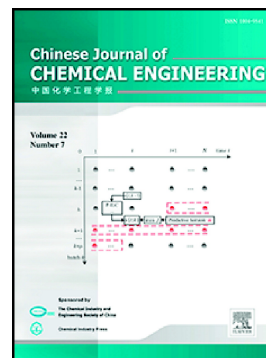# Journal Pre-proof

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Article

Comparison of catalyst-coated membranes and catalyst-coated substrate for PEMFC membrane electrode assembly: A review

Lim Bee Huah[1,3], Edy Herianto Majlan[1,*], Ahmad Tajuddin[1], Teuku Husaini[1], Wan Ramli Wan Daud[1,2], Nabilah Afiqah Mohd Radzuan[1], Md. Ahsanul Haque[1,4]

[1] Fuel Cell Institute, Universiti Kebangsaan Malaysia, UKM Bangi43600, Selangor Darul Ehsan, Malaysia

[2] Research Centre for Sustainable Process Technology (CESPRO), Universiti Kebangsaan Malaysia, UKM Bangi43600, Selangor Darul Ehsan, Malaysia.

[3] Faculty of Engineering and Built Environment, Mahsa University, Jenjarom42610, Selangor Darul Ehsan, Malaysia

[4] Department of Applied Chemistry & Chemical Engineering, Islamic University, Kushtia 7003, Bangladesh

Abstract

Catalyst-coated membranes (CCMs) have gained popularity among membrane electrode assembly (MEA) fabricators for their abilities and advantages compared with those of other methods, such as catalyst-coated substrates (CCSs). CCMs show a profound new analysis for reducing platinum (Pt) catalyst loading. In addition, they increase the total number of reactions that occur on the MEA because of their active area amplification, which leads to an improved catalyst-utilization efficiency rate. Moreover, several characteristics are involved in the MEA fabrication methods. Material-manufacturing effects with regard to catalyst inks and analysis of the overall performance of MEAs prepared by the CCM and CCS methods are deliberated. This deliberation emphasizes the practical approaches in minimizing performance deterioration during the fabrication of MEAs using the CCM method and converses the commercialization of the CCM fabrication method toward developing an end product. Novel research is required for MEA fabrication using the CCM methods to ensure

Corresponding author: Fuel Cell Institute, Universiti Kebangsaan Malaysia, UKM Bangi 43600, Selangor Darul Ehsan, Malaysia. Tel.: +60 3 89118521; Fax: +60 3 89118530

E-mail address: edy@ukm.edu.my, (Edy Herianto Majlan).

that the fuel cell performance is improved. Therefore, this review is focusing on the pros and cons of both distinguished methods, that is, CCM and CCS fabrication, for better comparison.

1. Introduction

At present, the continual use of fossil fuels contributes to global warming as greenhouse gasses, including carbon compounds, are trapped in the atmosphere. These fossil fuel-burning activities, which are produced by vehicle combustion engines, factory wastes, and stationary power generators, have increased the CO_2 emissions levels to a critical state [1,2]. In the last Convention of Parties 21 in 2015, the global climate change debates have agreed upon reducing the CO_2 emissions particularly from the current industrial levels, and campaigned against the global temperature increasing by over 2 °C. New energy policies and changes toward greener and cleaner energy production are expected in the next 10 years. These conferences also discussed green energy technologies, including the use of fuel cells as an alternative to the existing fossil fuels. Therefore, as an alternative energy source, fuel cells lead to future research areas in green and renewable energy [3–6]. Fuel cells exhibit an interesting feature in which hydrogen gas is used as the fuel. Hydrogen gas is an excellent energy carrier because of its unique properties and ability to produce water when integrated with fuel cells. Hydrogen is used to initiate electrochemical processes, which are converted into electrical energy for mechanical use. Moreover, these prominent chemical reactions further result in high power density and fuel cell efficiency [7,8]. Therefore, fuel cells are the potential substitute for fossil fuels in the energy sector, and various applications have been introduced through research development [9,10]. In particular, among the many types of fuel cells, proton-exchange membrane fuel cells (PEMFCs) have been a popular fuel cell since the

early 1960s because they have rapid activation during operation, a simple system, and proven feasibility in a wide range of applications, particularly in space shuttles [11,12]. In the PEMFC system, several components are integrated to produce the required power, including membrane electrode assemblies (MEAs); bipolar plates, consisting of an anode and cathode; and current collector plates, which are usually copper-based materials. However, among the main components, MEAs are the most important components, as they are fabricated by combining several parts, which usually include a carbon paper, catalyst layer containing platinum (Pt) and Nafion, and polymer membrane. These individual parts provide the main function of the PEMFC, as the chemical reactions occur and indicate the performance level of the integrated PEMFC system [13]. Theoretically, fuel cell performance is governed by its individual components as a whole. However, notably, the techniques used for MEA fabrication include two distinct methods, that is, (i) catalyst-coated substrates (CCSs) and (ii) catalyst-coated membranes (CCMs), which have significant roles [14]. Studies have reported that different fabrication techniques often result in different fuel cell performances. Meanwhile, several studies have indicated that the performance depends on specific mechanisms related to catalyst loading and the overall working temperature [15–17]. This review focuses on the latest research development techniques for fabricating MEAs that apply to PEMFC applications using CCM techniques. This review also claims that the CCM fabrication methods show a profound new way to reduce Pt catalyst loading and increase the total number of reactions occurring on the MEA. These reactions consequently initiate a reactive area amplification, which leads to an improved catalyst-utilization efficiency rate. In addition, this review discusses the advantages and disadvantages of the two distinguished methods, that is, CCM and CCS fabrication. As studies have indicated that the CCM fabrication methods have better performance than that of the CCS fabrication methods, many studies have emphasized the CCM fabrication method. Studies on the CCM fabrication

method have focused on the effects of a catalyst ink on the manufacturing and performance analyses of CCM-based materials compared with CCS-based materials. Furthermore, studies have considered practicable approaches to reduce performance deterioration of MEAs on the basis of the CCM fabrication methods and ways to commercialize them. This review aids in sorting the existing reports and research on the MEA fabrication methods with regard to the CCM fabrication methods to advance and broaden studies in the future.

2. MEAs

MEAs consist of a membrane and an electrode with regard to the anode and cathode. The membrane is sandwiched between two electrodes to form a type of single cell (Fig. 1) [12,18]. The electrochemical activity occurs in the membrane, producing a current by manipulating the hydrogen reactions at the anode sides to act as a fuel, while the oxygen or purified air at the cathode sides serves as an oxidant. These electrochemical reactions instantaneously react with the catalyst, either a Pt catalyst or another catalyst, which is used on both sides of the electrodes. Then, the reaction results in the decomposition of the oxidants into an ion and electron, which appear at the electrodes. Meanwhile, the conjoined hydrogen and oxygen ions further produce water (H_2O) throughout the MEAs [12]. Hence, this process indicates that the MEAs function as the important component that ensures that the fuel cell system works.

The MEA is the heart of the system, which contributes to the reliability, feasibility, and durability of the overall fuel cell system [19,20]. The MEAs attract much attention regarding the parts of the fuel cells, which reduce the production cost, because the only highly conductive catalyst available to date is platinum (Pt), which is expensive [21–25]. Therefore, previous studies have focused on developing Pt-free electrocatalysts and reducing the weight-loading percentage of the catalyst for each electrode [26–33].
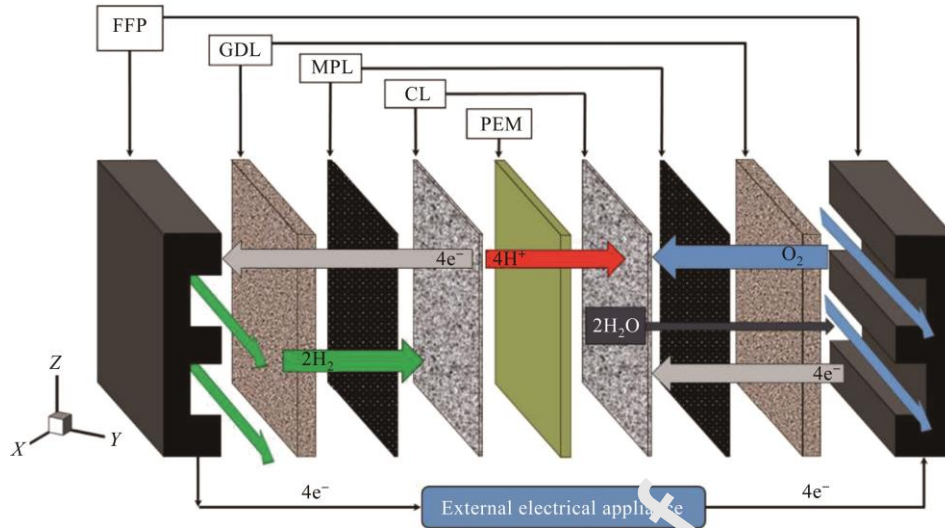
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Fig. 1 PEMFC layout consisting of a MEA and flow field plate [18]

A review conducted by Wang *et al*. [34] indicated the three main issues of non-precious metal MEA durability. These issues include the leaching of non-precious metal catalyst, attacking of H_2O_2, and protonation of the active side. Simultaneously, some research focuses on determining the best technique to produce better catalyst dispersion and increase mass transport at the fuel cell electrodes [12]. Theoretically, MEAs can be prepared using two types of fabrication methods, which are the CCS and CCM (Fig. 2). In the early stages of MEA fabrication, researchers tend to use the CCS fabrication method, as it allows separate media fabrication, which consists of the polymer membrane, gas diffusion layer (GDL), and catalyst inks for coating. The catalyst inks are coated onto the diffusion layer before combining it with the polymer membrane using the hot-press processing method to form the MEA.
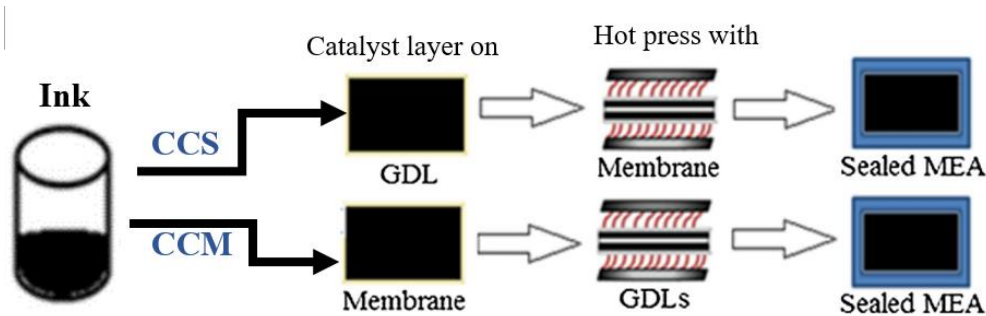

Fig. 2 Comparison of different MEA fabrication methods [35]

The overall CCS fabrication methods are simple and can be effectively applied to develop an extensive and bulk production of MEAs [36,37]. However, the high costs of the Pt loading, heterogeneous catalyst dispersion, and lack of mass transport in the MEAs are the issues in fabricating the MEAs using the CCS methods [12]. Hence, recent developments of MEA technology have proposed other methods identified as the CCM methods. This recent development uses a new approach that is distinct in many aspects compared with that of the previous CCS methods. The major distinction recognized by many studies is the ability of the CCM-MEA to generate a remarkable performance with regard to the electrochemical reaction rate while reducing the resistance effects of the MEA. An experimental study conducted by Shahgaldi *et al*. [35] showed that at high Pt loading (0.5 mg·cm^{-2}), the CCM membrane has shown higher power density compared with the CCS fabricated membrane. In addition, at Pt loading of 0.125 mg·cm^{-2}, both fabrication methods have shown a reduction of power density as the PT loading is reduced. However, the CCM-MEA has shown higher power density (0.69 W·cm^{-2}) compared with the CCS-MEA (0.23 W·cm^{-2}). These devices demonstrate a higher power density than that of the CCS-MEA with similar Pt loadings. One of the factors is the direct integration between the polymer membrane and catalyst inks because the reactions between the oxidant and catalyst occur on the membrane surface [38,39]. To date, all the methods invented are distinguished by the approach of where the catalyst inks are deposited, either on the diffusion layer or directly onto the polymer membrane layer to form an electrode.

1.1 CCS

In general, the CCS is a conventional method of the MEA fabrication containing the catalyst layer, known as the GDL, which is sandwiched into a polymer membrane using a hot-press machine. Studies on the different hot-press parameters have been undertaken to create optimum MEAs that contribute to good fuel cell system performance [40–42]. The

schematic diagram in Fig. 3 explains the fabrication of the CCS-MEA method that involves a carbon paper, catalyst, and membrane using the hot-press technique [43]. In addition, the illustration shows that GDLs are often integrated as a part of the MEA because of its ability to support the overall structure of the MEA. Furthermore, the GDLs primarily diffuse the reactants over the entire catalyst layer, which utilizes the catalysts and collects the electrons produced by the reaction on the electrodes. Basically, the GDL prevents water flooding into the gas channel of the bipolar plates. This phenomenon must be avoided, as it hinders the reactant transport, which deteriorates cell performance. At present, the GDL fabrication methods involve catalyst-coating processes, such as spraying, screen printing, and rolling [43–48]. The studies reviewed show that the different layers of the GDLs have different functions. The first GDL layer serves as a reactant dispenser for the entire active area of the MEA, whereas the second layer manages the two-phase water flowing in the MEA [49–51]. Previous studies have shown that the highest performance of the CCS-MEA is achieved by the presence of the second layer of the GDL, as it functions as the waterproof layer. These effects occur as the hydrophobic materials are added and supported by the carbon paper, which produces a great aperture volume, transports the reactants, and utilizes the catalysts. These factors further lead to the overall CCS-based fuel cell performance [52–55].
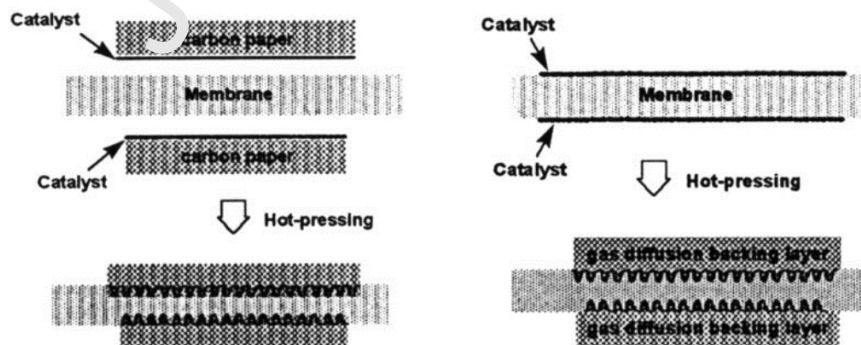

Fig. 3 MEA fabrication by the CCS technique [43]

The performance of the CCS-based fuel cell is not solely dependent on the types of GDLs utilized, although it is applicable for certain catalyst-loading compositions. However,

the effects of the catalyst loadings are crucial, particularly in evaluating the overall performance of the fuel cell. A study conducted by Gasteiger *et al.* [56] showed that as the catalyst loading was reduced, the performance of the fuel cell, with regard to voltage and current density, was maintained at optimum conditions. These findings are contrary to the theoretical fundamentals, as the fuel cell largely depends on the catalyst loading. However, the insignificant voltage losses that occur during the test indicate that the catalyst loading still plays a major role in determining the CCS-based fuel cell performance. Some studies have been conducted on the catalyst layer to analyze the impact, influence, and optimization of the Nafion content, with the Pt distributions across the active area of electrodes and thickness and porosity of the GDLs [57–61].

1.2 CCM

Researchers believe that the CCM method for MEA fabrication was founded first in the US by Mahlon S. Wilson on May 18, 1993. The patent description stated that "the catalyst layer is formed by applying a Na$^+$ form of a perfluorosulfonate ionomer directly to the membrane." This method was later expanded and applied in current studies on MEA fabrication [62]. As the technology started to develop, Hohenthanner *et al.* in 2002 coined the term "catalyst-coated membrane" referring to the patent number CA2420455C, although the patent was published on Jul 1, 2004 [63]. Later that year, another patent on the CCM method was published by Frank Baumann *et al.*[64], in which the term CCM was used for their fabrication method. The term continued to be used in 2006, as the first journal published the CCM fabrication method for 10 kW PEMFC applications performed by Mingruo Hu *et al.* [65]. This brief history shows how the past advancements regarding the CCM fabrication method proceeded over the years of research.

Theoretically, CCMs are prepared by applying a catalyst ink directly onto a polymer electrolyte membrane using specific techniques. Studies have revealed that the direct catalyst spray technique is a popular technique used to prepare CCMs on polymer membranes, a process known as CCM-DS and the decal transfer technique. These techniques coat the catalyst directly on the polymer membrane surface using a spray technique. Then, the catalyst layers are molded temporarily on the substrate form before integrating them with the polymer membrane using the hot-press method [66,67]. However, several techniques for implementing the CCM fabrication method have been reported by some studies, such as screen and inkjet printing methods, the doctor blade coating method, and the layer-by-layer (LbL) method. However, the CCM fabrication methods have several advantages over the CCS fabrication methods, with regard to lowering the Pt loadings. These methods result in high utilization efficiency and excellent fuel cell performance because the membrane and catalyst layer facilitate the electrochemical reactions [65]. In comparison with the MEA fabrication using the CCS fabrication methods, known as CCS-MEAs, the reaction theoretically occurs on the carbon paper before the protons (H^+) travel back to the membrane. Consequently, this process is a lengthy process compared with that of the CCM fabrication method, and it includes a performance drop during the process. Hence, membrane swelling issues are encountered because of the close contact between the catalyst layer and polymer membrane, while the catalyst utilization and power density produced are high. Therefore, suitable fabrication methods are important, and the Pt loadings can be minimized without neglecting the overall fuel cell performance. A study by Tang *et al*. [38] compared fabricated CCM-MEAs and CCS-MEAs under similar experimental conditions. The study showed that the CCM-MEA demonstrated better electrochemical performance than that of the device from the CCS-MEA fabrication method. Another study carried out by Hnat *et al*. [68] showed that the catalyst load can be reduced by 75% for CCM-MEA compared with CCS-MEA.

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Several factors that might have a significant role in preparing the MEAs for PEMFC applications using these two main methods are identified, which are discussed later in this paper. Considering that researchers are concerned with the fabrication costs, which are related to marketability issues, the CCM fabrication method has a great advantage in reducing the Pt catalyst loadings. The performance of the CCM-MEA, with regard to efficiency, power density, and Ohmic and charge transfer resistance, is increased compared with that of the CCS-MEA. This increase is due to the capability of the CCM-MEA fabrication method to boost the overall performance even when applying the same Pt catalyst loadings as those used in the CCS-MEAs [38].

Despite having some advantages, particularly regarding the performance, the CCM also has a drawback that may compromise the performance of the MEAs in the long term, which is the durability, as several studies conducted have found that the MEAs fabricated using the CCM method are short-lived. Hence, further studies on the CCM fabrication methods must solve these current issues. Sadeghi Alavijeh *et al*. [69] studied the issue of creep behavior on the CCM because creep is a type of mechanical damage that can occur in the CCM during fabrication. This consideration is important, as creep is undeniable and is known to reduce the membrane durability and later deteriorate the PEMFC performance. However, considering that the creep will eventually occur and worsen the durability, researchers have discovered solutions. Hence, the membrane durability is still manageable if the three main factors, including creep stress, temperature, and relative humidity, are controlled. Therefore, reducing the operation temperature and keeping the membrane hydrated are sufficient methods to alleviate the creep issues [69]. Xu *et al*. [70] established the palygorskite-based catalyst layer and spread it onto the membrane to enrich the mechanical stability of the catalyst layers using the CCM fabrication method. This treatment also aids in preventing impure metal ions from the perfluorosulfonic acid (PFSA) ionomer

poisoning. Such poisoning is a major drawback because the contaminant Fe^{2+} metal ions in the catalyst ink lead to mechanical damages between the catalyst and membrane. These damages include microcracks, delamination, pinholes, and debonding, which worsen overall fuel cell performance [70,71].

Based on the prior discussion, the CCS and CCM methods used in MEA fabrication have great advantages and disadvantages. However, the main downside for the CCS fabrication method is the requirement of high Pt loadings to achieve a similar performance to that of the CCM fabrication method. These factors have attracted numerous researchers to further investigate the CCM fabrication method because of its potential and ability for marketability at low production costs. However, the issue of the CCM fabrication method involves the durability of the MEA, which leaves the CCS fabrication method as the only option. However, the CCS is more difficult to fabricate than the CCM because it involves a complex technique that requires dealing with several layers of catalysts. Moreover, the CCM fabrication method does not have an issue with membrane wrinkling and swelling during fabrication. Hence, the CCM fabrication method has many improvements and has shown potential of becoming the main method in preparing MEAs in the future.

3. CCM Fabrication Techniques

Several techniques are applied in the CCM fabrication method to fabricate the MEAs, which include the direct wet spray, decal transfer, painting, screen and inkjet printing, doctor blade coating, and LbL techniques [47,72–76]. As mentioned by Silas Towne *et al*. [37], different sizes, shapes, and quantities of MEAs are the key elements to consider in MEA fabrication. These considerations are important in maintaining the high-quality production of MEAs, as it affects the PEMFC performance [37]. The three-phase boundary-containing

porosity allows a reaction to take place easily; the details on this type of technique, which is applied in previous studies of the CCM fabrication method, will be discussed [77].

1.3 Direct Spraying

A simple direct-spray technique is a popular technique to date [78]. This technique generates a uniform catalyst ink layer on the membrane layer. This technique involves using the spray gun as a spray module. The catalyst ink is initially deposited onto the membrane at each electrode, anode, and cathode at 70 °C using a hot plate. Considering that it is sprayed manually, an appropriate manner was used to feed the ink onto the membrane. This approach ensures that the catalyst ink can cover the active parts of the membrane. However, some studies use different types of spraying modules, depending on the work required. These types include a regular spray with manual adjustment or an ultrasonic spray, which offers a flexible spray pace and width adjustment. These techniques have the potential to minimize the catalyst loss, which will lead to a cost reduction [79]. H.N. Su *et al*. (2008) studied the use of infrared light during spraying, which aided in uniform catalyst distribution on the membrane layer [73,78]. These techniques have great advantages, particularly in fabricating effective and inexpensive electrodes at low Pt loading with high utilization efficiency [79]. The main challenge of this technique includes membrane swelling during spraying. Swelling and wrinkling of the membrane are caused by the reactions that occur between the membrane and certain solvents used in the catalyst ink [65,80]. By contrast, the conventional methods use a functioning vacuum board to hold the Nafion membrane to avoid membrane swelling during spraying and hot-pressing. Yang *et al*. [81] suggested using ethylene glycol (EG) during the fabrication of the catalyst ink to prevent the swelling issues and eliminate the use of the vacuum board. In addition, studies reported that a glycerol-presaturated membrane encounters the same swelling problem [62]. Hence, these results show that membrane

swelling during spraying is an issue that researchers must consider, as it is a critical parameter, particularly in the CCM fabrication method [82]. However, Xie *et al.* [83] researched on the use of electrostatic spraying during MEA preparation. They reported that electrostatic spraying could improve the adhesion strength and formation of a flat and uniform catalyst layer. Moreover, they concluded that using electrostatic spraying with Pt loading of 0.3 mg/cm^2, the power density could reach 1.75 W/cm^2.

1.4   Decal Transfer

The CCM fabrication method is still feasible for the mass production of MEAs by using the decal transfer method. This technique can produce low-resistance MEAs because its fabrication process (Fig. 4) reduces the interfacial resistance issues faced by conventional MEAs [84–90]. Different from the direct-spray technique, the decal transfer consists of various techniques used to implement MEA fabrication. Initially, the membrane is treated by converting the hydrogen-form membranes into sodium-form membranes because hydrogen-form membranes are relatively free of other cations. Hence, with this technique, a purification procedure is not necessary. Then, the catalyst layers are formed by casting the catalyst ink onto the Teflon substrate before it is transferred onto the treated membrane for hot-pressing. The temperature of the hot-press machine is set in the range of 160 °C to 210 °C to obtain optimum results. The substrate is later peeled off to obtain the sodium-form MEAs before it is treated in the H$_2$SO$_4$ solution to obtain the hydrogen-form MEAs in the final step, which involves rehydration and ion-exchange [86,91,92].
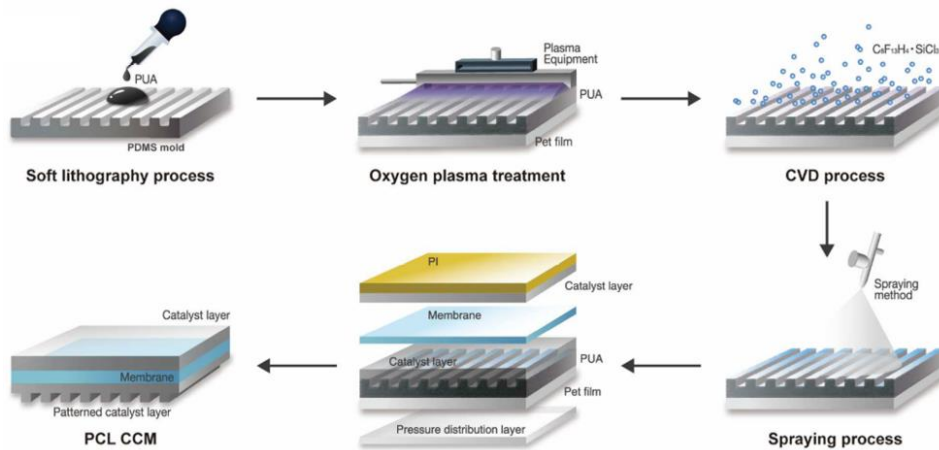
Fig. 4 Fabrication of decal transfer technique [90]

Apart from all the advantages, the decal method also has some drawbacks, such as that it is a time-consuming process with high manufacturing costs. Therefore, several studies have reported on the latest innovation, that is, a new low-temperature decal transfer method, which aids in reducing the overall cost and time consumption [93]. This technique involves four key steps: the catalyst is prepared in slurry form; the catalyst is deposited onto the substrate; the hot-press process is used, and the substrate layer is delaminated to obtain the best catalyst layer (Fig. 5) [74,93–95]. Hence, the improved decal transfer method may be the solution for a better CCM fabrication in the future.
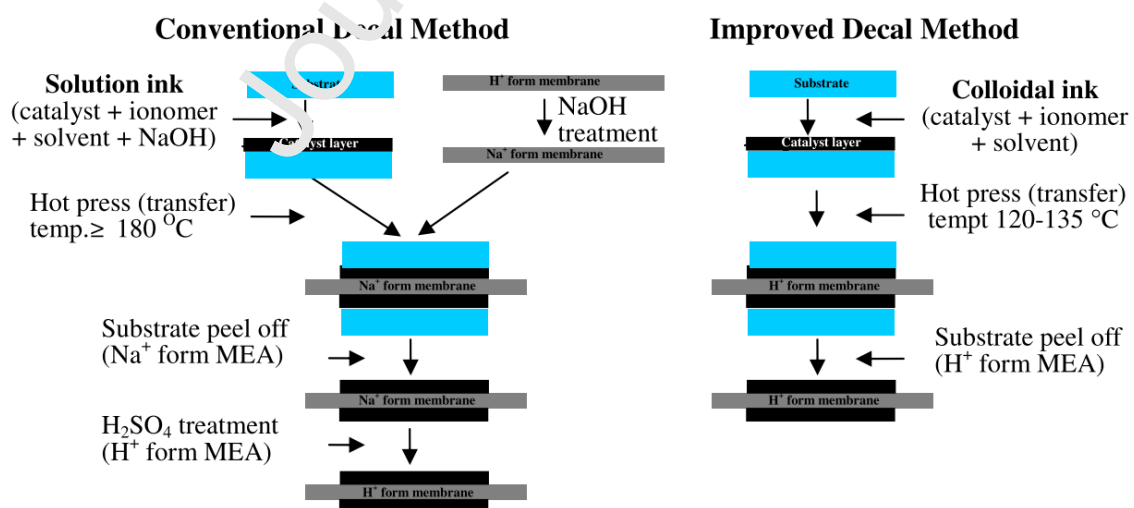

Fig. 5 MEA fabrication technique by a conventional and improved decal method [74]

Considering that the decal transfer technique can inhibit membrane swelling, researchers have tended to believe that this technique has great potential as a CCM fabrication method. The separate catalyst layer preparation before applying it onto the membrane layer using a hot-press machine makes this technique feasible, and it has the potential to avoid the conventional direct-spray technique issues. However, the decal transfer technique still has a few main flaws, as this technique transfers the imperfect Pt catalyst from the substrate to the membrane layer [53]. Simultaneously, other difficulties include the challenge in defining the ideal parameters for the targeted settings and water elimination in the catalyst layer. In addition, during the catalyst ink preparation for decal transfer, the dissolvent rate of the Pt catalyst and other ionomer solutions often produce high catalyst utilization and conduction.

1.5   Screen and Inkjet Printing

Screen and inkjet printing are other techniques applied as CCM fabrication methods for MEA fabrication. These techniques enable the fabricator to deposit the catalyst layer onto the membrane in complex structures. These techniques are adaptable with regard to applications, particularly for industrial purposes. Moreover, such techniques involve the use of inkjet printers as the main medium to transfer the catalyst layer onto the membrane (Fig. 6) [96]. The cartridges are first filled with the catalyst ink using a syringe, whereas the membrane, which acts as the printed layer, is protected by a cellulose acetate sheet for printing purposes. These steps can be conducted using illustrator software to control the printer parameters. The printer parameters are important as they change the electrode dimensions, including the thickness, image format, and hue-saturation-lightness and hue-saturation-value factors of the catalyst ink [35,44]. A comparison between direct spray and inkjet printing was reported by Wang *et al*. [96]. They concluded that inkjet printing has

increased the utilization of catalyst with the same amount of Nafion loading for both techniques (Fig. 7).
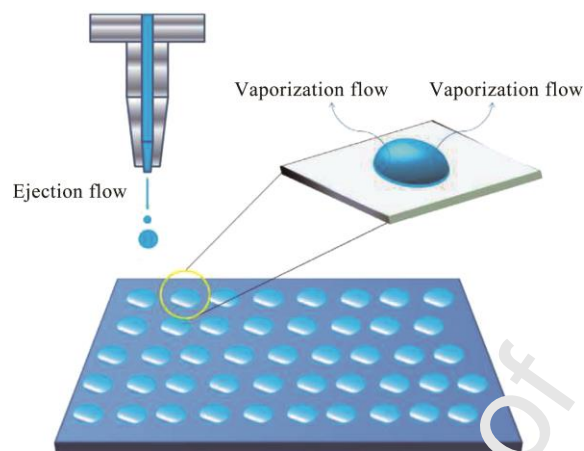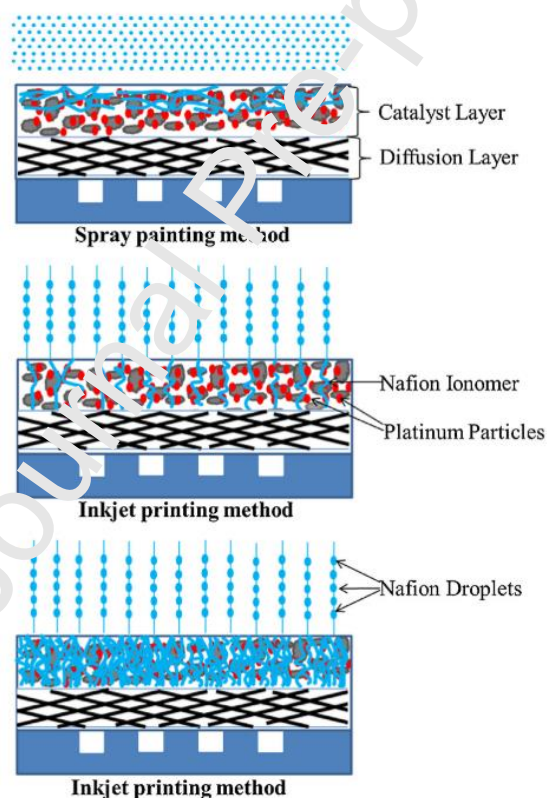

Fig. 6 Inkjet printing techniques [96]

Fig. 7 Comparison between direct-spray and inkjet printing techniques [96]

The screen and inkjet printing techniques have several disadvantages compared with those of the previously mentioned techniques, that is, direct spray and decal transfer. These disadvantages include the difficulties of the catalyst ink preparation and formulation. The

formulation of the catalyst ink composition is important as it aids in the smoothness of the printing process while preventing the ink from clogging at the printer nozzle. Proper formulation involves tuning the ink viscosity, surface tension coefficient, and ink particle size, which will solve the aforementioned difficulties [37]. Another issue is the difficulty in preparing the printer machine, particularly in removing and cleaning the ink cartridge. These setbacks indicate that the relatively high complexity of the MEA fabrication using this technique is undeniable compared with that of the direct-spray and decal transfer techniques. However, the main advantage is its ability to reduce the Pt loading amount while maintaining the same MEA performance [86]. One way to achieve this performance is by classifying the Pt loading required per thickness of the catalyst layer. In addition, this technique can serve as a large-scale printer that is capable of holding various containers of ink solutions based on the desired applications. The CCM fabrication methods have evolved with regard to instruments and facilities to improve the MEA performance [37].

1.6   Doctor Blade Coating

Despite all the techniques applied as the CCM fabrication methods, the focus of MEA fabrication includes the deposition of the catalyst ink onto the membrane using simple, yet effective, techniques. Hence, another technique that has been commonly applied as a CCM fabrication method is doctor blade coating (Fig. 8) [97]. This technique uses a tool known as a doctor blade or knife, which is used to coat and deposit the catalyst ink onto the membrane layer. In addition, this tool is used to ensure that the catalyst inks are distributed homogenously throughout the membrane areas. The doctor blade coating technique provides an advantage with regard to significant accuracy throughout the process, compared with that of the hand painting procedure [94]. Moreover, this technique is capable of coating high-quality catalyst ink for the mass production of MEAs. Hence, Park *et al.* [75] reported that

the membrane was first treated before the coating process started. This study showed that the Nafion membrane was treated to avoid swelling. Throughout the process, the studies reviewed show that the parameters, with regard to tools, methods applied to spread the catalyst ink, and the experimental conditions, are important. Therefore, based on the abovementioned discussions, the doctor blade coating technique is a suitable technique for the mass production of MEAs.
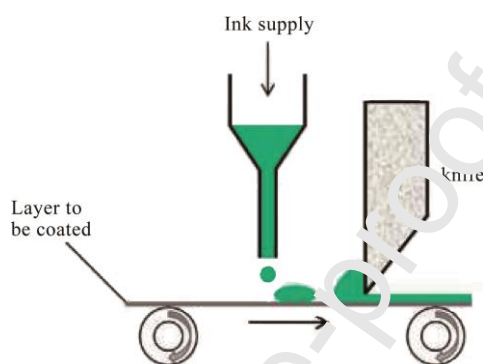

Fig. 8 Doctor blade coating technique [97]

1.7   LbL

In 1997, Gero Decher discovered a technique, namely, the LbL method, for preparing MEAs, which involved a multilayered catalyst ink and GDLs on the membrane layer [98]. Subsequently, advanced research was used to adapt the LbL technique for MEA fabrication [99–104]. After a decade, the LbL technique was applied as a CCM fabrication method for MEAs because of its great advantage with regard to decreasing the fabrication costs, using an environment-friendly electrolyte, and reducing fabrication complexity. In addition, the LbL technique used simple electrochemical components compared with those of the other CCM fabrication techniques [99,105–108]. Yılmaztürk *et al*. [76] conducted extensive research on the LbL technique to study its effects on the performance of PEMFCs. The LbL technique was tested by performing Pt salt precipitation inside the LbL film, which resulted in the best performance. However, the study showed that the LbL technique had tremendous potential of

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becoming the best technique for CCM fabrication because of its ability to produce high PEMFC performance at ultra-low Pt loading on both electrodes [76,100,101,104,109].

Table 1 shows the summary of the comparison between all the aforementioned CCM fabrication methods. Among the techniques used as the CCM fabrication methods, the direct-spray and decal transfer techniques have been proven to be the direct techniques yet sufficiently efficient to attain high PEMFC performance. Meanwhile, the indirect coating methods require more steps and high production costs, although these techniques have shown potential in obtaining high MEA performance. Therefore, based on the abovementioned discussions, the techniques used as the CCM fabrication methods can be divided into small-scale and mass-production techniques depending on the capability of the techniques. However, future investigations of the CCM fabrication methods must focus on reducing membrane swelling, which will lead to decreasing production costs of MEA fabrication.

Table 1: Comparison among the CCM fabrication methods

CCM Fabrication Method	Advantages	Limitations
Direct Spray	Simple process	High percentage of ink loss and low speed. Membrane swelling occurred frequently.
Decal Transfer	Low percentage of ink loss.	Complex process and tedious choice of decal transfer material.
Screen and inkjet printing	Evenly distributed deposition control and suitable for mass production.	Long preparation time due to ink formulation and ink stability.
Doctor blade coating	High accuracy in deposition and suitable for mass production.	High cost.
Layer-by-layer	Low fabrication cost and simple fabrication process	Low surface area and less active site.

4. Effect of the Materials Used in CCM

The materials are the main components used to control the MEA performance on the basis of the application requirements. Hence, this section focuses on the materials used as the catalyst ink in the CCM fabrication method. Theoretically, particular materials have their own functions and chemical characterizations that enhance the MEA performance after the

CCM fabrication method. These components include the main materials and solvents applied, which are a Nafion solution, IPA, and water as solvent. Previous studies have indicated that Nafion solutions and IPA are commonly used to produce the catalyst inks. These solutions aid in increasing the mobility and conductivity of the catalyst inks, which further increase the PEMFC efficiency and energy output.

1.8   Effect of Nafion Solution Content

The catalyst is the main material used in the MEA, as it allows a chemical reaction to occur. These catalyst inks will develop as an electrode in which the Nafion solution enables the Pt loadings to react. The fabrication of the catalyst ink is important during the overall preparation, as it will be deposited onto the membrane layer [110–112]. In theory, the Nafion ionomer functions as a binder and proton conductor within the catalyst layer. This Nafion ionomer serves as a bridge that allows the H^+ ions to travel through the Nafion membrane. The H^+ ions and electrons are separated during the reaction between the H_2O and catalyst layer at the anode side. Simultaneously, the Nafion ionomers will enhance proton conductivity while accumulating the Pt catalyst. These effects simultaneously aid in reducing the overall MEA resistance. The interfacial bond between the membrane and electrode affects the MEA performance [115–117]. Moreover, some studies have reported that the existence of Nafion aids in intensifying the Pt deployment during the reaction. Furthermore, Nafion boosts the electrochemically active surface area as the Pt disperses homogenously within the catalyst layer. These effects further result in three-dimensional reaction zone formations, which are affected by the Nafion content that develops a passageway in the catalyst layer for proton conveyance. These properties demonstrate that the CCM fabrication methods have an innovative method, as they can reduce the resistance between the catalyst layers and the membrane [58,59,61,86].

By contrast, previous studies have indicated that when using the same MEA-CCM fabrication methods, fluctuations in the MEA performance are observed. Some studies have shown that the Nafion ionomer content increases the MEA performance initially before decreasing. Studies on direct methanol fuel cell applications have indicated that dimethylacetamide, a new organic solvent, is often used with the Nafion solution during catalyst ink preparations. The outcome indicates remarkable adhesion between the membrane and the catalyst layer, which leads to an improvement in the durability of long-term system operation [118]. Therefore, those studies have proven that applying a low loading of the Nafion solution in the catalyst layer can lead to a weak interaction between the Nafion membrane and the catalyst layer, thereby resulting in poor MEA performance. However, applying a high content of the Nafion solution also results in an inadequate outcome because the unnecessary Nafion will block the Pt catalyst and electrode pores. The blocking further leads to a reduction in the gas permeability and increase in the mass transfer resistance, which can cause deterioration in the MEA performance [119–121]. Therefore, the association of the Nafion solution with a NaOH solution has significantly shown a positive result to obtain homogenous catalyst dispersion within the membrane. Suli Wang *et al*. (2007) proved that a catalyst ink with the addition of NaOH and Nafion solution could achieve higher performance than that of a catalyst ink without NaOH solution [122]. Another study has shown that the Nafion-SiO$_2$-PWA composite membrane can improve water absorption compared with the pure Nafion membrane [123].

1.9 Effect of Water and Isopropyl Alcohol (IPA)

The preparation of the catalyst ink has involved the use of IPA and water as the customary solvents [124–128]. The use of the Nafion-based catalyst has been explained

extensively by other studies with regard to MEA fabrication. The IPA dispersion rate in the catalyst ink has an influence on the Nafion ionomer morphology, which affects the overall MEA performance. These findings are supported by the study of Ngo *et al.* [129], which indicate that the morphology of the Nafion ionomers is strongly dependent on the IPA dispersion rate in the catalyst inks. In addition, studies have shown that reducing the IPA content may increase the Pt surface area. Therefore, the parameters of the IPA loading are important, as it affects the fuel cell performance accordingly. However, another study has been conducted to study the effect of the Nafion solution composition on the Nafion molecular morphology by applying different IPA concentrations in the range of 20 wt% to 80 wt%. The morphological analysis has shown that increasing the concentration of the Nafion from 20 wt% to 60 wt% results in particle formation in the primary and secondary layers. However, at a 70 wt% concentration of IPA, the accumulated particles start to transform into a coil-like structure that is different from their original rod-like structure. The researcher has determined that the size of the accumulated particles decreases inversely with the increase of IPA concentration. Additional studies have also reported that the overall performance of the fuel cell decreases as the concentration of the IPA increases. This result further relates to the decrease in the IPA concentration, which results in an increase in the surface area activities of the catalyst layer. The results obtained are also supported by the existence of IPA and water as the solvents in preparing the catalyst ink. However, the overall PEMFC performance can be influenced by adjusting the concentration and composition of solvents and their properties. Hence, based on the abovementioned discussion, the Nafion solution seems to directly affect the overall fuel cell performance [117,129–133].

The catalyst ink consists of several materials that are altered on the basis of the required performance. As previously discussed, the Nafion solution, IPA solution, and deionized water are the main components in the development of the catalyst ink. These

catalyst inks are then deposited onto the Nafion membrane using the suitable CCM fabrication methods, which have been discussed. The presence of such materials in the catalyst inks is necessary because their properties affect the whole MEA performance. Notably, the optimum Nafion loading is the key to maintaining and avoiding both drying and flooding of the MEAs.

5. Performance of CCM-MEA

In general, the membranes for the CCM-MEAs exhibit remarkable PEMFC performances because the CCM method has solved the Ohmic resistance issues experienced by the CCS-MEA membrane. This remarkable performance is due to the ability of the CCM-MEA membranes to enhance the ionic contact between the Nafion membrane and the catalyst layer. Hence, this section focuses on the effects of several parameters, such as temperature, hydrogen flow rate, and platinum (Pt) loading, on the overall MEA performance. In addition, the performances of two major fabrication methods in the CCM, that is, either using the hot-press method or not using the hot-press method, are discussed.

1.10   Effect of Temperature and Humidity on CCM

Temperature control and humidity setting are the main parameters that contribute to increasing the system efficiency of the fuel cell. These factors are important when utilizing CCS-MEAs by using PFSA ionomer membranes. In general, the PFSA membrane must be humidified at a certain temperature level throughout the system at the anode and cathode to prevent membrane dehydration, which may affect the proton transferability rate and deteriorate the overall fuel cell performance [134–136]. In CCM-MEAs, the influence of temperature and humidity affects both the MEA and fuel cell performances. However, the ability to increase the transportability of the ions and protons during the chemical reactions

on both electrodes gives rise to positive feedback, as it affects the whole fuel cell performance. However, the excessive temperature and humidity factors applied will result in a decrease in the fuel cell performance because the pores forming between the catalyst layers and GDL have trapped liquid water, which affects the gas transport rate and deteriorates the cell voltage. In PEMFC applications, as the current density increases, the membrane flooding caused by the excessive water generation will cause the performance to drop.

The fabrication of the CCM-MEA still cannot resolve the membrane flooding issues. Some studies have concluded that the rate of water production during the reactions is supposed to balance the rate of water removal from the system. This balance ensures that the entire system is able to provide sufficient proton conductivity and gas transfer rates. In addition, the water generation and water removal rates are intended to balance and produce proton conduction and gas transfer rates simultaneously. Meanwhile, the water generation rate is used to determine the current density. Studies have indicated that the water removal rate depends on the ratio (RH) of the equipped gases and water retention properties of the catalyst layers. The RH results on the PEMFC performance levels show that the MEAs serve as a steady ionomer content, whereas the operation temperature improves the PEMFC performance [137,138]. These findings indicate that as sufficient humidity conditions are applied, the PEMFC performance improves significantly with the increase of the operation temperature. However, as the operation temperature increases above the gas stream humidification temperature, the performance of the cell decreases, particularly at low-current density region. These results indicate that the anode humidification temperature has a considerable effect on the cell performance. Simultaneously, a low degree of humidification will further decrease the cell performance. However, at high current densities, the impact of the anode humidification temperature is not important. The cathode humidification temperature also shows no vital effects on cell performances, particularly at high current

densities. The fuel cell performance increases with pressure owing to the rise in the exchange current density and chemical gas partial pressures [134,139–142]. The cell performance gradually increases with the ratio of the cathode gas, providing the best performance at the totally hydrated condition while oxygen or purified air is supplied to the cathodes. Unpressurized air as a cathode gas can be attributed to high cell voltage when it has an intermediate humidity. Furthermore, the performance drops while the air approaches a totally humidified condition [135,143–145].

1.11   Effect of Platinum Loading

Researchers have struggled to perform various studies regarding MEA manufacturing to develop MEAs with high current density and long-term durability [146–148]. One factor that contributes to the MEA performance is platinum (Pt) loading. Hence, studies on the connection between the Pt catalyst content in the carbon and the overall PEMFC performance have been performed. The Pt distributions on the conductor play an important role for the catalyst, as it is related to the chemical reactions. The influence of various Pt concentrations within the carbon in a single-cell stack on the conductor performance has been reported by various studies. However, researchers have found that increasing the Pt concentration within the carbon does not directly improve the MEA performance. However, researchers have reported that no vital effect is found on the single-cell performance when using different Pt/C catalyst loadings of 20 wt% and 40 wt%. Moreover, at 60 wt% Pt/C catalyst loading, the cell performance diminishes significantly at the high-current density region. This decrease caused by the conductor structure, which contains 60 wt% of Pt/C catalyst, develops massive micrometer-sized pores. These pores further result in difficulties for removing water at the cathode and transporting the chemical gases at each electrode. These findings indicate that the catalyst loading and Nafion solution ratio, which are relative to the carbon support, are

important, as the Pt loading will influence the microstructure and fuel cell performance [149,150].

Studies have indicated that the Pt loading content can reduce the fabrication cost [78,151–153]. Hence, preparing the MEAs at low Pt loadings is important. Su *et al.* [78] reported that the best Nafion content for the MEAs was 25 wt%, with Pt loadings of 0.12 and 0.04 mg·cm^{-2} in the cathode and anode, respectively. These Pt loadings are considered low compared with those of similar MEAs prepared by different methods. However, these ultra-low Pt loadings show notable performance and high current density because of the thin catalyst layer, which reduces the mass transfer limitations. Hence, at 70 °C cell temperature and 30 psi air backpressure, the maximum power density and current density are recorded as 0.71 W·cm^{-2} and 0.7 A·cm^{-2} (at 0.7 V), respectively. The results reported are good compared with those of the previously reported MEAs at low platinum loading operating at ambient air conditions. Therefore, this study recommends the use of a thin catalyst layer, which can minimize the contact between the catalyst layer and the membrane. In addition, the uniform porous structure of the catalyst layers is another crucial factor that requires attention.

Meanwhile, Liang *et al.* [154] investigated an improved CCM fabrication method that was used to reduce the Pt loading and improve the Pt utilization using a phosphoric acid-doped poly(2,5-benzimidazole) (AB-PBI) membrane. These methods can improve the MEA performance and increase the power density of the high-temperature PEMFC compared with that of the conventional method at the same Pt loadings. The power density produced is reported to be 760 mW·mg^{-1} with a current density of 850 mA·cm^{-2}. These results indicate that the Ohmic resistance and the cathode charge transfer resistance for the CCM-MEAs are significantly decreased [155–158]. Garsany *et al.* [159] also investigated on the effect of Pt loading on PEMFC performance, and they concluded that the decrease of current density and power was not linearly dependent on the Pt loading. They have shown that significant loss is

recorded as the Pt loading is reduced from 0.16 mg·cm^{-2} to 0.04 mg·cm^{-2}. However, the reduction of Pt loading from 0.16 mg·cm^{-2} to 0.08 mg·cm^{-2} has shown low performance difference.

Although sufficient MEA performance has been achieved using low Pt loading in the catalyst layer, most of the techniques applied in the CCM fabrication method still cannot produce a mass-production product [160,161]. Long-term PEMFC applications are required, such as for vehicle batteries to achieve a minimum run time of 5000 h, while residential applications must achieve times longer than 20,000 h. Therefore, durability must be assessed as a function of time under realistic operating conditions in a PEMFC stack. Cho *et al.* [162] reported that the increase in the MEA performance declined at high Pt loading at the cathode side, which diminished the MEA degradation rate [162]. Hence, this study used various Pt loadings at the cathode side of the CCM-MEA-CCM, while 50 h of cyclic loadings was applied. These findings indicate that the fuel cell performance decreases proportionally with the increase of Pt loadings. This result is explained by the low Pt loadings on the cathode side, which severely increases the charge transfer resistance because of the decrease in the oxidation reduction reaction (ORR) activity in the catalyst layer. However, an adequate Pt loading will aid in maintaining high ORR activity for single-cell performance [163,164]. Another study is carried out to determine the effects of Pt loading using CCM with different bipolar plates. Lijuan *et al.* [165] concluded that using a water transport bipolar plate reduced the catalyst layer decay. The reduction of the catalyst layer decay will increase the durability of MEA as the carbon corrosion will further enhance the loosing of Pt particles.

1.12   Effect of the MEA Fabrication Methods on the Overall Performance

The CCM fabrication method has been recently developed to fabricate MEAs because of its effective technique, particularly for obtaining high PEMFC performance. These

improvements include the electrochemical reactions, power, and current density. As previously discussed, the CCM fabrication methods have a great potential over that of the conventional CCS fabrication methods with regard to Pt loading reductions without sacrificing the overall MEA performance. Moreover, two fabrication techniques are usually used to prepare the MEAs: direct wet-spray (CCM-DS) and decal transfer techniques (CCM-DT). Hence, the effect of both techniques on the overall performance is further discussed as follows.

1.12.1 CCM by Direct-Spray Technique

Recent research has discovered that the direct-spray technique is the most significant method to fabricate MEAs. However, these techniques also experience challenges to ensure that the Nafion membrane does not swell because of the solvents used in the catalyst ink. Hence, the popular strategy is to introduce some pretreatment methods for the Nafion membrane, as suggested by several researchers [62,65,73,166]. They have demonstrated that the MEAs prepared using certain tools and driving gas settings for the spray reach a current density of over 400 mW·cm^{-2} in the cell voltage of 0.6 V to 0.8 V (Fig. 9) [73].
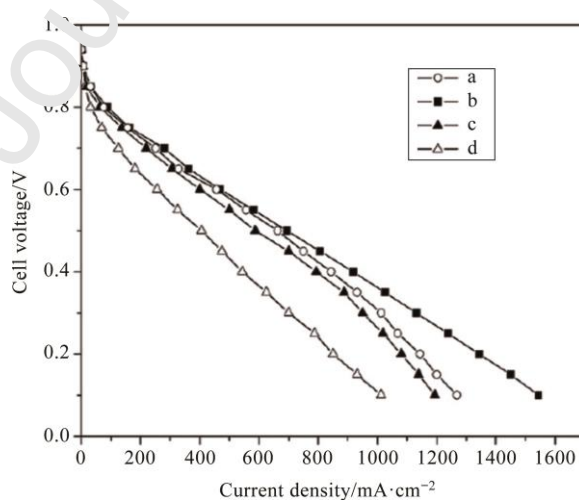

Fig. 9 Performances of single cells at different cell temperatures: (a) 50 °C, (b) 60 °C, (c) 70 °C, and (d) 80 °C

The flow rate of the O_2 is 250 ml·min^{-1}, and that of H_2 is 200 ml·min^{-1}, with anode humidification temperature of 10 °C higher than the fuel cell operating temperature at ambient gas pressure for the anode and cathode [73].

Notably, this result indicates how the operating temperature of the MEAs affects the fuel cell performance. The results show that the performance deteriorates at a working temperature of 80 °C. Sun *et al*. [82] reported that CCM-MEAs fabricated using the direct-spray technique could produce 430 mW·cm^{-2} of power density for 0.3 mg·cm^{-2} of Pt loading. However, the fabrication of CCM-MEAs using a single-cell PEMFC is also conducted by applying the direct-spray technique at 150 °C with a high-temperature hot plate. These findings indicate that the membrane is laid out, which affects catalyst deposition onto the membrane layer. At ambient temperature as seen in Fig. 10 (a), cracks are found on the surface morphology throughout the layer, which results in the drastic decrease of the MEA performance. However, at 150 °C, the ethanol solvent is completely evaporated before the catalyst ink reaches the membrane surface. These effects can be seen clearly in Fig. 10 (b), indicating that at high temperature, no visible cracks are found throughout the catalyst layer surface. In addition, Fig. 10 (c) shows that the catalyst layers are connected perfectly at the electrolyte membrane surface without any delimitation even after the water has boiled off.
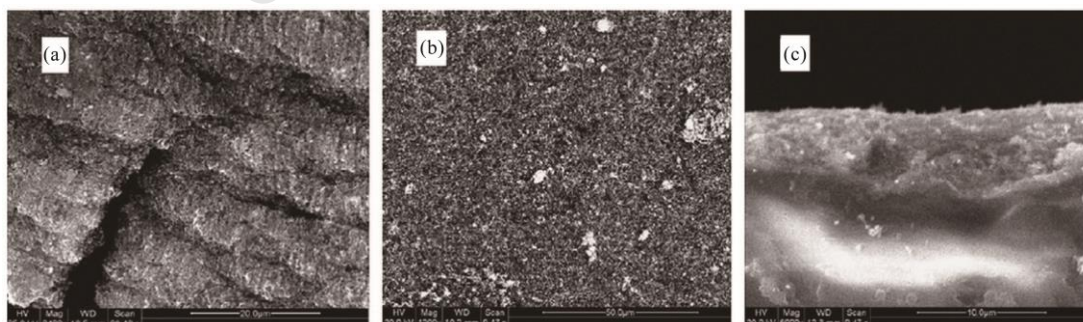

Fig. 10 SEM images of (a) the catalyst layer fabricated at ambient temperature, (b) the CCM prepared by the hot spray method at 150 °C, and (c) the cross-section of a CCM

prepared by the hot spray method at 150 °C with the immobilization of the Nafion membrane by a Pyrex glass during fabrication [82]

On the basis of the MEA surface morphology, studies on fuel cell performance with regard to the current density-voltage (I-V) curve and current density-power density (I-P) curve are conducted. These properties are important to determine the whole performance of the CCM-MEAs at different hot-plate temperatures. Studies have indicated that a stark difference can be observed between the CCM-MEAs prepared under ambient temperature and over 100 °C. Fig. 11 shows that the power density for CCM-MEAs prepared at 110 °C, 130 °C, and 150 °C was 550, 650, and 715 mW·cm^{-2}, respectively. At 150 °C, the prepared MEAs provide higher power density than that of the MEAs prepared at low temperature because high temperature causes the solvent in the ink to evaporate in the air before it reaches the membrane surface. These phenomena play a role in avoiding the occurrence of cracks on the membrane surface.

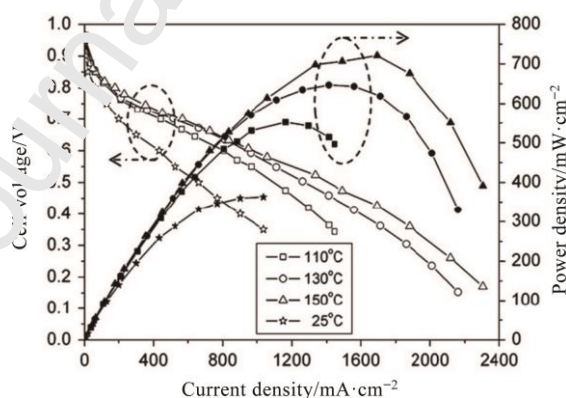Fig. 11 Current density-voltage (I-V) and current density-power density (I-P) curves for cells with CCMs prepared by the direct high-temperature spray deposition technique at room temperature and elevated temperatures of 110 °C, 130 °C, and 150 °C [82]

The results obtained indicate that the CCM-MEAs produced can achieve higher performance results than those of the conventional CCS-MEAs. By contrast, studies show the

CCS-MEAs using the same Pt loading of 0.4 mg·cm^{-2}. Fig. 12 shows the I-V curve with regard to power density fabricated using hot-sprayed CCM and hot-pressed MEA using the CCS fabrication method. The CCM-MEAs reach a peak power density at 715 mW·cm^{-2}, whereas the CCS-MEAs deliver approximately 650 mW·cm^{-2}. The high-power density results obtained by the CCM-MEAs are due to the improved electrochemical interaction between the electrolyte Nafion membrane and catalyst layers.
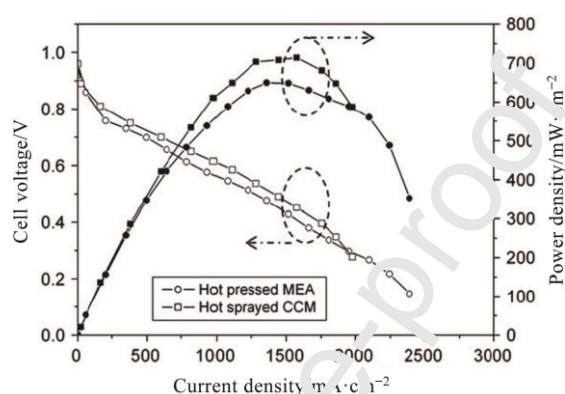

Fig. 12 Current density-voltage and current density-power density curves of single cells made from hot-sprayed CCM and hot-pressed MEAs [82]

Thanasilp *et al*. [167] showed that the two fabrication techniques, that is, direct spray and decal transfer, are not much different with regard to performance, particularly the Ohmic resistance. Studies have demonstrated that a slight change in the Ohmic resistance can significantly affect the charge transfer resistance and open-circuit voltage (OCV). Liang liang Sun *et al.* [82] highlighted that the main drawback of the CCM fabrication method using the direct-spray technique is due to its tendency to develop serious membrane swelling. This swelling occurs as the electrocatalyst ink is sprayed directly onto the membrane surface. However, the swelling can be addressed by using IPA as the primary liquid medium with EG as an active additive during direct spraying on the membrane. In addition, the wrinkling and cracking of the Nafion membrane during fabrication can be suppressed by applying a high-temperature spray deposition and immobilization of the membrane using a Pyrex glass via

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van der Waals forces. These steps will further minimize the occurrence of damage and enhance the fuel cell performance. Studies have also reported that at 45.5 wt% of Pt/C electrocatalyst loading and a high amount of ionomer content, the performance of the MEAs improves. The MEA performance increases proportionally to the ionic conductivity through the ionomers in the electrocatalyst layers and flow rates [73,82].

1.12.2 CCM by Decal Transfer Technique

The decal transfer technique uses a similar technique to that of the direct-spray technique in depositing the catalyst layer, that is, depositing a polytetrafluoroethylene (PTFE) sheet onto the membrane by hot-pressing. Xie *et al.* [167] studied the effects of the decal transfer technique on the MEA performance using variations in the catalyst loading, Nafion content, and distinctive porosimetry of the catalyst powders. Then, a few modifications were performed on the decal transfer technique, including using of Kapton, a lesser hydrophobic surface than that of Teflon, and eliminating the use of a hydrophobic lubricant in printing [168]. Despite such results, Chisaka and Daiguji [166] reported that glycerol affected the MEA performance particularly the catalyst dispersion. However, the low amount of glycerol also affects the MEA performance, as it affects the volume of the pores in the primary and secondary catalyst layer. Recently, the CCM-DT technique is modified to achieve optimum fuel cell performance results. Saha *et al.* [74] showed the modification of the CCM-DT technique by emulating the H^+ form of the membrane instead of the Na^+ form of the membrane. In addition, studies have modified and improved the catalyst ink, using a colloidal ink instead of a solution ink, which minimizes the steps in the MEA fabrication compared with those in the conventional decal transfer technique. Moreover, studies have reported that the MEA performance improves by 45% when using the colloidal ink instead of the solution ink, at a fixed cell voltage of 0.6 V. Park *et al.* [169] conducted a MEA fabrication using the

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modified decal transfer technique. This improved technique requires a carbon-breaking layer to achieve a high catalyst transfer ratio when the reaction occurs. These findings indicate that a modified CCM-DT technique is capable of achieving a 30% increase in power density compared with that of a conventional CCM-DT technique because the Pt catalyst transfer ratio is a factor that ensures the optimum MEA performance.

In addition, the detailed findings on the impedance analysis and performance measurement indicate that the fuel cell performance is related to the mass transfer resistance, and these findings are supported by the analysis conducted, which show that the impedance magnitude increases for the thick microporous layer (MPL) at a cell voltage of 0.30 V. Furthermore, the impedance magnitude increases in the power density peak by 30% when applying oxygen and air in the operations system. These phenomena indicate that appropriate thickness may provide a well-balanced water management over the electrode, which certainly improves the fuel cell performance. However, studies have suggested that the use of gas diffusion media with a low PTFE content will enhance the fuel cell performance because the mass transfer inside the electrode is easily modulated, which results in a 15% improvement in the power density. Hence, the fuel cells can achieve high power densities of ca. 1.66 and 844 mW·cm^{-2} for oxygen and air operations, respectively. These results indicate that the modified decal method constitutes a reliable electrode fabrication method that can yield high-performance fuel cells.

Although the improved CCM-DT technique appears to be a potential method that aids in the fuel cell performance, researchers tend to modify this technique to optimize it. Hence, these adjustments have led to studies of the modified CCM-DT technique, which uses the low hot-pressing temperatures with protonated Nafion. In addition, studies have also reported that the typical CCM-DT technique may suffer from an incomplete catalyst layer transfer if no modifications are made [74]. The researcher has suggested that with over 8 min of hot-

pressing and sufficient pressure and temperature, the MEAs can achieve high transfer yields. Moreover, Cho *et al.* [93] claimed that the incomplete transfer occurs when the outer ionomer layer is not applied, regardless of whether the hot-pressing conditions are appropriate. However, Park *et al.* [169] suggested that applying the carbon-breaking layer from a carbon colloidal dispersion can increase the transfer yield. In their studies, they provided a 100% CCM-DT yield by the carbon-breaking layer. However, the proposed procedure is more complex than that of the conventional CCM-DT technique because of the addition of the carbon layer, which has to be coated prior to the catalyst layer. Recently, Cho *et al.* [84] reported that liquid nitrogen treatment was used to remove the decal film to achieve a high transfer yield under both high and low hot-pressing temperature and pressure conditions.

Of all the techniques applied, the MEA-DT method with the use of an optimum catalyst ink composition appears to be achievable. Jung *et al.* [170] showed the progress in the MEA-DT technique for achieving the optimum MEA composition. In these research works, two types of catalyst ink are used, which are glycerol-based and Nafion-based. The optimum amount of Nafion-based ink results in a higher performance than that of the glycerol-based ink. Therefore, the problem with solvents in the catalyst ink for the CCM-DT technique is more complex than that for the CCM-DS technique [171].

1.12.3 Comparison Between CCM-MEAs Using Direct-Spray and Decal Transfer Techniques

In general, the different fabrication methods of the MEAs will result in different cell performances depending on the fabrication techniques applied, that is, direct-spray (CCM-DS), decal transfer (CCM-DT), and CCS techniques. Thanasilp *et al.* [167] studied the effect of the MEA fabrication techniques, which are CCS, CCM-DS, and CCM-DT, on the oxygen reduction performance of a PEMFC under identical conditions of Pt-Pd/C electrocatalyst

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loading. Fig. 13 shows the current density-potential curve or polarization curve of a single PEMFC with the MEA fabricated by CCS, CCM-DS, or CCM-DT. Notably, the fuel cell performance fabricated using the CCM-DT technique has remarkable results over the MEAs fabricated using the CCS or CCM-DS techniques under identical test conditions. Meanwhile, the findings indicate that the fuel cell fabricated using the CCM-DT obtains a power density of 230 mW·cm^{-2}. The results obtained are higher than those of the MEAs fabricated using the CCS and CCM-DS techniques with power densities of 160 and 204 mW·cm^{-2}, respectively. These MEA results show that the CCM-DT technique appears to be the most effective method to improve the PEMFC performance without increasing the electrocatalyst loading.
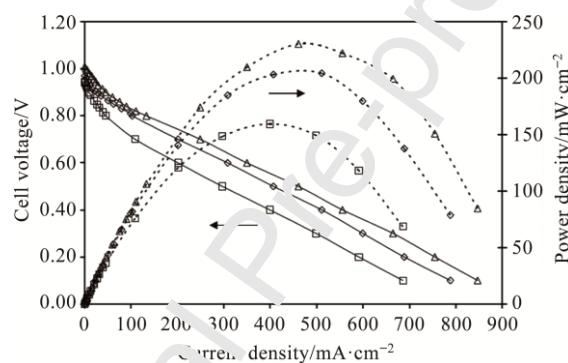

Fig. 13 Cell voltage (—) and power density (– –) of a PEM fuel cell, under H$_2$/O$_2$, with the MEA fabricated by the CCS (□), CCM-DS (◇), and CCM-DT (△) techniques [167]

Moreover, Fig. 13 shows the exchange current density, in which the highest value is obtained by the MEAs fabricated using the CCM-DT technique because of its low resistance, R, and the sum of the charge transfer, mass transfer, and Ohmic resistances. These findings indicate that the MEAs fabricated by the CCM-DT technique have smaller charge transfer overpotential and higher cell performance than that of MEAs fabricated by the CCS and CCM-DS techniques. Although the calculated exchange current of MEAs produced using the CCM-DT technique is 1000 times greater than that of MEAs produced with the CCS technique, the MEA current density using the former technique is only twofold higher than

that of the latter technique. This phenomenon occurs because the exchange current density of the electrocatalyst is dominated in the activation-controlled region [167,171]. However, Fig. 13 also shows that the OCV values obtained by the MEA from the CCM-DT technique are higher than those of MEAs from other fabrication techniques studied. As reported, the findings indicate that the OCV obtained by the CCM-DT is 1.009 V, which is greater than the OCV obtained by CCS and CCM-DS at 0.038 and 0.0066 V, respectively. Hence, the effect of the MEA porosity prepared by different fabrication techniques must be considered to explain this behavior. Therefore, Fig. 14 shows the distribution size and mean flow pore diameters of the MEAs fabricated by different techniques. Based on these findings, the size distributions of the MEAs fabricated by the CCS, CCM-DS, and CCM-DT techniques are distributed in the range of 0.146 μm to 3.724 μm, 0.242 μm to 2.391 μm, and 0.170 μm to 3.037 μm, respectively. Simultaneously, the mean flow pore diameters for the CCS, CCM-DS, and CCM-DT techniques reported are（3.709 ± 3.170）μm,（0.676 ± 1.406）μm, and（0.604 ± 0.865）μm, respectively. Based on these findings, the researcher has demonstrated that a large flow pore diameter will lead to a high fuel crossover from the anode to the cathode, which results in a low cell performance.
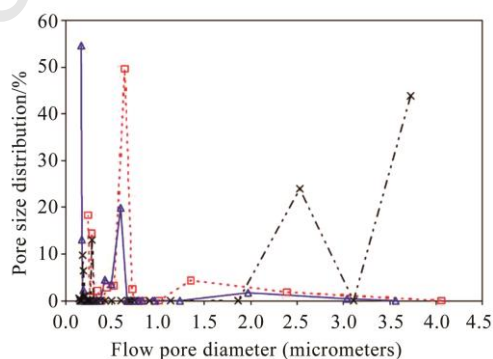

Fig. 14 Flow pore distribution of MEAs prepared by CCS (×), CCM-DS (□), and

CCM-DT (△) [167]

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Simultaneously, studies have indicated that through impedance analysis, the obtained spectra are fit by the equivalent circuit, which consists of the Ohmic resistance (R_Ω). These circuits are then connected in parallel combination with the constant phase element (CPE), double-layer porous electrode capacitance, and the charge transfer resistance (R_{ct}). These properties are used to associate the charge transfer resistance across the catalyst/electrolyte interface. These findings further indicate that the MEAs fabricated using the CCM-DT technique experience low Ohmic resistance. This resistance is followed by MEAs from the CCM-DS and CCS techniques. These phenomena show that the MEAs fabricated using the CCM-DT technique have good contact with the polymer electrolyte membrane. However, the studies conducted have also reported that the MEAs fabricated using the CCM-DT technique experience a low CPE compared with that of the CCM-DS technique. Moreover, these findings indicate that the reaction of the MEAs fabricated using the CCM-DS is faster than that of the MEAs fabricated by the CCS technique. However, studies have demonstrated that the MEA made by CCM-DT is closer to unity than the other two fabricated MEAs. This result indicates that the MEA fabricated by the CCM-DT technique possesses a uniform and smoother composition than the other MEAs. Referring to the studies of the impedance analysis, one can anticipate that the MEA prepared by CCM-DT has lower charge transfer resistance compared with those prepared by the CCS and CCM-DS techniques [167].

Hence, studies have indicated that the cell consisting of the MEAs fabricated using the CCM-DT technique provides a fast charge transfer reaction for the oxygen reduction reaction at the electrode and electrolyte interface because the MEA fabricated by the CCM-DT technique has good contact between the catalyst layer and the membrane. These effects lead to an increase in the electrochemical active area and three-phase boundary. Meanwhile, compared with the cell performance and other MEA properties, studies have reported that good cell performance and properties are obtained by the MEAs fabricated by the CCM-DT

technique. Based on these outcomes, an electrochemical active area of 36.20 $m^2 \cdot g^{-1}$, OCV of 1.009 V, exchange current density of 4.51×10^{-7} $mA \cdot cm^{-2}$, Ohmic resistance of 0.359 $\Omega \cdot cm^{-2}$, and charge transfer resistance of 0.315 $\Omega \cdot cm^{-2}$ are obtained. In addition, a high cell performance of 350 $mA \cdot cm^{-2}$ and power density of 210 $mW \cdot cm^{-2}$ are obtained by the MEAs fabricated using the CCM-DT technique at 0.6 V compared with those of the MEAs fabricated by the CCS and CCM-DS techniques. However, despite all the advantages of the CCM-DT technique, researchers must ensure a balance between the MEA performance and the manufacturing process [167].

High Pt loadings in the catalyst layer will increase the active area, improve the electronic conductivity, and limit the mass transport. Based on the aforementioned effects, the findings indicate that the increase in the active area is caused by the increase in the catalyst amount. Meanwhile, the initial improvement of the electronic conductivity in the current collector is due to the close Pt/C particle contact. In addition, the increase in Pt loading affects the appearance of the mass transport limitations at high catalyst loading. These effects are caused by the increase in the electrode thickness, which results in increased flooding and reactant gas diffusion. Notably, the materials used in the catalyst ink fabrication also influence the efficiency and overall performance of the CCM-MEAs. Moreover, the humidity and temperature control are other factors that must be considered. These factors are important because correct temperature aids in maintaining high levels of fuel cell performance while avoiding membrane and ionomer dehydration. Comprehensive studies between the two main techniques in the CCM fabrication methods, that is, direct spray and decal transfer, show that each technique has its own pros and cons. Decal transfer is an excellent choice to obtain a high fuel cell performance. However, the difficulties of the decal transfer fabrication make the direct-spray technique interesting and easy to apply. Hence, future research must focus on the direct-spray technique and its ability to produce a mass

production of the PEMFC using the CCM-MEA fabrication method.

6. Future Trend of CCMs in PEMFC

Several important criteria are required for the future CCM fabrication methods, particularly in predicting the research trends and developing CCM-MEAs. As previously discussed, the CCM fabrication method has great potential because of its ability to reduce the processing steps required for MEA production. Hence, an extensive study is required to minimize the necessary processing steps while maintaining and improving the cell performance. In addition, future studies must focus on and explore the capability of adapting the hybrid technique onto the fabrication process. These approaches include studying a hybrid technique between the CCS and CCM or combining of CCM techniques, that is, the decal transfer and direct-spray techniques. These considerations are important, as the diversity in adapting any type of MEA fabrication method is supposed to be an innovative fabrication technique. However, the involvement of the CCM fabrication method must not be underestimated, as these techniques are capable of producing MEAs for various types of fuel cells. However, studies on CCM-MEAs must also continue until the MEA parameters with regard to size, shape, and quantity of MEA production are optimized. These parameters are important because the MEA fabrication method is the key process to promote fuel cells as an alternative application in the future to replace fossil fuel. Moreover, researchers must focus on the ability to cope with market demand by introducing an adjustable fabrication technique as an adaptable and flexible companion to the current technologies. In summary, the CCM fabrication methods are an alternative method for better and innovative MEA fabrication methods, which ensure high product-quality control with associated manufacturing metrics.

7. Conclusions

CCMs using the direct-spray technique are an alternative method to other MEA fabrication methods because of its simple processing steps. In addition, the overall fuel cell performance is improved with regard to current density and power density compared with that of MEAs fabricated using conventional methods with similar conditions and parameters. Despite all the data produced and studied to date, MEAs still cannot operate over long periods of time. Hence, studies on durability and membrane mechanical failure must be included to obtain improved fuel cell performance in the future.

Acknowledgements

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