

Catalytic Particle Aggregation in the MEA of DMFC Systems*

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Abstract

During the development of the Membrane Electrode Assembly in Direct Methanol Fuel Cells it is not unusual for the Pt and Pt-Ru particles to aggregate forming an uneven dispersion on the Proton Exchange Membrane. It has long been known that the aggregation occurs over time when the catalyst is stored and can to a large extent be dispersed again through vigorous mechanical shaking or sonication. This paper aims to determine the time needed in order to disperse the catalytic particles to a degree that is suitable for the production of MEAs in DMFC.

Keywords: Fuel Cells, DMFC, Electrochemistry, Catalyst, Pt, Catalyst Production, Particle Dispersion, Particle Aggregation

1 INTRODUCTION

The worlds growing demand for power has been for some time a pressing problem to the finitely limited natural resource. Not only is humankind faced with the problem that conventional resources are running out but also due to the fact that all the bi-products of these conventional resources are changing the planet we live on [1], having already increased the mean European temperature by 1.3°C since pre-industrial levels [2]; this problem goes further than most people realise as this creates a accumulating effect where any climate change encourages more climate change and as such once a tipping point is reached the detrimental process will be self-sustaining [3,4].

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This very limitation has led to a hybrid solution, it can be considered that any further advances with the internal combustion engine is rather minute and so the efficiency of these engines will never improve far beyond the current 25% or so [5]. Increasing the engine efficiency requires a completely new engine, one in which the device would produce electricity on the spot with a higher efficiency. For this electrochemical cells, or fuel cells, are seen as a viable alternative to the problem at hand.

Currently a large range of different fuel cells are available, each serving a different segment of the market, this makes the term fuel cell very broad as no single system will come out as being perfect for all applications. The one of current interest however is the DMFC.

The DMFC operates at low-temperature and uses a dilute methanol solution as its fuel source; as such it is ideal for the use in small electronics where large power output is not necessary. However due to its high catalyst loading it is hard to develop a cost effective DMFC. Variations of the DMFC exist such as the Direct Ethanol Fuel Cell (DEFC) which uses a dilute ethanol solution as its fuel as opposed to methanol.

However at the heart of the DMFC there is a Membrane Electrode Assembly (MEA) where methanol reacts with the catalyst in order to produce the electrons the relationship between particle size and its active surface area will define its potential to reach the maximum power density.

As such the particle surface area, calculated per gram of particles, is directly linked to the performance of the cell. Knowing that the average particle size in the quality analysis is 2.8 nm the total surface area can be calculated.

Knowing the density of platinum to be 21.4 g/cm³ and ruthenium to be 12.4 g/cm³ the volume per gram can be calculated.

$$V = \frac{m}{\rho}$$

Where V is volume, m is mass and ρ is density; thereby receiving an answer of 0.047 cm³ or 4.7x10⁻⁸ m³ and for ruthenium 8.1x10⁻⁸ m³. As each component represents 50% of the solution this would give an average volume of 6.4x10⁻⁸ m³.

Assuming the particles to be near spherical [6] the volume per particle can be calculated as:

$$V = \frac{4}{3} * \pi * r^3$$

Where π is taken as 3.14; the individual particle volume of one gram is 1.15x10⁻²⁶ m³.

In order to determine the number of particles in a gram the total volume is divided by the individual volume proving there to be 5.57x10¹⁸ particles. To calculate the total surface area of all the particles the following equation is used:

$$A = 4 * \pi * r^2 * N_{particles}$$

These results in a total surface area of 137.1 m² per gram.

2 EXPERIMENTAL SETUP

In order to be able to screen print a catalyst onto a membrane it is necessary for the catalyst to be in a viscous form. In order to achieve this viscous form several components are added in succession. This mixture of components is referred to as the catalyst mixture.

The catalyst mixture consists of two main ingredients. This is the catalyst and the Nafion (DuPont) solution. The anode catalyst is a HiSpec 6000 (Alfa Aesar™) consisting of 50% platinum black and 50% ruthenium. The cathode side is a HiSpec 1000 (Alfa Aesar™) consisting of pure platinum black. The Nafion used is either of 5% or 10% concentrations (purchased from fuelcellstore.com), with the amount used during MEA production changed to match the concentration.

In addition METFE powder has been added as a support material to stabilize and increase the power density of the cell.

Furthermore a solvent is added to increase the volume in order to allow for easy screen printing. If only the catalyst, Nafion and METFE were to be screen printed there would not be enough liquid to cover the surface area thereby depositing all the slurry in one section.

2.1 Slurry Creation

The catalyst mixture was made in accordance to previously published research on the topic by the same author.

The slurries were created by adding each component in succession into a 1 ml glass vial using a Mettler AE 100 scale set capable of 0.1 mg precision. All of the parts that were in contact with the MEA were cleaned, with ethanol, before use and let dry properly in order to ensure that the catalyst would not react with any leftover ethanol on the equipment. The slurry was then mixed in the following order:

1. Catalyst
2. Solvent
3. METFE
4. Nafion

After mixing of the components the glass vial was inserted into a Finnsonic m03 water bath sonicator; the slurries were sonicated between 30 minutes and 48 hours. The sonicator was constantly cooled by inserting blocks of ice into the water.

2.2 Application

The airbrush method involves using an airbrush (Badger AirBrush model 200) with 1.5 bars of air pressure to create a fine mist of catalyst solution that is layered onto the membrane.

A Nafion membrane is first placed on a 90°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 mm².

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 of 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.

The then completed MEAs were then boiled in different concentrations of HCl (between 0.1M to 2M) in order to remove any metallic contamination from the membrane followed by rigorous washing with DI water.

2.3 Analysis

Analyses of the produced MEAs were done using the available laboratory microscope with an attached camera for taking images. The images were transferred into a custom program that allowed for measuring the seen particles aggregates. Repeated measurements were then used to create an overall analysis of the particle aggregate sizes and their coverage of the surface of the MEA.

3 RESULTS

These results have been achieved with the help of a microscope camera for capturing the images in order to measure the particles.

The first tests were done by increasing the sonication time used during production of the catalyst slurry.

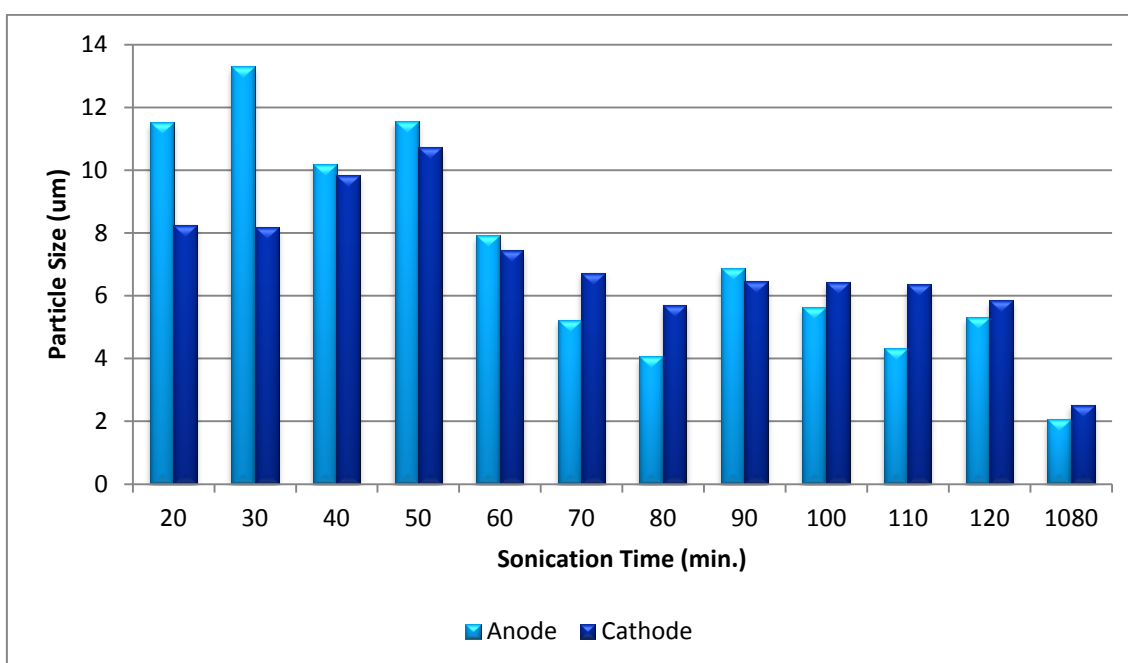


Figure 1: Catalyst particle sizes measured at intervals during sonication, taken as an average of six measurements.

In Figure 1 it can be seen how the particle sizes decrease over time during sonication in water. Taking the smallest particle size at 2.1 μm a new surface area can be calculated at 0.2 m^2 this is a reduction of 99.85% in surface area. Similarly after one hour of sonication the average anode particle size is 8.0 μm with a surface area reduction of 99.99%.

Further tests were done using HCl in an attempt to remove the oxidation layer from the particles.

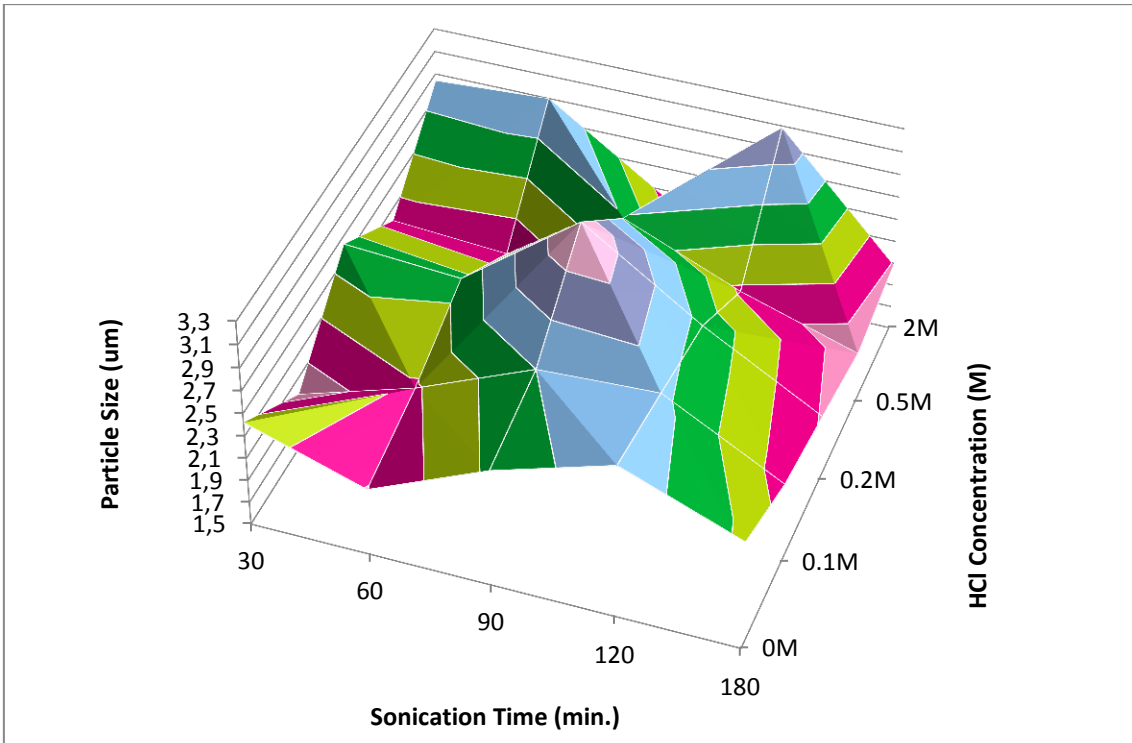


Figure 2: Anode particle sizes measured at 100x magnification.

This method caused varying results which cannot be seen as reliable when measuring the particle sizes. In an attempt to improve the accuracy software was written to calculate the number of particles seen in a taken picture. As nano-sized particles cannot be seen at 100x magnification it would stand to assume that as more particles become the original nano-size the overall mass of particles seen in a picture would decrease.

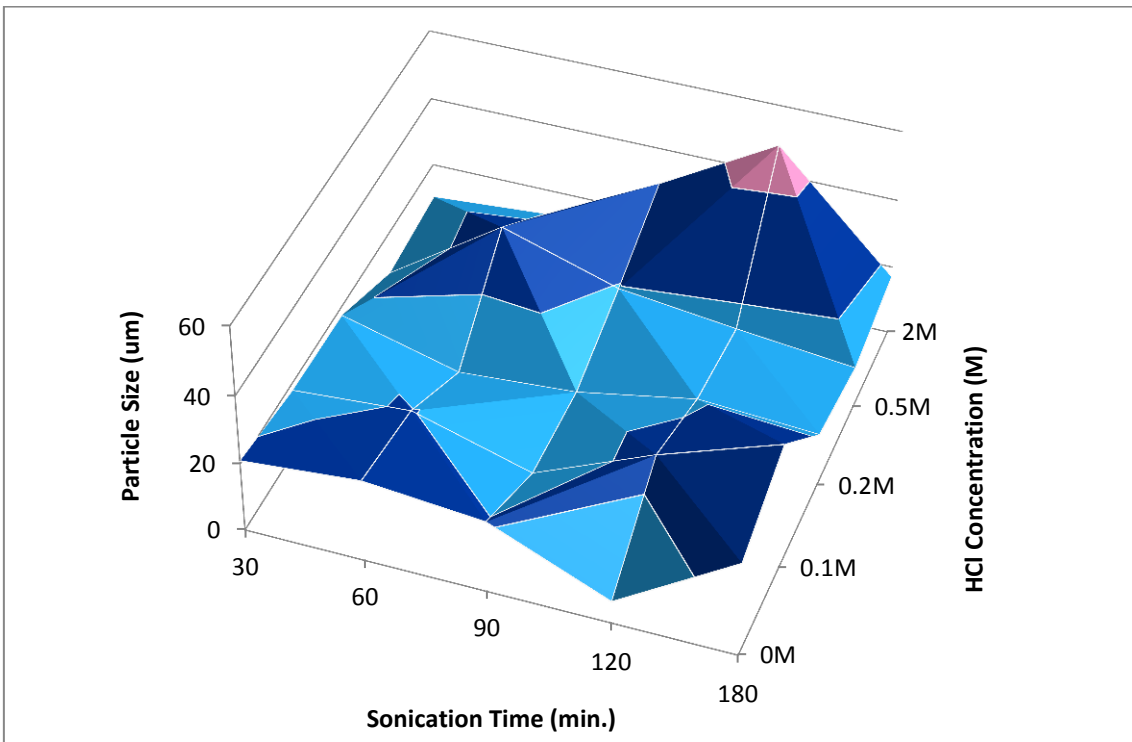


Figure 3: Anode surface coverage area at 100x magnifications.

This method produced slightly more accurate results.

4 DISCUSSION

As was expected the particle aggregation reduced greatly over time during sonication of the slurry. However unexpectedly the distribution of particles greatly slowed down after an hour of sonication at which point only small improvements were observed.

While the paper did not go into detail regarding the power input of the sonication this is a variable that can also be used to regulate the time needed for separation of the aggregates. However as the Nafion solution and catalyst are both sensitive to heat fluctuations, especially above 70°C, caution should be practiced.

Over time the metal particles will aggregate once again and slowly deposit at the bottom of the flask once more. The time for this sedimentation is inversely proportionate to the time spent sonicating the slurry in the first place. This is important to note, as the slurry should ideally be used immediately in order to reduce as much as possible any aggregation of the particles.

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