

# Pt and Pt-Ru Based Catalyst for DMFC\*

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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 Pt and Pt-Ru catalyst creating a redox reaction. The mechanical properties and composition of this catalyst will be main driving factor in determining how well the fuel cell will perform. This research paper replicates and furthers the research in the catalyst structure used in the DMFC and as such the work represents research in progress.

**Keywords:** Fuel Cells, DMFC, Electrochemistry, Catalyst, Pt, Catalyst Production

## 1 INTRODUCTION

Currently, Platinum and Ruthenium alloys are considered as ideal catalysts for methanol oxidation on the anode, due to the high activity and resistance to carbon monoxide poisoning [1,2], typically these loadings consists of 1:1 Pt and Ru however it has been suggested [3] that a higher ratio of Pt is used to that of Ru. However, it has been suggested that further improvement in activity and stability requires the development of novel catalysts, such as bi-metallic or tri-metallic alloy catalysts containing other metals, such as Sn, Mo, Pd, W, Nb, Co, Ni, Rh, Ir, Os [4] or PdAg [5]. The addition of transition metal oxides such as MoO<sub>x</sub>, VO<sub>x</sub> and WO<sub>x</sub> to Pt–Ru has also been evaluated for enhanced methanol oxidation reaction [6]. The catalyst in DMFC cathodes for

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\* This research has been made possible through the generous grant from Fonden för Teknisk Undervisning och Forskning (TUF).

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oxygen reduction is Pt; research to develop novel electro-catalysts tolerant to methanol, materials that are active towards the oxygen reduction reaction and relatively inactive for methanol oxidation, is under way. Catalysts based on Pt–Cr or Pt–Ni [7,8] and Pt–Pd [9] seem to be a good alternative for this purpose.

Both anode and cathode catalysts of Pt–Ru and Pt, respectively, are typically dispersed on carbon supports at a loading 40-70 w%. A common support is carbon black with a high electrical conductivity and a high surface area, though recently silica supported Pt–Ru catalysts have shown promising results [10]. Nevertheless, these materials have high micro-porosity, which have a crucial effect on the catalyst utilization and the mass transport inside the catalyst layer. It is known that metal-support interaction enhances the catalyst efficiency, decreases the catalyst loss, governs charge transfer, and increases the catalyst performance and durability by reducing catalyst poisoning, by compounds such as CO and S. In order to improve the metal-support interaction, other carbon supports have been tested, such as mesoporous carbon, carbon nanotubes, carbon nanofibers, and recently graphene [11-14].

There are several well-known methods to manufacture the catalysts cited above, namely methods based on wet chemistry (impregnation-reduction, colloidal route, polyol synthesis, carbonyl route, micro-emulsion and electrochemical methods) [15], mesh coating [16], magnetron sputtering [17], or more recently on atomic layer deposition [18]. Among them, the “wet chemistry” methods offer the best ratio throughput/cost, with particle size ranging between 2–10 nm; optimal distribution of the catalyst particles is critical to the performance of the cell [19,20].

## **2 EXPERIMENTAL SETUP**

Preparation of the MEA begins with the PEM and the catalyst structure is constructed upon it.

### **2.1 Preparation of PEM Membranes**

Nafion 117 (DuPont) membranes were purchased in bulk from a third-party supplier of fuel cell components and prepared in batches in order to reduce MEA production time.

- Sections of the Nafion sheets were cut to size.
- Followed by cleaning with 1 M Sulphuric Acid (J.T. Baker Analysed) for 2 hours at 75°C.
- Then further cleaned by boiling the membranes three times in de-ionized water (Millipore Direct-Q, >18.2 MΩ).
- While still wet the membranes were placed in 3 w% Hydrogen Peroxide (J.T. Baker Analysed) for 1 hour at 60°C.
- Followed by again cleaning the membranes by boiling them three times in distilled water.
- The membranes were then placed in an oven for 1 hour at 60°C to dry.
- Once dry the membranes were stored in a sealed, cool dry container.

The membranes were never stored for more than a month in order to ensure that the membranes were perfectly clean.

## 2.2 Catalyst Slurry

Two catalyst solutions were prepared at the same time, one for the anode and one for the cathode side of the membrane. All slurries were made in new and clean 5ml glass flasks, and all equipment used was cleaned with ethanol and allowed to dry. A waste factor of 15% was added to both catalyst inks. Solutions were always made in the amounts needed based on the active surface area needed for the DMFC, measured in  $\text{cm}^2$ .

- Anode catalyst ink preparation:
- $1.5 \text{ mgcm}^{-2}$  of powder Platinum-Ruthenium (1:1, Alfa Aesar HiSPEC 6000) measured on a micro-scale (Mettler AE 100).
- $1.2 \text{ gcm}^{-2}$  of de-ionized water was added.
- Using a stick sonicator (Sonics Vibra Cell VCX 134) with a Titanium alloy rod, the solution was sonicated for 10 minutes while cooling the flask with an ice bath.
- $3.2 \text{ mgcm}^{-2}$  of Nafion solution (10 w%, FuelCellStore.com) was then added using a pipette.
- The solution was then further sonicated for 10 minutes in an ice bath.

Cathode catalyst slurry preparation:

- $1 \text{ mgcm}^{-2}$  of Platinum Black (Alfa Aesar HiSPEC 1000) was measured.
- $1.2 \text{ gcm}^{-2}$  of de-ionized water was added.
- The solution was sonicated for 10 minutes using a stick sonicator while cooling the flask with an ice bath.
- $3.2 \text{ mgcm}^{-2}$  of Nafion solution (10 w%, FuelCellStore.com) was then added using a pipette.
- The solution was then further sonicated for 10 minutes in an ice bath.

Once either catalyst ink was completed it was deposited onto a proton exchange membrane as quickly as possible in order to prevent sedimentation, agglomeration and evaporation of the solvents used. During deposition the catalyst inks were also stirred in order to ensure a homogenous solution.

## 2.3 Application

A Nafion membrane is first placed on a  $90^\circ\text{C}$  hot glass plate giving it a clean and straight surface, the Nafion will also adhere to the surface of the glass making handling of the process easier. On top of this a polydimethylsiloxane (Atos Medical Silatos) sheet, with a rectangular opening in the middle, is placed. The PDMS template adheres lightly to the Nafion further aiding to keep the membrane in place during operation as well as creating a stencil formation of how the catalyst will be placed onto the membrane. The dimensions of the opening varies according to need however the main

bulk of experiments have been using an opening of 3.6x21 mm, thus creating a catalyst area of 75.6 mm<sup>2</sup>.

The surface is heated from above by an IR heater supplying ~300°C (measured using an IR thermometer on the surface of the heating element) at a distance of 50 cm, thus providing a surface temperature of 80°C as verified by a thermal imaging camera (FLIR i50). This IR heater is turned on only once the production is fully ready to begin and turned off immediately afterwards. During the spraying process the heat increases the water evaporation from the solvent thus creating a finer mist than would be if no IR heater was used. The heat also evaporates solvents used in the Nafion solution. At the same time the strong IR heater replaces the heat lost due to evaporation during production thus reducing the overall production time.

Once the temperature of the membrane had stabilised the catalyst ink was sprayed onto the surface of the membrane using the airbrush. The cathode ink was sprayed first as it was slightly less likely to be damaged due to the relatively higher Nafion content. This was done by pointing the airbrush nozzle towards the membrane at an angle of around 45° and a distance of 20 cm. Then manoeuvring the fine mist across the surface of the membrane, where it was visible through the PDMS. Once a layer of the mist had coated the membrane it was allowed to dry for 5-15 seconds when the next layer was the sprayed in the same manner. This was repeated 10-15 times when the position of the airbrush nozzle was rotated 90° clockwise to the membrane surface, this creates a more three dimensional structure of the particles as they are sprayed onto the surface. This process was repeated until all of the catalyst ink was used up.

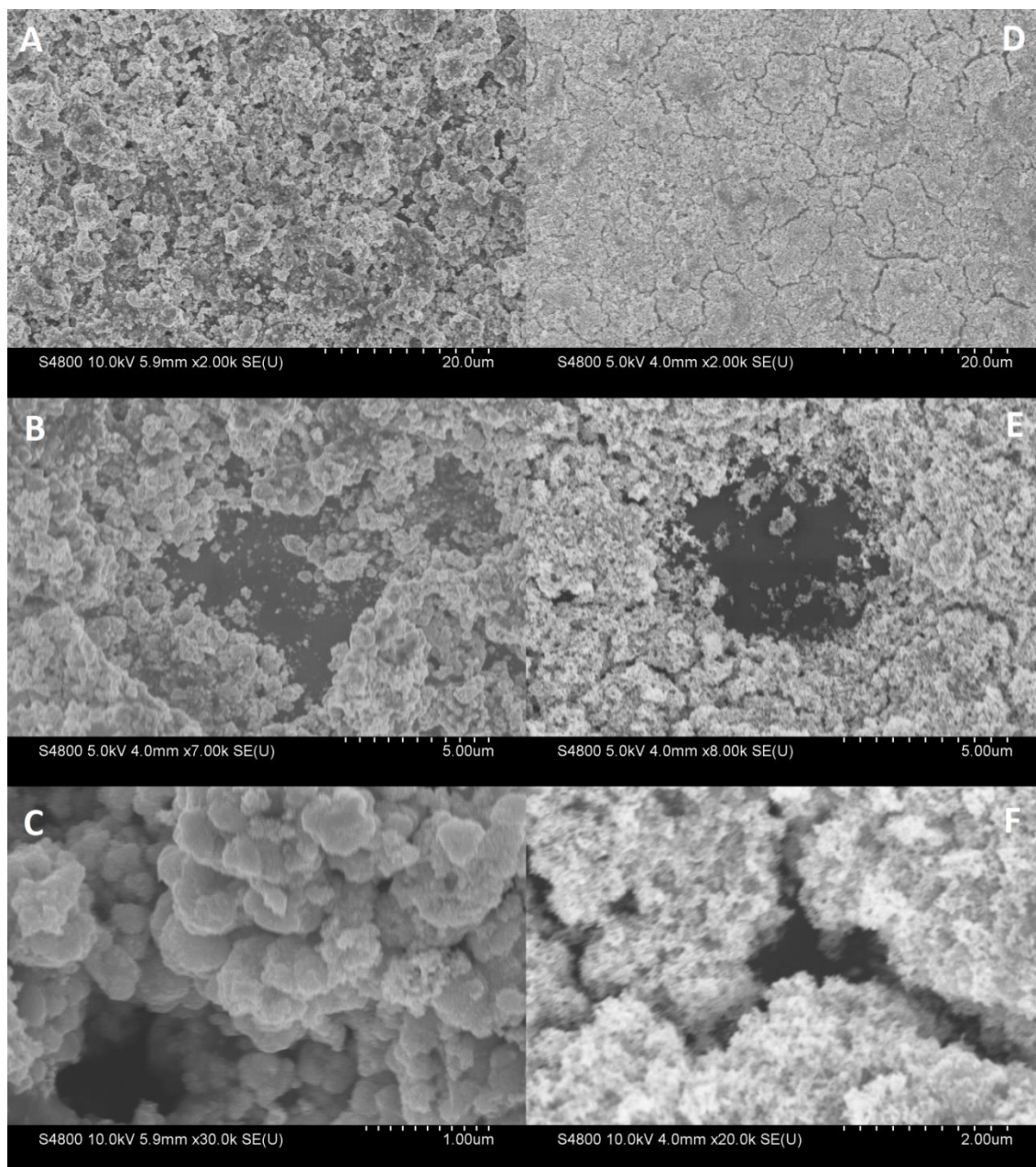
Once one side of the membrane was coated with the catalyst ink the IR heater was turned off and the PDMS template was removed. The membrane was left on the glass plate at 90°C to completely dry for 20 minutes. This allowed the Nafion solution to dry on the membrane and was then turned around to coat the other side.

The membrane was taken off the hot plate and allowed to cool down for 10 minutes in order to make it easier to detach the membrane from the glass plate and turn it around for coating the anode side.

Having successfully sprayed the catalyst layer onto both sides of the membrane, the MEA was placed in a glass container with an opening, in order to allow any solvent to evaporate. The container was then placed in an oven at 60°C for 24 hours ensuring that no solvent was left on the MEA.

### **3 RESULTS**

Scanning Electron Microscope (SEM) imaging was done on an MEA sample in order to determine the catalyst dispersion on the Nafion membrane.



*Figure 1: SEM image of anode and cathode surface of MEA; (a) shows an overview of the anode catalyst surface, (b) it can be clearly seen that it is a layered formation with spots of little-to-none catalyst (c) the average catalyst particle is 600 nm, far larger than expected. (d) The cathode surface is far more porous (e) yet still suffers from 'dead' spots where there is little-to-no catalyst, (f) the average particle size is also far smaller at less than 200 nm.*

In Figure 1, six images are shown, three of the anode at different resolutions and three of the cathode at different resolutions. It can be clearly seen that the porosity of the cathode surface is far higher than that of the anode surface, even though the two surfaces were done at the same time using the same technique. Large 'dead' spots were also seen on both anode and cathode where there was little-to-no catalyst covering the Nafion membrane.

The size of the catalyst particles on both the anode and cathode surfaces vary greatly with an average particle size of 600 nm on the anode side and less than 200 nm on the

cathode. This is far more than the expected particle size of 2-10 nm. This can be accounted for by the agglomeration of particles in the production process. Due to the Pt-Ru composition of the anode catalyst ink the attraction between particles is far greater than on the simple Pt catalyst ink of the cathode. Once the ink is airbrushed at high speed any clustering between particles will not separate due to the presence of the Nafion solution acting as an adhesive.

## 4 DISCUSSION

In order to achieve the best efficiency of the catalyst the aim is to produce a layer that consists of a high surface to increase the reaction area yet a low volume to decrease the cost of the catalyst. The SEM imaging of the surface of the MEA shows that a completely uniform layer is not fully achieved. This is further complicated by the fact that the deposited layer is densely packed resulting in layers of unresponsive catalyst on the surface of the membrane.

In an attempt to further increase the catalyst surface area while decreasing the volume it is logical to produce nanowire strands between the base of the membrane and the GDL surface layer. This in turn would create a direct connection for the current while keeping the surface area high.

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