Performance of Catalyst Coated Membrane (CCM) at different operating conditions in Proton Exchange Membrane (PEM) fuel cell.

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Abstract
In this paper, performance of Catalyst Coated Membrane (CCM) has been studied. Effect of various parameters on current density and power density has been analysed. Observations has been depicted using polarisation as well as power curves. CCM always gives better performance as catalyst it has direct ionic contact with membrane. CCM manufactured by Paxitech fuel cells, France has been used to perform the experiment along with stack fabricated. It is prepared with catalyst coating of 0.5mgPt/cm² by ultrasonic spray coating method. The SEM analysis has been carried out to study morphological characteristics of CCM. Out of other parameters, hydrogen humidification and air stoichiometry have good effect on CCM performance. Maximum current density obtained was 1.28A/cm² with hydrogen humidification temperature as 55°C. The performance has been analysed by polarization curve, Description of various parameters has been given in detail.

Keywords: CCM, SEM analysis, Ultrasonic spray coating, GDE

1. Introduction
As there is a surge energy consumption due to more involvement of human activity in last past two decades and release of greenhouse gases following the uses of fossil fuels such as carbon dioxide has increased drastically. Despite of the tremendous consumption of fossil fuels, the energy requirements are increasing and projected to grow even further. Thus, human beings are facing an increasingly severe energy shortage crisis [1].

Numerous nations and companies have been contributed towards employing green energy sources such as wind, solar, hydropower and bio fuels etc. so as to maintain sustainable growth for upcoming generations. Fuel cell offers greatest efficiency compared with available green energy conversion devices with minimum greenhouse gas emission and emerged as another solutions for supportable development[2].

A single PEM fuel cell stack consist of end plates, current collectors, sealants, monopolar plates, Membrane Electrode Assemblies (MEAs)[3]. MEA is the heart of fuel cell. Catalyst utilisation is one of the key parameter which determines overall cell activity. Usually at initial stage catalyst usage is limited causing the activation losses[4]. This results in an increase of the catalyst loading or finding an effective method for complete utilisation. Increase in catalyst loading is not economical. So for maximum utilisation effective method of catalyst loading is better[5].

MEAs broadly characterized into two types: a) MEA prepared by fabricating CCM with two Gas diffusion layers (GDL’s) is three layer MEA b) MEA prepared by coating catalyst on GDL’s i.e. called as GDE sandwiched between two membrane called as five-layer MEA[6]. CCM technique
always gives better results than GDE method. As in CCM method, catalyst will be in direct contact with membrane which gives good ionic contact between membrane and reactant. There are various methods used to fabricate CCM [7][8].

The chemical reaction takes place at PEMFC

Anode: \(2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^- \) (HOR)

Cathode: \(\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \) (ORR)

Total reaction: \(2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{Heat} + \text{Electricity} [9]\)

Compared with other methods, ultra-sonic spray coating method gives improved power performance. This paper discusses performance of CCM coated by ultrasonic spray coating method at various operating condition [10][11].

2. Experimental

During conduct of experiments different types of operation conditions related to temperature and humidity has been analysed. A single PEMFC stack and an active area of 25cm² was used to analyse the impacting parameters on different operating conditions. The MEA used is prepared by CCM-MEA method. The stack and CCM used to perform the experiments imported from the Paxitech fuel cells, France. Detailed specifications of each part of MEA are given as follows.

**Table 1: Specification of 3 layer MEA (CCM-MEA) Assembly**

| Specification of CCM | Specification of GDL |
|---------------------|----------------------|
| Membrane type       | Nafion 212 membrane  |
| Membrane thickness  | 0.05mm                |
| Platinum loading    | 0.5mgPt/cm²(same on both sides) |
| Catalyst chargement | 70%Pt/C              |
| Method of catalyst coating | Ultrasonic spray coating |

Material of GDL: Carbon paper (woven carbon paper)

Type of GDL: P75T on anode side and EP 40Ton cathode side

Thickness of GDL: 0.26 mm on anode side and 0.2 mm on cathode side

Manufacturer of GDL: AvCarb®

This CCM-MEA is self-assembled, hot pressing is not required [12]. This self-assembled, sealed MEA is sandwiched between two graphite monopolar plate having flow pattern single continuous flow on anode side and parallel flow pattern on cathode side. The graphite monopolar plate is having 25cm² active area. These are enclosed by current collector plates made up of gold plated copper plates which are then compressed by aluminium end plates by torque wrench of 5Nm/kg. Testing of this CCM is done at Sainergy fuel cells, Chennai. The polarisation curves were obtained for various operating conditions by measuring the voltage using stepwise increment of current density.
Before this cell stack put on dynamic testing, activation procedure had been performed. It is necessary to perform this procedure as it will properly humidify the membrane portion of MEA which was dried during ultrasonic spray coating[13]. For Air, activation was done at constant voltage mode at 0.7V or 0.6V. This is done by using electronic load on activation mode. For activation, temperature was kept constant at 50°C on anode as well as cathode side. For oxygen, activation was done cyclically, starting at 0.93V it should come to 0.35 V or current 35 amps. This was in one cycle. Like this it should complete 10 cycles. Cut off voltage and Cut off current is maintained at 0.35 V and 35 Amps respectively. Hydrogen, Air and Oxygen flow rate at 300 ml/min, 1575ml/min and 150ml/min respectively. After conditioning of MEA, static and dynamic testing of MEA was done at constant voltage and constant current mode respectively.

3. Result and Discussions

3.1 Effect of hydrogen humidification
In this experiment, Effect of hydrogen humidification on CCM has been studied by using membrane humidifier. Hydrogen flow rate is maintained at 250ml/min. Air flow rate is maintained at 1575ml/min. Using stoichiometry of 1.2/3.0, stack temperature is maintained constant at 65°C. Cathode side humidification temperature is maintained at 60°C. Anode side temperature has been varied from 50°C and 55°C.

![Figure 1:](image1.png) a) Image of CCM used b) Experimental set up at Sainergy fuel cell, Chennai.

![Figure 2:](image2.png) a) Polarisation curve b) Power curve for effect of hydrogen humidification at 50°C and 55°C.
From the above polarisation and power curve, CCM-MEA has worked well at a temperature of 55°C. At Sainergy fuel cells, Chennai, membrane humidifiers are used on both sides of cell i.e. anode and cathode side. This humidifier allows only humidified gasses to pass through it & not condensed water with it. Enhanced cell performance can be achieved by maintaining water poised between anode and cathode at acceptable level, as the Nafion membrane works properly in well humidified condition. The dampness of membrane can be well maintained when anode reactant is fully moist[14]. If the fuel is insufficiently humidified there could be membrane dehydration which causes decrease in membrane conductivity. At 55°C, the maximum current density obtained is 1.28 A/cm² at 0.3 v. Peak power obtained is 0.51w/cm² at 0.49 v.

3.2 Effect of different air stoichiometry
Air flow rate directly affects the performance, its effect and performance of CCM has been given by following figure. The performance is studied for different air stoichiometry of 3.0, 3.5 and 4.0 which gives air flow rate of 1575 ml/min, 1850 ml/min and 2100 ml/min respectively. Hydrogen flow rate is maintained constant at 250 ml/minute with constant Hydrogen humidification temperature at 60°C. This effect has been observed at constant stack temperature of 65°C.

Air Stoichiometry plays a vital role in fuel cell performance. As the ORR is the rate determining step in the PEM fuel cell working. More the flow rate of oxygen more will be the rate of reaction & more current density will produce. As air is having 0.21 mass fraction of oxygen. If air flow rate is increased, the concentration of oxygen reached will be more [15].

In this experiment, when air flow rates are compared, stoichiometry of 4.0 has given good results. It can be seen in ohmic region i.e. in 0.7-0.6 v range. At voltage 0.39V maximum current density obtained is 1.2 A/cm². Peak power gained is 0.52 w/cm².

![Figure 3: a) polarisation curve b) power curve for effect of different air stoichiometry of 3.0, 3.5, 4.0.at const. Stack temperature of 65°C.](image)

3.3 Effect of Air Humidification
In this paper, effect of air humidification on the performance of CCM. H2/ Air stoichiometry used is 1.2/2.0 that means hydrogen flow rate is 250 ml/min, while air flow rate is 1050 ml/min. Stack temperature has been kept constant at 65°C. Hydrogen humidification is given at 60°C.Cathode humidification temperature has been varied from 50°C and 55°C.
From the above polarisation curve, current density has been increased as the cathode humidification temperature increased. As stated earlier, rate of ORR is higher than that of HOR. With increase in current density, proton flow and water quantity generated at the cathode rises linearly. When in excess, water gets accumulated at the cathode reaction site and tries to block apertures of the membrane and similarly restrains species carriage. So if anode side temperature has been kept higher than that of the cathode side, the membrane is sufficiently hydrated by just taking in water available from the fully humidified anode gases. Though, the current density is increased by reducing cathode relative moisture at low cell voltage. But, the cell performance enhances with increasing comparative moisture of air at low current densities. At end of ohmic polarisation curve, means in mass transport losses region, voltage has dropped steeply, this is due to more water accumulation on cathode side.

Maximum current density obtained at a voltage of 0.41 V was 1.16 A/cm². 0.8A/cm² current density was obtained at 0.6v. Peak power obtained is 0.5W/cm².

3.4 SEM analysis of CCM

Morphological and catalyst loading of CCM has been studied by SEM analysis (JEOL, JSM-6380LA at ICT, Mumbai). Also the layering of catalyst over membrane surface can be seen properly in this analysis. It gives the complete idea that how CCM will always gives better performance. This is attributed in CCM catalyst is always in good ionic contact with membrane. This can be cleared by various images taken of SEM analysis. These images will show that catalyst layer has been formed uniformly over the surface of membrane by using ultrasonic spray coating method.

SEM images shows that ultrasonic spray coating method has formed continuous catalyst layer over membrane Nafion 212. This is the advantage of this method. This can prove that CCM will always give better performance. Thickness of various segments of CCM has been given by fig. Figure b) lower layer is little thicker than upper this is may be due to cross sectional area chosen. There are the chances ,during this procedure cracks and bubble formation takes place but this can be avoided by using correct viscosity of the solvent or correct solvent during catalyst ink preparation [16]. Figure d) gives close view of top surface of CCM. This shows that uniformity in catalyst coating done by this method. SEM analysis done for CCM is in good agreement with polarisation curve obtained.
Figure 5: a) Cross sectional image of CCM showing membrane, upper and lower layer of catalyst (platinum) loading. b) Cross sectional image of CCM showing various thickness of membrane and catalyst layer. c) Top image of CCM showing catalyst layer coating, cracks developed and bubble formation (with 250 magnification) d) close view of top surface showing catalyst layer and small cracks formed (with 1500 magnification).

4. Conclusion
In the paper, detailed performance analysis of CCM prepared by ultra sonic spray coating method has been given. This CCM is having 0.5 mgPt/cm² catalyst loading on both side. The effect of various parameters analysed using polarisation and power curve. From this experiments the following conclusions were obtained: higher hydrogen humidification temperature gives a good enhanced performance as it makes the membrane humidified which is a basic requirement of Nafion membrane. Higher the air stoichiometry, more the amount of oxygen will reach to the surface of catalyst, more will be ORR, and more will be current density produce. Air humidification causes increase in current density at initial i.e in activation region and ohmic region, but in the mass transport region, Performance decreases gradually. This is due to membrane becomes flooded due to higher cathode humidification which blocks the reaction site. SEM analysis has given effectiveness of spray coating method. Catalyst layer uniformity can be achieved by this method. SEM analysis gives good agreement with polarisation data obtained.
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