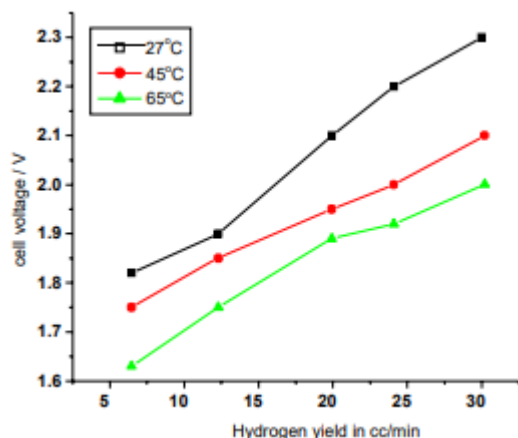


Figure 5: Polarization curves for 10 wt% Pd on activated carbon at 27<sup>o</sup>C, 45<sup>o</sup>C, 65<sup>o</sup>C for composite membrane



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

**Table 1:** Experiments carried out for 10 wt% Pd on activated carbon for Nafion Membrane 115

Cathode: Pd on activated carbon; Anode: RuO<sub>2</sub>:

Experimental Hydrogen yield (cc/min)	Current density (A/cm <sup>2</sup> )	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

**Table 2:** Experiments carried out for 10 wt% Pd on activated carbon for Composite Membrane (Nafion/TiO<sub>2</sub>):

Cathode: Pd on activated carbon; Anode: RuO<sub>2</sub>:

Experimental Hydrogen yield (cc/min)	Current density (A/cm <sup>2</sup> )	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. Conclusions

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 membrane 115 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, 30.20 cc/min respectively at current densities 0.1, 0.2, 0.3, 0.4, 0.5 A/cm<sup>2</sup> at temperatures 27°C, 45°C, 65°C. 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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