

Screen Printing of DMFC Catalyst*

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Abstract

Direct Methanol Fuel Cells have been a promising source of alternative energy as the supply of conventional fuels is slowly being diminished. At the heart of this electrochemical cell a Proton Exchange Membrane laced with a catalyst creating a redox reaction. This catalytic layer is time consuming and expensive to manufacture prohibiting large scale manufacture. This research paper studies the possible use of screen printing of the catalyst onto the PEM in a DMFC in order to allow for cost effective mass production of the MEA.

Keywords: Fuel Cells, DMFC, Electrochemistry, Catalyst, Pt, Catalyst Production, Screen Printing, DMFC Mass Production

1 INTRODUCTION

Mass production of the Membrane Electrode Assembly (MEA) on Direct Methanol Fuel Cells (DMFC) remains as one of the key priorities in creating a low cost and easily mass produced DMFC. Though several possible solutions have been given to the problem [1-3] no feasible mass production of MEA for fuel cells have started as of yet.

In an attempt to test and verify the different techniques found in patents and further the research in rapid MEA manufacturing a testing rig was setup in order to screen print the catalyst slurry onto a Proton Exchange Membrane (PEM) thereby reducing production time and increasing porosity of the catalyst layer.

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The method of screen printing [4] is a technique derived from the printing industry. Screen printing works by having a woven mesh covered by a filler material, such as wax, with the exception of a specific area. This open area will determine the final pattern which will be printed.

This technique is ideal as it can be easily and cost effectively tested. It can also be utilized for use in the industry where machines can perform the printing action at high speed on a continuous feed. By actively removing and replacing the mesh onto the same area of the membrane many layers of catalyst can be coated thereby increasing porosity.

Screen printing may also be performed without a mesh, only a film with a clear opening for the catalyst mixture to lie in. However due to the surface tension of water, the mixture would not dry homogenously. Also in order to coat the membrane several times with catalyst in order to create a layered structure each pass would require a slightly thicker film.

1.1 Screen Printing vs. Spraying

Previously, the catalyst layers had been sprayed onto the membrane using an airbrush. However several problems have arrived with this method.

The spraying nozzle is a complex unit which is highly costly and requires a large amount of maintenance both before use and after. During spraying the catalyst slurry moves at so high speed within the system and the rough particles 'pick up' metal ions from the contact surface of the spraying tool. These contaminants are deposited onto the membrane which in turn causes instability and lower power output from the final system.

In order to prevent this, the tool has been gold plated through electroplating ensuring that only minute gold particles, which are non-toxic to the cell, are covering the surfaces. However this method is time consuming, expensive and not permanent.

The air brush sprays a mist of catalyst slurry in the general direction of the membrane. This results in a number of foreign particles which may be picked up from the air through which the slurry travels. A large amount of catalyst is lost due to the lack of control of the spray direction.

The system does produce a very fine layer of catalyst onto the membrane. When several fine layers are sprayed in succession onto the membrane a very high porosity is achieved.

1.2 Screen Printing vs. Stamping

Stamping can be seen as a direct alternative to screen printing as it employs many of the benefits of screen printing, mainly the lack of contamination and the speed at which it can be performed. Methods of stamping have not been found in journal articles however stamping has been described in a couple of patent applications. The direct benefit of stamping is the ability to make MEAs at a high speed in a continuous process.

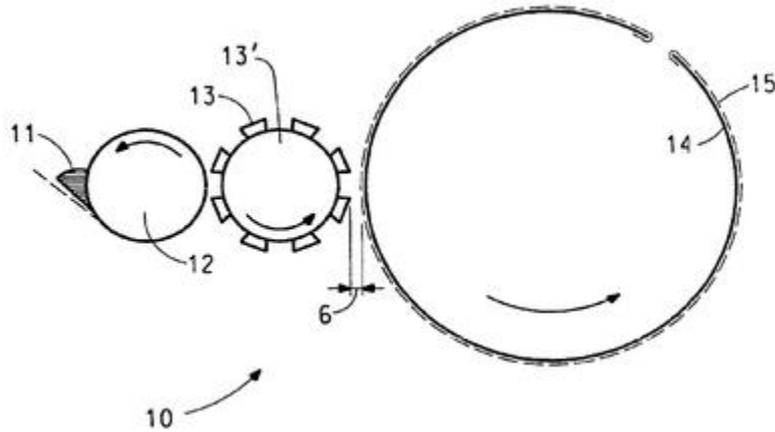


Figure 1: A method for continuous production of catalyst coated membranes for fuel cells. [3]

As seen in Figure 1 three rollers are used; seen from left to right, the first roller (12) introduces the catalyst slurry at a slant into the system (11). This is then transferred onto a second roller (13') with pre-made stencil outlines (13). The final roller (14) carries the membranes (15) which are continuously stamped with the catalyst slurry.

While the method of stamping can be seen as good for the industry when it comes to producing large numbers of MEAs at high speed. However for laboratory testing it may be seen as far too costly and complex.

2 EXPERIMENTAL

The mesh defines the screen printing outcome, in the case of a thin mesh being used then a thin layer of catalyst is deposited onto the membrane. Similarly the spacing between the mesh fibres determines the volume of catalyst which can be printed at any one time.

The mesh is held in tension by a frame, which can be made out of a number of materials such as wood, aluminium or plastic. Aluminium was chosen due to its light weight and low cost as well as being available immediately. The frame was made by Serifantasy, a company specializing in screen printing equipment. When referring to the screen printing mesh the aluminium frame is assumed to accompany it. The aluminium frame is the size of an A4 paper. This allows for a large working surface area thereby ensuring that the metal does not come into contact with either the catalyst or the membrane; this also allows it to be easily clamped onto a test bench.

In order to ensure that the mesh did not release any contaminants onto the MEA, a plastic mesh was chosen. For this purpose SEFAR, a company specializing in screen printing mesh equipment, has a product range named PET 1500. The meshes found in the PET 1500 range are specifically designed to be used in the circuit printing industry. The PET 1500 range meshes are made from PET plastic and as such do not release any contaminants during screen printing.

The mesh will have further specification such as the type of tweed, spacing between fibres, weight of the fibres, thickness of the fibres (also a representation of the mesh

thickness) and open area in between the fibres. The two factors of most importance are the thickness of the fibres and the open area of the mesh.

2.1 Catalyst and PEM

The catalyst used for screen printing is described in previous working papers on the subject. As for the PEM two different membranes were tested, ETFE-SA and Nafion.

The ETFE-SA membrane is produced in-house at Arcada based on the methods described in the materials original patent application [5]. The membranes were then stored in distilled water until use.

The Nafion membranes have been prepared through the following means:

1. Nafion was cut to 40x40 mm pieces
2. The membranes were boiled at 80°C for two hours in 1M H₂SO₄
3. Nafion was further boiled at 60-80°C for one hour in 3w% H₂O₂

In between each step the Nafion was washed vigorously in water (with at least three fresh water changes). The Nafion was then stored in distilled water until use.

2.2 Application

The printing process was devised so that the slurry would travel across the opening of the mesh at regular intervals so that each slurry layer printed would have time to dry before the next layer came on top. This process was repeated until all the slurry for one side was gone; afterwards the MEA was dried between 30 seconds and 3 minutes and then turned around for printing the other side of the membrane. In the case of screen printing Nafion membranes the membranes were boiled in water at 76°C for 2 minutes at regular intervals.

As the slurry is dragged across the screen it spreads towards the sides of the squeegee, this makes the screen procedure more complex. In order to compensate a smaller amount of slurry was added to the mesh for each printed layer. The slurry was always taken directly out of the sonicator and placed onto the mesh using a glass pipette. This ensured that the slurry is as homogenous as possible. Once the slurry was placed onto the mesh the squeegee was used to gently and slowly drag the slurry across the opening. Only marginal downwards force was applied to ensure that the slurry would seep through the mesh openings but not underneath the mesh. Once a single layer had been printed onto the membrane, the printing of the next layer began.

3 RESULTS

At first inspection the catalyst layer appears to be even on any printed membrane. However analysis through a microscope shows that dented canals are scorched throughout the catalyst layer.

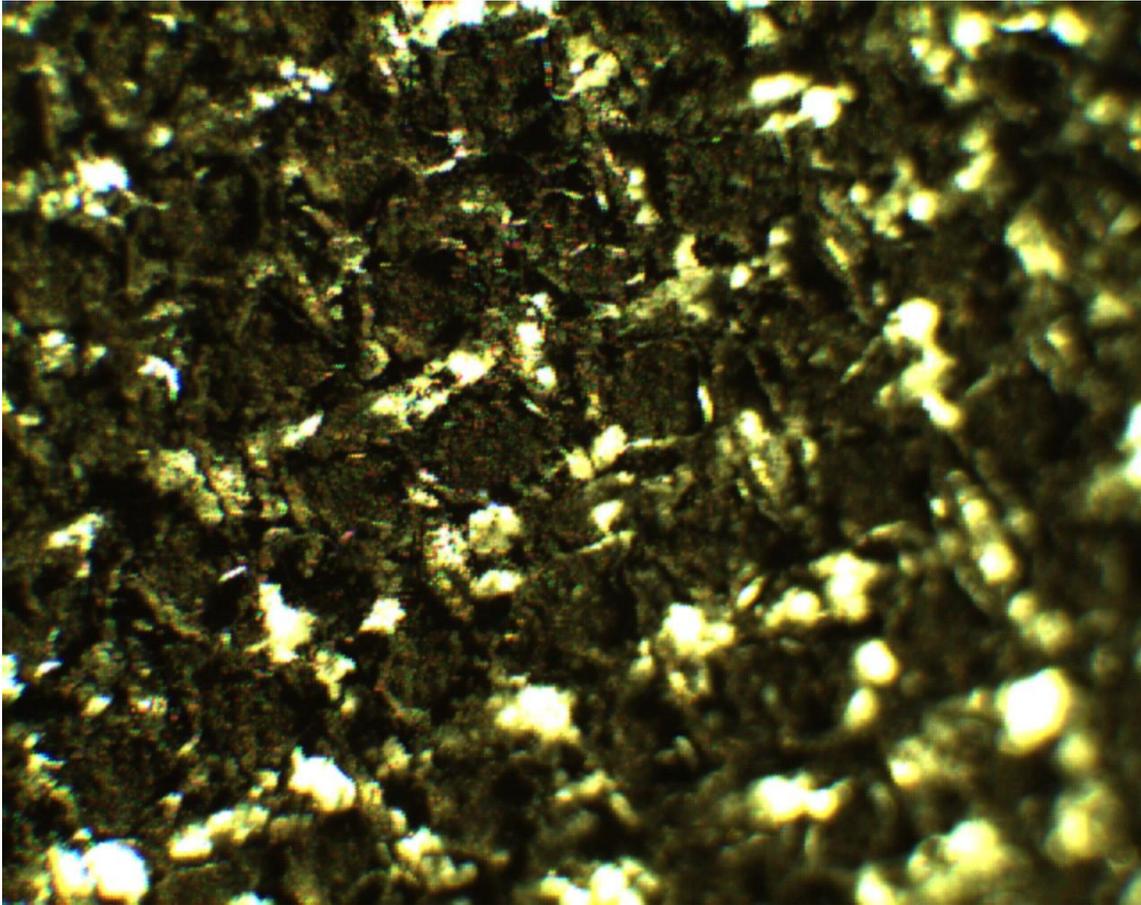


Figure 2: Anode catalyst layer printed on an ETFE-SA membrane seen through a microscope at 10x magnification.

In Figure 2 the canals left behind by the mesh fibres can be clearly seen. No evidence has been found that this effect degrades the quality or power density of the MEA.

3.1 Swelling of the Nafion Membrane during Screen Printing

In the conventional method of screen printing, Nafion must be temporarily ion exchanged to Na^+ form to avoid swelling [6]. Experimentation has shown that it is possible to compensate the swelling in the Nafion membrane without changing its form.

Due to the heated work bench, the Nafion membrane will start to evaporate its water content thus returning it to its original 'dry size'. As a result of this effect the catalyst slurry which is being screen printed onto the, now dry, membrane will cause the membrane to re-swell again. However due to adding only slurry in a specific area of the membrane the swelling will also be specific causing warping of the membrane.

In order to compensate for the swelling of a specific area of the Nafion membrane, a beaker of distilled water was kept at 76°C . The membrane was then placed in the beaker at regular intervals during the screen printing process. The membrane was allowed to boil in the water for around 2 minutes. This ensured that the swelling was even and no warping would occur. It was found to be of specific importance to boil the membrane in a beaker of water in between the anode and cathode printing.

4 DISCUSSION

The development of the screen printing process has been considered a success. It has been possible to accurately and repeatedly screen print high quality catalyst layers onto membranes of either Nafion or ETFE-SA. This has been accomplished by changing the catalyst slurry for it to suit the needs for the screen printing technique. The problems regarding the swelling of the Nafion membranes along with the slipperiness of the ETFE-SA membranes have also been solved for the screen printing process.

In earlier DMFC MEA works, the production time of producing one complete MEA has been around 3 hours (one hour sonication, one hour for spraying and one hour for cleaning the MEA in HCl). With the screen printing process this time has been reduced to around 1.5 hours (one hour sonication, five minutes screen printing, five minutes hot pressing and 15 minutes boiling in water). This is a significant increase in the speed of production, especially for the depositing of the catalyst slurry onto a membrane.

The MEAs suffered heavily from having only a few layers of catalyst slurry. In the air brush method of producing MEA the catalyst slurry is layered onto the membrane between 12-22 times. The screen printing method has only been able to layer the slurry less than five times. This will affect the results of MEA greatly. In order to resolve this problem, it is suggested that a new screen printing mesh with a higher open area and thinner fibres is taken into use. This would force the screen printing to be done a higher number of times thereby increasing the porosity of the catalyst.

It is estimated that around 20% of the catalyst is lost during air brushing yet only an estimated 5% is lost during screen printing. This is a large cost benefactor towards making DMFCs a reality on the consumer market.

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