

Performance Studies of Nitrogen doped CNTs Supported on Palladium as Electro Catalyst for Hydrogen Evolution Reaction (HER) Different Loadings on MEA in Proton Exchange Membrane (PEM) Water Electrolysis

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Abstract

The present study of this paper describes experimental analysis of the optimum loading of noble metal Pd/NCNTs (30 wt% of Pd) in electrocatalytic layers of the polymer electrolyte membrane (PEM) water electrolysis cells. The prepared electro catalyst was coated on membrane electrode assembly (MEA) with different loading from 0.3-1.0 mg.cm⁻² and tested in a proton exchange membrane water electrolyser in single cell setup. The performance and characteristics of the prepared electrocatalysts are reported along with the corresponding yields of hydrogen at different temperatures 27, 40, 50, 60, 70, 80°C, current densities from 0.1 to 2.0 A cm⁻². The performances of the water electrolyser developed by increase in the loading of catalyst overpotential has decreased with increasing the temperatures were compared.

Keywords: Hydrogen production, Electrolyser, Polymer electrolyte membrane (PEM), Nafion, Palladium.

INTRODUCTION

Hydrogen was play an important role as an energy carrier for sustainable development in the future[1-3]. Hydrogen was used in fuel cells to generate electricity efficiently, with water as the only byproduct [4,5]. Hydrogen was the lightest element and any

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leakage of hydrogen gas can disperse quickly, thus hydrogen has safe as other commonly used fuels [4]. However, hydrogen was not an energy source, but an energy carrier. Hydrogen must be produced from other sources with energy input from which is neither renewable energy sources [6-8]. From the solar energy, hydrogen can be produced from water, via photocatalysis, thermochemical cycles, and water electrolysis [9,10]. These methods offer renewable and clean production of hydrogen fuel and, therefore, have attracted increasing research interests in recent years. Water electrolysis was the most promising technology for large-scale hydrogen production [10]. Compared with traditional alkaline electrolysis, in which corrosive potassium hydroxide (KOH) solution was used as the electrolyte, proton exchange membrane (PEM) electrolysis have more advantages, such as ecological cleanness, high degree of gases purity, and easy maintenance [11]. The cost of hydrogen production by PEM electrolysis can be further reduced due to continuous technology development. Investigations on PEM electrolysis for hydrogen production are focused on demonstration of PEM electrolysis for hydrogen production [12], development of new catalysts [11,13], and development of new proton exchange membrane electrolytes [14,15].

In PEM water electrolysis commonly noble metals were used such as Pt, Pd, Ru, Ir, Rh etc., due acidic environment inside the cell [15]. Predominantly reduce the economic feasibility we can use the different carbon supports. Carbon supported platinum/palladium is a traditional electrocatalyst for proton exchange membrane water electrolyser (PEMWE) /fuel cell (PEMFC). The support material for the palladium is the key to the performance of the water electrolyser. The catalyst performance can be enhanced by increasing the surface area as well as the electrical conductivity of the support material. Nitrogen doped Carbon Nano Tubes (CNTs) are high electrical conductivity as well as very high surface area as compared to carbon (Vulcan XC-72). Nitrogen is an important additive for controlling the structural properties of CNTs. Nitrogen incorporation into aromatic graphitic carbon materials contributes to enhanced electrical conductivity [16], improved oxidation resistance [17], and leads to different surface properties, with consequences on adsorption performances [18]. Nitrogen doping is an effective way to modify the properties of CNTs [19]. Nitrogen doped CNTs demonstrate negative differential resistance behavior, high electrocatalytic activity for oxygen reduction reaction and can also be used as a suitable support for uniform distribution of palladium catalyst. The interest of using NCNTs as an electrocatalyst carrier is expected to come lower resistivity which will increase electron transfer during electrochemical reactions.

The present study noble metals are required because they yield the best performance catalytic activity and stability for the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) in acidic media in PEM water electrolysis cell. The different loadings of Pd/NCNTs from 0.3 mg.cm⁻² to 1.0 mg.cm⁻² on Membrane Electrode Assembly's (MEAs) and performance evolution studies were observed for HER electrocatalysts.

MATERIALS AND METHODS:

Synthesis of Nitrogen doped Carbon nanotubes (NCNTs):

The Nitrogen doped Carbon nanotubes (NCNTs) were synthesized using spray pyrolysis chemical vapour deposition method. A quartz boat and introduced in the center of a quartz tube, mounted in an electrical tube furnace. The temperature of the furnace was maintained at 850°C, Argon (Ar) with a flow rate of 2.0 slpm was supplied throughout the experiment to maintain inert conditions. A mixture of acetonitrile and ferrocene in sufficient quantity was passed through the peristaltic pump at a flow rate of 3 ml/min into the reactor chamber for 60 minutes. After which the furnace was cooled to room temperature under Argon flow. The synthesized Nitrogen doped carbon nanotubes were purified by acid oxidation method [20].

Membrane Electrode Assembly (MEA) Preparation:

Catalyst ink for the cathode was prepared electrocatalysts mixing electro catalyst in isopropyl alcohol and 5wt% Nafion solution (E 1005) in appropriate proportions, thus formed catalyst ink was sonicated for 30 minutes in a sonicator. The catalyst ink after sonication was directly sprayed on Nafion membrane in a defined area of 25 cm² (5 cm X 5 cm) with a loading of 0.3, 0.7 and 1.0 mg.cm⁻² for cathode side have prepared respectively. The anode catalyst was prepared in similar manner using RuO₂ with approx. 3 mg.cm⁻² area, the catalyst films thus sprayed on nafion membrane was sandwiched with Teflon sheets on both sides and hot-pressed at 60 bar pressure and at temperature of 120 °C for 3 minutes. The prepared MEAs (Fig 1) were tested in in-house prepared PEM single cell electrolyser of area 25 cm².

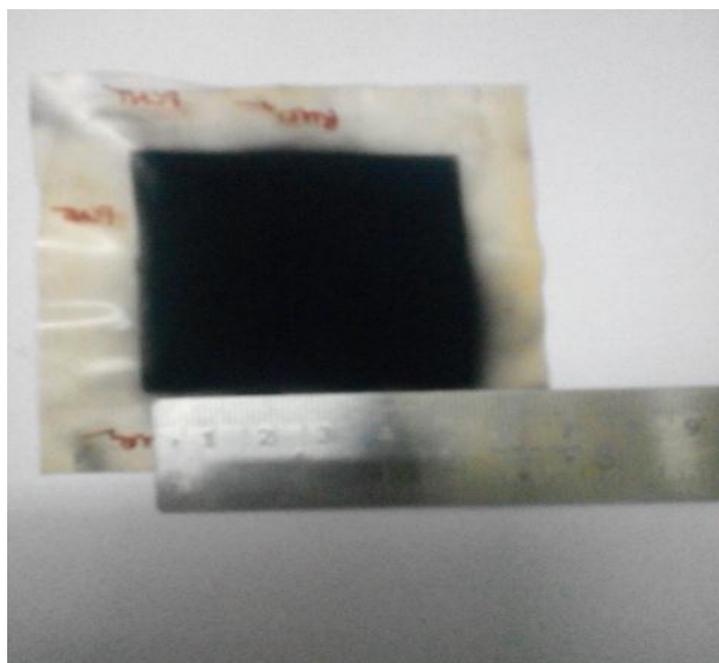


Figure 1: Membrane Electrode Assembly (MEA)

Operation of PEM Single cell:

The PEM water electrolyser was operated in electrolysis mode at 1 atm pressure and at temperatures from 25 to 80 °C. The water used for this experiment was purified (resistivity > 18 MΩcm) by reverse osmosis (Millipore Milli Q equipment). Thus obtained pure water was supplied from water reservoir atop and supplied to the bottom to both electrode sides of the single cell. The gases Hydrogen and Oxygen gases were evolved from top of the cell. The PEM single cells experiments were studied in area 25 cm² single cells with Stainless Steel (Fig 2).



Figure 2: Proton Exchange Membrane (PEM) Single Cell

RESULTS

Physico-chemical characterization

NCNT's SEM image shown in Fig. 3, It shows the long length of NCNT's is of 100 μm and average diameter range around 50-60 nm. It was observed that the palladium nano particles were uniformly dispersed into the CNT's with diameter size ranging from 40 to 60 nm. Fig. 4 shows the EDS spectrum of the PdNCNT, which confirmed the presence of Pd.

X-ray diffraction (XRD) patterns of PdNCNTs were represented in Fig. 5 The major diffraction peaks of Palladium was observed with {111}, {002}, and {022}, plane at 2θ values of 40.01°, 46.26°, 68.03°, for PdNCNTs. All the diffraction peaks corresponds to PdNCNTs only[21].

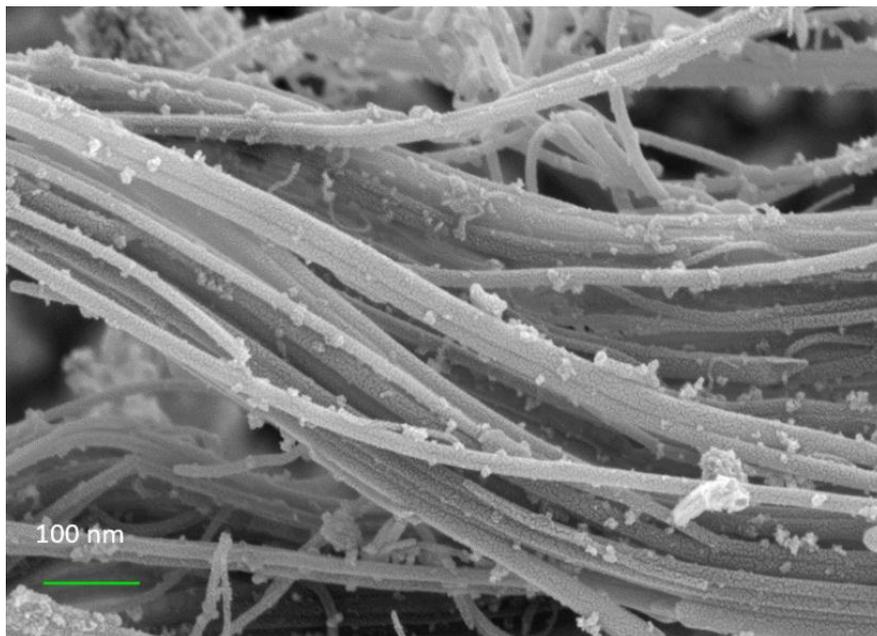


Figure 3: FESEM analysis of PdNCNTs

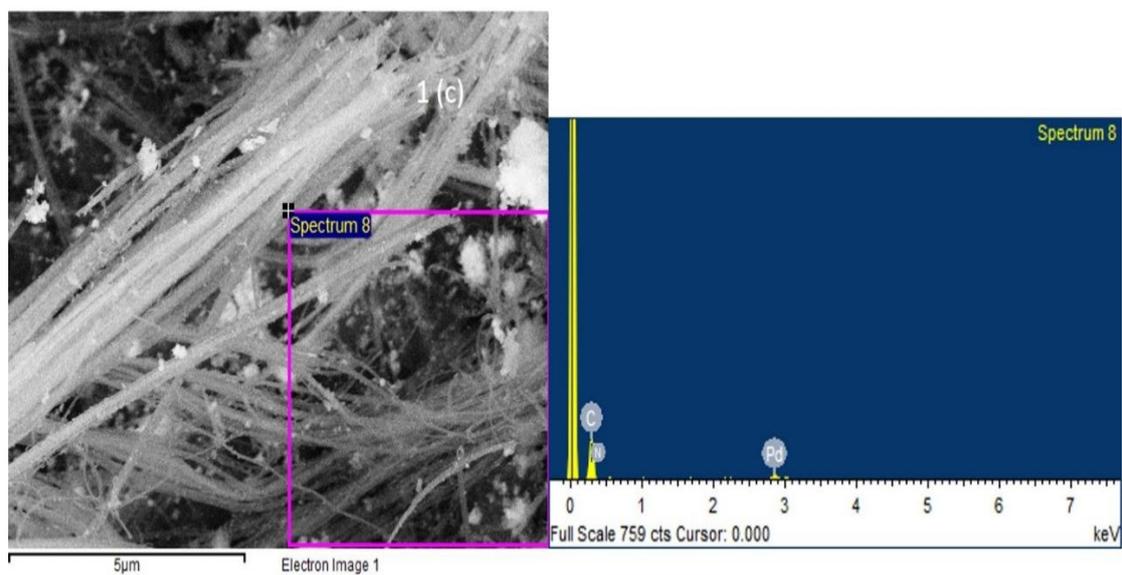


Figure 4: EDS analysis of PdNCNTs

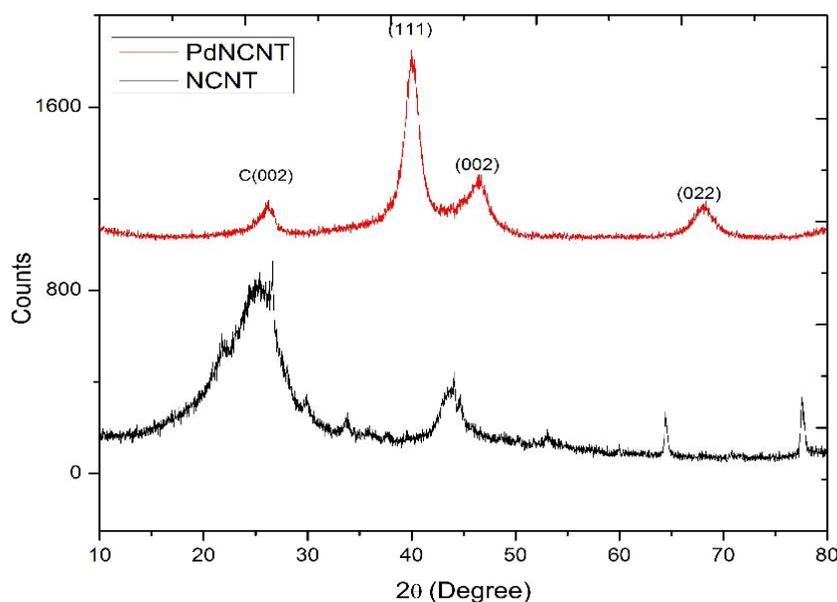


Figure 5: XRD analysis of PdNCNTs

Performance of the Pd/NCNTs in single cell assembly:

The performance studies of different weights of electro catalyst Pd/NCNTs (30 wt% of Pd) loadings like 0.3, 0.7 and 1.0 mg.cm^{-2} as cathode respectively and RuO_2 with 3.0 mg.cm^{-2} fixed as anode. In this we have observed that, the current density and hydrogen production rates are increased with increase in cell temperature at different cell voltages studied. The performance with respect to current density with Voltage (I-V) was represented as figure 6, 7 and 8 for 0.3, 0.7 and 1.0 mg.cm^{-2} respectively. In Fig 9 shows the MEA with 30wt% Pd/NCNTs as HER catalyst has shown 2.13 V, 2.09 V and 1.89 V voltages obtained for 0.3, 0.7 and 1.0 mg.cm^{-2} respectively at an operating current density 1 A.cm^{-2} at 80 °C. The performances of the water electrolyser developed by increase in the loading of catalyst overpotential has decreased with increasing the temperatures were compared. In comparison view from the Fig 9 and 10 shows that increasing the metal on the MEAs performance was increased and also hydrogen production rate was also increased. It may be attributed to the enhanced electrocatalytic activity and decrease in cell ohmic resistance. In this we have seen that, the current density and hydrogen production rate is increased with increase in cell temperatures at all cell voltages.

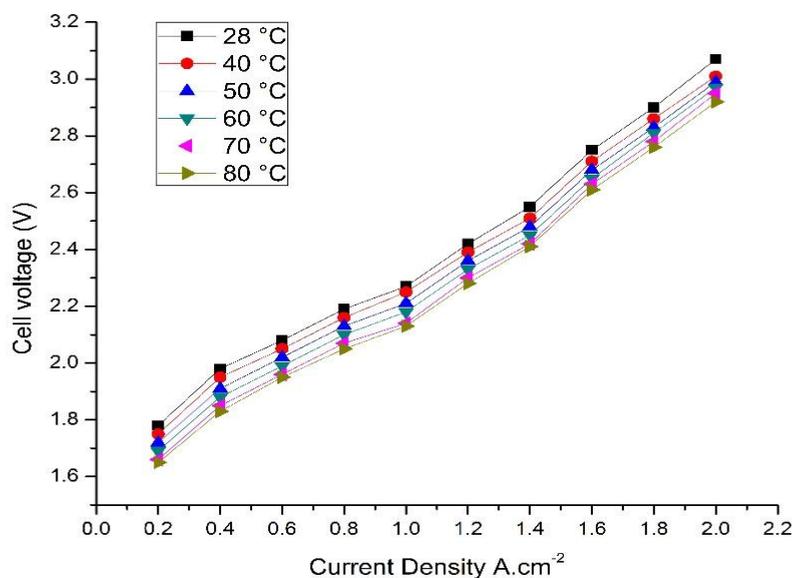


Figure 6: Current- voltage polarization of Pd/NCNTs MEA in 25 cm² area single cell assembly at various temperature 28, 40, 50, 60, 70 and 80 °C(0.3 mg.cm⁻²)

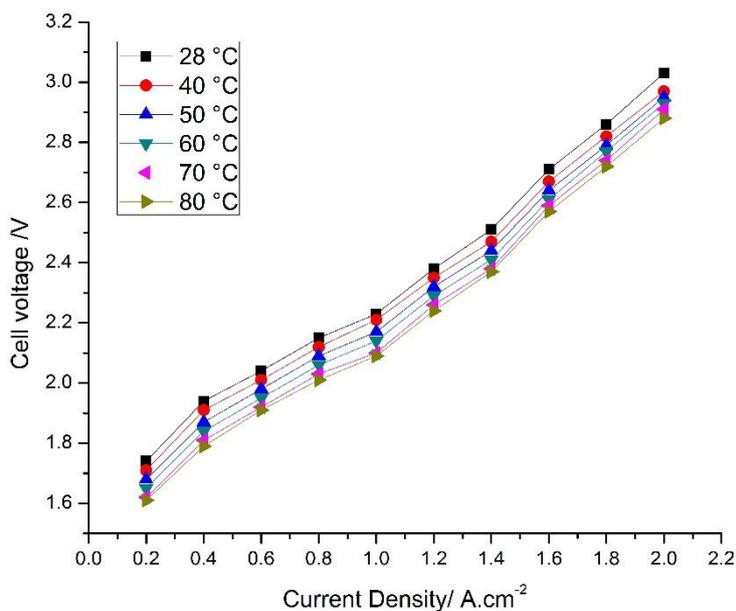


Figure 7: Current- voltage polarization of Pd/NCNTs MEA in 25 cm² area single cell assembly at various temperature 28, 40, 50, 60, 70 and 80 °C (0.7 mg.cm⁻²)

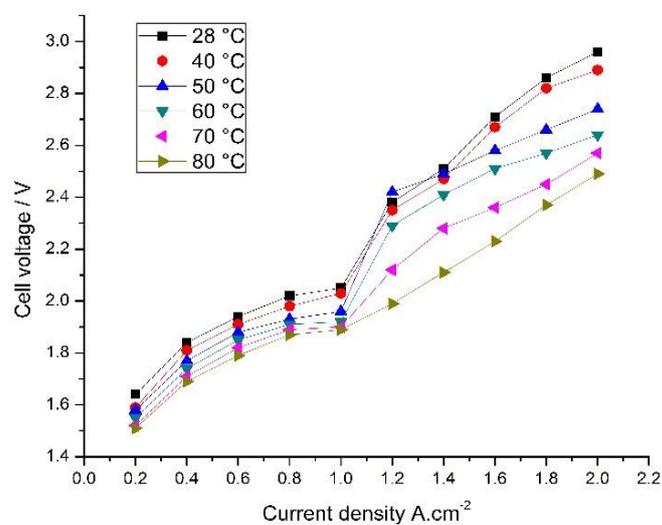


Figure 8: Current- voltage polarization of Pd/NCNTs MEA in 25 cm² area single cell assembly at various temperature 28, 40, 50, 60, 70 and 80 °C(1.0 mg.cm⁻²)

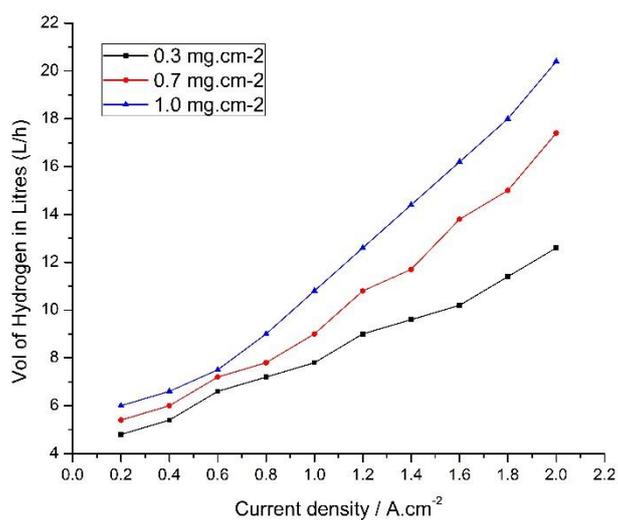


Figure 9: Current vs voltage polarization curves 0.3, 0.7, 1.0 mg.cm⁻² at 80 °C respectively

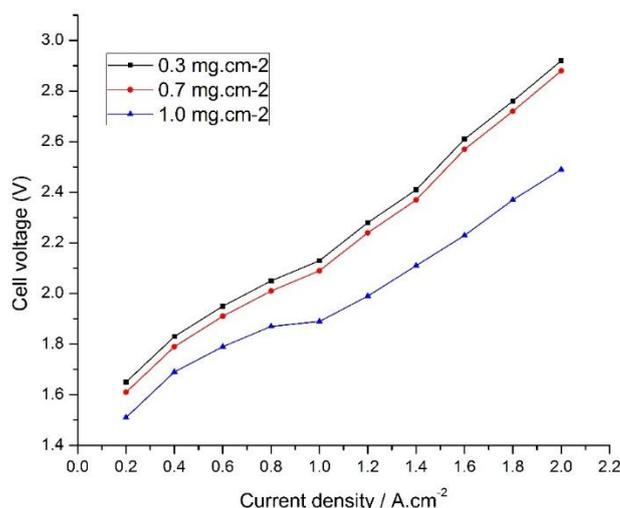


Figure 10. Current vs Hydrogen production 0.3, 0.7, 1.0 mg.cm⁻² at 80 °C respectively

CONCLUSIONS AND PERSPECTIVES

In this present study, structural properties and electrochemical performances of NCNTs supported Pd catalyst has been investigated in-house PEM single cell and compared with different weight loadings on membrane. Results show that NCNTs supported Pd catalyst exhibits increasing electrochemical activity with increases of metal loading on MEAs compared to the hydrogen evolution reaction rate were also increases. Water electrolysis based on a Nafion[®] 115 membrane and MEA with 25 cm² active area and fabricated with the above specified noble metals loading demonstrated a typical cell voltage of ca.1.89 V at a current density of 1 A.cm⁻² at 80 °C, that corresponding conversion efficiency is of ca.78%. The good stability of this MEA's performances were verified within 500h of operation. This is probably due to a better structure of the electrocatalyst and possibly to a higher activity of the substrate.

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