A comparison of catalyst application techniques for membrane electrode assemblies in SO_2 depolarized electrolysers

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Soli Gloria Deo

Abstract

Hydrogen production via the electrolysis of water has gained a lot of attention in the last couple of years. Research related to *electrolysers* is mostly aimed towards decreasing the noble-metal catalyst content.

In this study the presently used catalyst application techniques were reviewed and critically examined to find commercially applicable and effective methods. Selected methods were then practically applied to determine their feasibility and to gain "know-how" related to the practical application of these techniques. The selected techniques were the hand paint, inkjet print, screen print and spray paint techniques.

Meaningful comparisons were made between the methods in terms of parameters such as practicality, waste of catalyst and microstructure. The results point out that the hand paint and spray paint methods are feasible methods although there are improvements to be made.

The hand paint method was improved by applying a carbon micro porous layer to the gas diffusion layer before the painting is carried out. The addition of the carbon layer reduced the soaking of the catalyst-containing ink through the gas diffusion layer.

A method not initially investigated was identified an evaluated and showed promising results in lowering the mass of catalyst applied. This method comprised of sputtering a layer of catalyst material onto a prepared gas diffusion layer.

It also came to light from the results that electrodes, and therefore membrane electrode assemblies, can be produced at a much lower cost than the commercial available membrane electrode assemblies.

Keywords: Carbon micro porous layer, catalyst application techniques, catalyst layer, electrolyser electrode, fuel cell electrode, hand paint, inkjet print, membrane electrode assembly, screen print, spray paint, sputtering, water electrolysis.

Uittreksel

Die produksie van waterstof deur die elektrolise van water is vir die afgelope aantal jare ‘n belangrike navorsingsonderwerp. Die fokus van dié navorsing is hoofsaaklik gemik op die effektiewe deponering van die edelmetaal-katalisator met die doel om die massa katalisator, en sodoende die produksiekoste, te verminder.

In hierdie studie is ‘n oorsig van die huidige katalisator-aanwendingstegnieke gedoen en is dié tegnieke krities bestudeer met die doel om kommersiëel-belangrike tegnieke te identifiseer. Dié tegnieke is prakties uitgevoer om die lewensvatbaarheid daarvan te bepaal, maar ook om insig in te win aangaande die praktiese aspekte van die tegnieke.

Onder dié metodes was die handverf-, spuitverf- en *zeefdruk-* (*screen print-*) tegnieke, asook ‘n relatief-nuwe *inkjet*-druk tegniek.

In hierdie studie is betekenisvolle vergelykinge getref tussen die tegnieke in terme van aspekte soos praktiese uitvoerbaarheid, katalisatorbenutting en mikrostruktuur. Die resultate het getoon dat die handverf- asook die spuitverftegniek lewensvatbaar is, maar het ook sekere verbeteringe aangetoon in verband met dié tegnieke.

Die handverftegniek is verbeter deur ‘n poreuse koolstoflaag aan te wend op die oppervlakte van die gasdiffusielaag voordat die handverftegniek uitgevoer word. Dié koolstoflaag verminder die versadiging van die totale gasdiffusielaag deur die katalisator-bevattende ink.

‘n Tegniek wat nie aanvanklik geselekteer was om geëvalueer to word nie, het belowende resultate getoon in verband met die vermindering van die totale massa katalisator benodig. Die uitvoer van dié tegniek behels die deponering van die katalisator-metaal op ‘n voorbereide gasdiffusielaag deur ‘n proses genaamd *sputtering*.

Dit het aan die lig gekom vanuit die studie dat elektrodes, en dus gevolglik membraanelektrode-samestellings, teen ‘n veel laer koste vervaardig kan word as waarvoor dit kommersieel beskikbaar is.

Sleutelwoorde: Brandstofsel-elektrode, handverf, *inkjet*-druk, katalisator-aanwendingstegnieke, katalisatorlaag, membraanelektrode-samestelling, poreuse koolstoflaag, spuitverf, waterelektrolise, waterelektroliseerder-elektrode.

Table of Contents

List of Figures

List of Tables

List of Symbols

A	:	Ampere
˚C	:	Degrees Celsius
cm	:	Centimetre
Hz	:	Hertz
K	:	Kelvin
m	:	Meter
mm	:	Millimetre
nm	:	Nanometre
V	:	Volt
W	:	Watt

List of abbreviations

CB	Carbon Black
CCM	Catalyst Coated Membrane
CH_4	Methane
CNT	Carbon Nanotube
CO_2	Carbon Dioxide
CVD	Chemical Vapour Deposition
DMFC	Direct Methanol Fuel Cell
dpi	Dots Per Inch
EIS	Electron Impedance Spectroscopy
GDL	Gas Diffusion Layer
H_2	Hydrogen
H_2O	Water
H_2PtCl_6	Hexachloroplatinic Acid
HP	Hand Painting
HP-C	Hand Painting on Carbon Micro porous Layer
IJP	Inkjet Printing
MEA	Membrane Electrode Assembly
MPCVD	Microwave Plasma Chemical Vapour Deposition
NASA	National Aeronautical and Space Administration (USA)
NOx	Nitrogen Oxide Gasses
O_2	Oxygen
OMC	Ordered Mesoporous Carbon
PEMFC	Proton Exchange Membrane Fuel Cell (also Polymer Electrode Membrane Fuel Cell)
PCE	Porous Carbon Electrode
PFSF	Perfluorosulfonyl Fluoride
pl	Picolitres
Pt	Platinum
SEM	Scanning Electron Microscopy
SiC	Silicone Carbide
SO_2	Sulphur Dioxide
SCP	Screen Printing
SP	Spray Painting

1. Introduction

Hydrogen, being the most abundant element, is used in a variety of industrial and laboratory applications. One of these industrial applications is the production of ammonia via the Haber-Bosch process [**1**] where hydrogen and nitrogen are used to produce ammonia via the reaction:

$$N_2\,(g) + 3H_2\,(g) \rightarrow 3NH_3\,(g)$$

Hydrogen is also used as a coolant for high temperature industrial machinery such as power plant turbo-generator sets. Hydrogen's very high specific heat capacity and the low power required to pump hydrogen gives it the competitive advantage over other cooling fluids. Other applications of hydrogen include the saturation of fats and oil, the reduction of metallic ores and has even in some cases, been used for the floatation of lighter-than-air aircraft as in the Hindenburg.

Figure 1: A power plant turbo generator cooled with hydrogen [**2**].

Although abundant, hydrogen is mostly found in compounds in nature and has to be produced from these compounds [**3**]. The hydrogen currently available on the market is mainly produced via the removal of hydrogen from hydrocarbons. This is achieved by the steam reforming of natural gasses where high temperature steam reacts with natural gasses to produce hydrogen and carbon compounds (C,CO or CO_2). Other feedstock for hydrogen production includes animal waste, wood and coal.

In an attempt to meet research and development goals for sustainable energy production, the source of hydrogen has shifted to other non-polluting sources such as water. The ideal that hydrogen can be used as future energy carrier favours this shift since it highlights the possibility of renewable hydrogen production where the production energy can originate from solar-, thermal- or hydro-energy [**4**].

Hydrogen production without a carbon footprint is not new to science and has been done for many years on small scale. In the laboratory preparation of hydrogen, sulphuric acid reacts with metals such as zinc according to the reaction:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

Another non-carbon emitting production method of hydrogen is the electrolysis of water where the electrolysis energy can come from a renewable source. Water electrolysis entails the production of hydrogen and oxygen from water by the application of a potential difference over two electrodes exposed to water. This basic electrolysis of water however can be carried out a lot more efficiently by the introduction of a catalyst to the reaction [**4**].

Research regarding water electrolysis catalyst materials has shown that the most suitable electrolysis catalyst currently is platinum [**5**]. Since platinum is extremely expensive, its use in industrial electrolysers increases the running and manufacturing cost of this type of electrolysers [**6**].

In an attempt to reduce the catalyst cost factor of the electrolyser production, the application of a catalyst has to be carried out as efficiently as possible to yield optimised results. There are some requirements for this catalyst application in the manufacturing of membrane electrode assemblies (MEA’s) for fuel cells and electrolysers that makes the application process complex.

The first requirement is related to the electrochemical reaction surface area versus the total MEA size. As the electrochemical reaction surface increases, more catalyst is exposed to the chemical reaction resulting in increased hydrogen production. An increase in surface area will increase the assembly size except if the increase in surface is achieved by means of finer catalyst particles/substrate particles or/and an increase in the catalyst layer microstructure porosity.

The second requirement relates to the catalyst loading. In order to decrease the manufacturing cost of electrolysers, as little as possible catalyst has to be applied, yet as much as possible of it exposed to the electrochemical reaction. The efficiency of catalyst utilization is not only a function of the fineness of the particles, but also a function of the application technique that dictates the catalyst distribution and loading.

In order to ensure an even distribution of electrochemical reaction across the catalyst layer, it is essential that the catalyst is applied evenly and without agglomerations of catalyst particles. It is also crucial that the microstructure of the catalyst layer is porous with open structures to prevent water-clogging of the reaction surface, but also to ensure the accessibility of water, oxygen and hydrogen to and from the reaction sites.

From the above mentioned requirements it can be deducted that the microstructure of the catalyst layer and the production thereof is an important factor in the overall production of the electrolysers. This in turn reflects on the practicality and efficiency of the methods used to produce these catalyst layers and any eventual commercialization of electrolysers for, for instance, transport purposes.

Aim of the Study

The aim of this study is to review and compare catalyst application techniques employed in the manufacturing of catalyst layers for MEA's used in the production of electrolysers. The aim also includes the determination of the feasibility of such techniques. This is achieved by applying a selected number of techniques in practise to gain know-how related to the techniques and to obtain insight into the effect of microstructure on MEA integrity.

2. Background

In the previous chapter the current situation regarding hydrogen consumption and production was discussed briefly. In this chapter the electrolysis of water is discussed starting with the analogy of basic electrolysis of pure water in order to familiarize the reader with the process and the technical terms used in the dissertation.

2.1 Basic water electrolysis

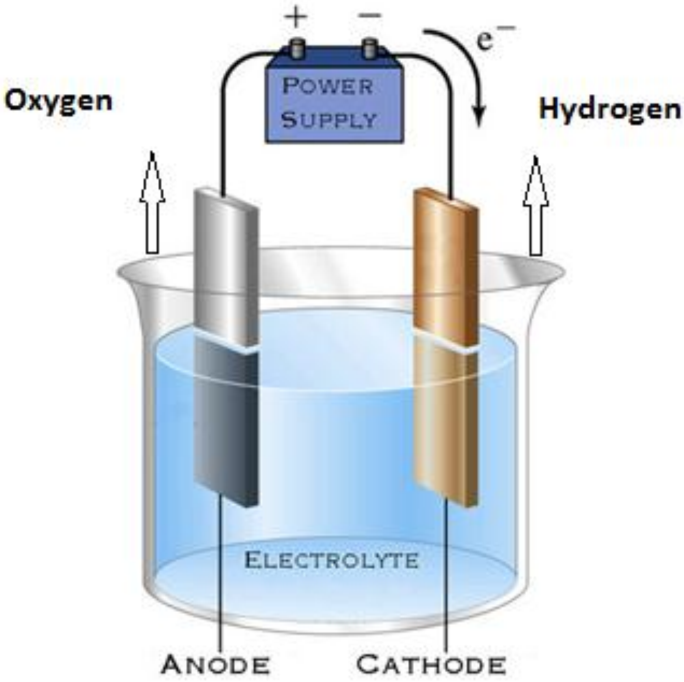

Figure 2: Illustration of the basic water electrolysis process (Modified after [**7**].).

Basic water electrolysis is per definition the decomposition of water into hydrogen and oxygen via the application of an electric potential difference [**3**]. In the basic setup two electrodes are placed inside water and a potential difference applied over the electrodes. As soon as the current starts to flow, bubbles of hydrogen appear at the cathode and bubbles of oxygen at the anode.

Cathode side reaction (reduction): $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Anode side reaction (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(g) + 4e^-$

An excess amount of electrolysis energy, called *overpotential,* is required when pure water is decomposed via electrolysis. This overpotential is due to the activation energy required for the chemical reaction to start. If this excess energy is not present, the rate of decomposition is very low if at all present. The rate of electrolysis of pure water can be increased by adding an electrolyte such as salt, which dissociates the water, and/or a catalyst such as platinum.

2.2 PEM Electrolysers and Fuel Cells

In an attempt to improve on the efficacy of basic water electrolysis, *Proton Exchange Membrane (PEM)* electrolysers have been developed [**8**], [**3**]. The working and subcomponents of these electrolysers are discussed in this section to provide the necessary background to the evaluation and research conducted.

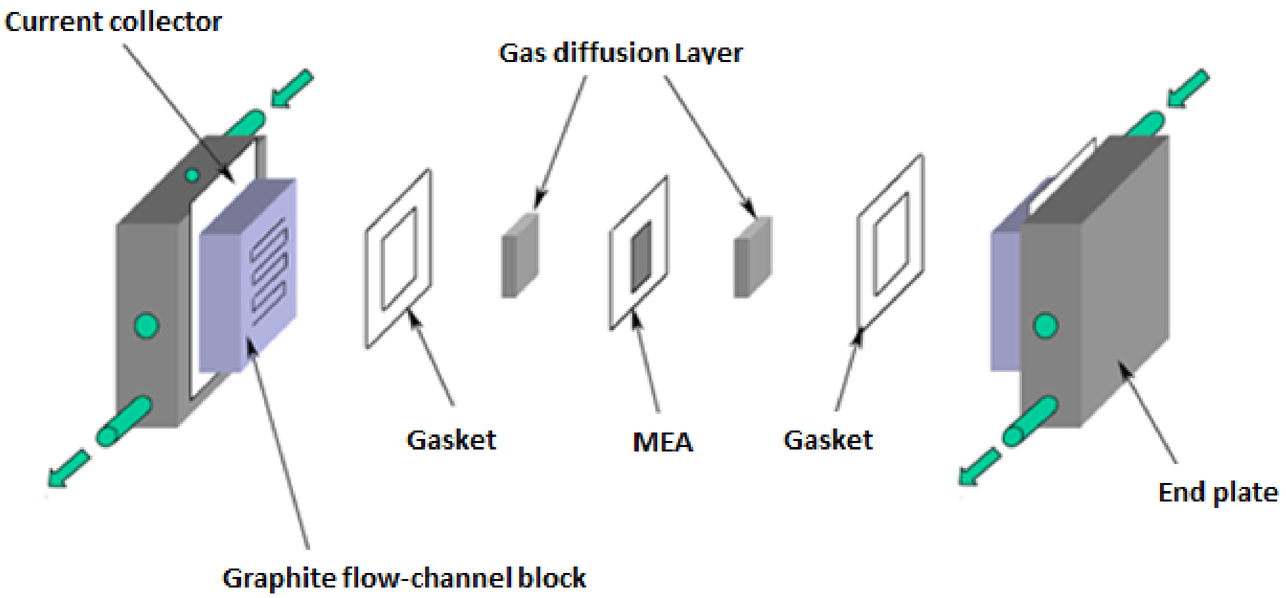

Figure 3: The basic components of a water electrolyser modified after Gland *et al*. [**9**]

Currently standard water electrolysers consist of components as shown in Figure 3. The standard design consists of end plates, current collectors, flow channels, gas diffusion layers and the MEA. The design and design requirement of each of these components will now be reviewed [**10**] [**11**].

- **End plates**

The purpose of the end plates is to hold the electrolyser assembly together. In some instances it also provides a connection for the external couplings to the flow fields. The end plates are bolted together to a specified torque to hold the other components in place and to ensure contact between the gas diffusion layer and the flow fields. Common end plate materials include stainless steel or aluminium because of the sometimes corrosive environment and the fact that the end plates should not deform under applied torque to prevent gas leaks.

- **Current collectors**

The purpose of the current collectors is to collect/supply the current required/produced by the process, whether it is a fuel cell or an electrolyser. The current collectors are normally produced from copper/ copper alloy as a very high electrical conductivity is required.

- **Flow fields**

The flow fields extract the reaction products from the electrolyser and supply the reactant gasses (hydrogen and oxygen/air) to the MEA in a hydrogen *fuel cell*. The flow fields are machined into graphite or polymer-impregnated graphite composite plates. The impregnation of the graphite is essential to prevent gas leakages through normally porous graphite. In some cases the coupling for the external gas supply is fitted/machined into the flow field instead of the end plates. Different patterns of flow fields exist including serpentine and parallel flow. Each of these patterns has its own characteristic pressure drop and mass flow characteristics.

- **Gaskets**

The gaskets are used to seal the assembly preventing gas or water leakages. The gasket material in most instances is a silicone elastomer. In other instances EPDM (Ethylene Propylene Diene Monomer) rubber gaskets are used especially in Direct Methanol Fuel Cells (DMFC).

- **GDL (Gas Diffusion Layer)**

The GDL removes water from the reaction site but maintains enough moisture to ensure the transport of protons through the membrane. The ability of the membrane to transport protons decreases as the membrane dries out. The GDL must be a porous substrate and can be produced from various substrate materials, but usually variations of carbon such as carbon cloth or carbon paper are useful [**12**]. In some instances a very fine titanium mesh is used as a GDL. Each of these gas diffusion layers has its own characteristic water transport and pressure drop characteristics. The GDL is in some instances used as the substrate onto which the catalyst is applied and is the path electrons follow from the reaction site to the current collectors. This adds to the requirement that the GDL has to be electrically conductive.

- **MEA (Membrane Electrode Assembly)**

The MEA is an assembly consisting of the membrane, gas diffusion layers and catalyst layers. The membrane (usually Nafion) allows the transport of hydrogen cations but does not conduct electrons. This characteristic of the membrane completes the circuit in the fuel cell/ electrolyser by forcing the electrons to travel along the external circuit. The catalyst layers and gas diffusion layers are located on both sides of the membrane. The catalyst (in most instances platinum or platinum alloys deposited on carbon designated Pt/C [**12**]) is either deposited directly on the membrane or onto the gas diffusion layer. If the catalyst layer is applied to the gas diffusion layer, it is subsequently referred to as the Gas Diffusion Electrode (GDE). The gas diffusion layer, the catalyst layer and the membrane are held together by the clamping force of the end plates or bonded together by exposing the assembly to a high pressure at temperatures between 100˚C and 140˚C [**12**] [**13**] [**14**].

2.3 PEM Electrolyser/ Fuel Cell Operation

The components discussed in the previous section are similar to that of a fuel cell since the process of water electrolysis is basically the reverse process of that taking place inside the hydrogen fuel cell. Figure 4 illustrates the similarities and differences between the two processes. The basic operation of the electrolyser and fuel cell is discussed in broad terms with reference to Figure 4.

- **PEM Fuel cell**

In the fuel cell operation, hydrogen is supplied from an external supply directly to the anode flow field or via the anode end plates. This hydrogen can originate from any source, be it compressed hydrogen, liquefied hydrogen or metal hydrides.Pure oxygen or air is supplied in the same fashion to the cathode flow field. This oxygen/ air can be extracted from the atmosphere or supplied via a compressed oxygen source. The gasses travel along the flow fields where they diffuse through the gas diffusion layer until they reach a point where an ionomer (Nafion), reaction catalyst and an electron conduction medium exists. These areas are sometimes referred to as the *triple phase boundaries* since electrons, protons and gasses exist at these points [**13**] At the anode side triple phase boundary, the hydrogen atom, in presence of the catalyst, is split up into a hydrogen cation and an electron according to the half reaction:

$$H_2(g) \rightarrow 2\,H^+(aq) + 2e^-$$

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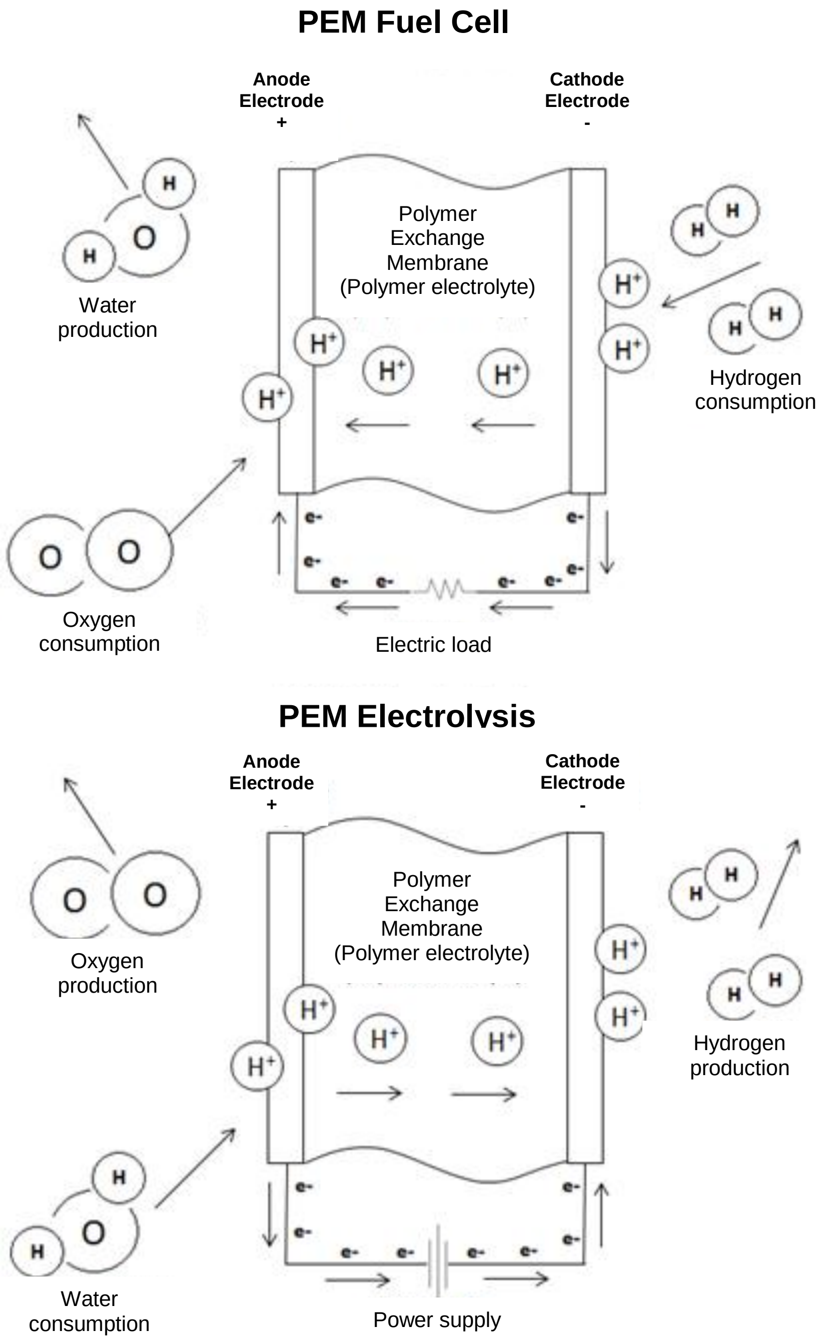

Figure 4: The PEM electrolysis and fuel cell process (modified after Barbir *et al*. [**3**])

The hydrogen cations diffuse through the membrane to the cathode side whilst the electrons are forced to travel along the external circuit because of the electrical insulation characteristic of the membrane producing the fuel cell's electrical output. Once on the cathode side, the hydrogen cations react with electrons and the oxygen supplied to form water according to the reaction:

$$O_2(g) \quad + \quad 4\,H^+(aq) \quad + \quad 4e^- \quad \rightarrow \quad 2\,H_2O$$

This reaction is catalysed with the aid of the essential catalyst.

- **PEM Electrolyser**

The oxidation reaction occurs at the anode where water molecules are split into oxygen, hydrogen cations and electrons according to the reaction:

$$2\,H_2O \rightarrow O_2(g) + 4\,H^+(aq) + 4e^-$$

Because of the applied voltage over the electrolyser, the electrons travel through the applied circuit and force the hydrogen cations to diffuse through the membrane to the cathode side. The reduction reaction at the cathode side produces hydrogen according to the reaction:

$$2\,H^+(aq) + 2e^- \rightarrow H_2(g)$$

The hydrogen and oxygen produced escapes from the electrolyser by traveling along with the water that is being circulated through the flow fields.

One particular modification of the basic water electrolyser is the SO_2 depolarized electrolyser. The advantage of this type of electrolyser is the fact that the potential difference required to decompose the water molecules is lowered significantly because of the SO_2 depolarizing the anode [**15**].

A mixture of SO_2 gas and water circulates through the anode side flow field. At the triple phase boundary, the water and SO_2 is converted to sulphuric acid and hydrogen according to the reaction:

$$2\,H_2O + SO_2 \rightarrow H_2 + H_2SO_4$$

The hydrogen is decomposed into hydrogen ions which diffuse through the membrane and electrons that travel through the external circuit. At the cathode side the hydrogen ions combine with the supplied electrons to produce hydrogen gas.

2.4 Electrolyser and Fuel Cell Catalyst Application

The efficiency of any electrolyser is a function of the operating parameters and the design of the subcomponents mentioned. In a similar way the production costs and performance depends on the amount of material used. This cost of material and material utilization is of utmost importance in the manufacturing of the electrolysers/fuel cells. By using the right application technique the minimum catalyst should be applied to yield optimal performance per mass of catalyst.

3. Literature

3.1 Introduction

In the previous chapter the components and operation of electrolysers have been discussed. This chapter deals with the literature regarding the application of catalyst for the manufacturing of electrolysers. In this chapter the term *loading* is often referred to indicating the mass of catalyst applied in the catalyst layer produced. This *loading* refers to either the total catalyst present in the catalyst layer (mg Pt/catalyst layer) or the catalyst mass per square centimetre of catalyst layer (mg Pt/cm^2).

3.2 Techniques

In the open literature studied several techniques of membrane electrode assembly catalyst application were encountered. For some of the techniques large amounts of literature were found while some techniques were merely mentioned. A summary of the most relevant information regarding these methods found in the literature is presented below.

3.2.1 Method(s) of Electrodeposition/ Electroplating

Platinum electrodeposition is a process currently being used in the manufacturing of various products, including the fabrication of aviation components, electrodes, turbine blades as well as in the jewellery and aesthetics industry [**16**]. The process was developed in 1805 by chemist Luigi Brugnatelli when he first plated silver objects with gold [**17**]. Electrodeposition and electroplating are terms that are used interchangeably. This process creates the possibility of very efficient utilization of precious metals as catalysts on porous substrates [**18**], [**19**] and assures that the catalyst is deposited in an area on the substrate with both ionic and electronic accessibility [**20**]. However, a drawback of this process is that the catalyst particle diameter is relatively large resulting in a relatively low surface area per unit mass of catalyst [**8**]. In this process an electric current induces the formation of thin metallic layers forming consecutively one upon another [**17**]. The deposition is achieved by applying a negative charge to the part to be plated and immersing it into a solution containing a salt of the metal layer to be formed. The part to be coated then fills the role of the cathode in an electrolytic cell. The metal ions in the solution that originate from the metal salt carry a positive charge and are drawn towards the part’s negative surface. The part supplies electrons which reduce the positively charged ions to the metallic state [**17**]. Figure 5 gives an illustration of the electrodeposition process.

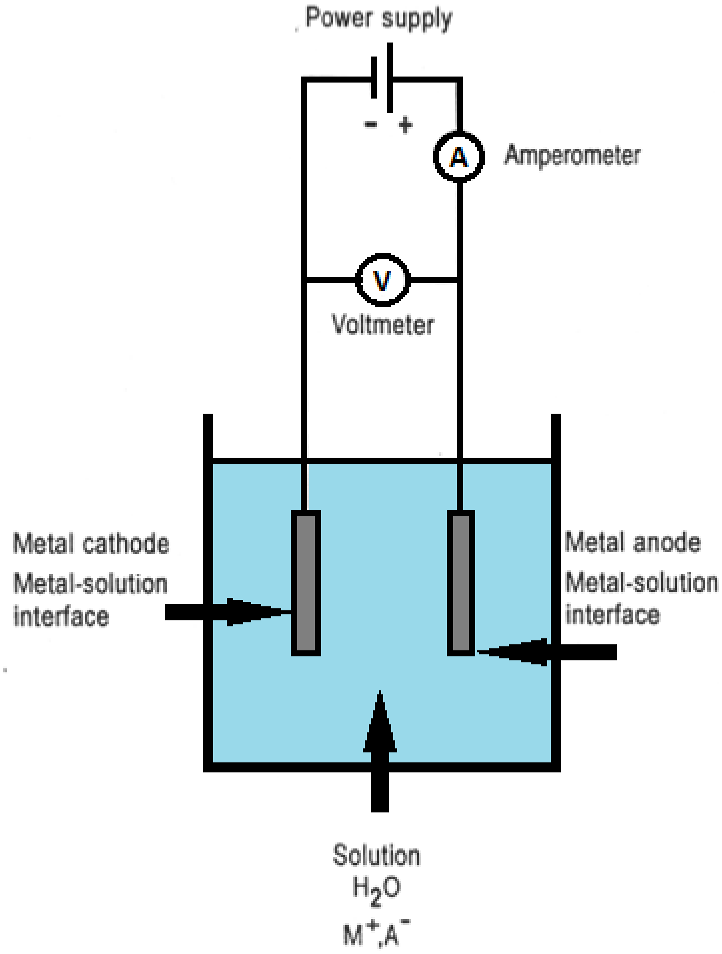

Figure 5: Schematic illustration of the electrodeposition process (modified from Mordechay *et al*. [**17**])

Since carbon is used as a supporting substrate in hydrogen fuel cells and water electrolysers, electrodeposition is carried out on the carbon surface. The carbon can be in various forms, including carbon nanostructures, carbon black and carbon cloth. Since carbon is hydrophobic, the carbon has to be treated prior to electroplating. This treatment creates a hydrophilic layer on the carbon surface. In most processes where platinum is electrodeposited on carbon, the platinum precursor is hexachloroplatinic acid (H_2PtCl_6) which is a product of the refining of platinum concentrates by solvent extraction [**16**].

In the most basic approach, carbon black or carbon nanostructures are treated to create a hydrophilic layer as mentioned. This carbon is then applied on top of another layer of hydrophobic carbon, usually carbon paper by forming a mixture with Nafion which is a sulfonated tetrafluoropolymer. This helps to ensure that only one side of the substrate/electrode will be electroplated. The carbon electrode/substrate is then immersed into a plating bath containing the platinum precursor. In this step the hydrophobic face of the electrode/substrate is usually masked with a non-conducting tape to further prevent platinum access. Platinum is now deposited now on the hydrophilic layer. Lister and McLean [**21**] reported this process to achieve platinum loadings as low as 0.05 mg/cm² [**21**]. In a later study by the same research group, the performance of this catalyst/electrode was found to be similar to those of a PTFE bound catalyst/electrode with a platinum loading of 0.5mg/cm².

In a study performed by Liao *et al.* [**20**] a Pt/PCE (Platinum/Porous Carbon Electrode) has been prepared by the displacement of electrodeposited Cu-particles by platinum particles. Electrodeposition was used to deposit Cu-particles on a PCE in a four-step process. The Cu/PCE was then dipped into a solution of a platinum salt in which the displacement of the Cu-particles took place resulting in the desired Pt/PCE. With a Pt loading of 0.196 mg/cm² the MEA produced a power output of 0.45 W/cm² in comparison with 0.3 W/cm² power output produced by commercial Nafion bonded 40%Pt/C catalysts with the same platinum loading.

An alteration to the standard process has been introduced by Pollet [**22**]. The platinum catalyst was galvanostatically (i.e. at a constant current) pulse electro-deposited in the presence of 20 kHz ultrasound. This was then compared to a catalyst prepared under silent conditions (i.e. no ultrasound) and also compared to the results of a conventional process. The conclusion of the study was that the galvanostatic pulse (i.e. potential cycling) electrodeposited catalyst yielded better performance than that of (i) a catalyst prepared under the same silent conditions and (ii) a catalyst prepared by the conventional method. A power density of value of 98.5mW/cm² was found when the anode was prepared sono-electrochemically and a power density value of 91.5mW/cm² was found when the anode was prepared in the same silent conditions. When the conventional method was applied, the power density value was found to be 86mW/cm² [**22**].

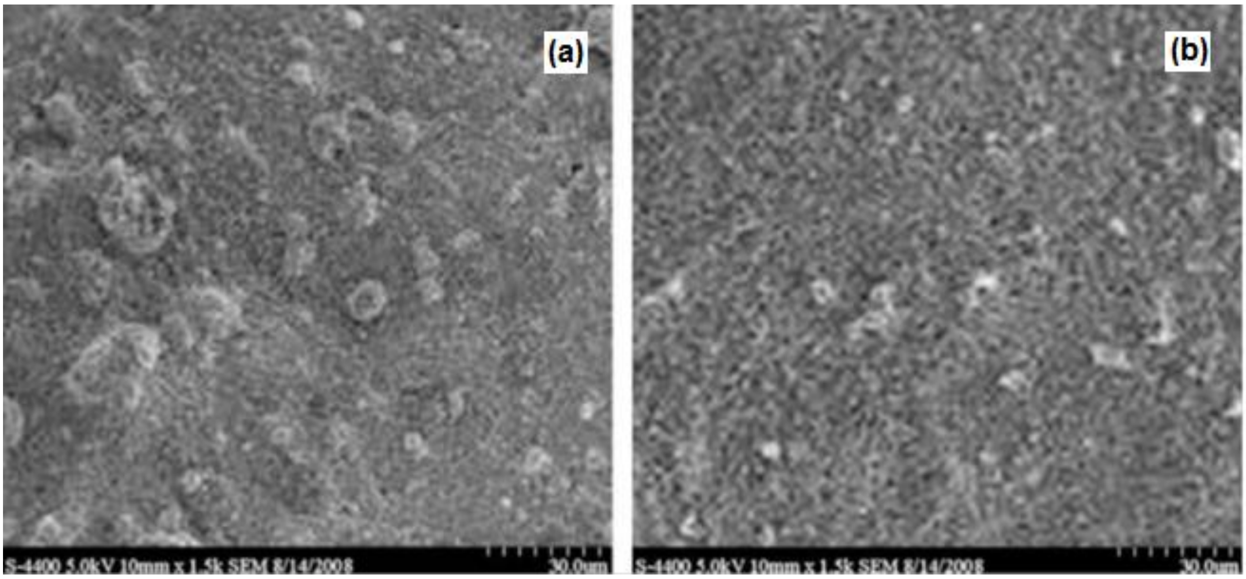

Figure 6: SEM micrographs indicating the difference of the in the surface microstructure of anodes prepared (a) by a galvanostatic pulse method (silent) and (b) galvanostatic pulse method with ultrasound [**22**].

Figure 6 shows a comparison of the microstructure of the galvanostatic pulse electrodeposition in (a) silent conditions and (b) in the presence of ultrasound. In Figure 6a agglomerates of platinum are observed which is an uneven distribution of platinum that can lead to a decrease in the utilization of the total amount of platinum deposited. Figure 6 (b) shows an even distribution of platinum with less agglomerates of platinum. This results in a larger catalyst surface area per unit catalyst deposited.

3.2.2 Method(s) of Catalyst Ink

A less complex method of MEA fabrication is the Pt/C catalyst ink approach. Lister and McLean [**21**] states that thin film methods (i.e. Nafion bound catalyst) are the current conventional method for preparing catalyst layers and that thin-film catalysts operate at almost twice the power density of that of PTFE bound catalyst layers. Pt/C powder, which can be bought off-the-shelf or prepared by *in situ* reduction of a platinum precursor, is formed into an ink by mixing it with an ionomer (usually Nafion solution). Before the use of Nafion as a binder was developed, catalyst particles were bound by hydrophobic PTFE that was cast into the diffusion layer. This PTFE layer had to be impregnated with Nafion to achieve ionic transport. PTFE was preferred because of its hydrophobicity but showed no real benefit after the incorporation of Nafion as a binder [**23**]. The ink prepared is applied either directly onto the membrane or onto the gas diffusion layer. Another alternative is to apply the ink onto a transfer decal and then hot-pressing it onto the membrane to ensure proton conductivity. This application can be done by spraying, hand painting, screen printing or inkjet printing. The brushing (hand painting) process does however have some disadvantages. Firstly is the fact that it is hard to control the uniformity of the catalyst applied and secondly it is time consuming, requiring iterations of painting/brushing, drying and weighing. Uptake of ink into the brush and evaporation of the solvent can severely affect reproducibility [**13**]. Another problem encountered with any catalyst ink approach is the fact that the Nafion membrane tends to wrinkle and swell when in contact with some solvents [**24**].

In their study, Bender *et al.* [**25**] proposed a method in which a doctor’s blade is used in an x-y plotter setup, screen printing catalyst ink onto a substrate. The doctor’s blade approach assures an even distribution of catalyst ink. Their study proved that their proposed method can largely reduce the amount of time consumed by the hand brushing technique.

Another improvement in the field of catalyst ink deposition is that spray painting severely reduces the drawbacks of the brushing process and creates a more uniformly distributed catalyst layer. Since the process is easily automated, it opened the door for commercialization.

Using this method only requires an air pressure line and a spraying head. Spraying has been used in different forms either with a commercial hobby-class spray gun or an industrial spray gun with satisfying results. Taylor *et al.* [**13**] found that there is however still an amount of catalyst wasted due to periodic clogging and amounts of overspray.

The process of inkjet printing (IJP) reduces the time of production by a significant amount as indicated by Figure 7. A drawback of this process is that, since electrochemical reaction only takes place at triple phase boundaries where reaction materials, electrolyte and electrically conductive catalyst are all in contact simultaneously [**8**], an amount of the platinum cannot be utilized because it is not exposed as a reaction surface [**26**]. With reference to this, the deposition processes where the catalyst is applied onto the carbon support after it had been set into the desired form is advantageous, as all the platinum deposited is exposed to reactants resulting in a better utilization of deposited platinum.

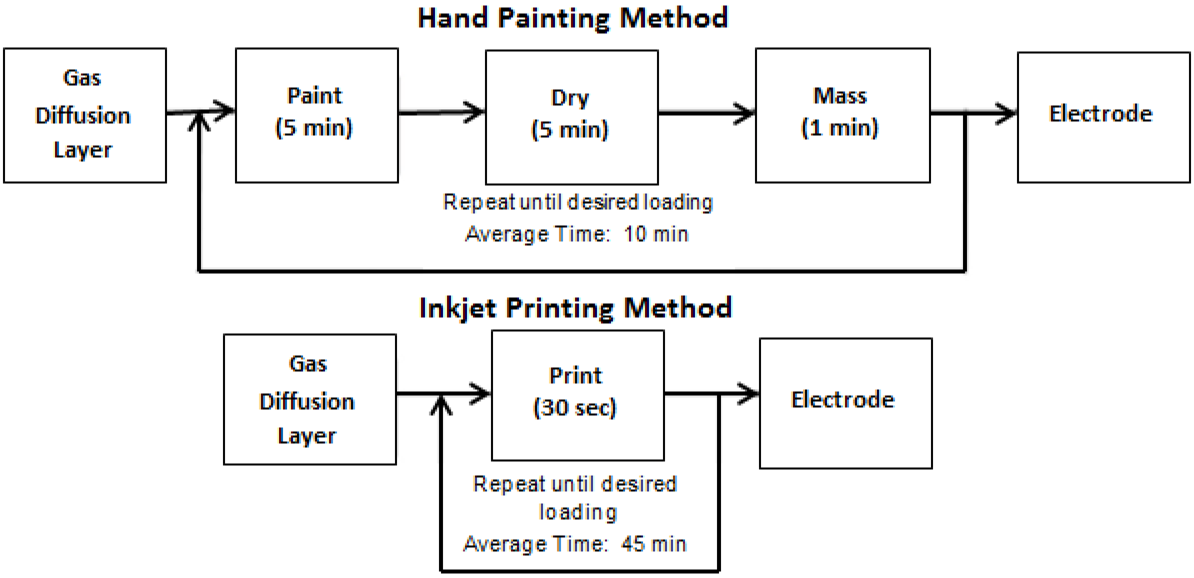

Figure 7: Time consumption comparison between inkjet method and hand painting method [**13**].

In a study done by Taylor *et al.* [**13**], inkjet printing (IJP) was used to deposit catalyst material onto gas diffusion layers. According to this study the advantage of using IJP is that the ink can be applied with extreme precision (picoliter precision) if the catalyst ink is compatible with the printer cartridge design. In this study MEA's with platinum loadings of 0.02 mg Pt/cm^2 were produced. It was found that in order to utilize this technique successfully the ink consistency and dispersion of the particles must be taken into account to prevent clogging of the nozzle. In their study a commercial Lexmark Z32 inkjet printer was used with the ink cartridge emptied, cleaned and filled with the Pt/C ink. Carbon cloth, used as GDL, was cut into the desired dimensions and taped to standard printer paper.

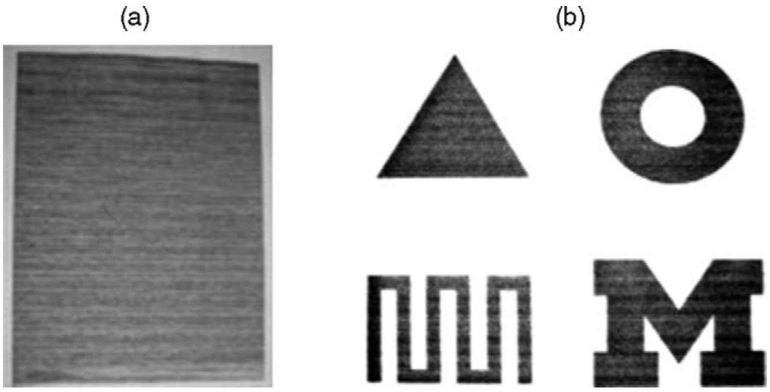

Figure 8(a) a catalyst layer and (b) various shapes printed by the IJP technique [**13**].

The shape of the carbon cloth was then printed on top of the cloth on the “best printing quality” setting to ensure the best resolution. This step was then repeated to obtain the desired loading. Figure 8 shows the product of this method and also illustrates the possibility of printing various shapes and sizes. Printing was also done successfully directly on carbon cloth and Nafion membranes. After printing, the electrodes were placed in an oven for one hour at 180˚C to dry any remaining solvent. To obtain the MEA, the anode, membrane and cathode were hot-pressed at 135˚C and 10 MPa for 5 minutes.

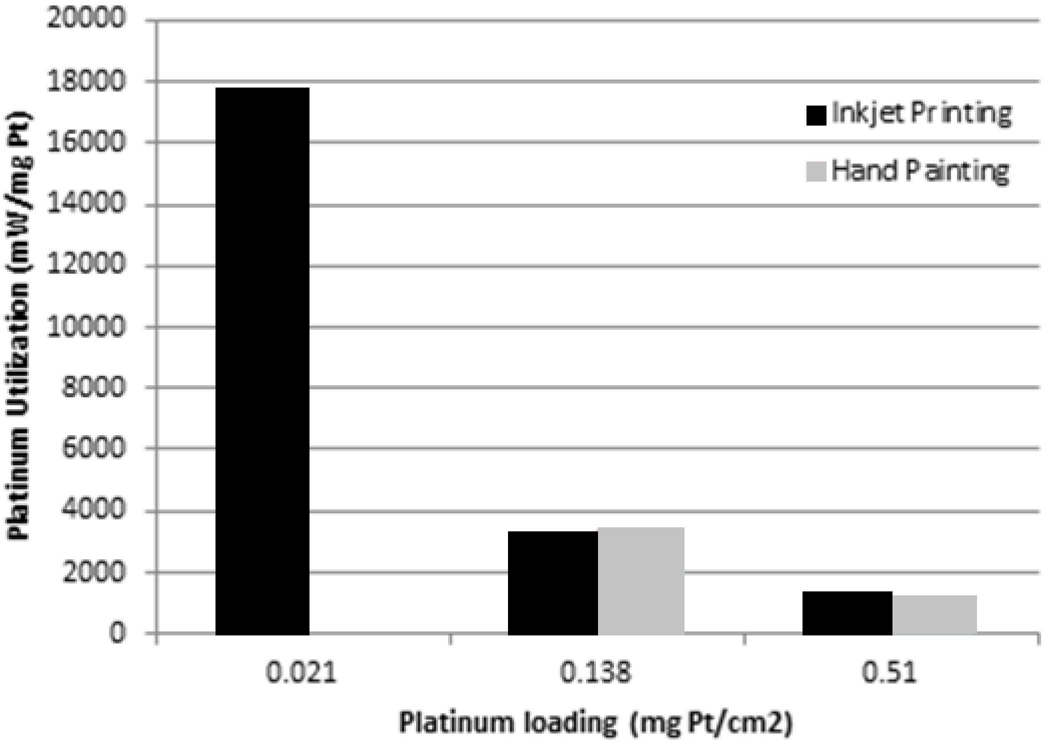

Figure 9: Histogram of the platinum utilization as a function of platinum loading for the Inkjet Printing and Hand Painting techniques [**13**].

At ultra-low Pt-loadings (0.021 mg Pt/cm^2) the IJP produces a platinum utilization of 17600mW/mg Pt (Figure 9). This low loading can however not practically be achieved with the hand painting method because of the difficulty to achieve uniformity and also the difficulty to achieve the correct loading without overloading. The study by Taylor et al. also found that the catalyst was better utilized when concentrated near the membrane. This can be achieved using different concentrations of catalyst ink for each layer printed resulting in a graded catalyst. A schematic illustration of the graded catalyst created is shown in Figure 10.

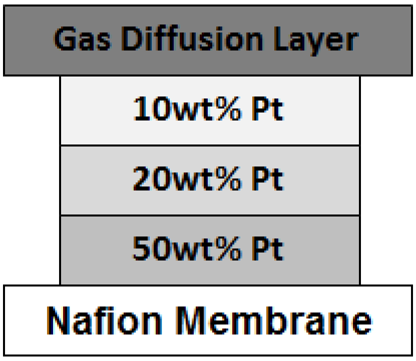

Figure 10: Drawing indicating the cross-sectional distribution of platinum for the graded catalyst layer by Taylor *et al.* [**13**].

In a study performed by Kim *et al.* [**27**], CCM's (Catalyst Coated Membrane) were produced by making using the catalyst ink spraying method. The aim of the study was to compare relative efficiencies of different ionomer loadings in the catalyst ink.

In their study, ink of 20, 25, 30 and 35% ionomer content (relative to total solid content of the ink) was spray painted onto untreated Nafion membranes (H^+ form). No hot pressing was used in this case. Results obtained from the study revealed that an ionomer content of 30wt% in the cathode and 25wt% in the anode was the optimum loading. A defect of the catalyst ink spraying method observed from this study is the fact that a relatively uneven/non-uniform surface is created making it difficult to determine layer porosity and thickness. Figure 11 presents a cross section of one of the resulting MEA's showing the uneven surface.

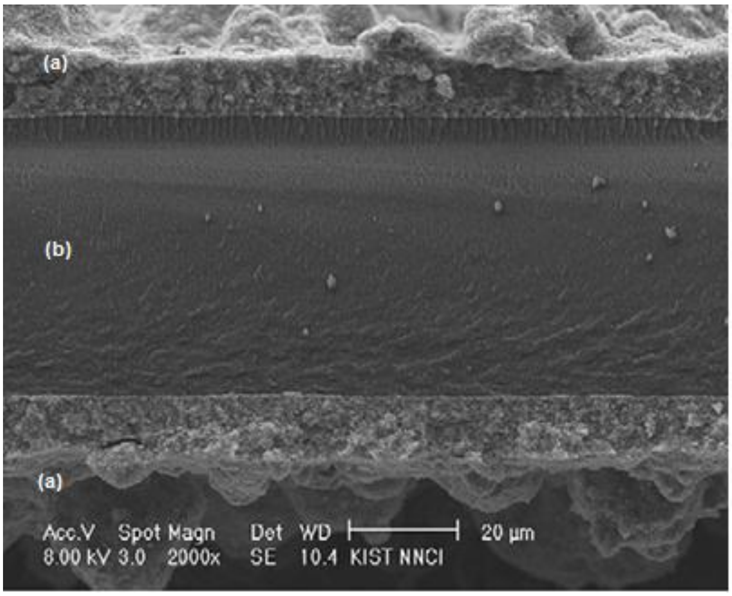

Figure 11: A cross section of a MEA in the study by Kim *et al.* (2010) indicating an uneven catalyst surface (a) applied to the membrane (b).

3.2.3 Method(s) of Impregnation

Fabrication techniques like melting, moulding and extruding would be of great benefit for the MEA industry as the current MEA's are not melt-processable [**21**]. In this fashion Kim *et al.* [**28**] produced a membrane by hot-pressing perfluorosulfonyl fluoride (PFSF) powder at 200-250℃. A catalyst ink containing only Pt/C, glycerol and water was applied to both sides of the membrane. Since the membrane can now be melted, no Nafion ionomer was required. The ink was then hot pressed onto the membrane at 200℃ embedding the catalyst into the membrane. The results were not significant but the process does show some potential in MEA manufacturing [**28**].

Ambrosio *et al.* [**29**] prepared platinum supported on mesoporous carbon by an impregnation-reduction method. Ordered mesoporous carbon (OMC) powder was impregnated with chloroplatinic acid hexahydrate dissolved in acetone. The platinum loading was determined by the amount of chloroplatinic acid hexahydrate in the solution. After stirring for 5 hours, the reduction was accomplished by treatment in hydrogen gas under vacuum at 573 K for 3 hours. An ink was created by the addition of Nafion, isopropanol and water in a certain ratio. The ink was then painted onto a 5 cm^2 area of the electrode. The platinum loading obtained was 0.5 mg Pt/cm^2. Since the study focussed on the performance of OMC as catalyst support, the study does not give any useful information on the viability of the impregnation-reduction technique as application technique for MEA's

3.2.4 Method(s) of Sputtering

Sputtering has been widely used for the manufacturing of integrated circuitry and has undergone many investigations as to its application to prepare effective low catalyst loading fuel cells [**30**]. According to Hirano *et al.* [**31**], sputtering has the potential for large scale production of fuel cell electrodes with ultra-low Pt loadings.

Taylor *et al.* [**13**] states that although thin film methods such as sputtering can achieve very low Pt loadings, there are several associated drawbacks. Probably the biggest drawback is the high capital expenditure due to the required clean rooms, high vacuum equipment and platinum targets. Another factor is that only a two dimensional catalyst surface can be created. To improve on the fact that only two dimensional surfaces can be created, separate layers can be deposited, but these are quite time consuming.

In a study conducted by Wan *et al.* [**30**], sputtering was used to produce a series of two dimensional surfaces resulting in a three dimensional reaction surface as indicated in Figure 12.

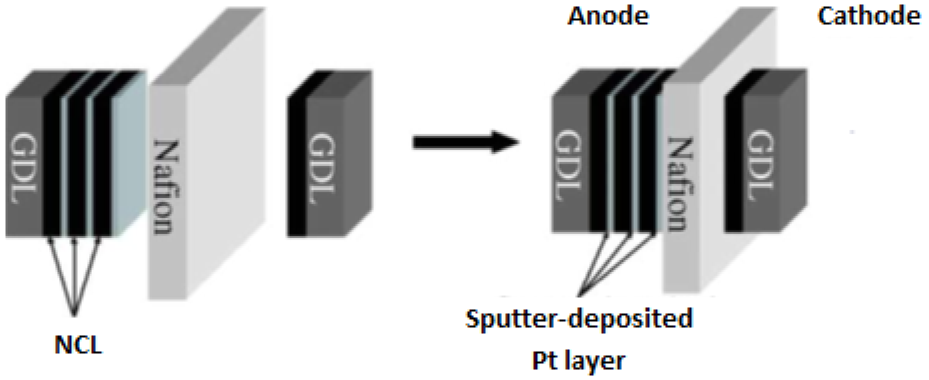

Figure 12: Schematic illustration of the series of two dimensional layers mentioned in the study (NCL = Nafion-Carbon Layer).

In their study, they state that sputtering shows great potential in reducing catalyst loading by facilitating the production of nano-scale layers as it provides a uniform distribution of catalyst. Other advantages according to them include the fact that sputtering allows the preparation of precise platinum content and thickness as well as microstructure morphology.

In their study the layers were produced in the following sequence: Firstly the Nafion-carbon ink was screen printed onto the gas diffusion layer. The GDL was then sputtered with the catalyst under vacuum. After sputtering, a layer of Nafion was impregnated on the catalyst layer by the hand brushing method. This sequence was repeated until the required amount of layers had been reached.

In a study performed by Hirano *et al*. [**31**], a catalyst layer of 1µm was deposited on top of an un-catalysed gas diffusion layer. The resulting loading was 0.1 mg/cm² and the performance thereof was similar to those of a loading of 0.4 mg/cm² produced by a standard loading method.

Kim *et al.* [**32**] performed platinum sputtering on a blend of carbon nanotubes and carbon black (Vulcan XC 72) with a specific area of 250m²/g. The reason for the blending is the fact that the sputtered platinum penetrates deeper into the carbon nanotubes (CNT) than it does into the carbon black (CB) where it is merely deposited on top of the surface as illustrated in Figure 13. The deeper penetration of the catalyst means that more catalysed reaction surface is created.

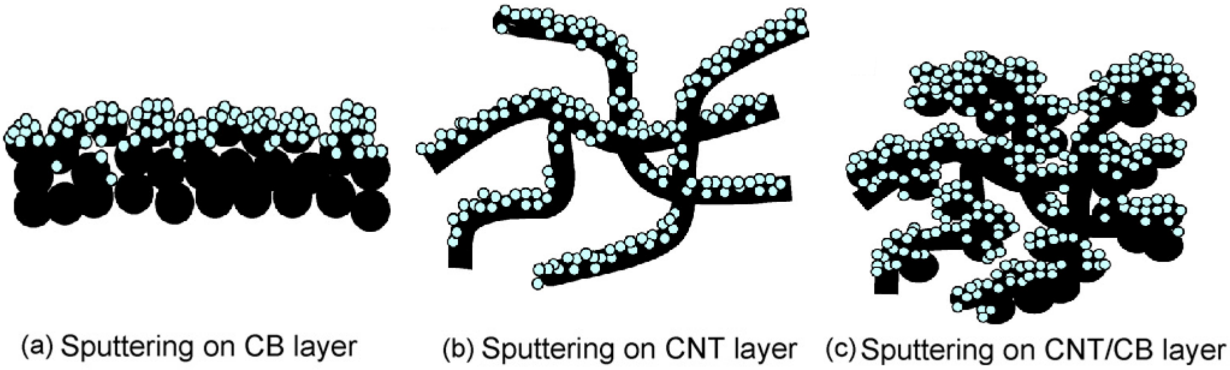

Figure 13: The effect on catalyst distribution by sputtering on (a) a CB layer (b) a CNT layer and (c) a blended layer of CB and CNTs [**32**].

The sputtered platinum penetrates deeper into the CNT because the filamentous tubes provide a more porous substrate. The idea of the mixing was to create a more porous substrate with the carbon nanotubes and to increase the specific area with the carbon black. Platinum was sputtered on the blended carbon layers with a platinum loading of 0.05 mg Pt/cm². To be able to control the Pt loading accurately, the rate of sputter deposition was kept at 0.005 mg/min.

O'Hayre *et al.* [**33**] performed a study on the sputter preparation of a catalyst on a membrane producing a very low platinum loading. In their study, platinum was sputtered directly onto membranes without carbon substrate or binder. The membranes were roughened with silicon carbide (SiC) sandpaper to test the effects of prior surface treatment. Different roughness of sandpapers, smooth-, fine-, and course, were tested (using no sanding, 400 grit and 600 grit paper). Their study concluded that the thin film on the membrane performed remarkably well in comparison with commercial technology but that it was not safe to assume that the performance would remain the same under other conditions.

One of the problems with the thin film method is their lack of water management which might hamper performance under high load performances. The roughening of the membranes showed no increase in performance and required a higher Pt load to produce the same performance as the smooth membrane. The optimum thickness of catalyst layer for the smooth membrane was 5 nm which corresponds to a platinum loading of 0.014mg Pt/cm². Performance decreased in thicker and thinner platinum layers, most probably due to changes in layer morphology. A sputtered layer of MEA with a 0.04mg Pt/cm² was produced and compared to a conventional 0.4 mg Pt/cm² MEA (Electrochem Inc.). The fabricated MEA produced a maximum power of 33mW/cm² and the conventional MEA a maximum power of 50mW/cm². This means that the fabricated MEA produced 66% of the power of the conventional one at only 10% of the platinum loading [**33**].

In a study performed by Marcinek, Song and Kostecki [**34**], microwave plasma chemical vapour deposition (MPCVD) was used to produce nano-crystalline graphitic carbon with Pt-nanoparticles. It is reported that the method is simple, fast and inexpensive. Figure 14 presents a schematic illustration of the setup used in this technique.

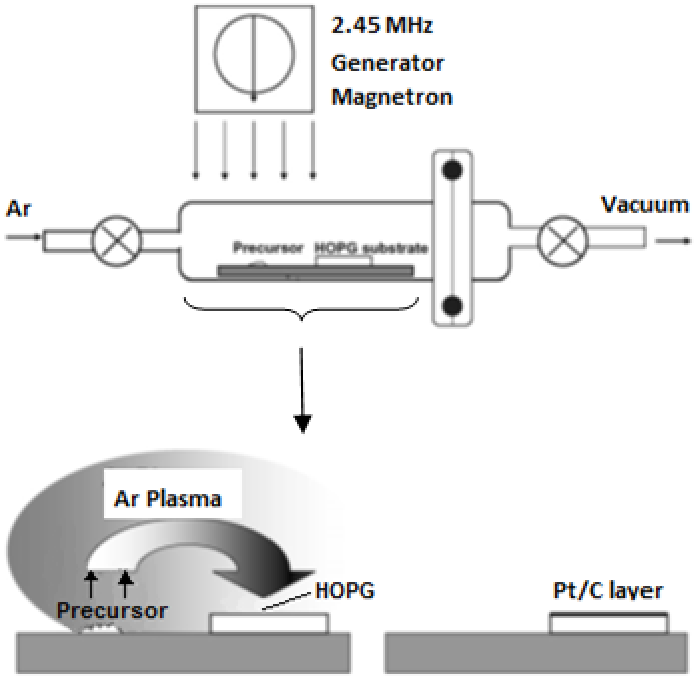

Figure 14: Illustration of the experimental setup in the study by Marcinek *et al*. [**34**] showing the components and layout.

Figure 14 shows the glass tube with fitted vacuum valves. At the one end an Argon supply was fitted while the other end was coupled to a two stage vacuum pump. The platinum precursor ($Pt(C_5H_7O_2)_2$) was placed on a glass plate with the highly-oriented pyrolitic graphite (substrate) at the other end (~5mm away). The glass tube was purged with argon and then evacuated to 1.2 x 10^{-1} Torr. The glass tube was placed close to a 2.45 GHz, 1200 W magnetron in such a way that the hot edge of the resulting plasma was near the platinum precursor and the cool edge near the substrate. The dipolar polarization of the magnetron leads to fast evaporation of the organic precursor. After 20 seconds the process produced a ~2µm thick nano-composite Pt/C layer on the substrate. The authors claim that the results were reproducible for the given precursor and deposition time. The average Pt particle size was calculated to be ~4nm.

From the literature it is evident that even though the maximum power output obtained from electrodes produced by the sputtering method does not necessarily improve on those of commercial methods, the platinum utilization is improved to a great extent as stated by Lister and McLean [**21**]. They refer to a study where 3/5 of the power of a commercial process was obtained from the sputtering process at 1/10 of the platinum loading.

3.2.5 Relevant Aspects regarding catalyst application

Apart from the actual catalyst application, some important aspects related to the application have been observed. These aspects are discussed next.

- **Ink Ionomer Content**

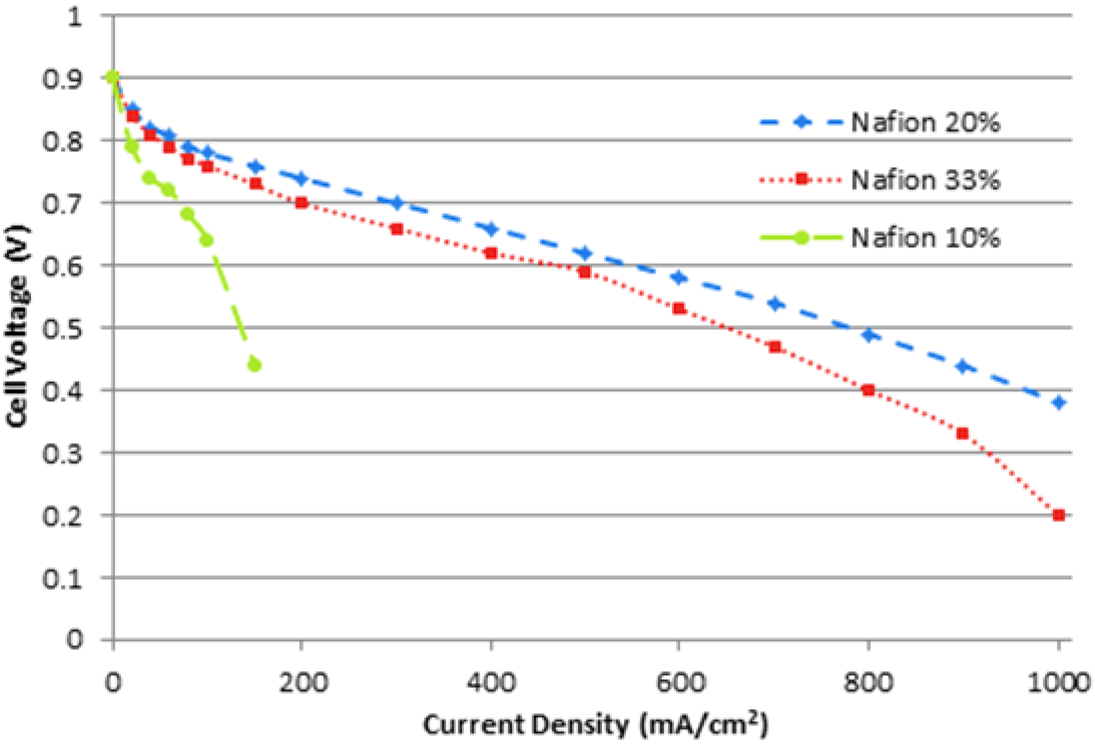

Figure: 15: Line chart of the cell voltage as a function of the current density for fuel cell electrodes with different Nafion contents as determined in the study by Sasikumar *et al.* [**12**].

The ratio of the constituents of the ink plays a very important role in the MEA performance. Not only does the constituent ratio determine the loading and practical issues like clogging, but also the chemical characteristics like mass transport and chemical activity [**21**]. Too little ionomer inhibits proton transport while a high concentration could isolate catalyst particles and lead to a reduction in electrode porosity [**35**], [**27**]. This highlights the importance of the ink ionomer content.

Sasikumar *et al*. [**12**] concluded in their study on the optimum Nafion content for polymer electrolyte membrane fuel cell electrodes that the optimum ionomer content for the electrode decreases as the catalyst loading increases. This optimum Nafion content ranges from 50wt% (50wt% Nafion and 50wt% platinum) for 0.1mg Pt/cm^2 to 20% for 0.5 mg Pt/cm^2. Their study showed the most suitable Nafion content for a Pt loading of 0.5 mg Pt/cm^2 is in the region of 20% Nafion (Figure: 15).

- **Gas Diffusion Layer**

The two types of gas diffusion layers that are commonly used in the catalyst ink approach are carbon paper and carbon cloth (Figure 16). According to Radhakrishnan and Haridoss [**36**], the carbon paper fibres are held together by a carburized resin matrix whereas the carbon cloth fibres are woven and hence the use of resin is obsolete. Kowal *et al.* [**37**] concluded in their study that the carbon paper gas diffusion layer retains more water in the flow channel of the flow field resulting in performance loss due to the flooding. The rough structure of the carbon cloth gives it a better water removal property. Based on these observations one could conclude that the carbon cloth is more suitable for high humidity conditions and the carbon paper more suitable for lower humidity conditions. A study by Mukundan *et al.* [**38**] also revealed that the carbon paper degrades faster than the carbon cloth.

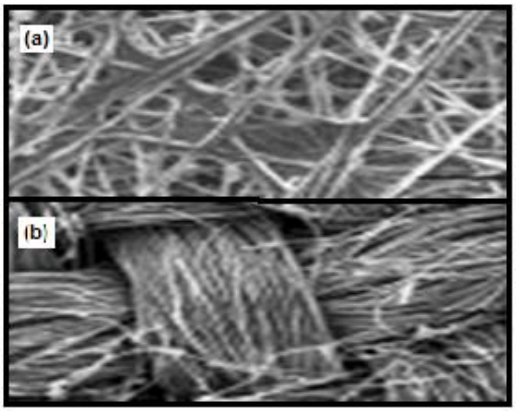

Figure 16: Structure of carbon paper (a) versus carbon cloth (b).

One drawback of the carbon cloth is however the fact that the carbon cloth can unravel at the cut edge and therefore requires careful handling whereas the carbon paper is cut and handled easily.

- **Hot-pressing**

In the literature encountered, there is a strong correlation between the hot pressing parameters (time, temperature and force) and the membrane thickness. Taylor *et al.* [**13**] in their study used Nafion 117 membranes (0.1778mm thickness) with hot pressing parameters of 135℃, 10MPa and 5 minutes. In their study on the electrospray deposition of catalyst layers, Martin *et al.* [**35**] used Nafion 112 (0.0508mm thickness) with hot press parameters of 120℃ at 10 MPa and 2 minutes. Kim *et al.* [**32**] in their study on platinum sputtered carbon nanotube electrodes used Nafion 112 (0.0508mm thickness) and hot pressing parameters of 130℃ at 7MPa and 10 minutes. The lower pressure is compensated for by the longer pressing time ensuring good interfacial bonds.

3.2.6 Summary and Discussion

A summary and discussion of the catalyst application techniques found in the literature is presented below with a focus on their advantages and disadvantages. A comparison between the techniques is presented based on the insight gained from the literature.

Electrodeposition

Since electrodeposition is a method that has been used in a wide range of applications for many years, the process is well documented in literature and equipment is readily available. Electrodeposition takes place on fine carbon particles resulting in a three dimensional reaction surface. Since the catalyst is only utilized when in the reaction zone, electrodeposition has another advantage over other methods of application because the catalyst is applied in the three phase reaction zone and no catalyst is “wasted” in areas not exposed to reactants. Problems with the dispersion of catalyst particles and mass transport in the electro deposition process can be addressed in a sono-electrochemical process. This process merely incorporates the use of a high pitch tone as described earlier in the literature study. Good results have been achieved using the simple electrodeposition of aqueous solution according to Martin *et al*. [**16**]. In their study it was found that electrodeposited electrodes show higher mass activities than standard electrodes.

Drawbacks encountered by this method include the non-uniform growth of particles and the overlapping of particles in the growing stage which in effect means that the catalyst is not utilized optimally [**18**]. A further drawback that comes to mind is that proper electroplating equipment and a fair amount of experience is required.

Catalyst Ink

The catalyst ink approach is the simplest of the techniques encountered and shows potential for improvements in various forms. Little equipment or skill is required since the catalyst is already applied to the carbon support particles. A wide variety of literature and results are available on this method. For example Lister and McLean [**21**] describe a step-by-step layout of the patent by Wilson [**39**] by which catalyst layers can be produced.

Uniformity is ensured by the fact that the binder/ ionomer (Nafion/ PTFE) is thoroughly mixed with the catalyst powder before application which results in a homogenous distribution of catalyst on the MEA [**40**] provided the ink is applied evenly.

The catalyst ink approach can however be time-consuming depending on the application method. When using the hand brush technique, several iterations of brushing, drying and weighing have to be done in order to achieve the desired loading of catalyst. When weighing, it is assumed that all solvent (ethanol/ isopropanol) is evaporated which is not always the case and can have an effect on the accuracy of the catalyst loading. This iterative process can range from 6 hours to several days depending on the degree of precision required [**25**] and even the best precision can deviate up to 12% to 13%.

There are other methods of ink application which can decrease the application time consumption. Firstly is the method proposed by Bender *et al.* [**25**]. As mentioned their doctor's blade approach drastically decreased the time consumption of the catalyst ink approach. Screen printing, from which Bender's method was derived, improves on the time consumption of hand brushing, although weighing might still be necessary. This method can be very easily mechanized leaving little room for human error and is therefore a good choice with respect to reproducibility. A serious concern regarding the screen printing method is the amount of catalyst wasted. This comes from the operating philosophy of the screen printer. A certain amount of catalyst paste is placed in front of the blade after which the blade is moved across the screen at a specified pressure, speed and angle. The blade/ spreader force the paste through the screen and onto the substrate resulting in the print. The drawback is the large amount of paste left over in front of the blade after the blade has crossed the screen relative to the amount of paste printed. This paste can hardly be used again since it may have become contaminated and its consistency changed due to the evaporation of the solvents.

The IJP method is probably the most accurate method in the catalyst ink category in terms of amount of catalyst deposited and deposition homogeneity. This accuracy is made possible by the extremely precise working of the printer. The printing also promises outstanding reproducibility which goes hand-in-hand with accuracy. Once the printer is calibrated the loading can easily be varied by changing the printing quality or amount of layers printed. The IJP method also delivers a very even distribution of catalyst and various forms or patterns can be printed depending on the design (refer to Figure 8b). Taylor *et al.* [**13**] demonstrated MEA catalyst layers successfully produced by Inkjet printing on various substrates as mentioned earlier. In their study a Lexmark Z32 printer was used with a specified droplet volume of 28 picoliters. Their article was published in 2007 indicating that the study was probably done in 2006. Printer technology has since evolved and printer droplet size currently varies between 1 and 3 picoliters which can alter the outcome of new studies. However, the small nozzle size increases the possible hazard of printer nozzles clogging.

Another commonly used method is the spray painting approach. Very little equipment is required as mentioned earlier (spray gun, compressed air supply). Better results are produced than with the hand painting method concerning reproducibility, homogeneity and accuracy. Spray painting can be mechanized with the promise of better uniformity and less time consumption. A severe drawback however the matter of time consumption since the sprayed catalyst layer has to be dried and weighed for several iterations to achieve the desired load within acceptable limits. Another drawback is the amount of catalyst wasted due to periodic clogging. This can however be overcome/ addressed since a vast variety of spraying nozzles are available. Spray painting has been used in several studies with satisfactory results especially for producing the control in the experimental setup ([**24**], [**41**], [**42**], [**8**], [**32**]).

Impregnation/ Impregnation-reduction

The impregnation of the membrane by the catalyst material was only encountered in one instance in the literature study. It appears that the impregnation method was mainly carried out as an experiment to evaluate its feasibility and is not used as a commercial method.

Sputtering/ Vapour Deposition

The sputtering process has the potential of creating a catalyst layer of very low loading. Extremely fine particles are dislodged from the target surface with high energy ions and deposited on the part surface resulting in a high specific surface area.

Advantages of this process include the fact that the catalyst loading can be controlled very accurately by controlling the duration of sputtering and that an ionic transport medium is not needed when a simple catalyst layer is formed on the membrane because of the intimate contact between the catalyst and the membrane. Sputtering is a highly commercialized technique in other industries used for thin-film deposition and can be used for the large scale manufacture of PEM fuel cell electrodes [**31**]. Wan *et al.* [**30**] state that the process is simple and should therefore be investigated as a preparation technique for PEMFC electrodes. Sputtering as a catalyst application technique does however have some drawbacks according to Kim *et al.* [**40**]. Firstly is the fact that very expensive equipment and platinum targets are required and secondly only two dimensional surfaces can be created. This problem can be addressed by depositing alternate layers of catalyst and Nafion to create a three dimensional reaction surface. The method is very time consuming since the sputtering process has to be stopped for each layer created, ionomer applied and the process resumed. It has to be kept in mind that a vacuum has to be formed again before the sputtering can continue. Another disadvantage of this method is that ultra-clean vacuum chambers are required.

Comparison of Methods

From the literature studied, a comparison of the methods based on qualitative parameters and perception of the feasibility of the application techniques is presented in Table 1.

Table 1: Qualitative comparison of techniques in literature

Method	Electrodeposition	Catalyst ink	Impregnation	Sputter
Available literature	Large amount of literature available	Large amount of literature available	Very little literature available	Literature available
Advantages	Have been used in commercial applications, promising results in terms of catalyst application	Promising results in terms of commercially, good experimental results, currently used commonly, Limited skill required, Few equipment required	Low loading can be achieved	Capabillity of producing thin layers and thus low loadings, very fine particles. High performance with low Pt loading.
Disadvantages	Expensive equipment required, Experience required	Limited catalyst exposure to gas, Waste of catalyst	Very little information available	Expensive equipment, expensive Pt target
Complexity	Medium	Low	High	Low
Practicality	Good	Very good	Bad	Good
Time consumption	Medium	Low-medium	High	Low-medium

Based on the findings as summarized in Table 1, variations of the catalyst ink approach to catalyst application were selected to be evaluated. The selected variations of the catalyst ink approach are the (i) hand painting technique, (ii) inkjet printing technique, (iii) spray painting technique and (iv) screen printing technique.

4. Experimental Procedures

4.1 Introduction

In the previous chapter the literature studied in terms of catalyst application techniques as well as aspects relevant to these techniques were reviewed and discussed. Based on the aim of the study, this chapter deals with the experimental procedures associated with the catalyst application via each chosen technique.

Before continuing with the experimental procedure, it is necessary to discuss some technical aspects related to the fabrication of MEA's in this study.

4.2 MEA Structure

Figure 17 shows a simplified schematic drawing of an electrolyser (current collectors, gaskets and fasteners omitted for clarity) to serve as a base for further discussion.

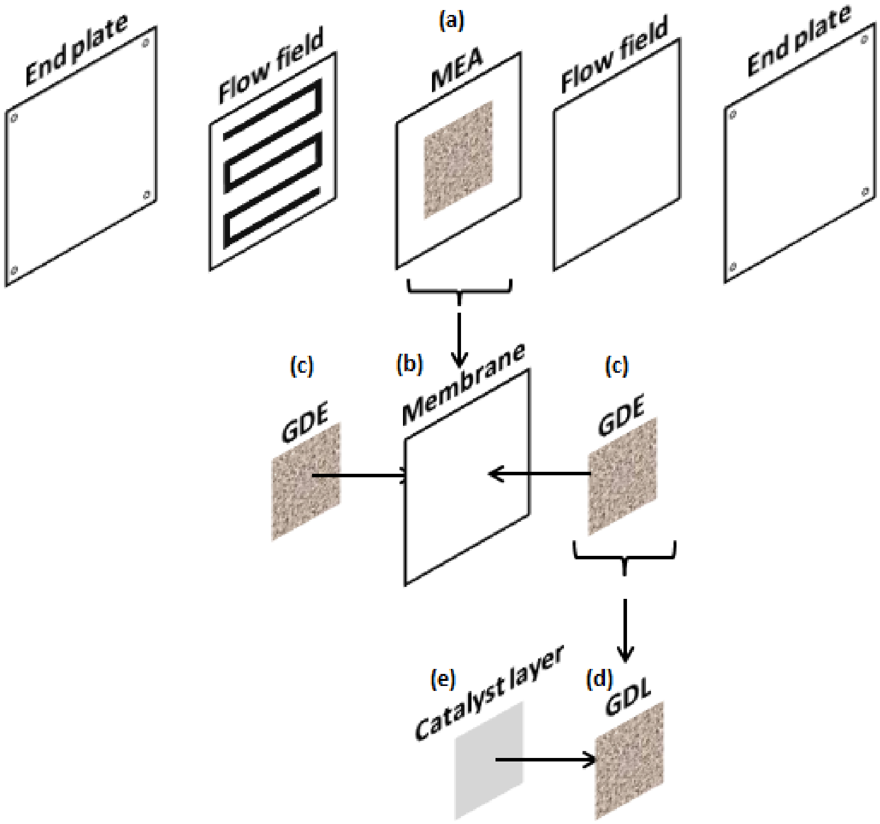

Figure 17: Schematic drawing showing the location of the applied catalyst layer.

Catalyst Layer Location

The Membrane Electrode Assembly (Figure 17a) is positioned between the flow fields in the assembled electrolyser. The MEA consists of the membrane (Figure 17b) and two identical gas diffusion electrodes (Figure 17c), one at each side. The GDE consists of a gas diffusion layer (Figure 17d), in this case carbon cloth, upon which a catalyst layer (Figure 17e) is applied.

Catalyst Layer

Two important aspects in the production of a catalyst layer using catalyst ink is the catalyst loading and the ink composition.

As one of the fixed parameters, the catalyst loading was chosen as 0.5mg Pt/cm^2 since good results have been obtained in various studies in the literature using this catalyst loading. This meant that a total dry ink mass of 78.1 mg had to be deposited onto each GDL.

The ink composition encountered in different cases in literature was studied. The most basic ink composition consisted of catalyst powder in the form of platinum deposited onto carbon black (Pt/C), Nafion solution and an alcohol solvent. In some instances ethylene glycol was added as a thickener.

In this study the same ink composition as in the study by Taylor *et al.* [**13**] was used because of the good results achieved and its suitability for Inkjet printing. The ink consisted of 75wt% Pt/C powder (20wt% Pt on Vulcan XC-72, Fuel Cell Store) and 25wt% Nafion (Sigma-Aldrich, 5wt%, in lower aliphatic alcohols and water). The 25wt% Nafion refers to the dry Nafion content of the Nafion solution. The Nafion content is in close accordance with the guideline given by the results of the study by Sasikumar *et al.* [**12**] for platinum loadings of 0.5 mg Pt/cm^2. The exact composition of a typical mixture of ink consisted of 50.3 mg Pt/C powder, 383 µl Nafion solution, 3.0 ml methanol as solvent and 200 µl deionised water.

The ink was prepared by carefully weighing the Pt/C powder and measuring the Nafion solution, deionized water and alcohol. Because of the small volumes, an insulin syringe was used to measure the volumes of Nafion solution, deionized water and alcohol. The same scale (Sartorius) was used for all the weighing carried out in this study. The deionized water was added to the Pt/C powder to prevent the alcohol solvent or the alcohol in the Nafion solution from reacting with the platinum resulting in platinum oxidation. The mixture was then stirred with a micro stir bar for one minute and ultra sonicated for one minute to ensure the dispersion of the water. Next the Nafion solution and the methanol were added and the mixture ultra-sonicated for 30 minutes and stirred for 30 minutes. The mixture was left overnight and inspected for settling or agglomeration.

This procedure was followed for the preparation of ink for all the methods with the addition of ethylene glycol as thickener for the screen printing technique. For each method the viscosity of the ink was adjusted by evaporating some of the solvent from the mixture by stirring in a well-ventilated room.

Membranes

In the catalyst ink related literature studied, a wide variety of Nafion membranes were encountered. The most commonly used membranes are Nafion 212 (0.002 in. thickness), 115 (0.005 in. thickness) and 117 (0.007 in. thickness) membranes.

Because the membrane electrode assembly is bonded by hot pressing at high temperatures and pressures, the thicker Nafion 117 membranes was used to prevent damage caused by the heat and pressure. To ensure accuracy when cutting the membranes, it was decided to use a locally available 30W laser engraving/cutting machine (Trojan).

The synthesis process by which the membranes are formed might leave behind an amount of organic matter. To prevent contamination from this organic matter, the membranes were cleaned by boiling in 3wt% hydrogen peroxide solution for one hour and again rinsing it twice in a 3% hydrogen peroxide solution. The membranes were thereafter stored in deionized water for further use.

Gas Diffusion Layer

Based on the insight into the water handling capabilities and degradation characteristics of carbon paper and carbon cloth gained from the studies by Kowal *et al.* [**37**] and Mukundan *et al.* [**38**], carbon cloth was used as gas diffusion media and catalyst layer supporting substrate. The carbon cloth was cut by a laser to ensure accuracy and prevent unravelling of the cloth.

MEA Dimensions

For evaluation in an electrolyser, the MEA’s physical dimensions had to be compatible with that of an available electrolyser, situated at the Chemical Research Beneficiary Focus Area of the North-West University. This meant that the following dimensions were fixed for the fabrication of the MEA’s:

- Membrane: 7x7 cm
- GDE: 5x5 cm

The membranes were at first cut to a square of 8x8cm to ease the centring of the GDE’s on the membrane. After the hot-press bonding, MEA’s were trimmed to the exact required dimensions.

MEA Materials

The following materials were procured for the experimental procedure that was followed:

- Membranes (Nafion 117, Fuel Cell Store)
- Carbon cloth GDL (AvCarb Grade 1071 HCB, Fuel Cell Store)
- Catalyst powder (20 wt% Pt on Vulcan XC-72, Fuel cell store)
- Nafion solution (5wt%, in lower aliphatic alcohols and water, Sigma-Aldrich)

4.3 Catalyst layer application techniques

In an attempt to get familiarized with the techniques selected, **test runs** were carried out producing mock electrodes with each of the selected techniques. These test runs revealed hidden difficulties regarding the techniques and are presented in **Appendix A.**

The application procedure followed for each of the application techniques is now presented.

Hand Paint (HP)

A setup (Figure 18) was built for the hand painting and spray painting techniques. The setup consisted of a steel backing plate (Figure 18a) heated from the back by a 40W incandescent lamp. The heated plate decreases the drying time of the applied ink. Holes drilled into the plate allowed suction to be applied from a suction device (Figure 18c) to hold the GDL in place on the steel plate while the ink was being applied. A holder and a disposable mask (Figure 18d) assisted to position the GDL while keeping the ink away from the rest of the setup. A very fine hand paint brush was used for the painting process. A carbon cloth square was inserted into the setup and iterations of painting, drying and weighing were repeated until the desired loading as calculated, was achieved. This same sequence was repeated for a second and third sample. The produced GDE’s were labelled HP1, HP2. At a later stage another GDE, HP3, was produced and mounted to investigate the cross sectional microstructure via Scanning Electron Microscopy (SEM) analysis.

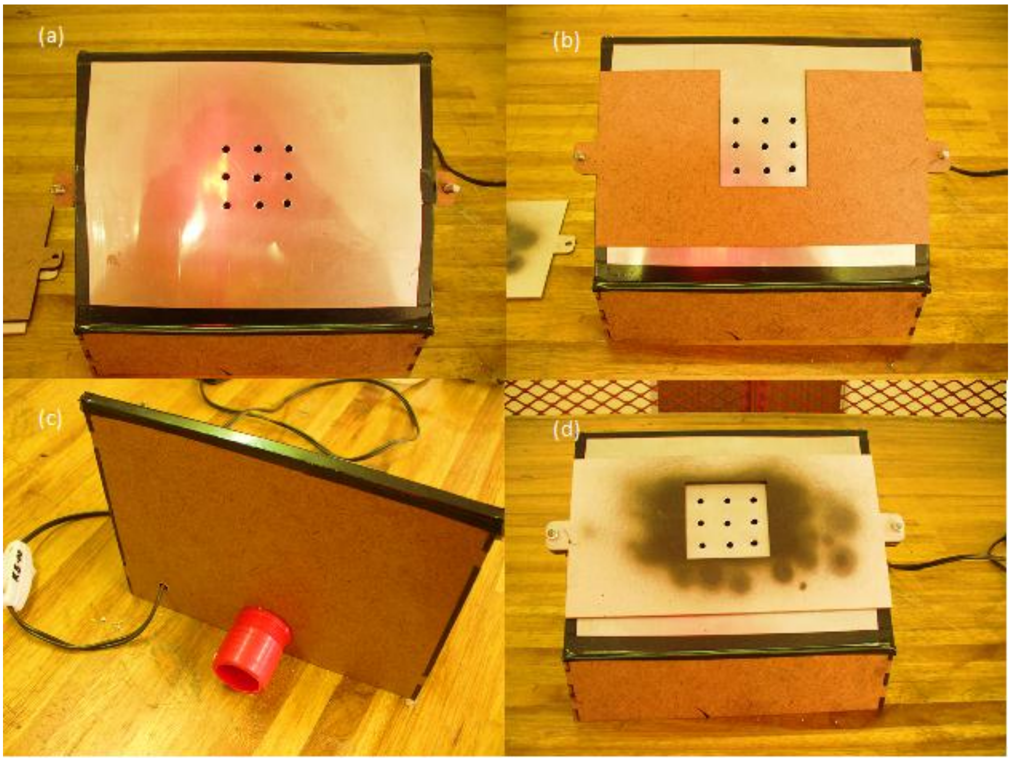

Figure 18: The setup built for the hand painting and spray painting of catalyst ink.

Spray Paint (SP)

An airbrush (Iwata Revolution, Tool & Professional Services) was used for the spray painting technique (Figure 19). The airbrush specifications specified a 7ml reservoir and a 0.5mm nozzle opening. Compressed air at a constant pressure of 200kPa was supplied via a hobby class compressor (Puma, Tool & Professional Services) and regulator (Figure 19). The optimum regulator pressure was determined by trial and error in the test run in order to optimise deposition and minimise overspray.

The cut carbon cloth was placed on the setup as described for the hand painting. The ink was then sprayed onto the cloth evenly in a z-pattern and dried to be weighed after each coat. This process was repeated iteratively until the desired loading was achieved. The first GDE made by hand painting was designated SP1. The same procedure was followed to produce the second electrode, SP2. At a later stage another electrode, SP3 was produced and mounted for the purpose of cross sectional investigation via SEM analysis.

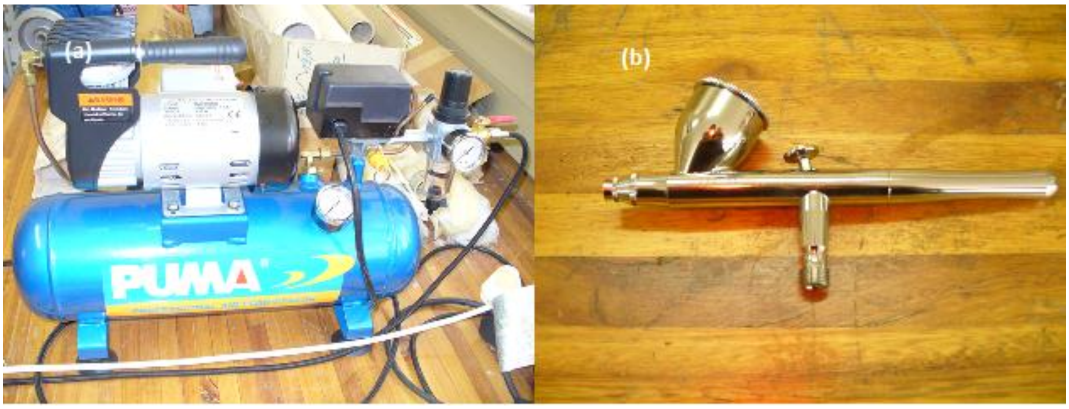

Figure 19: The compressor (a) and the airbrush (b) used for the spray painting.

Inkjet Print (IJP)

A HP Deskjet D1663 printer (Figure 20) was used for the inkjet printing technique with the printing settings set to black and white and *Best Printing Quality*. The specifications of the printer specify a maximum resolution of 600x600 dpi (black and white). The cartridge (Figure 20) specification specify a printer droplet size of 13.8 picolitre (13.8 x 10^{-12} litre).

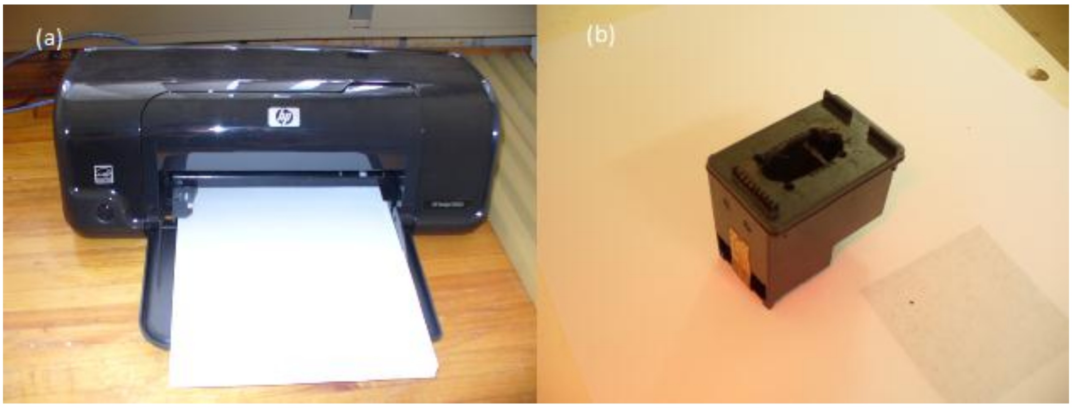

Figure 20: (a) The HP printer used in the study and (b) the cartridge with the machined hole.

In the case of the inkjet printing, the ink quality and viscosity is very important. Any settling or agglomeration could cause clogging of the printing nozzles resulting in poor printing quality. If the viscosity is too high the ink might get stuck in the printing head. On the other hand a low viscosity might cause the ink to leak out of the cartridge head.

Since no viscosity measuring facility was available, a procedure was invented to compare the viscosity of the manufactured ink to those of standard HP printer refill cartridges. This was done by a very simple method giving acceptable relative results. The viscosity was compared by placing two glass plates next to each other both at an angle of 7 degrees. Equal sized drops of the respective inks were then placed on the plates and the distance travelled in 30 seconds measured (Figure 21). The viscosity of the Pt/C ink was then adjusted by adding or evaporating some of the solvent (methanol). This does not affect the chemical ratio of the catalyst applied to the electrode since all the solvent is evaporated after the electrodes have been produced. Although an iterative process, the test was fairly simple since the initial viscosity achieved was in the range of those of the replacement ink.

Figure 21: The viscosity tests and adjustments showing the results for the replacement ink at the left and the adjustments (1-3). The final adjustment showed a good comparison with 10.5mm (3) compared to 11mm (control)

When printing with the catalyst ink, it is crucial that the printing cartridge is cleansed of any residual printer ink beforehand since this residual ink can influence the loading accuracy and also clog the printing head if dried.

The cartridge was cleaned by first machining a hole into the top of the cartridge. The content of the cartridge was disposed and the cartridge was immersed into acetone and cleaned in an ultrasonic bath for 30 minutes. After the 30 minutes the cartridge was removed from the acetone and left to dry.

Before the cartridge was removed from the printer, a square the size of the GDL (5x5cm) was printed onto a standard A4 photocopy paper to indicate the position of the GDL. This square was then cut out and the GDL inserted into the square. The GDL was taped at its back with masking tape to hold it in place. This setup also reduces the chance of the GDL colliding with the printer head as the GDL is much thicker than the paper.

The catalyst ink was then inserted into the cartridge and left for 5 minutes. A small square was printed onto a paper to verify the printing of the catalyst ink.

Screen Print (ScP)

The pressure regulator feeding compressed air to the screen printer (Systems Automatic, model SA F1-12) was set to 600kPa. Ink was drawn up into a suction tube and pipetted in front of the spreader (Figure 22). The carbon cloth square taped to a transparency was placed on the suction plate and its position relative to the screen mesh (160 mesh size, printing area 5x5cm) verified by switching on the vacuum pump and lowering the carriage. The foot pedal was then activated lowering the carriage after which the flood switch was activated. After the spreader had passed down the travel length over the screen, printing a square of catalyst ink, the flood switch was flipped back and the carriage lifted up and returned to its original position.

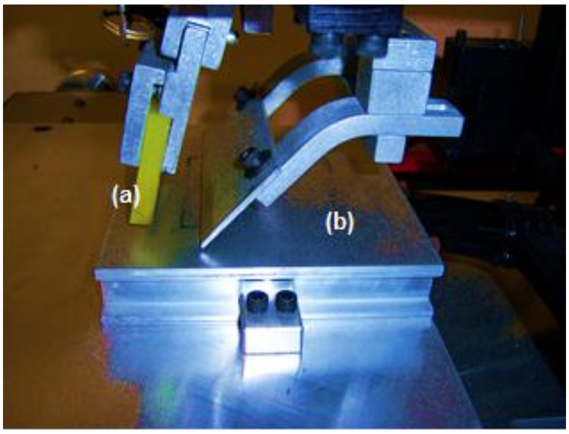

Figure 22: The (a) spreader and (b) suction pad of the screen printer.

After every second layer of catalyst ink was applied, the gas diffusion layer was placed in a drying oven (LABOTEC EcoTherm) at 55° C to dry the ink. After each layer the electrode was rotated to compensate for the fact that the screen printer prints from one side consuming the ink as it goes. After 5 minutes of drying the electrode was weighed and the steps repeated. This was repeated several times until the required loading was achieved. The GDE’s produced were labelled ScP1 and ScP2. Another GDE, ScP3 was produced at a later stage and used for cross sectional investigation via SEM analysis of resin-mounted samples.

4.4 Investigation of Microstructure

The microstructure of the catalyst layers applied to the GDL’s by each of the selected methods was investigated by SEM imaging and SEM element mapping conducted at the SEM Laboratory at the North-West University. The results of the SEM analysis are presented in the next chapter.

5. Results and discussion

5.1 Final Catalyst Loadings

The results of the catalyst application procedures as presented in the previous chapter is summarized and presented in **Table 2**.

Table 2: Final weight and loading figures for the manufactured electrodes

Materials	Samples					
	HP1	**HP2**	**SP1**	**SP2**	**ScP1**	**ScP2**
Dry GDL (g)	0.285	0.282	0.282	0.288	0.282	0.282
Req. GDE (g)	0.363	0.360	0.360	0.366	0.360	0.360
Final GDE weight (g)	0.365	0.361	0.362	0.366	0.370	0.369
Dry ink loading (g)	0.080	0.079	0.079	0.079	0.088	0.086
Pt loading (mg/cm²)	**0.512**	**0.503**	**0.508**	**0.502**	**0.563**	**0.553**

The GDE's was weighed after the allocated drying period and the weight verified after 48 hours. As indicated in Table 2, the desired catalyst loading of 0.5 mg Pt/cm^2 was achieved with satisfying accuracy, especially for the hand painted and screen printed electrodes. The little variation in loading for the different GDE's produced by each technique indicates the accurate repeatability of the techniques.

5.2 SEM Analysis and Results

Scanning electron microscopy images were used to investigate the microstructure of the produced GDE's. The distribution of the different constituents of the catalyst ink was verified by SEM element mapping. The SEM analyses are discussed next.

5.2.1 Microscope Imaging

- **Gas Diffusion Electrodes (GDE's)**

The microstructures on the frontal surface of the gas diffusion electrodes prepared by the various techniques were investigated by SEM imaging at magnifications varying from 60x to 5000x. Images were also obtained at the edge of the GDL to investigate the coating homogeneity at various positions on the GDL.

Figure 23 presents SEM images obtained at 60x magnification at the edges of the electrodes. It is clear from Figure 23a that the coating homogeneity of the catalyst ink is poor towards the edges of the electrodes prepared by hand painting. This is due to the experimental setup where the edges were not completely accessible to the ink or the ink brush. The geometric setup of the painting also had an influence on the poor homogeneity. Because of the fact that an amount of ink would be lost if the edge is overlapped by strokes of paint, it is possible that the brush strokes were applied at a small distance from the edge (approx. 1mm). This could have led to a catalyst gradient from the inside of the electrode frontal area towards the edge, as indicated in Figure 23a.

The edge coating effect is minimal if at all present with the spray painting and screen printing techniques as indicated in Figure 23b and Figure 23c. The spray painting technique produced an extremely homogeneous catalyst distribution on a macro level (Figure 23b). This in turn, however, is accompanied with an amount of catalyst ink wasted due to overspray.

The gas diffusion layer frontal area was almost completely covered with porous catalyst structures creating a nearly pseudo-continuous layer. The continuity of the layer would be better if a more even and continuous gas diffusion layer such as carbon paper was used instead of the relative uneven carbon cloth.

The images in Figure 23 clearly point out that the ink has penetrated deeper into the carbon cloth with the hand painting (a) and screen printing (c) technique than with the spray painting (b) technique. The ink penetrates deeper into the carbon cloth with the hand paint method since relative large amounts of liquid (ink) were deposited onto the layer with every stroke. This forces a large amount of ink deeper into the cloth. The second reason is the fact that once a layer has dried and another layer is applied, the repetitive strokes of the brush damages and even removes the relatively weak and brittle structures formed on the frontal surface while only the deeper more protected structures survive. In the case of the spray painting, the layers form consecutively on one another without damage to the previous layers resulting in the very porous and rough structure.

In Figure 23c it is clearly visible that ink (light-grey to white as indicated by backscatter images in Figure 23a and Figure 24c) is present at the edges of the electrode in contrast with those done by hand painting. This even distribution is due to the fact that the screen dimensions are exactly the same as the carbon cloth printed onto (5x5 cm), therefore giving equal access to all the areas on the cloth including the edges.

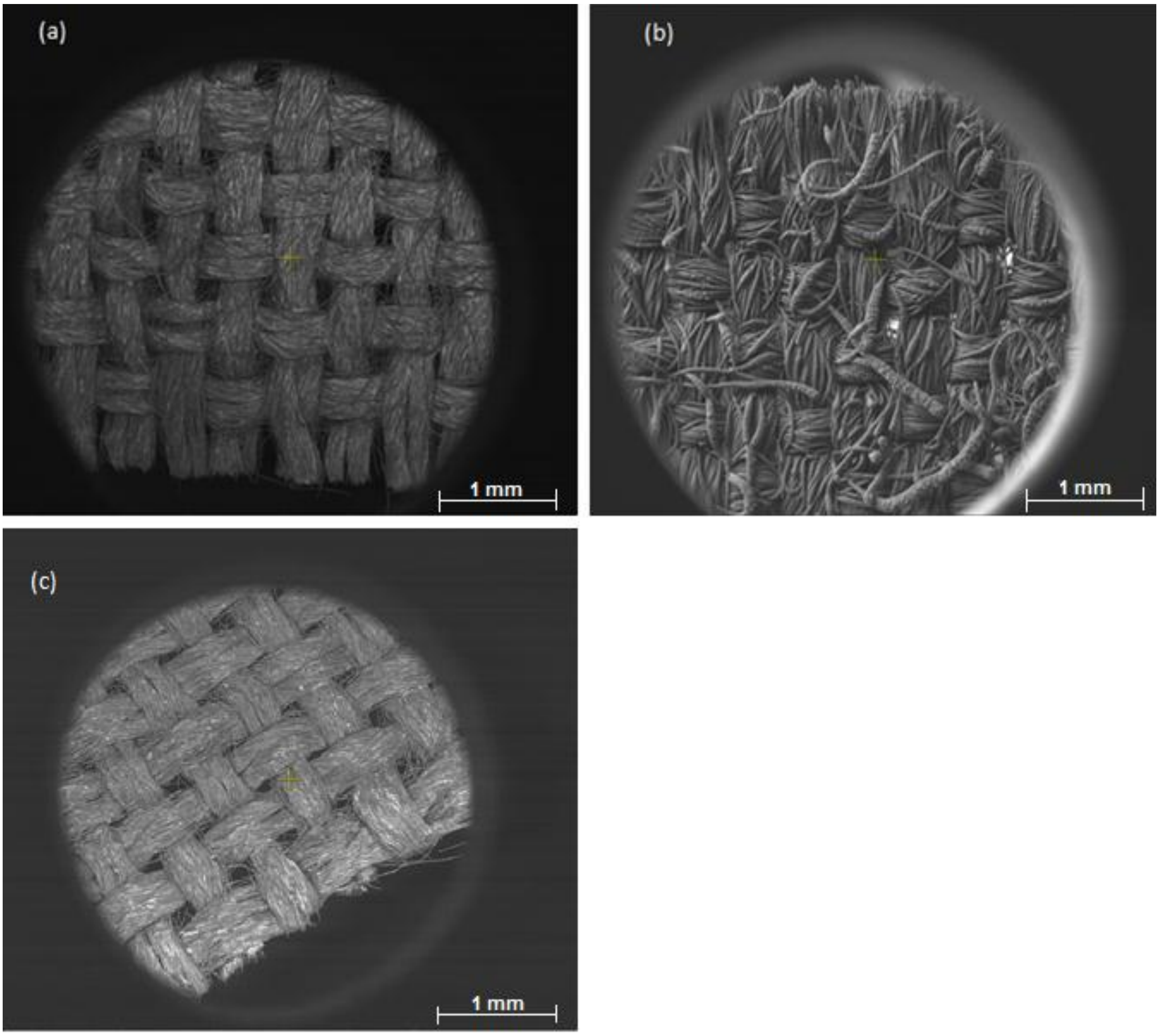

Figure 23: SEM photos taken at 60x magnification of the face of the GDE’s indicating an ink gradient towards the edge of the electrodes produced by (a) the hand painting technique (backscattered image), but none for the (b) the spray painting technique and (c) the screen printing technique (backscatter image).

Images obtained at 120x magnification are presented in Figure 24. This gives a good indication to the degree at which ink is concentrated to the surface of the electrode. Figure 24a presents the electrode prepared by hand painting having a concentration of ink just below the surface indicated by the white-grey areas between the carbon filaments. The reason for the lack of ink on the immediate top surface has been previously discussed.

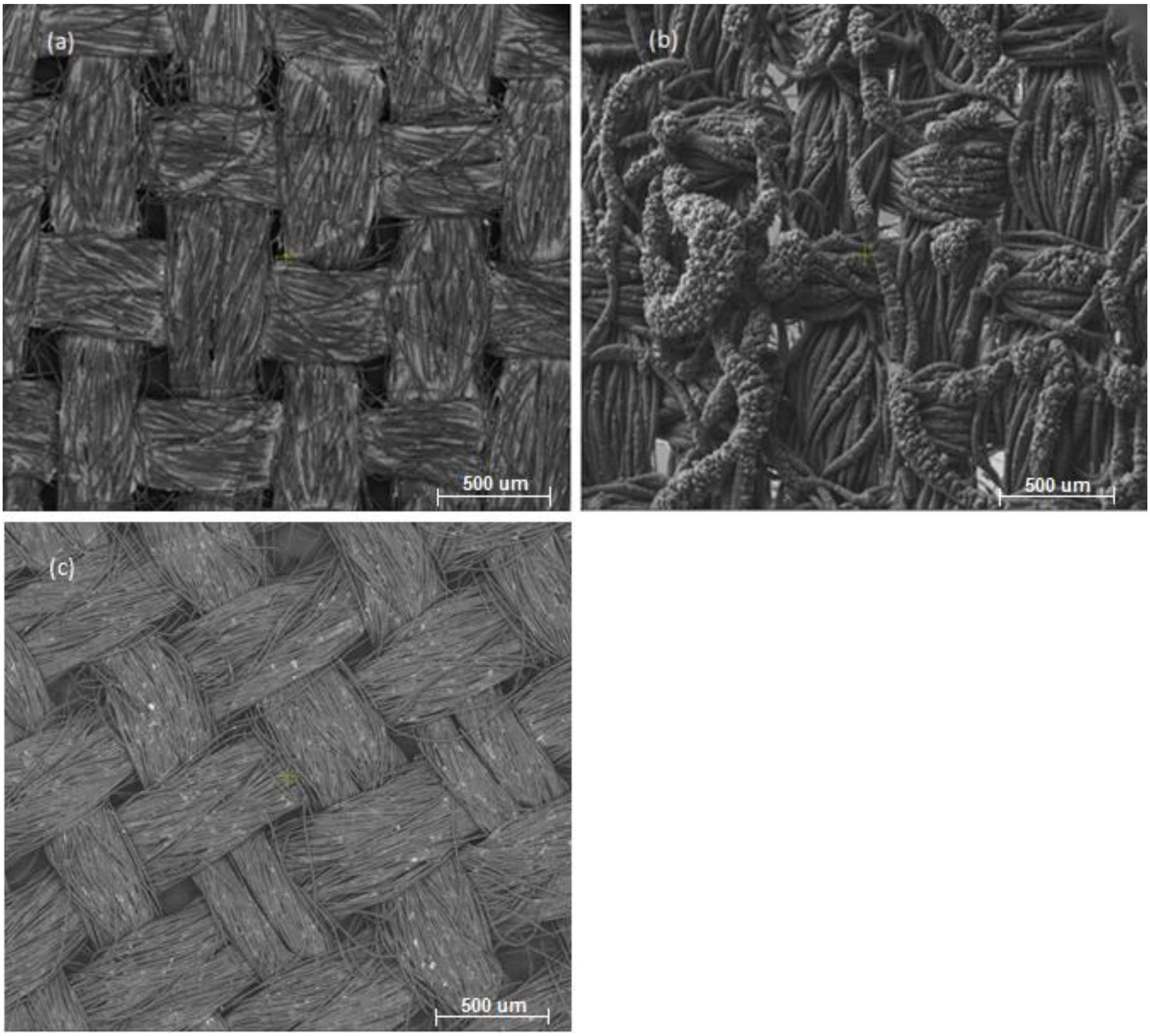

Figure 24: SEM photos at 120x magnification of the GDE's prepared by the (a) HP technique (backscattered image), (b) SP technique and (c) screen printing technique (backscattered image).

Electrodes prepared by spray painting (Figure 24b) indicate an intense concentration of ink at the immediate top surface with all visible carbon filaments covered with catalyst ink. This is due to the fact that the spray mist of ink arrives at the surface of the electrode with minimal or no force and adheres to the nearest surface where any residual solvent that has not evaporated in flight, evaporates. As the solvent evaporates, large amounts of open porous structures are formed creating a large surface area open to electrochemical reactions. None of the other techniques used so far in this study to produce GDE's have produced electrodes where the ink is so concentrated on the surface of the GDL.

Ink concentrations at the surface of screen-print prepared electrodes (Figure 24) are very low in comparison to the other methods. Weight gain measurements taken before and after application of the ink however verified that the same amount of ink was present on the electrode. This indicates that the ink had penetrated deeper into the carbon cloth.

Images taken at 5000x magnification (Figure 25) gives good insight into the porosity of the structures formed.

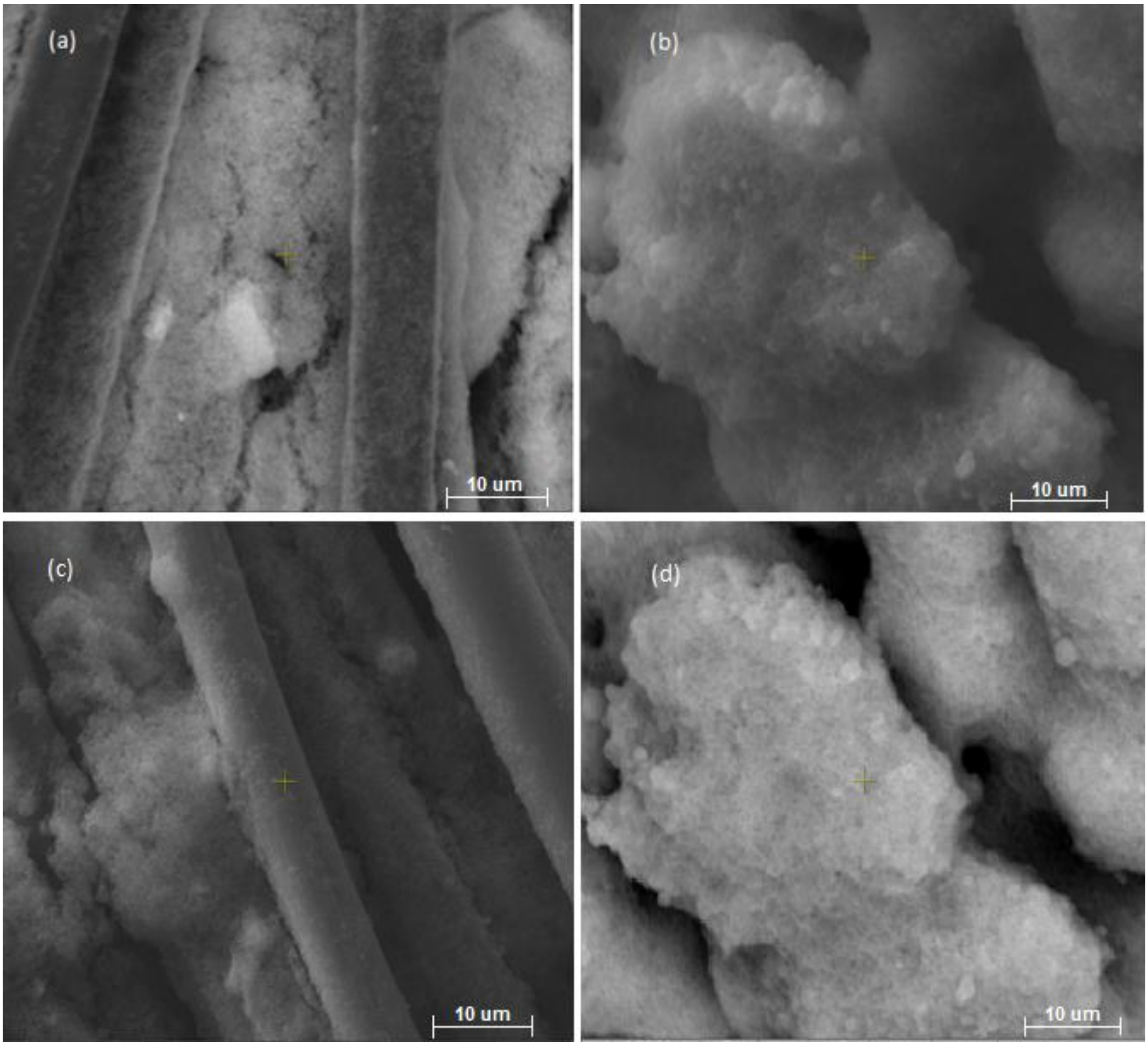

Figure 25: SEM photos at 5000x magnification of the (a) HP technique (backscattered image), (b)+(d) the SP technique and (c) the screen printing technique showing the porosity of the electrodes.

Even though the hand painting did not form large agglomerates, the ink structures that formed between the carbon-filaments are porous and open promising a large specific electrochemical area. The brighter white spots (Figure 25a) are more solid/dense ink structures although SEM element analysis have shown that large concentrations of platinum exists inside these “clumps”. This large platinum concentration could be due to the high ink concentration or more likely near-solid agglomerations. These agglomerations could have formed from platinum removed from the carbon black when exposed to ultra sonication. This effect is highly undesirable since this non-porous agglomeration reduces the active platinum area exposed to electrochemical reaction in effect reducing the platinum utilization.

Figure 25b shows one of the microstructures formed with the spray painting technique. These structures, even though more dense than those in Figure 25a, produced by the hand painting, are still mighty porous providing a high specific area. The porosity has been verified with a backscattered image of the same location and magnification as in Figure 25d. Although these microstructures repeat, they are not completely continuous allowing the transportation/migration of reaction products. The distribution of these microstructures on the GDE surface is illustrated in Figure 26.

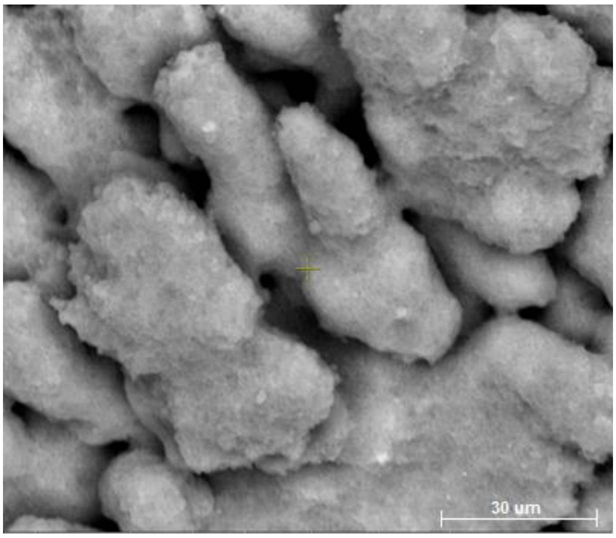

Figure 26: SEM image of the repeating structures formed on the GDE surface with the spray painting technique (2500x magnification).

It is thought that the cumulative reaction area produced with the spray painting technique will be even higher than those produced with the hand painting and screen printing because of the finer pores as well as the additional structures formed.

Photos taken at 5000x magnification of the screen printing electrode show that ink has adhered to the carbon filaments although the ink has a low distribution at the surface. Figure 25c shows a point where ink structures have formed between filaments with only a very thin layer of ink is left on the top surface of the filaments (Figure 27).

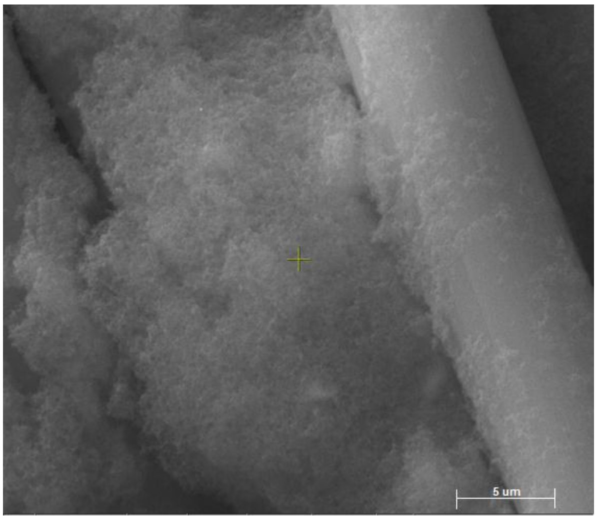

Figure 27: SEM photo of the surface of the screen-printed electrode taken at 10000x magnification showing a very thin layer of ink on the carbon filament surface.

The extent to which the ink had penetrated into the cloth was verified by SEM imaging of polished samples made (Figure: 28). These images show that the spray painted catalyst containing ink is indeed concentrated at the top surface while the screen printed and hand painted electrodes were saturated throughout.

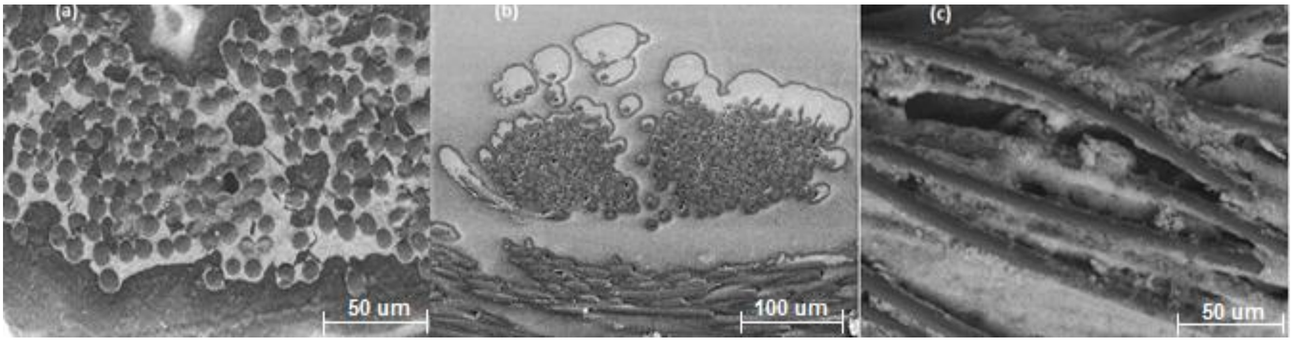

Figure: 28 Polished samples of the (a) hand painted electrode and (b) the spray painted electrode shows the relative penetration of the catalyst ink. The SEM image (c) of the screen printed electrode confirms the deep penetration of catalyst ink.

Figure: 28a and Figure: 28b are images of the polished samples made from the hand painted and spray painted electrodes, respectively. It was virtually impossible to prepare a polished sample of the screen printed electrode since the catalyst ink washed out during the polishing due to their fragile nature. The cross sectional ink penetration was however still investigated by SEM imaging of an un-mounted sample (Figure: 28c) and showed that the catalyst ink had penetrated through the thickness of the electrode.

5.2.2 Element Mapping

SEM element mapping was carried out on the electrodes fabricated by the hand painting, screen printing and spraying methods. The mapping was conducted at 30kV and 120x magnification with a horizontal field width of 2.5mm and vertical field width of 2.15mm. Element mapping at these parameters gave a good indication of the ink distribution over the surface area (agglomerates/concentrations, etc.) but also gave some insight into the extent to which the ink has penetrated into the cloth.

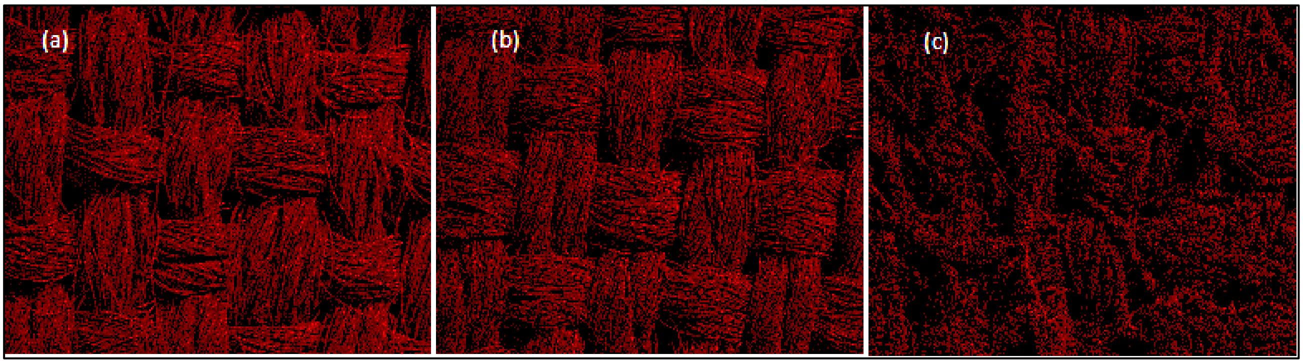

Figure 29: SEM element maps showing the carbon distribution for the electrodes manufactured by (a) Hand Painting, (b) Screen Printing and (c) Spray Painting showing no definitive pattern of ink application.

In Figure 29a and Figure 29b the fibres of the carbon cloth are clearly visible because of the fact that a large amount of the cloth is exposed or covered only in very thin layers of ink. This is in contrast to Figure 29c where the visible carbon is those in the structures created by the ink deposits (carbon content of the ink) and not the weave of the carbon cloth. The carbon fibres of the cloth are less visible/ less defined because of the large amount of ink deposited.

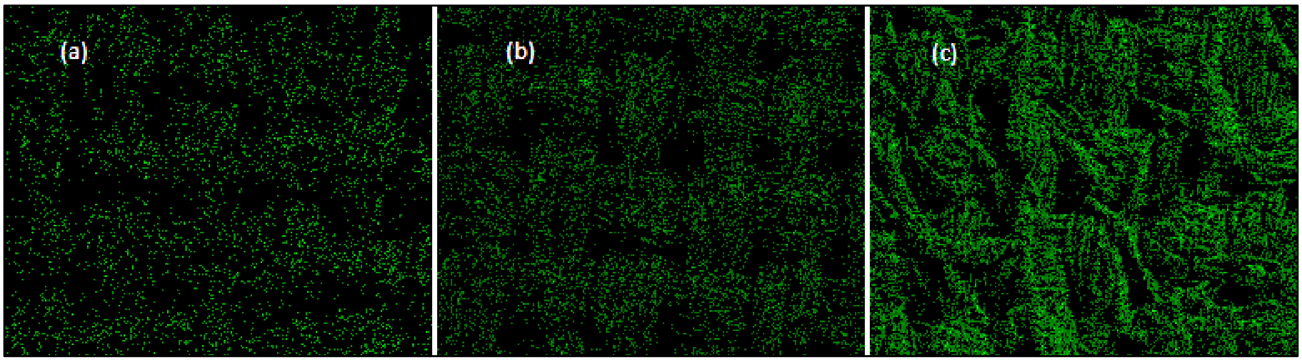

Figure 30: SEM element mapping showing the fluorine (Nafion) distribution for the electrodes manufactured by the (a) Hand Painting, (b) Screen Printing and (c) Spray Painting methods showing a larger surface concentration for the spray painted electrode.

The carbon distribution in Figure 29 also supports the statement that the larger amount of catalyst is situated below the top surface for the hand painted and screen printed electrodes, but concentrated at the very top surface for the spray painted electrode since the same (approximate) mass of ink was deposited onto all electrodes. Figure 30 and Figure 31 further support this statement by means of the display of the Nafion (fluorine content of Nafion indicated on the element maps in Figure 30) and platinum (Figure 31) distribution.

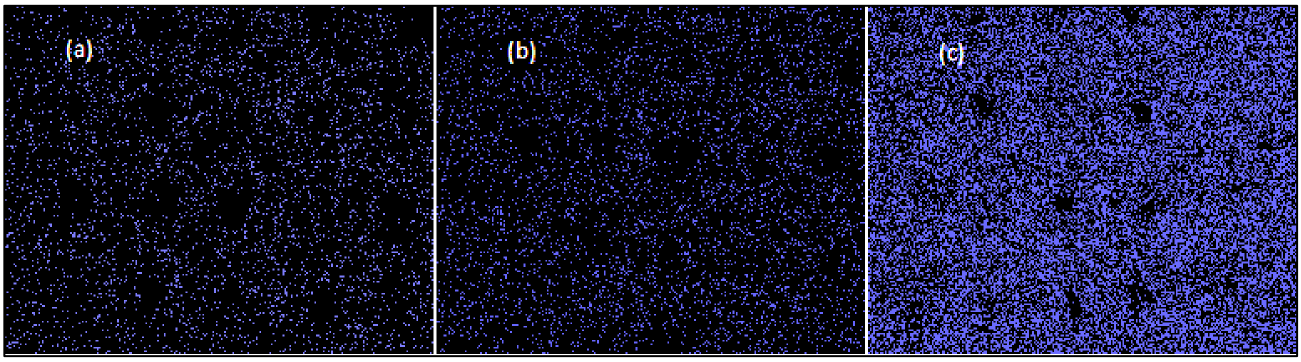

Figure 31: SEM element mapping showing the Platinum distribution for electrodes manufactured by the (a) Hand Painting, (b) Screen Printing and (c) Spray Painting methods.

The element maps revealed that the spray painting technique created a much more continuous layer with fewer weave-gaps than the other methods yielding a higher reaction surface area and less reaction concentrations and reaction product concentrations on the membrane, catalyst layer and flow field. The spray painted electrode (Figure 31b) has a concentrated distribution of platinum at the immediate top surface in comparison with the hand painted electrode (Figure 31) and the screen printed electrode (Figure 31b) which is a desirable characteristic as it would facilitate the electrochemical reactions close to the membrane shortening the diffusion distance of the cations.

5.3 General observations

5.3.1 Hand Painting

Catalyst ink was only wasted where the ink soaked through the carbon cloth onto the backing plate and via the uptake of ink into the brush. A few difficulties have been encountered using this technique.

The first is the matter of accuracy. When the first layer of ink was painted onto the cloth, it was clearly visible where ink had been deposited and where not. When the next series of layers were applied, however, it became more difficult to determine where to apply ink for consecutive layers while not overlapping strokes or leaving gaps between strokes.

Furthermore, when the ink is painted, the GDL is easily soaked with ink. To prevent the soaking of the GDL, only small amounts of ink has to be taken up by the brush which in effect increases the total amount of time required to produce a GDE by the hand painting technique.

The time spent preparing a sample of ink was also a matter of concern. The average preparing time for a sample of ink was roughly 5 hours. This time can however be decreased by heating the mixture during evaporation (which was not carried out in this study) but care has to be taken not to overheat the mixture. The ink preparation time was basically the same for all the methods.

5.3.2 Inkjet Printing

The viscosity of the prepared ink was compared to those of the refill ink as described previously. The distance travelled by the refill ink in 30 seconds was 10.5mm. After a second adjustment an acceptable viscosity was achieved with a travelling distance of 11mm.

A small test square was printed, but showed very poor printing quality. Another square was printed with even worse results after which no ink could be printed.

It was suspected that the relative low boiling point of the methanol could have caused rapid drying of the ink in the nozzle. Another mixture of ink was prepared with isopropanol instead of methanol because of its higher boiling point and therefore slower rate of evaporation. This ink was used in a new cartridge prepared in the same fashion as the previous one but the same problem was encountered. The error is attributed to a jam in the printer head. This was probably due to the relative larger size of the Pt/C particles in comparison to the printing nozzles as well as the rapid evaporation of the solvent. Because of the technical difficulties, the Inkjet Printing technique was therefore discarded as a catalyst application technique in this study.

Another observation made is the fact that since a relative large amount of ink had to be injected into the cartridge when refilling, an amount of ink and therefore platinum, would go to waste if small amounts were printed, for example when manufacturing small sized or small quantities of Gas Diffusion Electrodes (GDE's).

5.3.3 Screen Printing

Ink for the screen printing was prepared as described earlier with the added ethylene glycol to increase the viscosity. Very little wastage of ink was noted in comparison to the other techniques. Locations were spilling of ink was noted was on the screen at the end of the spreader travel path where the scraper was positioned and on the spreader itself. This wastage can be minimized by better adjustment of the screen printer to the screen size. The actual application of ink is very fast, effective and simple requiring no special skill or training and took approximately 5 seconds per pass and 5 seconds for ink placement for each coat.

5.3.4 Spray painting

Ink for the spray painting was prepared as described previously and a suitable viscosity was achieved with little effort.

Disadvantages noted were firstly the large amounts of overspray. Because of this overspray, the spraying had to be done in a well-ventilated room with the aid of a gas mask. The overspray is clearly visible on the top cover in Figure 32.

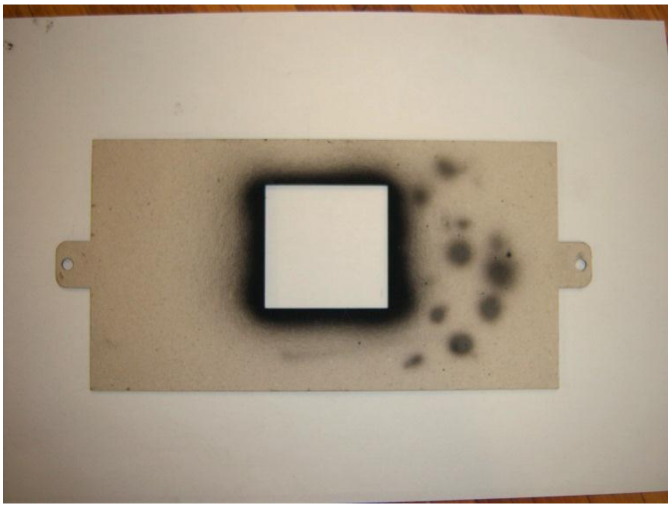

Figure 32: The spray painting setup top cover showing amount of overspray.

Apart from the amount of overspray on the cover, an amount of airborne overspray was present which floated in the environment and was carried away by the ventilation stream. All this overspray adds to catalyst wastage.

On the positive side, the loading could be controlled very accurately since small amounts of ink can be sprayed if desired. A second advantage is the fact that the ink does not penetrate through the thickness of the cloth in effect decreasing the waste of catalyst. In the literature, concern was expressed about the clogging of the spray gun causing unnecessary waste of catalyst and time. In this study however, at no time was any clogging noted or time or catalyst ink wasted due to clogging related difficulties.

5.4 Summary and Discussion

The reason for the higher average value of catalyst loading for the screen printing is due to the fact that every coat applied by the machine deposited roughly the same amount of ink whereas the person applying the ink has more control over the amount being deposited with the other two methods.

The reason for the distribution of the ink throughout the GDL prepared by the screen printing technique can be explained with reference to the mechanical working of the printer.

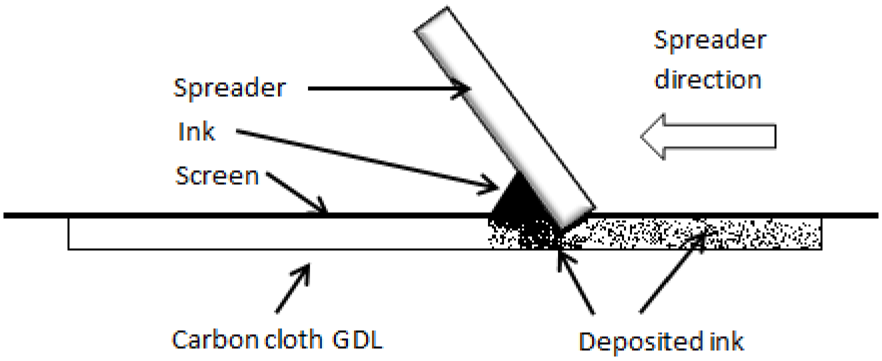

Figure 33: Illustration of the screen printing operation indicating the spreader, screen, ink and GDL

In the illustration in Figure 33 the ink is placed in front of the spreader. As the automatic sequence is activated, the spreader moves along the length of the screen applying pressure at a pre-set angle forcing the ink through the screen onto the printing substrate. Since the carbon cloth is soft it is compressed as the spreader moves over the cloth while the ink is forced into the cloth. The combination of the downward force on the ink and compressed cloth nearly saturates the cloth under the spreader edge with ink. As the spreader moves further along, the local force on the cloth is removed causing it to expand to its original form. The ink is now largely distributed through the cross section of the cloth and not only concentrated to the top layer.

The results of the SEM imaging indicated that no solid ink structures were formed by any of the application techniques although the density of the ink structures formed by the various techniques was not consistent.

The element maps indicate no visible catalyst ink concentrations or patterns of application over the surface of the produced GDE’s. The maps and the mounted samples do, however, indicate that the catalyst is more concentrated to the top layer of the GDE for the spray painted electrode than for the other electrodes.

The time consumed by the various methods differs significantly and is presented in Table 3. The ink preparation time for both the hand painting and spray painting methods was approximately 5 hours. The major part of this time was taken up by the solvent evaporation which was done under ventilation while being stirred in the absence of applied heat. The remainder of the time was spent weighing/measuring the constituents. The solvent had to be partly evaporated in order to achieve an ink viscosity suitable for hand painting/ spray painting. The spray painting required an ink with a lower viscosity (more paste-like) in order to function properly. A thickener, ethylene glycol was added to the mixture and subsequently the evaporating time increased. The solvent evaporation time can be decreased with the addition of heat, which will decrease the evaporation time for all the methods to the same extent, therefore not influencing the relative values listed in Table 3.

Table 3: Time consumption for the different electrodes produced

Method	Ink preparation time	Time per coat	Drying time between coats	Amounts of coatings	Final drying time	Overall time per electrode[1]
Hand Paint	5 hrs	1 min	5 min	10	30 min	85 min
Screen Print	7 hrs	10 seconds	5 min[2]	14	30 min	67 min
Spray Paint	5 hrs	15 seconds	1 min	32	5 min	44 min

The time per coat ranged from 10 seconds (screen print) to one minute (hand paint). The high degree of automation of the screen printer reduces the time consumption in comparison with the hand paint and spray paint method.

Because of the fineness of the spray drops formed with the airbrush, the drying time between coats as well as the final drying time is significantly shorter than those for the other methods. This drying time, however, increases as the distance between the airbrush and the spraying target is decreased.

The drying time between coats for the hand paint and screen print methods is much longer because of the fact that a larger volume of ink is applied with each coat. The fact that more than double the amount of coats were necessary to apply the same amount of ink with the airbrush supports this statement (refer to Table 3). The overall manufacturing time per electrode for the

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[1] Excludes ink preparation time

[2] Dried after every second coat

mentioned methods (excluding ink preparation) shows that the spray painting method is the most time efficient at 44 minutes per electrode.

6. Application Technique Improvements

6.1 Introduction

During the application procedures and the investigation of the microstructures, some points of possible improvements came to mind and the possibilities of some of these improvements were experimentally evaluated. The investigation into these methods and their results are discussed in this chapter.

6.1.1 Hand Paint Improvement

In an attempt to reduce the technical difficulties and disadvantages of the hand painting technique, a possible improvement was investigated. A micro porous carbon layer was sprayed onto the top surface of a carbon cloth similar to those produced for the sputter coating. The aim of this carbon layer was to limit the soaking of the ink into the carbon cloth and thereby enhancing the specific reaction surface area while reducing the raw exposed carbon cloth surface roughness.

After the micro porous layer had been formed by iterations of spraying and drying, ink with the same composition as that used for the hand painting was painted onto the carbon layer by hand painting. It took approximately one minute to apply a coat of ink. Ten coats were applied to achieve the desired loading. Five minutes of drying time was allowed between successive coats. Three of these electrodes were produced with the aim of 0.5 mg/cm^2 and designated HP-C1, HP-C2 and HP-C3.

Results: Hand Paint Improvement

The GDE’s were weighed after the allocated drying time and verified after 48 hours. The results of the weight measurements and the resulting catalyst loadings are presented in **Table 4**. From the results it is evident that the aimed catalyst loading was achieved with satisfying accuracy.

Table 4: Weight measurement results and catalyst loadings for the improved hand paint technique.

Materials	HP-C1	HP-C2	HP-C3
Dry GDL (g)	0.289	0.289	0.289
After carbon layer (g)	0.329	0.320	0.317
Carbon loading (g)	0.040	0.031	0.028
After hand paint (g)	0.418	0.404	0.401
Pt loading (mg Pt/cm²)	**0.575**	**0.539**	**0.535**

The applied micro porous layer formed a layer on top of the carbon cloth. The ink painted onto this layer saturated this layer creating a dense and solid-like layer (Figure 34a). The carbon layer structures formed were fragile and easily damaged by the painting strokes as seen in the stripped carbon filaments shown in Figure 34b. The cracks indicated in Figure 34b reveals the brittle nature of the dense catalyst layer created

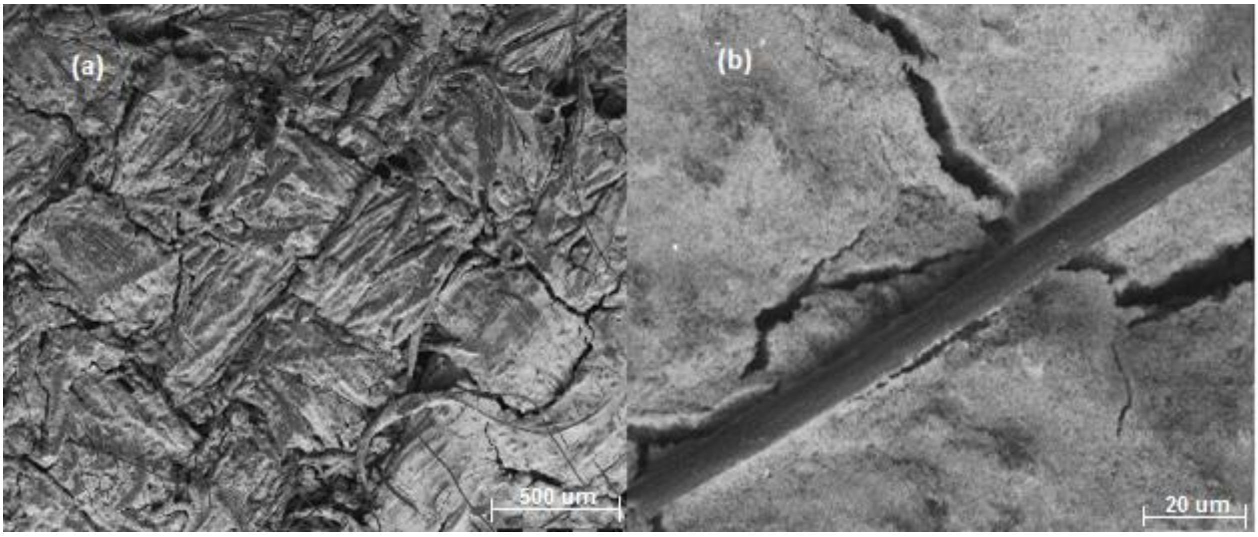

Figure 34: SEM backscattered electron images of the surface of the electrode produced by hand painting over a previously applied carbon micro porous layer showing a dense distribution of catalyst ink (a) with a close-up showing the development of cracks (b).

The presence of the platinum catalyst is visible in Figure 34 as the lighter shades. When taking the backscattered electron images as in Figure 34, the heavier elements (like platinum) appear brighter than the light elements (like carbon). This created a sharp contrast between the carbon/carbon micro porous layer and the platinum containing ink (Figure 34b and Figure 39 b). Apart from the extra time consumed due to the application of the carbon layer, no severe drawbacks were encountered. It is however unclear how the more dense catalyst layer will influence the pressure drop in the electrolyser setup.

It is expected that the electrode produced by this method will yield a bond superior to all the others when formed into a MEA by hot pressing because of the abundance of Nafion containing ink at the immediate surface (see Chapter 7).

6.1.2 Spray Paint Improvement

During the production of the GDE's by the spray painting technique, a significant waste of catalyst ink was noted due to overspray. In an attempt to reduce this large amount of overspray, the principle of the electrospray technique was adapted to the spray painting setup. The electrospray method was encountered in literature but not tested due to a lack of high voltage equipment and the accompanying danger of working with these high voltages.

Because of the above mentioned reasons the setup as described in the literature was modified using a reduced voltage of 12V. Firstly a variable power supply (Figure 35a) was coupled over the airbrush and a copper substrate below the airbrush (Figure 35d) at a distance of 15cm. A high intensity light source was aimed towards the location where the spray would take place (Figure 35b). The light source was used to illuminate the sprayed particles to see if a definite difference in flight pattern exists with and without an applied potential difference. A white photocopy paper (Figure 35c) was placed under the copper plate to determine if the diameter of the spray cone decreased as the potential difference is applied. In order to eliminate other possible variables, the same ink was used as was used for the unmodified spray paint.

The first run was done with the power supply switched off to serve as a control. In the next run the power supply was switched on and the spraying continued for a few seconds.

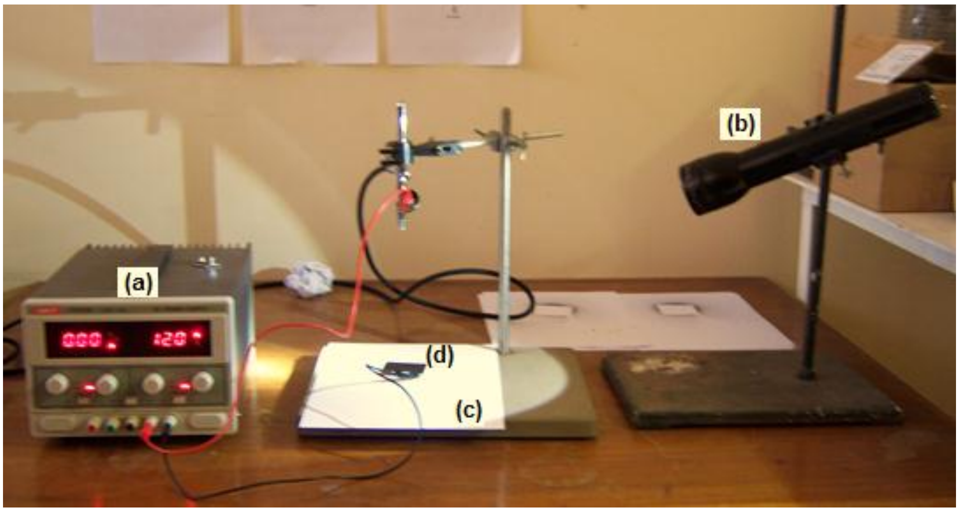

Figure 35: The electrospray setup with the (a) power supply, (b) light source, (c) white paper and (d) copper target.

The experiment was carried out twice for a regulator pressure of 200 kPa and twice for a regulator pressure of 400 kPa as the fineness of the ink drops might influence its flight pattern (Figure 36).

Results: Spray Painting Improvement

Although the spray cone was visible under the illumination of the light, no distinct difference in the spray cone shape was visible with extra or less airborne overspray. The white paper underneath the copper target also indicated no decrease in overspray pattern.

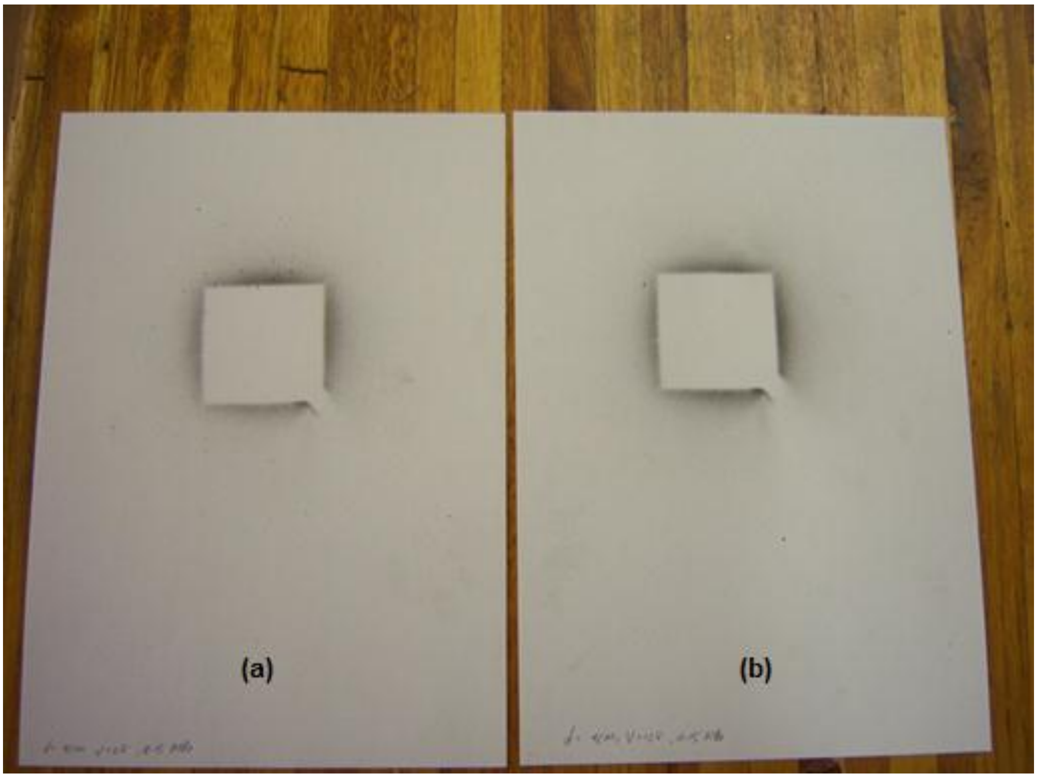

Figure 36: The white photocopy paper placed under the copper plate showing no difference in the spraying pattern between the control (a) and the test (b).

These results suggest that a much higher voltage needs to be applied over the spray cone to have an effect on the cone. The distance between the spray gun and the copper plate also play a role on the strength of the electric field created. This distance could not be decreased since it would influence the spraying characteristics. This test therefore showed no promising potential without major adjustments with respect to supply voltage and was therefore abandoned.

6.1.3 Sputtering

The method of sputtering has been encountered in literature but the option was not considered as a viable option because of the expensive platinum target and equipment needed. At a later stage however, a sputter device was found at the SEM laboratory which is used to prepare biological samples for SEM analysis. These samples were coated with a layer of gold-palladium or carbon.

No pure platinum target could be located, however a 95% platinum-gold alloy sheet used for metallurgical experiments was obtained. This piece of sheet was used to produce a circular target with a 5cm diameter to fit the sputter device target holder.

A micro porous carbon layer was produced on top of the carbon cloth by spraying an ink consisting of carbon black (Vulcan xc-72, Cabot) and a Nafion solution (Nafion 117, Fuel Cell Store) onto the top surface of the cloth. A layer of 32 mg dry carbon-Nafion ink to produce the carbon micro porous layer was applied with the same airbrush that was used for the production of the spray painted electrodes. The purpose of the carbon layer was to create a more even layer on top of the raw uneven wove of the carbon cloth. Secondly the porosity of the layer increased the surface area creating the possibility of increased reaction surface area.

A sputter coater (Eiko Engineering model IB2) was used to deposit platinum nanoparticles onto the micro porous surface. The platinum target was inserted into the target holder and kept in place with retaining circlips. The carbon cloth with a micro porous carbon layer was placed on top of the coater-button. The vacuum chamber was closed and the vacuum pump (Edwards model E2M5) switched on. At a vacuum of 2 torr, a valve was opened to introduce argon gas into the vacuum chamber. As the sputter coater power supply was switched on, purple plasma was formed between the gas diffusion layer and the platinum target indicating coating activity. The coating current was kept at 8 mA by regulating the argon flow via the flow-valve. The deposition was continued for 30 minutes after which the sample was taken out and weighed to determine the mass increase. The results of the weighing indicated that very little, if any, coating had taken place. The lack of coating activity was suspected to be due to some sort of surface layer existing on the surface of the platinum target. Because of this suspicion the platinum target was sanded with 400 grit sandpaper and the coating procedure was repeated for 10 minutes. The sample was then inspected in reflected light with a light microscope and the SEM, showing a very clear layer of deposited metal as indicated in Figure 37.

A scar was made on the coated surface (Figure 37) which clearly indicated the deposited layer of platinum-gold. The sample was then coated another 5 times for 10 minutes each with 5 minutes cool-down time in-between for the coater to cool down preventing damage to the electronics. Samples were then weighed and the deposited mass calculated. The electrode was designated SPUTTER 3. The same coating procedure was repeated twice to produce SPUTTER 1 and SPUTTER 2. SPUTTER 1 was used to produce a mounted sample to investigate the cross-sectional microstructure of the electrode whereas SPUTTER 2 and 3 were used to produce a MEA for electrochemical analysis.

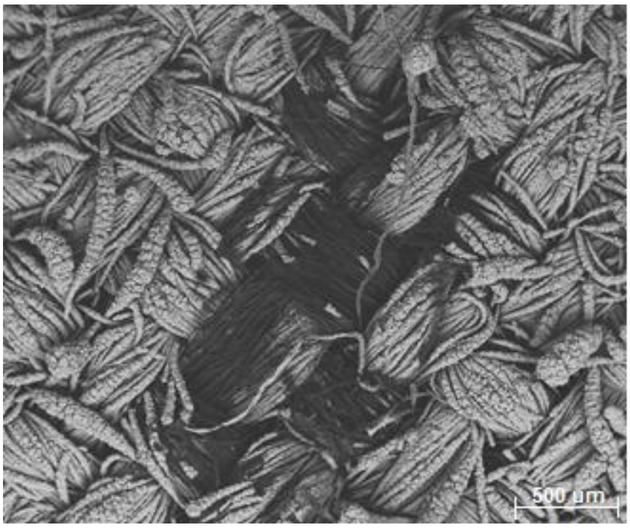

Figure 37: SEM image investigation of the surface of the electrode produced by sputter coating for 10 minutes. The surface was scratched with a needle showing the clear carbon-metal contrast.

Results: Sputtering

The sputtering was done with relative ease even though it consumed more time relative to the other methods. A fair amount of time was used to produce the carbon layer and a further amount of time was taken up by the actual coating. It took approximately 60 minutes of actual coating to coat an electrode to the desired loading. Between each 10 minutes of coating the coater was left to cool down for 5 minutes. This adds up to a coating time of one hour and 25 minutes of coating per electrode produced.

Table 5: Weight measurement results and catalyst loadings for the sputtering technique.

Materials	SPUTTER1	SPUTTER2	SPUTTER3
Dry GDL (g)	0.285	0.285	0.284
After carbon layer (g)	0.320	0.316	0.316
Carbon loading (g)	0.035	0.031	0.032
After sputter coating (g)	0.324	0.323	0.323
Pt loading (mgPt/cm²)	**0.156**	**0.300**	**0.296**

The loading of the sputter coated electrodes was designed to be 0.3mg Pt/cm^2 because of the homogeneous and continuous layer formed. Another reason for the lower loading is to protect the machinery. If a loading of 0.5mg Pt/cm^2 was to be coated, the coating time would almost have doubled.

The weighing of the samples showed a mass increase of 7mg for SPUTTER 1, a mass increase of 7.5mg for SPUTTER 2 and a mass increase of 7.4mg for SPUTTER 3. This gave an average rate of catalyst deposition of 0.123 mg/min.

Problems noted with the sputter coating were firstly the circular catalyst deposition pattern on the square substrate due to the circular button (Figure 38). It is thought that even catalyst distribution can be achieved by producing a square button with the dimensions of the GDL.

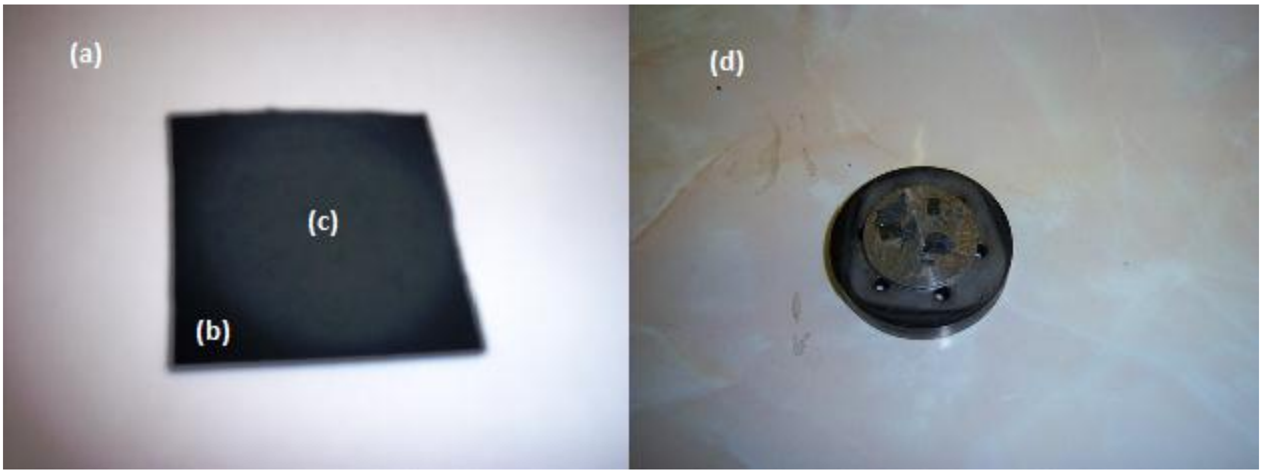

Figure 38: The electrode produced by sputter coating with the circular deposition pattern (a) and the button sample holder (d).

The sputter coated electrode was investigated by SEM imaging to verify the coating characteristics. The sputter coating of the electrode produced a very homogeneous catalyst layer. Except for the corners of the GDL where little coating had taken place, the layer formed is virtually continuous. According to Figure 39b the thickness of the catalyst layer formed was less than half a micron. From this view it is also clear that the catalyst is extensively concentrated at the surface of the carbon layer. The sputtered particles adhered to the immediate surface and did not penetrate deeper into the cloth (white particles on top of the structures in Figure 39c).

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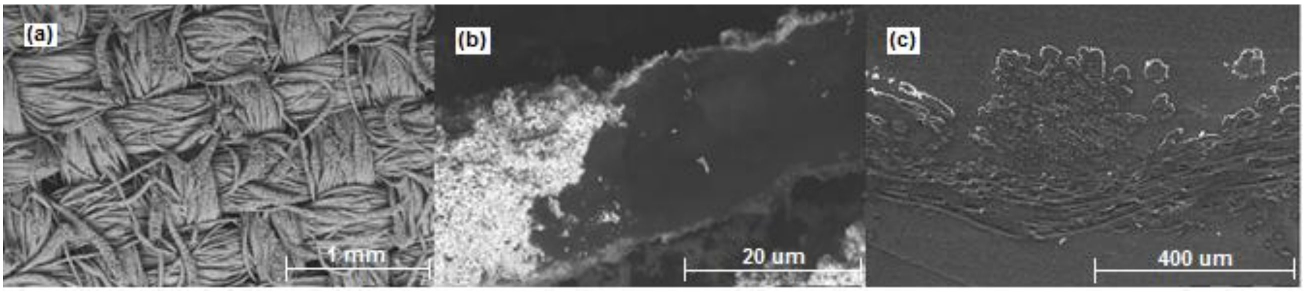

Figure 39: SEM images of the sputter coated electrodes. The exact location of the deposited catalyst can be seen in the SEM backscatter image of the mounted sample (c).

This concentration of the catalyst at the surface is a desirable quality as it would facilitate the electrochemical reaction in close vicinity of the membrane where ionic transportation is available. This would also limit problems regarding the mass transport of ions from reaction sites to the membrane via ionomer pathways.

There is however rising concern about the effect that the continuous catalyst layer will have on the bonding integrity between the membrane and the electrode but may be overcome by further experimentation.

6.2 Characteristics of Carbon Micro Porous Layer

Since the carbon micro porous layer was formed by mixing ultra-fine carbon black (Vulcan xc-72, CABOT) with Nafion solution, a high specific area was expected to be created. After the spray-deposition of the carbon layer, the layer was investigated by SEM imaging. At a first glance the layer created resembled the spray painted electrode. The carbon layer had adhered to all the carbon filaments exposed at the top surface as indicated in Figure 40a. The carbon had created a much denser top surface limiting the chance of catalyst particles penetrating deeper into or even through the thickness of the cloth when coated. The average size of the carbon particles or agglomerates was determined by measuring the size of a few randomly selected particles. First a few randomly selected measurements were taken of relative smaller particles (Figure 40d) and then a few randomly selected measurements of the relative larger particles (Figure 40c).

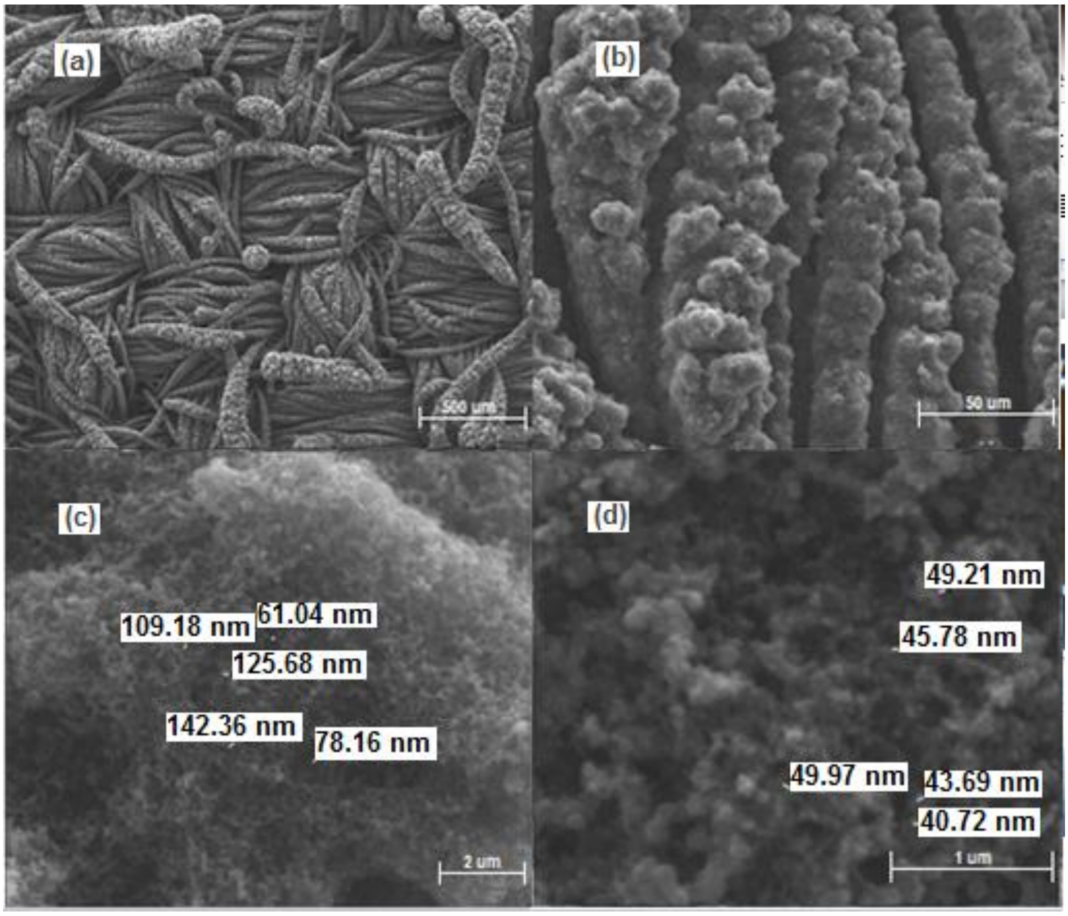

Figure 40: SEM image investigation of the carbon micro porous layer showing the (a) +(b) large reaction surface and (c)+(d) fine particles.

The results of these measurements are presented in Table 6. The average size of the particles was between 41nm and 143nm. This sized corresponds to specific areas between 70 m^2/g and 20.08 m^2/g respectively (assuming the particles are spheres and a carbon density of 2.09 g/cm^3).

Table 6: Results of carbon layer particle diameter measurements

Sample no.	Size [nm]	
	Smaller Particles	Larger Particles
1	49.21	61.04
2	45.78	109.18
3	49.97	125.68
4	43.69	142.36
5	40.72	78.16
Average size [nm]	45.874	103.284

The high specific areas, however, requires deposited catalyst particle diameter to be very small in order to utilize this porous surface of the carbon layer. This very small particle diameter creates the possibility of producing an extremely high specific reaction surface when coated in catalyst material by sputtering.

6.3 Summary and Discussion

The small difference in catalyst loading between HP-C1, HP-C2 and HP-C3 indicate the ability of the hand painting technique to repeat the procedure with the same results. This is also true for the SPUTTER2 and SPUTTER3 produced by the sputtering technique.

The weighing results indicate that the loading of SPUTTER1 is lower than those of sputter SPUTTER2 and SPUTTER3. The reason for this lower loading was the initial technical difficulties that were encountered. Because of this lower loading, SPUTTER 1 was used to produce the mounted sample for cross sectional investigation.

The time consumed to produce an electrode by each of the improvements is presented in Table 7. The hand paint method time consumption is the same as for the basic case except that the time needed to produce the carbon layer is now added to the total time. The time consumed to produce an electrode was basically the same for both methods discussed. This is however only true if the ink preparation time is excluded. The sputter method thus saves a lot of time since no time is spent preparing and adjusting the ink.

Table 7: Time consumed to produce an electrode by each of the improved methods

Method	Ink preparation time	Time per coat	Drying/ cooling time between coats	Amounts of coatings	Final drying time	Overall time per electrode	Total Method time per electrode (incl. carbon layer)
Carbon layer	2 hrs	15 seconds	1 min	12	5 min	22 min	
Sputter coat	-	10 min	5 min	6	-	85 min	**107min**
Hand paint	5 hrs	1 min	5 min	10	30min	85 min	**107min**

Very little ink wastage was encountered in the method where hand painting was done on the carbon layer. The soaking of the ink through the cloth to the back plate was limited with very little waste. The main waste of ink was due to the uptake into the brush.

In the case of the sputter coated electrode, the platinum was applied directly to the GDL from the platinum target by means of the formed plasma. This meant that the deposition of the catalyst could be controlled very accurately. It can be assumed that all the catalyst material removed from the catalyst material source was deposited onto the carbon cloth.

7. Hot-Press Fabrication of MEA’s

7.1 Introduction

In the previous three chapters the manufacturing and evaluation of the GDE’s by the various methods and improvements that were carried out, were discussed.

After the microstructure was evaluated, the GDE’s fabricated were used to produce MEA’s by hot-pressing with the view of evaluation in an existing electrolyser. The hot pressing procedure and the investigation of the resulting MEA’s are presented in this chapter.

7.2 Hot pressing procedure

The MEA is assembled by placing a Nafion membrane in-between two GDE’s with the catalyst layers facing the membrane and centred in the middle of the membrane. The assembly was then bonded by subjecting it to a high pressure and temperature in a heat-press apparatus (Carver, Figure 41). The faces of the press could be heated to a specific temperature. A dial shows the applied pressure which is applied by means of a manual hydraulic hand-jack.

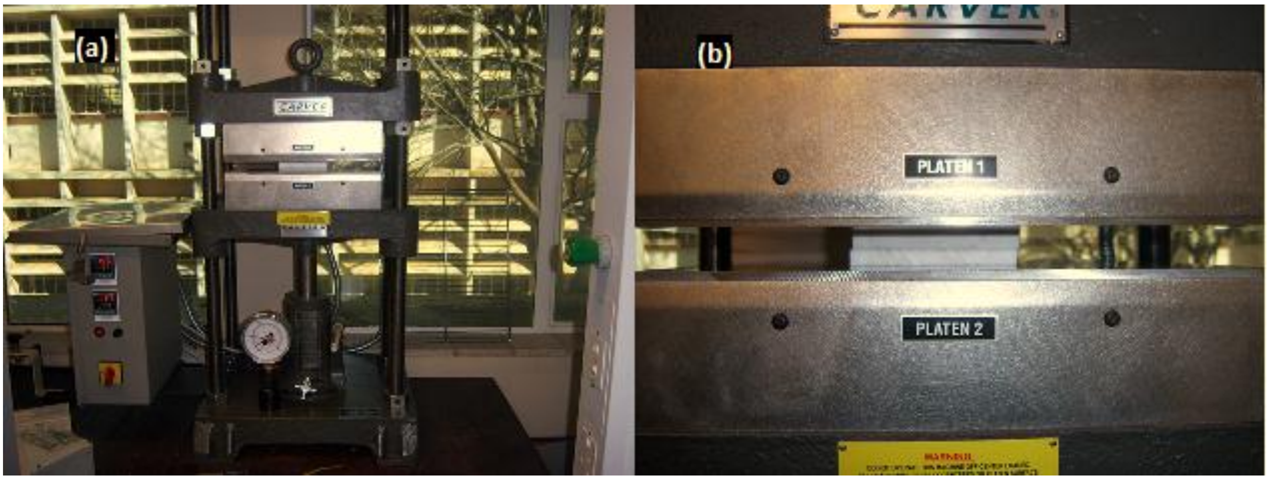

Figure 41a: The heated press that was used in the production of the MEA's with (b) a close-up indicating the Teflon plates between the press faces.

The following procedure was carried out for the production of the MEA':

1. The press temperature was set to the desired temperature (Press units in Farenheit)
2. The press was allowed to achieve the set temperature (approx. 10 minutes).
3. An electrode was placed on the Teflon plate[3] with the catalyst side upwards.
4. The membrane was placed over the electrode with the electrode centred under the membrane.
5. The second electrode was placed in the centre on top of the membrane with the catalyst side facing the membrane. The two electrodes were then aligned.
6. The Teflon block with assembly was then placed on the lower press plate.
7. The top Teflon block was carefully placed over the assembly without moving the assembly.
8. The lower plate was jacked up towards the top press plate to the desired force (calculated from the desired stress and GDE dimensions).
9. After the required bonding time, the press was opened by opening the relieve valve. Care was taken to ensure the Teflon plates do not stick to the press plates as this might tear the MEA apart.
10. The Teflon plates were opened and the MEA immediately placed in deionized water to prevent warping of the membrane.
11. The fabricated MEA was stored in deionized water.

* One of the two identical Teflon pressing plates (visible in Figure 41b)

Since the hot-pressing parameters in literature differed for the different studies, the hot-pressing procedure presented above was followed to determine the optimum temperature and pressing-time for effective hot-pressing experimentally. A detailed description of the procedure is presented in **Appendix B**.

Using Nafion 117 membrane, the experimental results indicated that the optimum parameters are:

- Temperature: 140℃
- Pressure: 10 MPa
- Time: 15 minutes

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[3] One of the two identical Teflon pressing plates (visible in Figure 41b)

After being produced, the MEA’s were evaluated in terms of GDE-membrane bond after various time intervals. The results and discussion of the results of this inspection are now presented.

7.3 Inspection of MEA’s

The first MEA to be produced was fabricated from the HP-C electrodes. This MEA was produced at the temperature, pressure and time as experimentally determined (140˚C, 10 MPa, 15 minutes). The MEA was immediately placed in deionized water after it was taken out of the press to prevent warping of the membrane. After about ten seconds the membrane had returned to its original shape.

The integrity of the bonds of the MEA’s produced was visually inspected at various time intervals. A summary and discussion of these results is now presented.

Table 8: Summary of the MEA’s after 5 days of inspection.

MEA electrode production method	24 hour inspection	48 hour inspection	72 hour inspection	5 day inspection
Hand painted on carbon layer (Improvement)	Good	Good	Good	Good
Spray painted	Good	Good	Good	Little parting (edges)
Hand painted	Good	Good	Centre started to part	One electrode parted
Screen printed	Edges starting to peel	Parted	N/A	N/A
Sputter coated	No bond	N/A	N/A	N/A

- **Direct inspection**

The visual inspection of the first produced MEA was carried out with the MEA still in the water to prevent damage.

The inspection revealed that the electrodes had bonded extremely well to the membrane with no GDE edges peeling away.It was however noted that the membrane had started to distort under the severe pressure. To prevent the damage of membranes the other MEA’s were pressed at a pressure of 5MPa instead of 10Mpa.

The sputter electrodes showed no bond at all when taken out of the press. As the Teflon plates were taken apart, the electrodes simply fell of the membrane.

All the other MEA's produced showed good results with no peeling away of the electrodes or distortion of the membranes.

- **24 Hour inspection**

After 24 hours the MEA's were once again inspected for bonding quality. At this time the MEA produced by the screen printed electrodes had started to peel away. Except for the Spu-MEA (MEA with sputter coated electrodes) and the ScP-MEA (MEA with screen printed electrodes), all other MEA's showed no signs of parting.

- **48 Hour inspection**

After two days the MEA's were once again inspected. All the MEA's were still completely bonded, except for the ScP-MEA (screen printed electrodes) which had completely parted.

- **72 Hour inspection**

Three days after the MEA's were produced they were once again inspected. The inspection revealed no changes except for the HP- MEA (hand painted electrodes). At first glance the MEA seemed fine but at closer inspection it was noted that the electrode edges had started to part.

- **5 day inspection (Final inspection)**

The final inspection took place 5 days after the production of the MEA's. The inspection revealed that the only MEA's with satisfactory bonding quality was the HP-C MEA (hand painted on carbon layer electrodes) and the SP-MEA (spray painted electrodes).

7.4 Discussion of Hot Press Results

The distortion of the first MEA pressed at 10MPa showed that the pressure exceeded the yield strength of the membrane at the pressing temperature. This temperature was set at 140˚C on the control panel of the press, but as the temperature test (described in the detail in **Appendix B**), the maximum temperature reached was approximately 113˚C after 15 minutes.

This high pressure can damage the membrane and lead to the possible failure of the produced MEA.

The sequence of MEA bonding failures followed a logical path with reference to their microstructure and the suspected method of bond. These will be discussed now.

- **Hypothesis of interfacial bond behaviour**

The hypothesis is that the bond between the membrane and the catalyst layer is not a pure mechanical mechanism where the Nafion membrane flows over the catalyst layer structures, but an interaction of the Nafion content present in the catalyst layer and the Nafion membrane. This would mean that an electrode with a high Nafion (i.e. catalyst ink) concentration at the surface would yield a bond with superior strength to electrodes where the ink is distributed through the gas diffusion layer because larger amounts of Nafion were present at the GDE surface to bond to the membrane (via sintering).

This hypothesis is confirmed by the behaviour of the sputter coated electrode versus the behaviour of the electrode prepared by hand painting on the carbon micro porous layer.

- **Differences in interfacial bond strength**

As illustrated in **Error! Reference source not found.**a the HP-C electrode has a high concentration of dense catalyst ink concentrated at the surface. This dense ink layer provides a large presence of Nafion at the membrane-catalyst layer interface which makes a strong bond possible.

To the contrary, the very homogeneous and almost continuous layer of catalyst material sputtered onto the Nafion containing carbon layer in the electrode in Figure 39b creates a barrier against the formation of any possible interfacial bonds. This explains the absence of any bond formed in the production of the MEA containing the sputter coated electrodes.

According to this hypothesis the bond strength of the MEA's will decrease as the presence of the ink at the surface decreases.

From the SEM image results shown in Figure 24 it would follow logically that the interfacial bond strength would decrease from the weak bonds produced by the screen printed electrode (Figure 24a) to the relative stronger bond of the spray painted electrode (Figure 24c) and the high interfacial bond of the electrode produced by the hand paint onto the (Nafion containing) carbon layer as confirmed by the sequence of MEA failures.

- **ScP-MEA bond integrity versus HP-C-MEA bond strength**

The hypothesis of the interfacial bond would predict that the spray painted electrode would yield a bond strength at the interface similar to those of the electrode prepared by the HP-C method because of the abundance of Nafion containing ink at the surface. The results of the hot press inspection however showed that the HP-C MEA was still as good as in the beginning whereas the ScP-MEA showed signs of parting at the edges after 5 days. Even after 7 days the HP-C-MEA still showed no signs of degradation.

It is thought that the reason for this behaviour lies in the method of production. In the production of the spray painted electrodes, the catalyst ink dried very rapidly once sprayed onto the gas diffusion layer. The reason is that a large amount of solvent evaporates along the flight between the spray gun and the carbon cloth. This suggests that small particles of “dry” ink forms as the solvent evaporates and upon reaching the cloth surface, simply adheres to the ink particles already deposited by cohesion forces or few chemical bonds due to the small amounts of remaining solvent. To make matters worse, the high porosity of the structures formed, severely decreases the tensile strength of the structures.

Both the above mentioned factors contribute to a significant decrease of the catalyst layer strength resulting in fragile ink structures formed on top of the gas diffusion layer. As these electrodes are used to manufacture MEA’s in the hot press, the catalyst does in fact form good interfacial bonds with the membrane. As the MEA is handled and moved however, forces, especially shear forces, act on the interfacial ink structures. Because of their relative weakness, the ink structures tear lose and breaks off, resulting in the parting of the electrode and membrane.

8. Conclusion and Recommendations

8.1 Discussion

In this study the different membrane electrode assembly catalyst application techniques were reviewed and studied. The techniques in the study were found to be used in a variety of applications from commercial production to laboratory experiments. In each of the cases found some of the characteristics of each method are reported. It was however nearly impossible to do a meaningful comparison based on commercial important parameters like time consumption, capital cost, microstructure, etc. because of the varying conditions of each approach as well as the fact that the MEA production business is known to be a “Black Art”. The reason why it is being referred to as Black Art is the fact that very important information is omitted from the literature as trade secrets that are protected by the authors in order to protect their competitive edge. This is the reason for some critical technical difficulties encountered by newcomers to the industry and first time researchers which this research now revealed and to some extent addressed.

In an attempt to solve these above mentioned problems, the comparison of the techniques was carried out by selecting promising methods from the literature and evaluating these throughout the production process. From this evaluation a more sensible comparison was made based on the above mentioned parameters.

It is important to note that a change in the parameters of this study would to a great extent change the outcome of the study. If, for example, carbon paper were used instead of carbon cloth, the ink concentration of certain methods might have been more concentrated towards the GDL surface. This carbon paper might also have influenced the outcome of the hot press fabrication because of its higher stiffness.

Table 9: Catalyst application techniques table of comparison

Production method	Time consumption per electrode (min.)	Cost per catalyst layer (ZAR)*	MEA production cost (ZAR)*	Cost of equipment (ZAR)[4]	MEA quality (directly after production)	MEA quality (after 5 days)	Catalyst location on electrode	Skill required
Hand Paint	85	R 85.02	R 332.77	R 115.00	Good	No MEA	Through GDL	Little
Screen print	67	R 97.77	R 358.27	R 63,900.00	Good	No MEA	Through GDL	Little
Spray Paint	44	R 106.28	R 375.29	R 1,800.00	Good	Acceptable	GDL Surface	Average
Sputter Coat	107	R 24.28	R 211.29	R 70,300.00	No MEA	No MEA	At membrane	Little
Hand Paint on Carbon (Improvement)	107	R 110.09	R 382.91	R 1,815.00	Good	Good	GDL surface	Average

A summary of the evaluation results is presented in **Table 9**. The calculations of the cost related aspects can be found in Appendix E.

With further study and development of the techniques, some of the drawbacks of each method can be addressed. The hand paint method, for instance, showed very promising results in all aspects except for the catalyst location and interfacial bond which is a result of the catalyst ink location. This issue can be addressed by doing a study on the influence of various ink constitution ratios and viscosities on the catalyst ink deposition location.

The promising effect of development of a technique and investigation of its drawbacks can be seen in the results for the hand paint on carbon method. This method gave good results in all aspects. Further study on this method should address the matter of time consumption.

The spray painting method greatly reduced the time consumption and cost of equipment. The spraying also yielded good catalyst application with the catalyst in direct contact with the membrane.

An important point to note from the results is the significant decrease in catalyst ink cost achieved by the sputtering process. If the matter of the GDE adherence to the membrane is addressed and a solution found; the sputter process will have the highest potential in decreasing MEA production cost. Although the initial cost of equipment is very high, it can easily be made up for by lower production cost in mass production.

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[4] Calculated at R 8.00/$, packaging and shipping excluded

MEA Quality versus MEA Storage Life

All the MEA’s produced apart from the sputtered MEA were in a desirable condition directly after the bonding in the hot press and could be evaluated in an electrolyser at that stage. It was only after some time that the MEA’s started to show signs of decay. It is suspected that the water might weaken the ink structures and thus decrease the overall MEA quality. This would explain the decay of the MEA’s over some extend of time.

It is concluded that the MEA’s should not be stored in the wet form, but rather produced directly before use or produced and dried. The drying of MEA’s is very challenging and requires some level of expertise. This remark is only applicable to MEA’s as produced in this study and does not necessarily apply to cases where the catalyst is applied directly to the membrane or any other gas diffusion layer like carbon paper.

8.2 Recommendations

At the end of the study, the results were investigated and compared. This investigation along with the reported difficulties that were encountered and recommendations made, can aid in further studies or investigations related to the catalyst application for membrane electrode assemblies. Recommendations for similar studies in the future are now presented:

- **Hand Painting Method**

  As mentioned in the discussion the hand painting results were greatly improved by the addition of the carbon micro porous layer. This shows the potential of improvements to standard methods.

  The hand paint method can be improved even further by investigating the time consumption. The time consumption can be improved by:

  a) Using ink of higher viscosity. This will decrease the amount of layers necessary and limit uptake into the brush. The effect of this higher viscosity on the drying time should however be determined first.
  b) Using drying apparatus between coats such as a ventilated oven.

- **Screen print**

  The screen printing method shows great potential in cases where the catalyst layer is applied directly onto the membrane or onto a stiffer substrate such as carbon paper. For its application to carbon cloth, the printing settings should be optimized in terms of spreader pressure, spreader angle, stroke length, etc. This would minimize the damage to the deposited catalyst ink and limit ink waste.

- **Spray paint**

  The spray painting method gave good overall results although the adherence of the electrode to the membrane should be optimized. A possible solution is to increase the amount of Nafion solution in the ink mixture. This will increase the strength of the catalyst ink structures formed and increase the interfacial bond strength. The effect of this increase in Nafion solution of electrochemical performance is unknown though and should be determined beforehand. Another possible solution to this weak catalyst ink structure strength is to increase the solvent content of the ink mixture to prevent smaller “dry” Nafion particles forming *in flight* thus enhancing the formation of larger Nafion structures on the catalyst layer.

- **Sputter Coat**

  As mentioned in the discussion, the sputter coating shows great potential however some trade secrets certainly exists as seen in the results of the hot pressing. The absolute failure of the bond is due to the non-wetting characteristics of the Nafion membrane on the platinum catalyst layer. These phenomena can possibly be solved in one of the following ways:

a) Alloying

   It is possible that some catalyst alloy can be designed to have properties enhancing the wetting of the catalyst by Nafion. This option could however require large amounts of study and research.

b) Nafion coating

   A more economical option is to investigate the possibility of coating the sputtered catalyst layer with Nafion before the hot press step. This coating can be done by spraying a layer of Nafion solution or by some sort of physical or chemical deposition.

c) Multiple layers

   A last possible solution is the investigation of creating multiple sputtered layers. This can be done by sputter coating multiple layers with lower individual loadings and applying very thin carbon micro porous layers in between the sputtered layers. This will however increase the time consumption.

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Appendix A: Test Run

Hand Painting (HP)

A test run of the hand painting was done using the standard HP 121 cartridge refill ink instead of the Pt/C/Nafion ink to minimize cost and waste. White cotton cloth was cut into 5x5 cm squares representing the carbon cloth GDL. The square was weighed and inserted onto the manufactured painting setup. The ink was then painted onto the squares using a fine brush and left for 45 minutes to dry. The painting was done by painting very fine strokes in a zigzag fashion. After the 45 minutes of drying the squares were weighed to verify the applied amount of ink.

Inkjet Printing (IJP)

A Hewlett Packard 1663 printer and standard commercial replacement ink (Print-Rite) was used for the test run. The aim of this test cycle was firstly to see if the method was practical and secondly to discover and learn to overcome potential problems in order to do the actual printing run more efficiently, accurately and with as few as possible waste of catalyst. To do the test run, 5x5 cm squares of white cotton cloth were cut representing the carbon cloth GDL in the actual printing. This square was then taped to a standard 8.5”x11” photocopier paper by cutting a printed square of the same dimensions out of the paper and applying masking tape to the back. This masking tape was applied in such a fashion that the cloth square can be stuck to the hole in the paper from the front. This means that the whole frontal area of the cloth can be printed on preventing wastage from the covered area of the tape when taped down from the front.

Before the square was stuck to the paper it was weighed carefully on a digital scale with the capability of weighing increments of 0.0001 g (same scale used for all weighing).

The printer cartridge was removed and a hole machined into the top. The sponge inside the cartridge was then removed and the remaining ink drained. Both the cartridge and the sponge were cleaned in an ultrasonic bath in acetone for 30 minutes. The sponge and the cartridge were then taken out of the acetone and left to dry. Once dried, the sponge was placed back and the cartridge refilled with the replacement ink. A piece of insulating tape was used to cover the machined hole. A square was printed onto a paper to make sure that the ink had refilled correctly.

The paper with the square was then fed through the printer and a 5x5 cm square was printed on top of the cloth square and weighed after drying for 3 minutes. This sequence was repeated three times with the printing quality settings set to *normal*. The same test run was repeated with the settings set to *best* printing quality. Lastly a square was fed through the printer four times on the *best* quality setting with drying periods of 3 minutes between cycles and a final drying period of 20 minutes. In each instance the change in weight was calculated and compared to determine the printing consistency and accuracy.

Spray Painting (SP)

The test run for the spray painting (airbrush) technique was done with the same HP replacement ink that was used for the hand painting and inkjet printing. An airbrush (Iwata Revolution, Tool and Professional Services) was used for the test run.

The air pressure regulator coupled to the compressor (Puma) was set to 200kPa. The same setup as specified in the section describing the hand painting was used. The cloth squares were weighed before being inserted into the setup. 2 ml of ink was drawn up with the cartridge ink replacement kit syringe and injected into the airbrush ink reservoir. Next the squares were sprayed with a coat of paint and left to dry for 5 minutes. After being weighed a second coat was sprayed onto the squares. In this second repetition the squares were not placed on the heated pad setup but rather stuck to a paper/masking tape template as in the hand painting technique. The painted squares were weighed again after being left to dry for another 10 minutes.

Screen Printing (ScP)

Other personnel working on the screen printer had already gained sufficient experience on the screen printer to deem a test run unnecessary.

The printing sequence consisted of firstly positioning the target to be printed onto on the vacuum plate. Next an amount of ink is pipetted in front of the squeegee. The foot operated pedal is then activated lowering the carriage and screen (160 mesh size) onto the target. The automatic sequence then sends the spreader along the pre-set travel length printing the ink through the openings in the screen. At the end of the travel length the carriage automatically lifts up and a flood switch is activated by hand bringing the spreader and scraper back to the original position where the flood switch is switched back on. This sequence is repeated to achieve the desired loading.

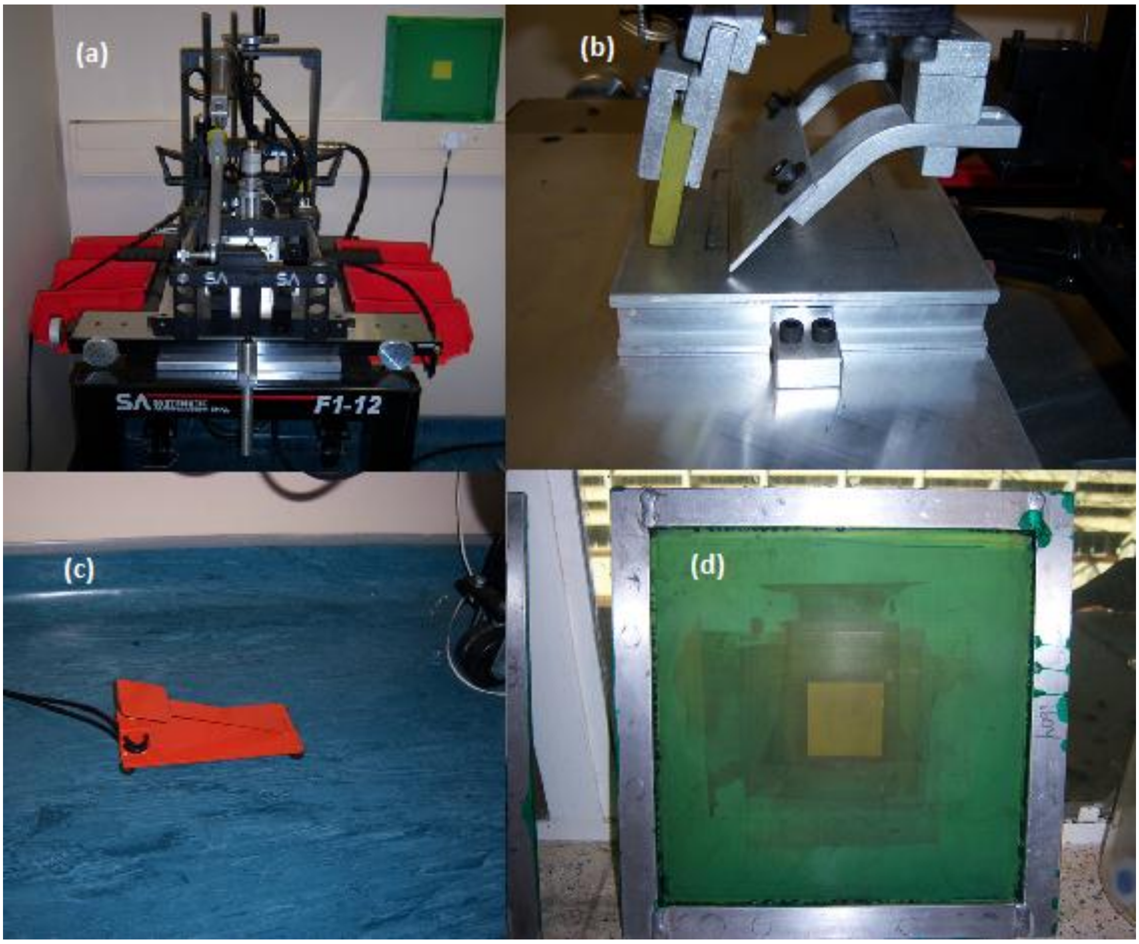

Figure 42: The screen printer (a) used in the study, suction plate with spreader (left) and scraper (right) (b), foot operated pedal (c) and 160 mesh size screen (d).

Results: Test Run

It is necessary to note that the loadings, although an indication of the degree of loading of each technique, is not as important **in this test run** as the difference between the loading of each separate method. This serves as a reflection of the accuracy and repeatability of each process.

- **Hand Painting**

The results for the test run done with the hand painting using standard HP 121 replacement ink is shown in table below.

Table 10: Results for the hand painting test run

Hand paint (One coat, 45 minutes dry time)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading(mg)**
0.5041	0.7995	0.2954	295.4
0.5066	0.7724	0.2658	265.8
0.4654	0.852	0.3866	386.6
		Average	**315.933**
		Average deviation	**47.111**

The results for the hand painting test run in Table 10 points out the problem of accuracy encountered in this specific method. Since it is very difficult to control the amount of ink uptake into the brush, it is also very hard to control the amount of ink deposited. Aside from this, another problem is that it is very difficult to deposit small amounts of ink accurately. Apart from the drawbacks, the hand painting is fairly simple and can be done with only a few practise rounds. Possible drawbacks have been identified as mentioned. These difficulties are discussed next.

Firstly is the matter of ink waste. Since it is not practically possible to control the uptake of ink into the brush, an amount of ink is wasted by getting stuck in the brush. Besides this, an amount of ink ends up on the template holding the cloth square in place and therefore goes to waste. This wastage of ink can however be minimized by improving on the painting skill and using finer brushes although this will have a major effect on the time consumption.

The second matter is those of time consumption. Since a larger amount of ink is deposited on the cloth, the time for drying increases. In the test run, the drying time was 45 minutes and even after these 45 minutes the solvents were still evaporating. This matter can be addressed by using an ink with a little higher viscosity in order to better control the uptake and deposition of ink. A smaller amount of deposited ink and solvent will result in a shortened drying time. This will also create the possibility of more accurate ink loadings.

- **Inkjet printing**

The results of the test run done with the replacement ink are presented below.

Table 11: Results for the inkjet printing test run (Normal quality)

IJP (normal quality, 3 minutes dry time)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading (mg)**
0.4353	0.45	0.0147	14.7
0.4491	0.4636	0.0145	14.5
0.486	0.5009	0.0149	14.9
		Average	**14.7**
		Average deviation	**0.133**

Table 12: Results for the inkjet printing test run (Best quality)

IJP (best quality, 3 minutes dry time)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading (mg)**
0.477	0.4968	0.0198	19.8
0.4801	0.4998	0.0197	19.7
0.429	0.4487	0.0197	19.7
		Average	**19.733**
		Average deviation	**0.044**

Table 13: Results for the inkjet printing test run (Best quality, 4 passes)

IJP (best quality, 3 minutes dry time, 4 passes)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading (mg)**
0.4233	0.4776	0.0543	54.3

The results show that the printer ink deposition is very accurate with an average deviation of 0.133 for the *normal quality* and an average deviation of 0.044 for the *best quality*. The accuracy is suspected to be even better since the deviations can be attributed to differences in the evaporation of the ink solvents during the detachment of the cloth and the measuring. As seen in the loading of the 4 pass cloth (table 6) the loading is slightly lower than would have been suspected (4 x 19.733g = 78.932g versus 54.3g). This inconsistency is attributed towards the longer drying period of the 4 pass run resulting in a more complete evaporation of solvents. This also highlights the importance of the drying time in the accuracy of the measurements and loading. From this test run the following possible problems have been identified.

The first is the adherence of the square to the template paper. Care should be taken towards adhering the GDL onto the template paper ensuring a flat even printing surface. This will prevent the cloth from uneven loading or warping due to collision with the printing head.

The second possible problem is the matter of solvent drying. To prevent inconsistency when loading, proper time should be allocated towards drying of the deposited ink. This drying period can be shortened by placing the coated substrate on a heated pad in a well-ventilated area. At ambient temperatures the period of drying should be no less than 5 minutes between successive coats.

A third matter is the feeding of the template paper into the printer. Although fairly simple, attention should be given to inserting the template paper into the paper tray. Misalignment of the paper can cause a paper jam causing a waste of ink and damage to or the possible discarding of the carbon cloth. In addition to this a template placed in the wrong orientation will result in the deposition of catalyst onto a position other than the determined GDL position, causing a waste of catalyst and inconsistency of the loading.

- **Spray painting**

Table 14: Results for spray painting test run (5 minutes drying time)

Airbrush (5 minutes dry time)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading(mg)**
0.4791	0.4899	0.0108	10.8
0.4375	0.4452	0.0077	7.7
0.4701	0.4832	0.0131	13.1
		Average	**10.533**
		Average deviation	**1.889**

Table 15: Results for spray painting test run (second pass, 10 minutes drying time)

Airbrush second pass (10 minutes dry time)			
Weight before (g)	**Weight after (g)**	**Delta Weight (g)**	**Loading(mg)**
0.4791	0.5324	0.0533	53.3
0.4375	0.5032	0.0657	65.7
0.4701	0.5274	0.0573	57.3
		Average	**58.767**
		Average deviation	**4.622**

The results show that the loading amount is much more controllable than that of the hand painting. This is clear in both the single coat and double coat. The results also highlight the amount of ink that can be applied. A low loading in the vicinity of 5mg can be applied as easily and effective as a load of 50 or 100mg. The drying time was sufficient at 5 minutes which is much shorter than that for the hand paint and in the same magnitude of that of the inkjet printing.

In the first run, the manufactured spray setup with heated steel back plate was used. The idea was that the cloth could be easily slid into place and sprayed while being dried by the backing plate. Although concept seems to work, it did have some technical difficulties. The first is that the high pressure jet of air that propels the ink dislocated the cloth square from its place and makes accurate spraying a daunting task. The second problem is that the material warps as some regions are still wet due to the paint while other regions are beginning to dry. This was overcome by using a masking tape backed paper template as mentioned earlier and using the heated pad only for the drying. This problem can also be solved by connecting a vacuum device to the backing plate and drilling holes through the plate. The applied vacuum then holds the square cloth in place. The warping can be overcome by the much stiffer carbon cloth used in the actual Pt/C ink deposition.

Appendix B: Optimum Hot-press Parameters

In an attempt to determine the optimum hot press procedures experimentally, the necessary steps were carried out as indicated in the MEA fabrication chapter (Chapter 7).

Four membranes (20x20mm) were cut from Nafion 117 hydrated membranes. GDE's fabricated by the spray painting method were cut to fit these membranes. Two of these electrodes were placed at the sides of a membrane and placed inside two Teflon blocks. The heated press was set to temperature and given sufficient time to heat up. The Teflon blocks were then inserted into the press and left for the specified time. After the fabricated MEA had been taken out of the press, it was inspected and stored in deionized water for 72 hours and again inspected for any signs of the electrodes parting from the membranes. A summary of these results are presented in Table 16.

Table 16: Summary of the experimental investigation of the pressing parameters

Sample	Temperature [˚C]	Pressing Time [minutes]	Pressure [Mpa]	Bond direct after press	Bond after 72 hours
1	90	10	10	Weak	none
2	95	10	10	Good	weak
3	100	15	10	Good	weak
4	140	15	10	Excellent	excellent

From the results of the experimental procedure, it was clear that the optimum parameters are:

- Temperature: 140℃
- Pressure: 10 MPa
- Time: 15 minutes

The temperature in Table 16 is the temperature as indicated and adjusted to on the heat-press control panel. It was however still unclear how accurate these temperature values were. It was also unclear how the temperature distribution that the MEA would feel would be, since the press was pre-heated when the cold Teflon blocks containing the unpressed MEA was inserted.

To investigate this uncertainty, these values were determined experimentally by first pre-heating the press and then inserting the Teflon blocks containing a thermocouple. The results of this test are now presented:

Table 17 Heated press interface test data

Time (min)	Interface Temperature[C]	Plate Temperature [C]
1	31.6	136.7
2	36.9	136.7
3	44.4	136.7
4	55.3	136.7
5	66	136.7
6	74.9	136.7
7	82.9	136.7
8	90.1	136.7
9	95.4	136.7
10	99.8	136.7
11	102.9	136.7
12	106.2	136.7
13	109	136.7
14	111.3	136.7
15	112.9	136.7
16	114.5	136.7
17	115.6	136.7
18	116.6	136.7
19	117.4	136.7
20	118	136.7
21	118.4	136.7
22	118.9	136.7
23	119.3	136.7
24	119.5	136.7
25	120.2	136.7
26	120.4	136.7
27	120.3	136.7
28	121.1	136.7
29	121.3	136.7
30	121.4	136.7
31	121.6	136.7
32	121.9	136.7
33	122.2	136.7
34	122.4	136.7
35	122.3	136.7
36	122.4	136.7
37	122.7	136.7
38	122.8	136.7
39	122.9	136.7
40	123.1	136.7
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42	122.8	136.7
43	122.9	136.7
44	123.3	136.7
45	123.2	136.7

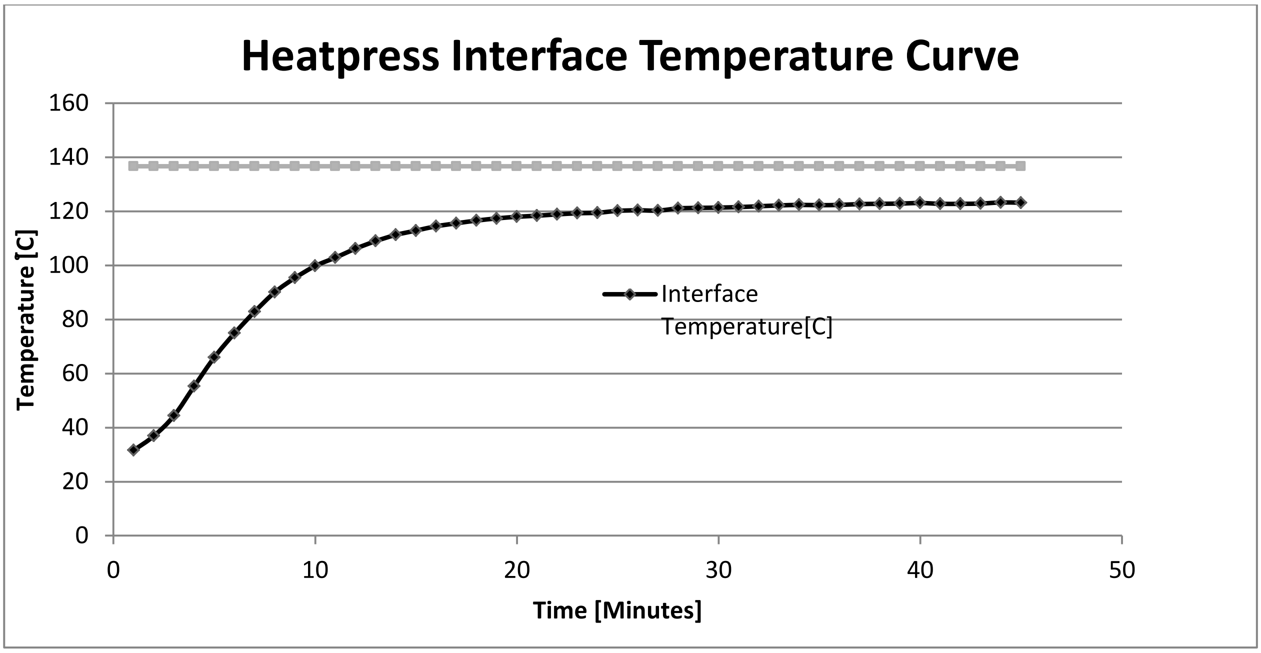

Figure 43: Results of the test done on the heated press temperature distribution

The results show that although the plate temperature was stable at 136.7 ˚C, the Teflon interfaces reached a maximum temperature of 123˚C. The difference in temperature can be ascribed to the heat loss because of radiation and convection. If a sample is pressed for 15 minutes, it will experience a temperature ranging from 31.6˚C in the first minute to 111.3˚C in the 15th minute.

Appendix C: MEA Fabrication Cost

The cost factor involved in the catalyst application mainly consists of two aspects, namely the cost of equipment and the cost of materials. These costs are discussed next.

Cost of Equipment

The equipment differed for most of the methods studied. There were, however, some equipment that were universal in the methods and is therefore not accounted for. The equipment cost for each method is presented in Table 18, but are not compared between the respective methods as it would involve taking variables such as life expectancy and mass production into consideration, which is beyond the scope of this study.

Table 18: Equipment cost for each method

Method	Equipment	Cost (ZAR)
Hand Paint	Paint brush	R 15.00
	Paint setup	R 100.00
	Total	**R 115.00**
Spray Paint		
	Air brush	R 700.00
	Compressor	R 1,000.00
	Spray setup	R 100.00
	Total	**R 1,800.00**
Screen Print		
	Screen printer	R 62,700.00
	Screen	R 1,200.00
	Total	**R 63,900.00**
Sputter Coating		
	Sputter coater	R 70,300.00
	Total	**R 70,300.00**
Hand Paint on Carbon	Air brush	R 700.00
	Compressor	R 1,000.00
	Spray setup	R 100.00
	Paint brush	R 15.00
	Total	**R 1,815.00**

Cost of Materials

The amount of catalyst ink needed to produce the GDE's reported in the study varied for all the methods. There is a remarkable difference in the fabrication cost based on the ink consumption.

The ink consumption for each method was measured in amounts of mixtures used. The mixture size was constant throughout and consisted of the following:

- 50.3 mg Pt/C powder (20wt%)
- 382 µl Nafion 117 solution (5wt% in alcohols and water)
- 3.0 ml Methanol
- 0.4 ml ethylene glycol (only screen printing)

In the calculation of the cost of materials, the cost of the ethylene glycol, methanol and deionized water was emitted because of their insignificant contribution. Table 19 presents the material cost per unit as purchased.

Table 19: The unit cost of various materials required

Description	Size/Quantity	Cost (ZAR)*	Unit cost (ZAR)*
20wt% Pt/C catalyst powder	1g	466.64	0.466 R/mg
Nafion 117 solution	25ml	1248	49.92 R/ml
Nafion 117 membrane	30x30cm	1600	1.777 R/sq.cm
AvCarb Grade 1071 HCB Carbon cloth	20x20cm	392	0.98 R/sq.cm

*Calculated at exchange rate of R 8.00/$. Costs do not include packaging and shipping.

The values in Table 19 were used to calculate the cost per mixture of catalyst ink prepared from which the cost per electrode for each method was calculated. The only material costs used in the calculation of mixture cost were those of the Nafion solution and the Pt/C powder as illustrated in Table 20.

Table 20: Mixture cost

Constituent	Amount	Unit cost (ZAR)	Cost per mixture (ZAR)
Pt/C powder	50.3 mg	R 0.47	R 23.44
Nafion solution	0.382 ml	R 49.92	R 19.07
Total cost (ZAR)			**R 42.51**

The cost per catalyst layer for the basic three methods has been calculated and is presented in

Table 21 (carbon cloth price not included, therefore catalyst layer cost).

Table 21: The catalyst layer cost for each basic method.

Method	Amount of mixtures used per electrode	Total cost per catalyst layer (ZAR)
Hand Paint	2	R 85.02
Screen Print	2.3	R 97.77
Spray Paint	2.5	R 106.28

The fabrication of the sputtered electrode and the electrode produced by hand painting onto a carbon micro porous layer had changes to the basic mixture cost. For both methods a mixture of Nafion solution, carbon particles and solution (methanol) were made. The cost per electrode catalyst layer for these methods can be calculated as follows:

Table 22: Catalyst layer cost for improvement methods

Method	Description	Amount	Unit cost (ZAR)	Catalyst layer cost (ZAR)
Sputter	Nafion solution (carbon layer)	0.382ml	49.92 R/ml	R 19.07
	Platinum deposited*	12.5 mg	0.417 R/mg	R 5.21
			Total	**R 24.28**
Hand paint on carbon				
	Nafion solution (carbon layer)	0.382ml	49.92 R/ml	R 19.07
	Basic hand painting mixtures	2	42.51 R/mixture	R 91.02
			Total	**R 110.09**

*****Calculated as the theoretical amount to be deposited, not the physical amount deposited in the study.

Total MEA Production Cost (Excluding Equipment)

From the results of all of the method catalyst layer costs, the total cost per MEA for each method was determined. These calculations included:

- 50 cm^2 carbon cloth (2 x 25cm^2 GDL's)
- 64 cm^2 Nafion membrane

2 x electrode catalyst layers from each method as presented in

- **Table 21** and **Table 22**.

Table 23: Total MEA cost as calculated for each method

Method	Total MEA cost
Hand Paint	R 332.77
Screen print	R 358.27
Spray paint	R 375.29
Sputter	R 211.29
Hand Paint on Carbon	R 382.91

The results indicate that the most expensive MEA had cost R 382.91 to produce. This is very low in comparison with the commercial available MEA's which cost approximately R1110 per MEA (at R 8.00/$, excluding packaging and shipping).