Synthesis and Performance of Carbon Supported Nano Palladium Electro Catalyst for PEM Water Electrolysis

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Abstract

In this current work Nano palladium electrocatalyst is synthesized with two carbon supports, Carbon black (CB) and flame made nano carbon (FC). The synthesized electrocatalysts performance is studied in PEM water electrolyser by varying cell voltage with respect to the hydrogen production and current density. The synthesized Nano-palladium electrocatalysts showed better performance compared to commercially palladium on activated carbon electrocatalysts.

Key wards: Flame synthesis, Palladium, carbon, Hydrogen, water electrolysis.

I. INTRODUCTION

Hydrogen production technologies have great importance in energy sector. Conventional processes [1] such as steam reforming, partial oxidation of natural gas and other fossil fuels due to simultaneous production of green house gases require CO_2 sequestration technologies. Hydrogen production by water electrolysis using proton exchange membrane (PEM) is an attractive route for CO_2 free production of hydrogen [2-3]. Compared to conventional process like steam reforming, partial oxidation of natural gases, PEM (proton exchange membrane) water electrolysis offers a number of advantages compared to fossils fuels such as higher safety, reliability and higher gas purity (above 99.99% of hydrogen).The main components in water electrolysis system is solid polymer electrolyte membrane (SPEM), electrocatalyst and current collectors. The first electrolysers using polymer membranes as electrolyte were developed by General Electric Co. in 1966 for space applications [4]. Extensive research and development on SPE electrolysers has been performed within the Japanese WE-NET program [5-7].A cell voltage of 1.68 V at 1 A cm^{-2} was obtained on a single cell of 50 cm^{-2} at 80^0 C. Kondoh et al. [8] tested two cell stacks of 0.25 m^2 ×10 for 2500 h at 1 A cm^{-2} with an average cell voltage of 1.74V at 1A cm^{-2} and 1.9 V at 2 A cm^{-2}, respectively. S. Stucki et al [9] tested two units of 100 kW for long time with an average voltage 1.75 V at 1 A cm^{-2} and 80 ^{0}C.

Palladium which is widespread in earth's crust, has been less studied for PEM applications despite its interesting electrolytic properties [10-11].In this paper an attempt has been made to study the carbon supports for palladium electrocatalysts. An in-house prepared single cell electrode assembly (as shown in Fig-1) with 10 cm^{-2} area at room temperature and 1atm pressure is studied. Ruthenium oxide as Anode electrocatalyst kept

constant for all studies, varying cell voltage from 1.8V to 3.2V and current density of 0.05 to 0.3 A/cm^2.Carbon supports for palladium electrocatalyst i.e. 10Wt % palladium on Activated carbon (10wt% Pd/Ac), 10Wt% Palladium on Carbon black (10Wt% Pd/CB) and 10Wt% palladium on flame synthesized nanocarbon (10Wt% Pd/ Nano carbon).Flame made Nano carbon and Carbon black support for palladium Electrocatlyst is synthesized by chemical reduction method [12]. The synthesized catalysts coated on a Nafion 115 membrane (Duo point) by Hot-pressing technique at temperature 120 ^oC and 110 bar pressure and tested in single cell assembly.

II. Material and Methods

II-A Material

Three different carbon supports for palladium electrocatalyst were used in this work i.e Activated carbon, Carbon black and Flame synthesized nano carbon. 10Wt% (Pd-AC) is procured commercially from sigma Aldrich, 10Wt % palladium on Carbon black (Pd-CB) and Flame made nano carbon (Pd-FC) is synthesized by reduction method using $PdCl_2$ (Sigma Aldrich India) as precursor salt. Carbon black procured from SRL chemicals (local made), flame made nano carbon is synthesized indigenously by flame reactor in JNTUH. Nafion 115 membrane is procured from Ion Power Inc, USA are used in this Experiments.

II-B Synthesis of Flame made nano Carbon

Flame made nano carbon is indigenously synthesized by using flame reactor setup [13] in JNTUH, LPG (Liquid petroleum Gas) as Fuel and Oxygen as oxidant with a flow rate of 1.2 slpm and 0.7 slpm respectively. The produced nano carbon was scanned using Phillips XL 30 series from National Center for compositional characterization of

materials (NCCCM), Hyderabad. The SEM images (Fig.1) of nano carbon resulted nano rods with an average diameter of 450 nm was found with lengths of up to 5 -8 μm.

XRD investigations for flame made nano carbon (Fig.2) was carried at Osmania University Hyderabad, using PW1830 Phillips X-ray Diffractometer (XRD) using CuKα1 type of radiation with a wave length (λ) of 1.54060 A^o .using PCPDFWIN-XRD database the peaks were identified for their lattice structure an the orientation The raw scan detected three strong peaks. The first peak at 2θ angle of 43.648^O was found with (002) orientation of atoms along its plane with peak corresponding to carbon molecule with a hexagonal type of system and a primitive lattice. The second peak at 2θ angle of 66.730^O was found with (109) orientation of atoms along its plane with peak corresponding to carbon molecule with a hexagonal type of system and a primitive lattice. The third peak at 2θ angle of 83.489^O was found with (112) orientation of atoms along its plane with peak corresponding to graphite with a hexagonal type of system and a primitive type lattice respectively.

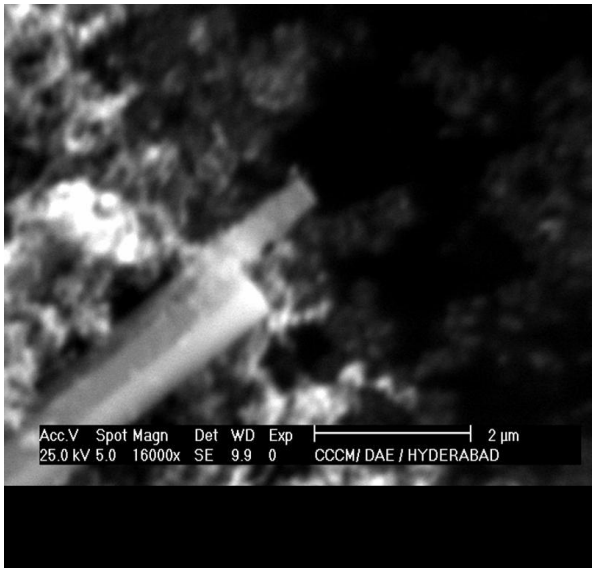

Figure 1 SEM image of Flame synthesized nano carbon

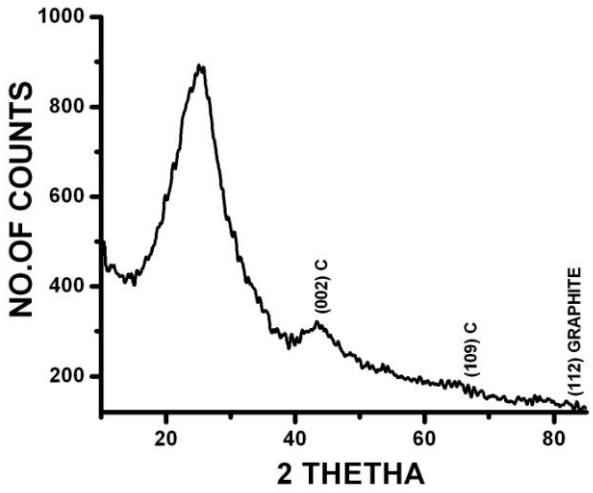

Figure 2 – XRD Pattern of Flame synthesized nano carbon.

II-C Catalyst synthesis

Palladium catalysts (Pd-CB and Pd-Flame made carbon) were synthesized in the form of metal nano-particles on Carbon black (SBET=120 m2/g) and Flame made nano carbon (SBET= 326m2/gm.) using chemical reduction of Pd complexes by ethylene glycol with addition of formaldehyde. The simultaneous sorption/reduction technique [14] briefly explained below was used. The required amount of precursor (0.1 M $PdCl_2$) and suspension of bi-distilled water, 2-proponal and Carbon black were mixed; the pH of the mixture was conditioned up to 8 using Na_2CO_3 Solution. Suspension was added to ethylene glycol, formaldehyde was added drop wise. The temperature of the obtained mixture was kept constant at 95^oC for 2 hours and after the heating was switched off. Leave the solution undisturbed for 12 hours, then excess of the solution was poured out the deposit (Pd/CB and Pd/Flame made nano carbon) was washed off 8-10 times by

decantation method in bi-distilled water. The synthesized electrocatalyst is dried and used to make Membrane electrode assemblies (MEAs) [15].

II-C Preparation of Membrane electrode assemblies (MEAs)

The Membrane electrode assemblies fabricated are 10wt% Pd-CB, 10wt% Pd-AC and 10wt% Pd-Flame made nano-carbon as hydrogen electrode and RuO_2 is used as Oxygen electrode. The membrane (Nafion 115) is pretreated by boiling for 1 h in 0.5M H_2SO_4 and in solution of 3% H_2O_2. The membrane is then thoroughly washed with deionized water dried and flattened [16]. The thin film electrocatalyst for hydrogen side (cathode) is fabricated by using 10Wt% Pd-CB, Pd-AC and Pd-Flame made nano-carbon catalysts is mixed with isopropyl alcohol and 5Wt% Nafion solution (EW 1005) is appropriate portions, thus formed catalysts ink is sonicated for 20 minutes in a sonicator. The catalyst ink after sonication is sprayed on the 0.8 mm Teflon sheet in the defined area of $10cm^2$(3.1 cm × 3.1 cm). The anode catalyst is prepared in the similar manner using RuO_2.The catalyst films thus sprayed on Teflon sheet are sandwiched on both sides of the Nafion 115 membrane and Hot-pressed at 110 bar pressure and temperature at 120^oC for 3 minutes, thus formed membrane electrode assemblies (fig-3) (MEA) are tested in single cell water electrolysis cell.

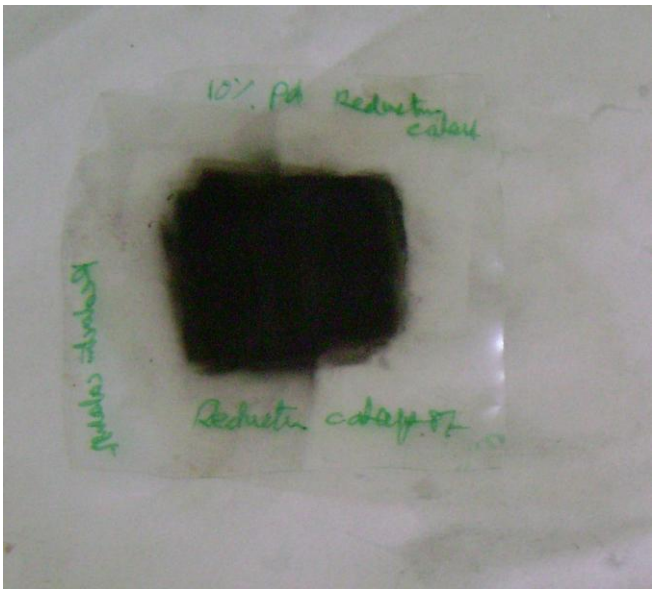

Figure 3 – Proton Exchange membrane with two electrocatalysts coated on each side (Pd/RuO_2).

II-D Description of single cell PEM water electrolysis system

The single cell PEM water electrolyser for 10 cm^2 is fabricated with SS316 material (fig-1). Current collectors used are perforated titanium sheets. The thickness of each end plate is 20mm, 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. The testing of prepared MEA (fixed in single cell) is operated in electrolysis mode at room temperature and 1 atm pressure. The water used for this experiment is purified (resistivity>18MΩcm) 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 (Fig-4). The produced gases hydrogen and oxygen is evolved from top of the cell at respective electrodes. Thus evolved water, gases are lifted by circulated water on both sides of the single cell and collected in vessels at top of the electrolyser.

Figure 4 Single cell water electrolyser system.

III Results and Discussion:

III-A Hydrogen Production

The hydrogen produced during the electrolysis operation is collected in vessels provided a top the single cell electrolyser Fig-1. The theoretical yield of hydrogen is calculated using faraday's laws equation (1) given below at STP conditions in cubic centimeter per minute (cc/min).

Faraday's laws equation (1)

$$w_{H_2} = \frac{I\,t\,M}{F\,N_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where **w** is the weight of the hydrogen produced at the cathode (*g*), 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 10 wt% of Pd on activated carbon, 10 wt% of Pd on Carbon Black and 10 wt% of Pd on nano carbon are calculated. Both experiments are run for 10 minutes at current densities 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 A/cm2 at room temperatures 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 hydrogen gas occupied in the vessel at 1 atm pressure

III-B Performance of the synthesized nano electrocatalysts in single cell assembly

The performance of the synthesized nano cathode electrocatalysts is tested using inhouse fabricated single cell assembly. A DC Voltage of 1.8 to 3.2V is applied during water electrolysis operation. The cell is kept under experimental condition for two hours. The performance is evaluated by current and voltage (I-V) characteristics curves (fig-5) during water electrolysis operation. In these Experiments three different cathode side electrocatalysts is varied by keeping anode side electrocatalysts as constant for all experiments. The performance of the synthesized nano catalysts is studied by varying voltage (1.8 - 3.2V) with respect to the current density is studied and hydrogen produced with respect to current is calculated using faradays first law as shown in table-1,2,3 as follows.

Table 1: experiments Carried out for 10 wt% Pd on Activated Carbon support
Cathode: Pd on Activated Carbon, Anode: RuO_2

Voltage of cell (V)	Current of the cell during Electrolysis (A)	Current Density of the Catalyst (A/Cm^2)	Experimental Hydrogen Yield Calculated at STP conditions (CC/Min)	Theoretical Hydrogen Yield Calculated at STP conditions (CC/Min)
1.83	0.5	0.05	2.65	3.48
2.15	1.00	0.10	6.01	6.96
2.36	1.50	0.15	9.71	10.44
2.50	2.00	0.20	12.89	13.92
2.72	2.50	0.25	16.96	17.40
2.91	3.00	0.30	19.08	20.88

Table 2: experiments Carried out for 10 wt% Pd on Carbon Black support
Cathode: Pd/CB, Anode: RuO_2

Voltage of cell (V)	Current of the cell during Electrolysis (A)	Current Density of the Catalyst (A/Cm^2)	Experimental Hydrogen Yield Calculated at STP conditions (cc/min)	Theoretical Hydrogen Yield Calculated at STP conditions (cc/min)
2.08	0.5	0.05	3.18	3.48
2.34	1.00	0.10	6.71	6.96
2.73	1.50	0.15	9.71	10.44
2.91	2.00	0.20	13.07	13.92
3.01	2.50	0.25	16.96	17.40
3.20	3.00	0.30	19.61	20.88

Table 3: experiments Carried out for 10 wt% Pd on Flame synthesized Nano Carbon support
Cathode: Pd/FNC , Anode: RuO_2

Voltage of cell (V)	Current of the cell during Electrolysis (A)	Current Density of the Catalyst (A/Cm^2)	Experimental Hydrogen Yield Calculated at STP conditions (CC/Min)	Theoretical Hydrogen Yield Calculated at STP conditions (CC/Min)
1.82	0.5	0.05	3.00	3.48
1.97	1.00	0.10	6.54	6.96
2.14	1.50	0.15	9.54	10.44
2.31	2.00	0.20	13.25	13.92
2.48	2.50	0.25	17.13	17.40
2.61	3.00	0.30	19.43	20.88

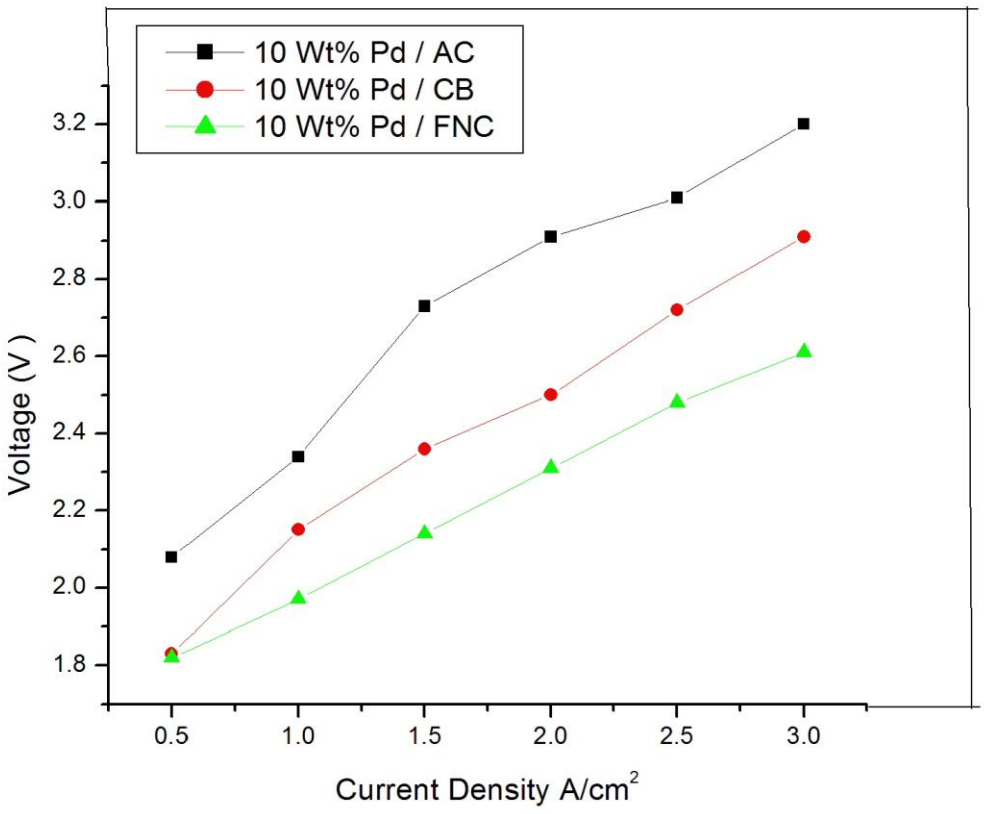

Figure -5 Hydrogen yield with respect to cell voltages

IV Conclusions

A Nano palladium electrocatalysts with Pd/Flame made carbon support and Pd/carbon black supported is synthesized by chemical reduction method. Its performance is studied in PEM water electrolyser by varying cell voltage from 1.8 to 3.2 Volts. The hydrogen produced in water electrolysis is calculated with respect to current density. The results shows at cell voltage of 2.08V for Pd/AC support, 1.83V for Pd/FNC support and 1.83V for Pd/CB support for current density 0.05A/cm^2. The over voltage of the cell is decreased in case of Pd/CB and Pd/FNC, Hence the results conclude that highly dispersed Nano-palladium electrocatalysts synthesized by reduction method is suitable electrocatalysts for water elctrolysers.

Acknowledgments

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