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Conventional Catalyst Ink, Catalyst Layer and MEA Preparation

Huamin Zhang, Xiaoli Wang, Jianlu Zhang and Jiujun Zhang

19.1 Introduction

The membrane electrode assembly (MEA) is the heart of proton exchange membrane fuel cells (PEMFCs), including direct methanol fuel cells (DMFCs), and determines both fuel cell performance and durability. The MEA component materials, structure, and fabrication technologies play important roles in performance improvement and optimization. For example, the catalyst layers, where the electrochemical reactions take place, are the most important of the several components in PEMFCs. An MEA contains an anode gas diffusion layer (GDL), an anode catalyst layer (CL), a proton exchange membrane (PEM), a cathode catalyst layer, and a cathode gas diffusion layer. An ideal MEA would allow all active catalyst sites in the catalyst layer to be accessible to the reactant (H_2 or O_2), protons and electrons, and would facilitate the effective removal of produced water from the CL and GDL. Over the past several decades, great efforts have been made to optimize the catalyst layer and MEA, and many catalyst layer/MEA structures and fabrication methods have been developed. As a result, MEA performance with advanced catalyst layers has been significantly improved by employing different fabrication methods [1–4], changing the catalyst layer structures [5–11], and using different components [5–8].

This chapter will address the preparation methods for catalyst inks, catalyst layers, and MEAs, with a focus on the fabrication processes.

19.2 Principles of Gas Diffusion Electrodes and MEA Structures

The electrodes in PEMFCs, including both cathode and anode, are multi-component and gas porous matrices, also called gas diffusion electrodes (GDEs). A GDE is generally composed of a reaction layer (the CL) and an accessorial layer (the GDL). The GDL, adjacent to the catalyst layer and the flow field, plays an important role in PEMFC performance and has several functions: (1) transportation

of reactants: the GDL should be able to provide reactant pathways from the flow field channels to the catalyst layer and uniformly distribute the reactants onto the whole reaction surface; (2) transportation of liquid water: the GDL offers pathways for liquid water removal from the catalyst layer to the flow field channels; (3) conduction of electrons: the GDL allows electron transfer from the bipolar plate to the catalyst layer or vice versa; (4) mechanical support: the GDL should be able to support the catalyst layers and the proton exchange membrane against pressure from the gases and the assembly force; and (5) heat conduction: the GDL should be able to effectively remove the produced heat from the catalyst layer. The GDL has a typical dual-layer structure with a macro-porous substrate layer (SL) and a coated thinner microporous layer (MPL), as illustrated in Figure 19.1.
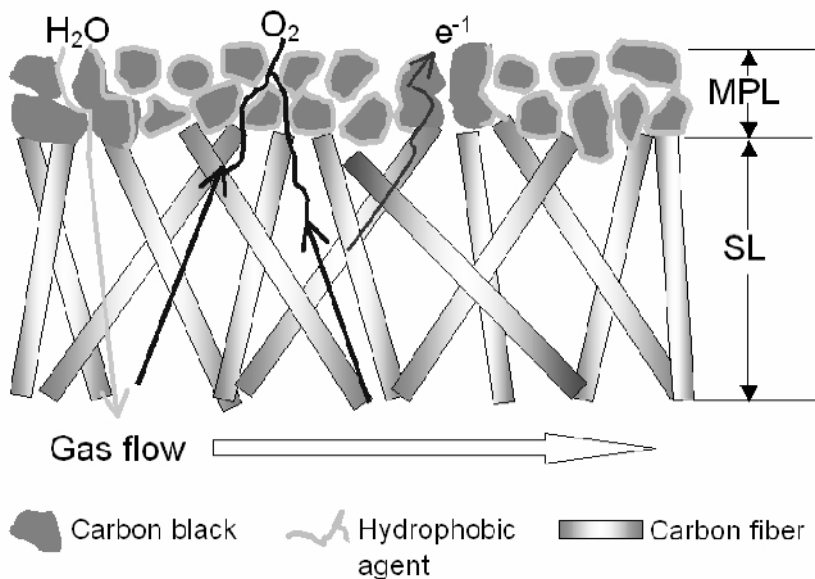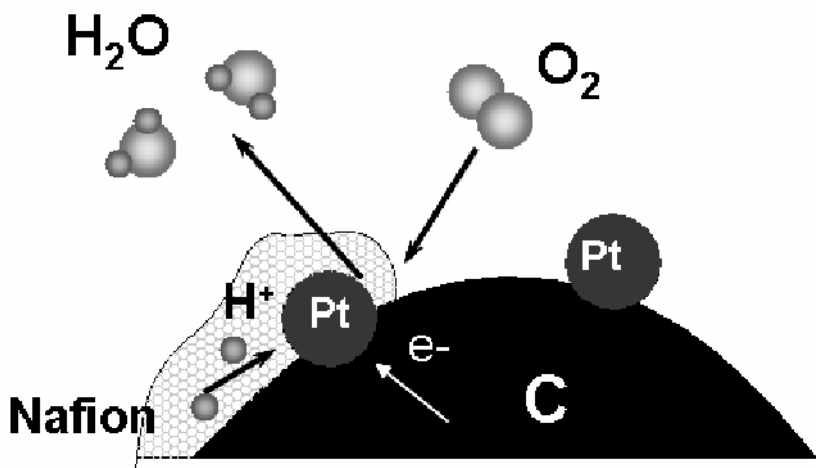

Figure 19.1. Schematic diagram of a dual-layer cathode gas diffusion layer

A well-qualified substrate layer should have excellent gas permeability, high electron conductivity, smooth surface, good mechanical strength, proper wettability, stable chemical and heat properties, as well as low cost. The most common SL materials used in PEMFCs are carbon-fiber-based products, such as non-woven carbon papers and woven carbon cloths. This is mainly due to their high porosity ($\geq$ 70%) and good electrical conductivity. Besides these carbon materials, some metal substrates such as sintered porous titanium and stainless steel fiber felt have also been explored as SLs [12–14] because of their high mechanical strength, ductility, and low cost.

Adding a surface layer onto the SL has proven to be an effective way of improving the water/gas management of the whole GDL [15–18]. The microporous layer (MPL, also called a carbon base, in industry) consists of carbon or graphite particles mixed with a hydrophobic agent, usually polytetrafluoroethylene (PTFE),

which serves as a binder. Typically, the MPL has a pore size in the order of the carbon agglomerates, between 100 and 500 nm, with a thickness of 5–50 μm, while the SL has a 10–30 μm pore size and 100–300 μm thickness. The primary purpose of the MPL is water management and reactant redistribution. It can provide effective wicking of liquid water from the cathode CL into the SL, and then effective transportation of gases in the opposite direction. It also contributes significantly to the reduction of electrical contact resistance between the SL and CL.

The catalyst layer (CL) is a key component in the GDE, as the location where electrochemical reactions take place. For example, in order to carry out the oxygen reduction reaction (ORR) ($\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$), the catalyst particles must be in contact with both electronic and protonic conducting materials, and there must be some passages for the transportation of the reactants to the catalytic reaction sites as well as paths for the reaction product (H_2O) to exit. In a catalyst layer, protons travel through an electrolyte (ionomer) and electrons travel through electrically conductive solids, including the catalyst itself. Therefore, the catalyst particles must be in close contact with each other, the electrolyte, and the adjacent GDL. Moreover, the reactant gas (O_2) and the produced water travel mainly through the voids, so the electrode must be porous enough to allow gas to diffuse to the reaction sites and liquid water to wick out. Figure 19.2 schematically shows a three-phase boundary where catalyst, reactants, and electrolyte meet for electrochemical reactions. In the diagram this reaction boundary essentially is a line, not an area, which would result in a limited current. However, the actual reaction zone is larger than a single three-phase boundary line because some reactant gases can diffuse through the electrolyte polymer to the catalyst surface.

Figure 19.2. Schematic diagram of a three-phase reaction boundary

In a PEMFC, the combination of anode/membrane/cathode is referred to as a membrane electrode assembly (MEA). Normally, the MEA is a five-layer composite structure that includes anode GDL, anode CL, membrane, cathode GDL,

and cathode CL. Two different typical MEA structures have been developed according to the CL location, as illustrated in Figure 19.3. Applying catalyst ink onto the GDL leads to a basic two-layer structure called a catalyst coated GDL (CGDL), while directly applying catalyst ink onto both sides of the proton exchange membrane results in a three-layer structure called a catalyst coated membrane (CCM). Then a final five-layer MEA is formed by sandwiching a membrane between two CGDLs or a CCM between two GDLs.
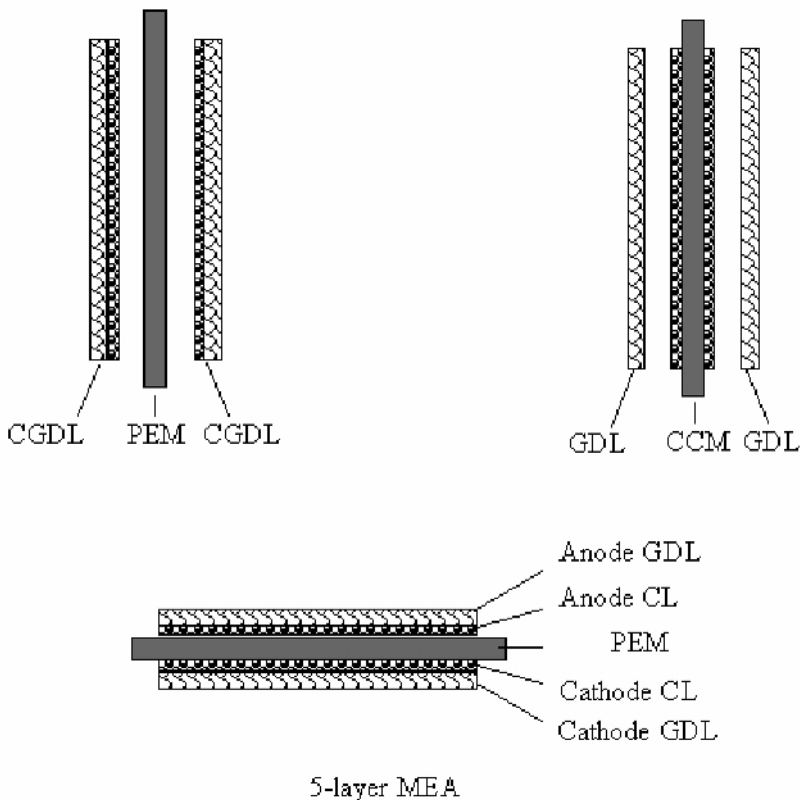
Figure 19.3. Schematic diagram of an MEA

The catalyst layers need to be designed to generate high rates of the desired reactions and minimize the amount of catalyst necessary for reaching the required levels of power output. An ideal catalyst layer should maximize the active surface area per unit mass of the electrocatalyst, and minimize the obstacles for reactant transport to the catalyst, for proton transport to exact positions, and for product removal from the cell; these requirements entail an extension of the three-phase boundary. In general, individual property specifications should be a compromise between conflicting requirements. The catalyst layer structure should be optimized with respect to the interactions between components, with trade-offs between several effects.

This chapter focuses on the preparation of catalyst inks, catalyst layers, and MEAs.
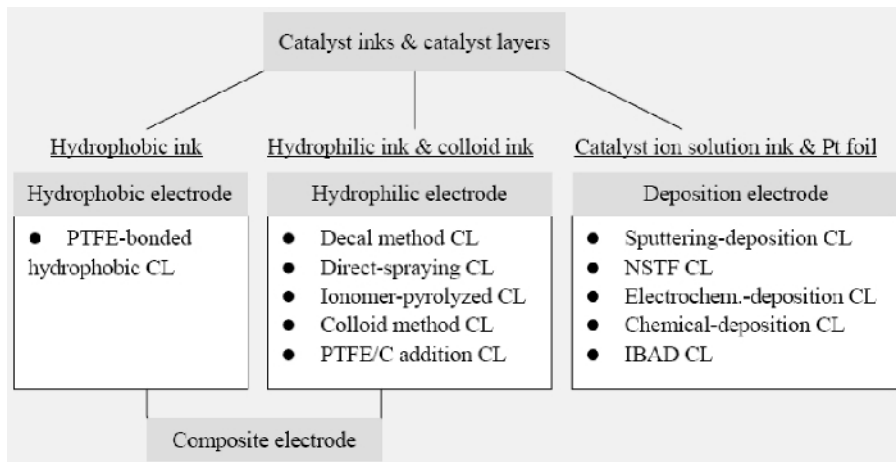
19.3 Catalyst Layer

The catalyst layer is the region where electrochemical reactions occur. The large challenges in PEMFC research arise from catalyst layers because their structures are quite complicated and heterogeneous. The first-generation CLs using PTFE-bonded Pt black electrocatalysts displayed high performance but at a prohibitively high cost [19]. These conventional electrodes generally have a high platinum loading, up to 4 mg/cm^2. One of the most significant improvements has been made by Raistrick [20], who fabricated a CL with dispersed Pt/C and by painting solubilized ionomer. These electrodes with 0.4 mg Pt/cm^2 loading demonstrated the same performance as the first-generation electrodes with 4 mg Pt/cm^2 [20]. With thin-film methods, the Pt loading was further lowered down to a level of 0.1–0.3 mg/cm^2 [8, 21–23], and even to 0.01–0.02 mg/cm^2 with the sputtering-deposition method [24]. The 2010 target of the United States Department of Energy, to have PEMFCs for transportation applications, needs to achieve a total Pt catalyst loading of 0.3 mg Pt /cm^2 (total Pt loading of cathode and anode) with a performance of 0.8 V @ 0.4 A/cm^2 or 0.85 V @ 0.1 A/cm^2 under 80 °C, 250 kPa, and H$_2$/air operation.

The important properties of a catalyst layer, such as electronic/protonic conductivity, porosity, active reaction area, as well as catalytic activity, are mainly determined by the fabrication method and the properties of the components. To date, several manufacturing techniques have been developed, such as blading, painting, printing, spraying, rolling, and screening. It is difficult to judge which method is the best because each has unique qualities.

19.3.1 Preparation of Catalyst Ink

Catalyst ink, containing the catalyst, an electrolyte (ionomer) and/or hydrophobic agent, and certain solvents, is a liquid precursor of the catalyst layer. When preparing the ink, the contents of each component are the first consideration, followed by its uniformity and viscosity. In general, catalyst ink should be stirred or ultrasonically dispersed thoroughly to ensure all the nano-scaled catalyst particles come into contact with the other components uniformly. If lower viscosity catalyst ink is being applied on a porous GDL substrate, the ink could penetrate the inside of the substrate, leading to wasted catalyst as well as a water "flooding" problem. However, if the viscosity is too high, the resultant catalyst layer will have problems with non-uniform dispersion or hard drying. According to the bonders used, there are three kinds of catalyst inks, as shown in Figure 19.4; the corresponding catalyst layers made from these inks are also shown.

Figure 19.4. Classification of catalyst ink and catalyst layers

19.3.1.1 Hydrophobic Ink

Hydrophobic ink, containing a catalyst and a hydrophobic agent (such as Polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF)), is used to prepare a hydrophobic type of catalyst layer. The typical process for the preparation can be summarized as follows:

1. Stir a mixture of Pt/C catalyst and solvent (e.g., ethanol) highly and disperse it in an ultrasonic machine;
2. Add a diluted PTFE emulsion to the above mixture, followed by thorough ultrasonic stirring to form a catalyst ink;
3. Heat the mixture in a temperature water bath to form a paste that is suitable for transferring onto a GDL.

PTFE induced in a CL not only acts as a binder to stabilize the catalyst particles but also imparts hydrophobicity to the CL and provides passways for gas transportation. However, if the PTFE content is too high the catalyst particles could become wrapped, resulting in decreased electron conductivity and catalyst utilization. Normally, a content of 10–40% is considered optimal.

19.3.1.2 Hydrophilic Solution and Colloid Ink

In a hydrophilic ink, the CL binder is replaced with a hydrophilic perfluorosulfonate ionomer (PFSI, e.g., Nafion). It is well known that Nafion ionomer exists in different states according to the dielectric constants of solvents, ε. For example, Nafion forms a solution in solvents with $\varepsilon > 10$, a colloid in those with ε between 3 and 10, and a precipitate in those with $\varepsilon < 3$. Typically, a solution state with ethanol or isopropyl alcohol and a colloidal state with butyl acetate have been widely used in prior studies.

One of the key parameters in such a hydrophilic ink is the PFSI content. The optimum amount and distribution of the ionomer in the CL is a trade-off between the requirements of maximum contact between ionomer and Pt particles, and

minimum electron/gas transport resistances. This maximum ionomer-Pt contact is required to guarantee maximum protonic conductivity. Gas transport inside the catalyst layer could be affected by both decreased porosity and liquid water trapping. Decreased porosity is caused mainly by occupation of the solid ionomer, while liquid water trapping is caused primarily by the hydrophilic property of the ionomer. For a supported catalyst like Pt/C, the carbon has a much larger surface area than that of the Pt particles. Therefore, only if the carbon surface is covered by the ionomer can contact between the ionomer and Pt particles be guaranteed. Normally, the ratio of ionomer to carbon (*I/C*) is about 0.8~1.

19.3.1.3 Pt Ion Solution Ink and Pt Foil

The third method is to use Pt ion solution ink, such as Pt^{2+} or Pt^{4+} salt solution, rather than using a well-prepared Pt/C or Pt-alloy/C catalyst. In this way, catalyst sites at desired positions in the catalyst layer can be formed through a reduction process. Alternatively, a Pt foil can also be used as the Pt resource in most of the sputtering-deposition method for CL preparation.

19.3.2 Preparation of the Catalyst Layer

In accordance with the component distribution in a catalyst layer, two categories of catalyst layer have been employed during the development of PEM fuel cells. The first is the uniform catalyst layer, in which all components distribute uniformly; this kind of CL is widely used in the fuel cell industry. The second is the non-uniform catalyst layer, in which one or more components have gradients across the whole catalyst layer, from the GDL side to the membrane side or from fuel cell inlet to outlet. The following sections will discuss these two categories in detail.

19.3.2.1 Uniform Catalyst Layer

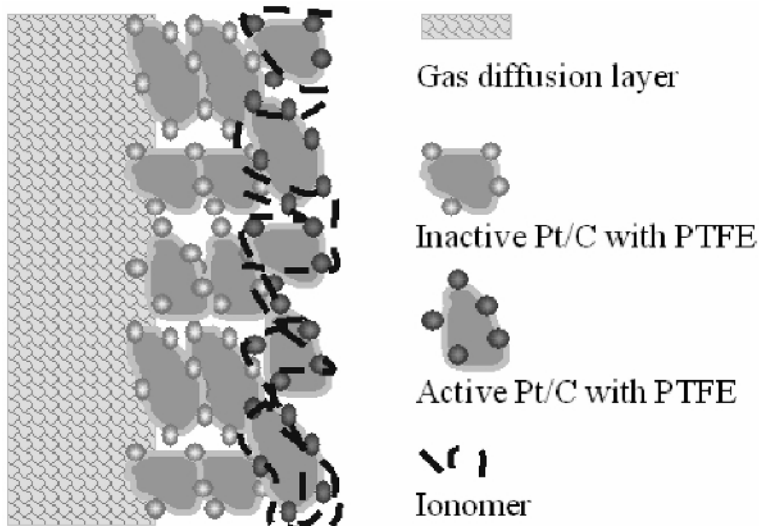#### PTFE-bonded Hydrophobic Catalyst Layer

PTFE-bonded hydrophobic electrodes are the modified versions of gas diffusion electrodes developed for PAFCs. In preparation, the catalyst particles are mixed with PTFE emulsion to form a catalyst ink, which is then cast onto the GDL. In order to provide ionic transport to the catalyst sites, the PTFE-bonded catalyst layers are generally impregnated with an ionomer, commonly Nafion, by brushing or spraying. A typical preparation process is detailed as follows:

1. Coat a PTFE-bonded hydrophobic ink onto the GDL and then dry to remove the solvent;
2. Bake the electrode subsequently at 240–340 °C for 40 minutes to remove surfactants in the PTFE emulsion and hydrophobilize the electrodes;
3. Spray a certain amount of Nafion solution onto the surface of the catalyst layer to form the ionic paths;
4. Dry the as-prepared electrode at room temperature to remove the solvents.

Such a PTFE-bonded hydrophobic catalyst layer is a breakthrough in catalyst layer preparation technology for PEMFCs. First, this technique uses a carbon-

supported platinum catalyst to replace a platinum black catalyst. This replacement can reduce platinum usage more than ten-fold without compromising catalyst layer performance. More importantly, proton transport is enhanced significantly by impregnating the CL with a proton conducting material (Nafion) between the electrode and the membrane. For fuel cell performance optimization, a PTFE content of 20~40 wt% and an ionomer to carbon (in a Pt/C catalyst-based catalyst layer) ratio of 0.8~1 have proven to be optimal parameters for forming an efficient electrode. To date, the performance of such an electrode has been improved significantly and corresponding mass production has been achieved.

Figure 19.5 schematically shows the structure of PTFE-bonded electrodes. The advantages and disadvantages of such electrodes depend on the preparation processes and materials used. The unique use of such a PTFE in the catalyst layer can improve the gas transport limitation considerably. However, if too much PTFE is used, negative effects can be observed. For example, the catalyst layer wrapping effect will cause a decrease in both electron conductivity and catalyst utilization. In addition, the process of impregnating the top of the catalyst layer surface with Nafion ionomer could lead to an asymmetric distribution within the whole CL. If the sprayed Nafion ionomer does not penetrate the electrode to a sufficient depth, the deeper layer catalyst particles will not come in contact with the ionomer, leading to a higher resistance in proton transport and leaving the uncontacted Pt inactive. These inactive Pt particles are denoted by blank circles in Figure 19.5. The platinum utilization in such an electrode is only 10–20% [7]. Note that assembled MEAs with such electrodes are prone to delamination due to the different swelling degrees of the electrode and membrane, resulting in a discontinuity in the ion path and decreased cell longevity.

Figure 19.5. Schematic of a PTFE-bonded hydrophobic electrode

Ionomer-bonded Hydrophilic Catalyst Layer

As discussed above, it is vital to extend the contact area between the catalyst and the protonic ionomer in order to improve catalyst utilization. To meet this requirement, ionomer-bonded hydrophilic catalyst layers have been developed. The hydrophilic ink, prepared by mixing the catalyst and ionomer directly, ensures sufficient contact between the catalyst particles and the ionomer. It was found that an ionomer-bonded hydrophilic catalyst layer could improve Pt utilization by up to 45.4% [25].

Ionomer-bonded hydrophilic catalyst layers can be classified into two categories, according to differences in preparation processes and structures: the membrane-based hydrophilic catalyst layer and the GDL-based hydrophilic catalyst layer. In addition, some modified versions of such hydrophilic catalyst layers have also been explored. These will be discussed in detail in the following sub-sections.

Membrane-based Hydrophilic Catalyst Layer. Wilson and Gottesfeld [8, 21–23] suggested an ionomer-bonded hydrophilic catalyst layer prepared with the decal transfer method. The so-called decal transfer process includes two key steps: (1) coating catalyst ink onto a blank substrate (e.g., PTFE film) then (2) transferring the coat onto the membrane (as shown in Figure 19.6). A typical preparation procedure is as follows:

1. Prepare a uniformly distributed hydrophilic ink (Pt/C catalyst, Nafion solution and water/glycerol as a solvent). The weight ratio of carbon/water/glycerol is about 1:5:20.
2. Paint the PTFE film with a layer of ink and then bake this catalyzed film in an oven until dry. If the desired catalyst loading is not achieved, more painting will help.
3. Decal the coated layer onto a polymer electrolyte membrane by a hot-pressing process (i.e., press at 70~90 atm for 90 seconds under 140 °C).
4. Cool down and then release the blank substrate from the coating film, leaving the film adhered to the membrane surface.
5. Place gas diffusion layers against the catalyzed film to form an MEA.

Normally, glycerol is used in the ink preparation, which prevents the decal film from spontaneously combusting during the drying process in an oven; this prevention is mainly due to the low evaporation rate of glycerol. A cation exchanged ionomer and membrane (such as tetrabutylammonium ion (TBA$^+$) or Na$^+$ form) are also used more frequently in ink preparation. With these agents, the transferring temperature can be increased to as high as 200 °C without any damage to the film structure, facilitating effective contact between the ionomer and the catalyst particles, as well as strong bonding to the membrane. In addition, a robust pseudo-crystalline structure of ionomer can also be formed in the catalyst layer. The catalyzed membrane assembly is thereafter converted to the H$^+$ form by light boiling in a 0.1 M H$_2$SO$_4$ solution and rinsing in deionized water prior to assembly into the MEA.
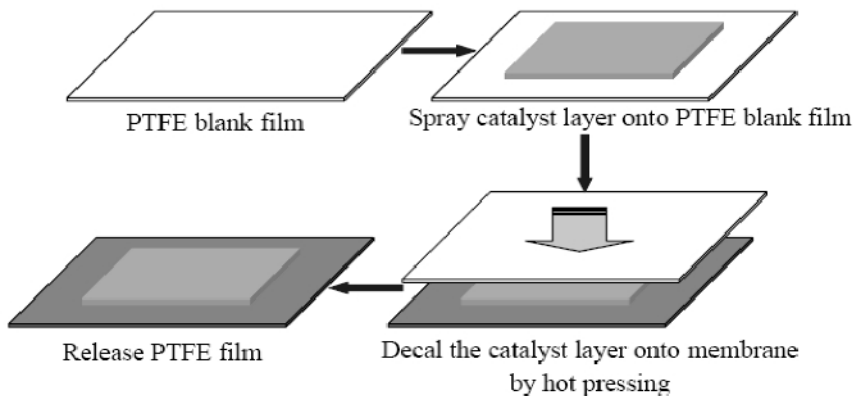
**Figure 19.6.** Process flow diagram of thin film decal transfer technology

In order to further improve the ionic connection between the membrane and the catalyst layer [8, 26–30], a technology called catalyst coated-membrane (CCM) has recently been developed. In a CCM, the catalyst ink composed of catalyst, proton exchange ionomer, and solvent is sprayed directly onto both sides of the proton exchange membrane (e.g., Nafion membrane) to form anode and cathode catalyst layers. In this way, a three-layer (anode catalyst, membrane, and cathode catalyst layer) CCM is formed. The CCM is then sandwiched with two GDLs to make an MEA. A hot-press bonding step for this MEA may not be necessary when it is assembled into a single cell. Of course, a hot-press step may help if the heating and pressing conditions are optimized. Commercially available CCMs can give a performance of 0.65 V at a current density of 1.0 A/cm^2 under operating conditions of 80 °C, 50% relative humidity (RH), and 7 psig.

Besides a wet-spraying method for CCMs, a dry-spraying method was also developed by Gulzow et al. [31, 32] without using solvents. In this process, composite catalyst powders, ionomer, and PTFE are mixed in a knife mill. The mixture is then atomized and sprayed with a nitrogen stream through a slit nozzle directly on both sides of the membrane, followed by a hot rolling procedure to improve both electric and ionic contacts. The advantages of the dry layer technique are its simplicity without solvent evaporation steps, as well as its unique ability to create graded layers with multiple mixture streams.

GDL-based Hydrophilic Catalyst Layer. Catalyst layers can also be formed by spraying hydrophilic catalyst ink onto a GDL [33–36]. Qi and Kaufman [36] presented a low-Pt-loading high-performance electrode for PEM fuel cells by this method. They simply mixed together the catalyst with cold Nafion solution and water, without any additional organic solvent, and then pasted the mixture onto the GDL to form the electrode. Using E-TEK 20 wt% Pt/C, the catalyst layer with 30 wt% Nafion content and 0.12 mg/cm^2 Pt loading yielded the best performance, 0.72 W/cm^2 under ambient pressure. This performance could be further improved using several effective activation methods. One was to boil or steam the electrodes or MEAs before fuel cell testing [37]. The second method was H$_2$ evolution on electrodes using an external power source [38]; H$_2$ evolution could change the

porosity and tortuosity of the catalyst layer and improve catalyst utilization and fuel cell performance. The third method was to operate the MEAs at elevated temperature and pressure before operation at normal conditions [39, 40].

Figure 19.7 shows a schematic structure of an ionomer-bonded electrode. The notable advantages of such an electrode can be summarized as follows: (1) improved bonding between the membrane and the catalyst layer, (2) a uniform continuity of the electronic and ionic paths for all catalyst sites due to the uniform dispersion of catalyst in the ionomer, (3) high Pt utilization, attributed to good contact between the catalyst and the protonic conductor, and (4) relatively low catalyst loading without performance losses. However, there are still some inevitable disadvantages for this kind of catalyst layer. First, due to the lack of hydrophobic passages, gas transportation from the GDL to the reaction sites is difficult, and the produced water tends to accumulate in the electrode and block the gas transport paths, leading to a decrease in fuel cell performance. Second, because the ionomer degrades, its ability to bind with the catalyst particles will decrease, causing lowered reliability as well as durability problems.
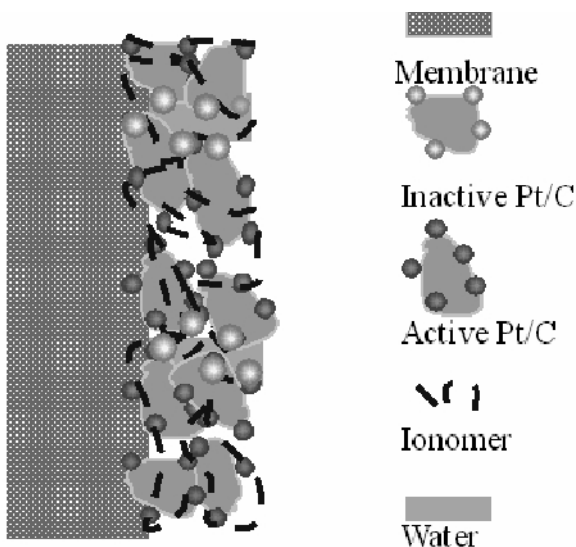
Figure 19.7. Schematic of an ionomer-bonded hydrophilic electrode

Modified Hydrophilic Catalyst Layer

Colloid Method: In order to improve gas transport through the ionomer-bonded hydrophilic catalyst layer, some modified hydrophilic electrodes have also been developed. One technique is called the colloid method, which changes Nafion into a colloid state. The colloid ionomer (such as Nafion) can adsorb catalyst particles to form larger catalyst/Nafion agglomerates. It is believed that the colloid method benefits the construction of the CL microstructure and enhances gas transportation [41–45]. Uchida et al. [41, 42] first proved that butyl acetate with a ε of 5.01 was the best solvent to form PFSI colloids for the preparation of a catalyst layer. The detailed steps are as follows:

1. Add butyl acetate into the PFSI solution to form an ionomer colloid.
2. Add the Pt/C particles into the above colloid solution; in this step, the mixture is transformed into a paste by ultrasonically coagulating the Pt/C catalyst adsorbed PFSI chains.
3. Spread the paste over the GDL to form an electrode.

A colloid method such as this should be more suitable for applying catalyst ink onto a porous GDL because the larger catalyst agglomerates do not easily penetrate deeply into the GDL. Improved cell performance was observed with the catalyst layer prepared using this colloid method, which could be attributed to the increased reaction area, the reduced internal resistance, and the enhanced reactant mass transport.

Ionomer-pyrolyzed Method: To improve gas transfer through the hydrophilic catalyst layer, another technique called the ionomer-pyrolyzed method has also been developed [46]. This method can effectively introduce hydrophobic gas paths into the catalyst layer through pyrolyzing a part of the ionomer, making it hydrophobic.

The preparation steps are as follows:

1. Prepare a hydrophilic catalyst ink consisting of catalyst, Nafion, and alcohol.
2. Spread this catalyst ink onto a gas diffusion layer, then dry it to form a pre-electrode.
3. Heat-treat this pre-electrode in a temperature range from 280 to 340 °C for 1 hour under inert gas.
4. Spray a small amount of Nafion ionomer solution onto the surface of the electrode with a Nafion loading of 0.05–0.2 mg/cm^2 then dry the electrode at room temperature.

It is known that Nafion has a hydrophobic Teflon-like backbone and hydrophilic sulfonic groups ($-SO_3H$) at the end of the side chains, which make it proton conductive. Thermogravimetric/mass spectrometric (TG-MS) measurement during heat-treatment in the temperature range of 275 to about 380 °C showed a sharp mass loss peak corresponding to the release of sulfur dioxide. This result indicated that the sulfonic group in the ionomer was decomposed in this temperature range to form sulfur dioxide gas. Similar results were also reported in [47].

In the ionomer-pyrolyzed method, after heat-treatment of the pre-electrode in the temperature range of 280–340 °C, part of the Nafion ionomer in the catalytic layer can be pyrolyzed, losing its sulfonic acid group. This part of the ionomer can act as hydrophobic material in the electrode, performing the same function as PTFE in a PTFE-bonded electrode. The rest of the unpyrolyzed ionomer can still serve as the proton conductive material. In the final step, a small amount of Nafion ionomer solution is sprayed onto the surface of the electrode to increase the adherence between the catalyst layer and the membrane. Therefore, the ionomer-pyrolyzed electrode not only guarantees ionic and electronic contact but also provides passage for the gases and avoids flooding, thereby improving Pt

utilization. Compared to a PTFE-bonded electrode, much better fuel cell performance can be achieved with an ionomer-pyrolyzed electrode, as shown in Figure 19.8.
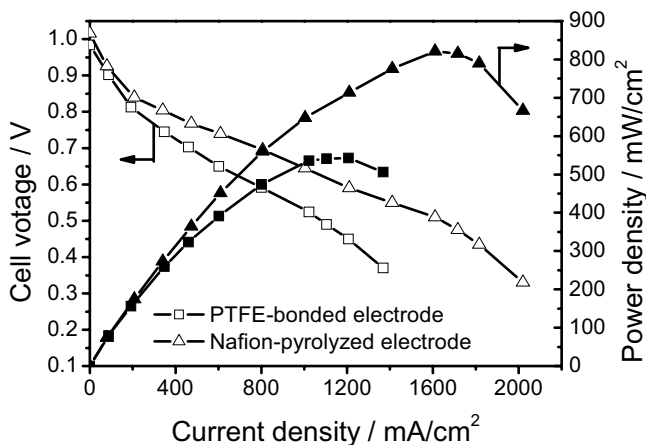

Figure 19.8. Performance of MEAs with different electrodes [46]. (Reproduced from Zhang J, Wang X, Hu J, Yi B, Zhang H. A novel method for preparing PEMFC catalytic layers. Bulletin of the Chemical Society of Japan 2004;77:2289–90, with kind permission from the Chemical Society of Japan.)

Adding PTFE/C in a Hydrophilic Electrode: Another method for modifying the hydrophilic ionomer-bonded electrode is to introduce hydrophobic materials into the electrode to form gas passages. PTFE-supported carbon (PTFE/C) composite powder is the first choice because of its excellent compatibility with the electrode. However, due to the high tenacity and low fluidity of PTFE, it is difficult to break PTFE/C into very small particles. Two ways have been proposed: (1) the mechanical milling method in liquid nitrogen [48] and (2) the intermittent microwave irradiation (IMI) method [49]. Mechanical milling is a complicated and time-consuming process, and the resultant PTFE/C powder is not uniform. The IMI method is more convenient and can achieve a uniformly distributed PTFE/C composite. Unfortunately, the drawback of IMI is that it is not easy to control the PTFE content precisely. Taking a PTFE/C with PTFE loading of 30 wt% as an example, the IMI synthesis steps are as follows [49]:

1. Mix 4.0 g carbon black and 150 ml deionized water together thoroughly under stirring.
2. Add 120 g PTFE emulsion (with a concentration of 5 wt% diluted by deionized water) to the above carbon suspension under stirring.
3. After the evaporation of water, a nominal 60 wt% PTFE/C mixture can be obtained and is treated by intermittent microwave irradiation (IMI); the IMI is cycled with "30 s on, 90 s off" to decompose the surfactant in the PTFE emulsion and recover the hydrophobicity of the PTFE until the final PTFE loading of 30 wt% is achieved.

The fabrication procedure for a catalyst layer modified by adding the as-prepared PTFE/C composite powder is as follows:

1. Prepare Nafion ionomer-impregnated Pt/C catalyst ink by dispersing Pt/C catalyst and Nafion solution in isopropanol, followed by a thorough ultrasonic treatment; the weight ratio of Nafion to the carbon support of Pt/C is controlled at ~4:5.
2. Add the butyl acetate to the dispersion to promote *in situ* deposition of Nafion on the Pt/C catalyst, forming a Pt/C/Nafion dispersion.
3. Mix the Pt/C/Nafion dispersion and PTFE/C composite powder together under stirring, forming Pt/C/Nafion-PTFE/C composite catalyst ink; the percentage of PTFE/C nanocomposite in the Pt/C/Nafion-PTFE/C catalyst layer is about 30%.
4. Spray the as-prepared composite catalyst ink directly on one side of the membrane to form a catalyst layer.
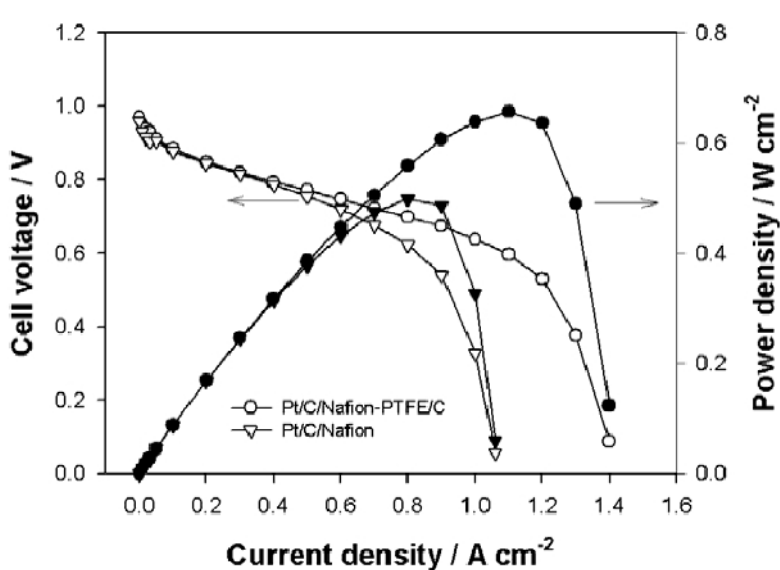
Figure 19.9. Polarization curves and the corresponding power density curves of fuel cells with a Pt/C/Nafion-PTFE/C catalyst cathode and a Pt/C/Nafion membrane-based cathode, respectively. Measured at 80 °C. The hydrogen and air reactant gases were externally humidified at 90 °C and 85 °C, respectively. The flow rates were 50 mL min^{-1} for hydrogen and 200 mL min^{-1} for air [49]. (Reprinted from Electrochemistry Communications, 8(7), Tian ZQ, Wang XL, Zhang HM, Yi BL, Jiang SP, Microwave-assisted synthesis of PTFE/C nanocomposite for polymer electrolyte fuel cells, 1158–62, ©2006, with permission from Elsevier.)

The polarization curves in Figure 19.9 show that incorporation of PTFE/C nanocomposite into the Pt/C/Nafion catalyst can significantly improve the mass transport property of the catalyst layer without any negative effect on the electrocatalytic activity of the Pt catalysts.

Dual-bonded Composite Catalyst Layer

Regarding the inherent problems with proton/gas transport for the hydrophobic or hydrophilic types of catalyst layers, a dual-bonded composite CL was suggested first by Zhang et al. [50, 51] in order to alleviate the drawbacks and promote the merits of the individual CL. Zhang and Shi [52, 53] also investigated such dual-bonded composite CLs by optimizing various components used. This dual-bonded CL cathode has two layers. The first is the hydrophobic layer with PTFE as a binder material, which is fabricated directly on the surface of the GDL. The second is a hydrophilic layer with Nafion as a binder material, which is fabricated on top of the hydrophobic layer surface. The typical preparation process can be summarized as follows:

1. Apply a PTFE-bonded hydrophobic ink on the surface of the GDL as the hydrophobic layer;
2. Bake this hydrophobic layer in an oven at a temperature of 200–350 °C for 30–60 minutes to hydrophobilize the layer;
3. Then apply a Nafion-bonded hydrophilic ink onto the top surface of the above hydrophobic layer as a hydrophilic layer, and at the same time can also ionize the hydrophobic layer.
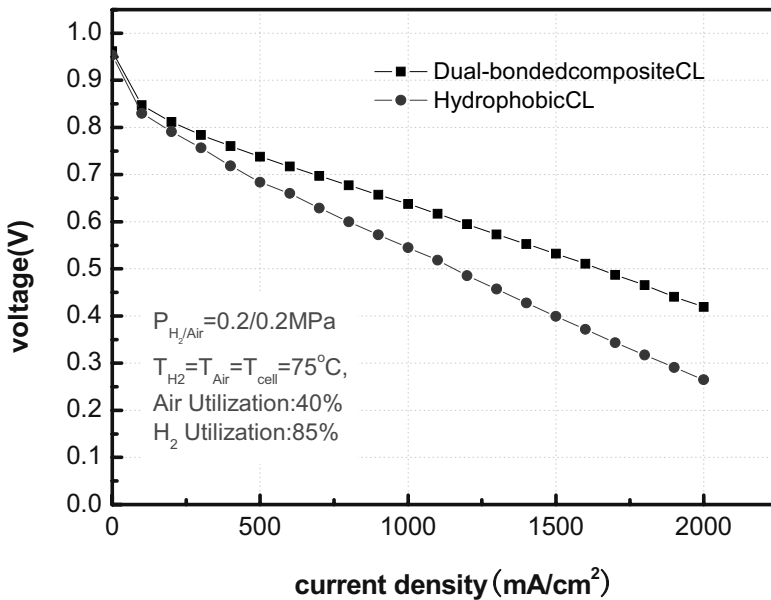

Figure 19.10. Cell performances with different catalyst layers

The dual-bonded CL has both hydrophobic and hydrophilic properties, ensuring enough protonic conductivity as well as smooth gas transfer pathways. As expected, the cell performance of such a dual-bonded composite CL is obviously higher than that of a conventional PTFE-bonded hydrophobic CL (as seen in Figure 19.10). Moreover, the catalyst dosage in such an electrode can be increased

in order to achieve the desired higher output power. Though the preparation process of such a dual-bond electrode is a little fussy, it is a promising and practical method to achieve relatively higher performance and better durability.

Super-thin Deposition Catalyst Layer

A trend in electrode preparation is to reduce the catalyst layer thickness to improve the mass transfer efficiency at the interface, such as the efficient movement of protons, electrons, and dissolved reactants in the reaction zone. In addition, a thinner electrode will be beneficial to reduce catalyst loading and increase mass power density. The deposition technique is an effective way to achieve a thinner electrode through depositing a nano-scale catalyst film on the substrate. Deposition methods include chemical vapor deposition, physical or thermal vapor deposition, sputtering deposition, electrochemical deposition, chemical deposition, as well as ion beam deposition. The following sections will focus on electrodes fabricated with these various deposition methods.

Sputtering-deposition Electrode. Sputtering is widely used in the preparation of thin catalyst layers. The resultant CLs have demonstrated high performance even at an ultra-low level of Pt loading [24, 54, 55]. In general, the sputtering process is carried out in an evacuated chamber. The typical sputtering steps are as follows:

1. Mount the substrate (either the GDL or the membrane) in the sputtering chamber, with one side facing up or down towards the catalyst target.
2. Evacuate the chamber and then fill argon to a pressure between 1.3 and 6.7 Pa.
3. Initiate the sputtering process by applying a high voltage between the target and the chamber wall. Depending on the desired catalyst loading, the process is continued until the targeted loading is achieved.
4. Upon completion of the sputtering, readmit air to the chamber and remove the substrate.

The performance of a sputtering catalyst layer is sensitive to the amount of sputtered catalyst, the substrate material, and the morphology of the substrate. The sputtering layer generally has a thickness of 2–15 nm (corresponding to an ultra-low level of platinum loading of 0.005–0.03 mg/cm^2). The surface roughness of the substrate has a significant effect on the Pt layer adhesion and morphology. Applying an additional thin layer on the substrate before catalyst layer deposition, such as a chromium, palladium, or gold thin film layer, can modify the substrate's seeding, improving the growth of the platinum catalyst film and enhancing electrical conductivity. In addition, to extend the three-phase reaction zone a two-dimensional active layer was developed by sputter-depositing alternating layers of Pt and Nafion-carbon ink onto the membrane or the gas diffusion layer [56–58]. The results demonstrated that such multiple sputtering could also effectively improve performance.

Nanostructured Thin Film (NSTF) Electrode. Debe et al. [59, 60] employed sputter technology and deposited catalyst on a nanostructured thin film (NSTF). This NSTF is an oriented crystalline organic whisker. Perylene red (PR) is a highly useful organic material for growing the NSTF. To form an electrode, the

catalyst/PR nanostructured film is decaled to the surface of the proton exchange membrane to form a catalyst layer. Scanning electron microscope (SEM) cross-sectional views of a nanostructured whisker support and a catalyst coated NSTF are shown in Figure 19.11. There are two primary differences between the NSTF catalyst layer and the conventional catalyst layer (using Pt/C): (1) the former is at least ten times thinner than the latter, which has significant implications for the electrochemically active area as well as for the water and heat generation rates per unit volume of the electrode, and (2) the former contains no additional ionomer, such as Nafion, for ion transport. But no increasing ionic resistance is observed because of the short distance between the proton exchange membrane and the active catalyst surface sites. The second difference becomes more significant when a fuel cell is operated at higher current densities. For conventional electrodes, only a fraction of the catalyst layer is utilized, whereas the NSTF layer appears to be 100% utilized at all current densities.
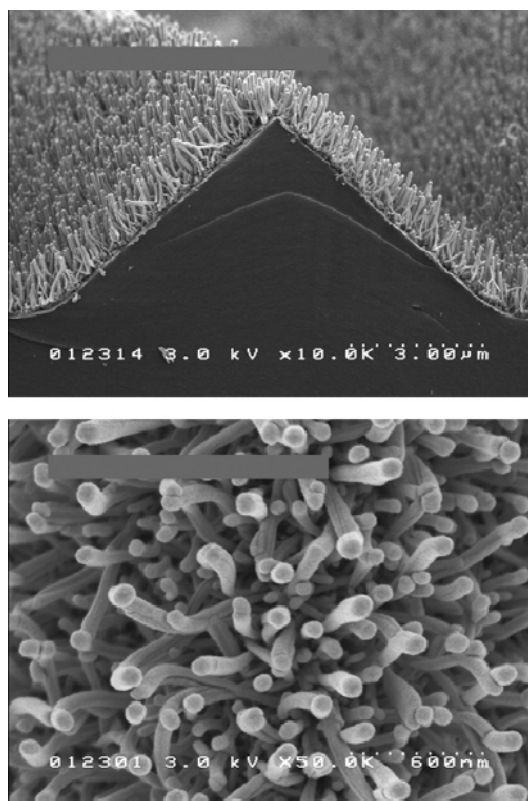
Figure 19.11. Scanning electron micrographs of typical NSTF catalysts as fabricated on a microstructured catalyst transfer substrate, seen (top) in cross-section with original magnification of ×10,000 and (bottom) in plane view with original magnification of ×50,000. The dotted scale-bar is shown in each micrograph [59]. (Reprinted from Journal of Power Sources, 161(2), Debe MK, Schmoeckel AK, Vernstrom GD, Atanasoski R, High voltage stability of nanostructured thin film catalysts for PEM fuel cells, 1002–11, ©2006, with permission from Elsevier.)

Besides Debe's electrode, Tang et al. [61] produced a carbon nanotube thin film with ultra-low Pt loading (Pt on multi-walled carbon nanotubes (MWNTs)) through a polycarbonate filtration membrane. Compared to the results presented by both Los Alamos National Lab (LANL) and 3M Corporation, as shown in Figure 19.12, this thin-film cathode catalyst layer with a loading of 6 μg Pt/cm^2 could give a mass activity of 250 A/mg Pt, which is the highest activity reported so far.
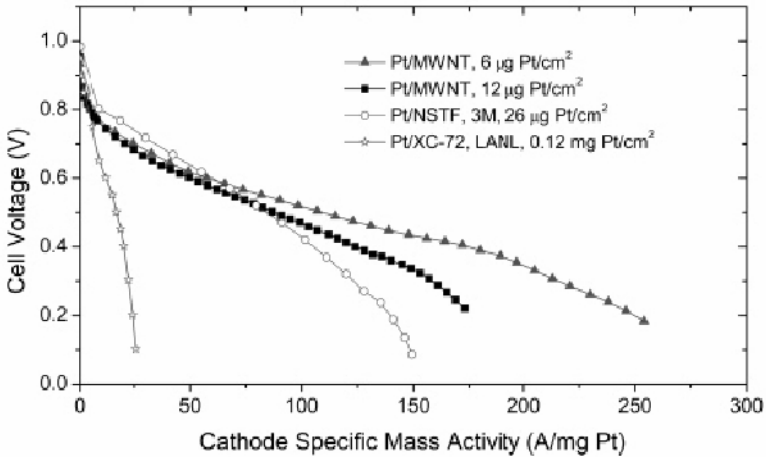

Figure 19.12. Comparison of mass activity of Pt/MWNTs thin film with Pt loading of 6 μg Pt/cm^2 (▲); Pt/MWNTs thin film with Pt loading of 12 μg Pt/cm^2 (■); 3M Corporation, Pt/NSTF with Pt loading of 26 μg Pt/cm^2 (□); Los Alamos National Lab, Pt/C with Pt loading of 120 μg Pt/cm^2 (☆) [61]. (Reprinted with permission from J Phys Chem C 2007;111:17901–4. Copyright 2000 American Chemical Society.)

As discussed, the sputtering technique is a very useful method to achieve an ultra-low Pt loading in the catalyst layer. A unique advantage of the sputtering technique is that the catalyst utilization is extremely high. In addition, the sputtering method facilitates the preparation of a nano-scale Pt catalyst layer with a precise thickness, which could simplify fuel cell water/thermal management and eliminate mass transfer loss. Furthermore, the sputtering process allows the deposition of Pt on various substrates, such as the GDL, membrane, and other supports. However, although the sputtering CLs showed remarkably higher mass activity than the conventional layer, the validated output power density still falls short.

Electrochemical-deposition Electrode. Vilambi-Reddy et al. [62] presented the early research on the electrochemical deposition electrode. They developed an electrochemical catalyzation (ECC) technique to deposit platinum catalyst particles selectively in the regions accessible to both ions and electrons. In the ECC technique, a hydrophobic porous carbon paper was first coated with dispersed carbon particles and PTFE to form a substrate. Then the Nafion ionomer was impregnated onto this carbon substrate. This substrate was then placed into a platinum acid-plating bath, along with a platinum counter electrode. One side of this substrate, without Nafion, was masked with a non-conducting film, which

could guarantee that the platinum would only be deposited on the regions impregnated with Nafion. When an interrupted DC current was applied to the electrodes in the plating bath, catalyst ions would pass through the Nafion to the carbon particles and be deposited on those areas where protonic and electronic conduction coexisted. The resulting platinum particle sizes ranged from 20 to 35 Å, with a Pt loading of 0.05 mg/cm^2. In terms of mass activity, i.e., mA/mg Pt, a tenfold increase was observed for the ECC prepared electrode, contributing to higher platinum utilization. In addition, the electrodeposited method was also used to deposit catalyst particles through the membrane and into the membrane-electrode interfacial region, or directly onto the carbon substrate [63, 64].

Chemical-deposition Electrode. Chemical techniques can also be employed in the fabrication of catalyst layers by platinizing the surface of a Nafion membrane. One approach [65, 66] is to expose one side of the Nafion membrane to a reductant solution (e.g., hydrazine solution) and the other side to a platinic acid solution. The reductant diffuses across the membrane to react with platinic acid and form a Pt catalyst layer. In another impregnation-reduction method [3, 67, 68] a cationic salt, such as $Pt(NH_3)_4Cl_2$, is first impregnated into the Nafion membrane, followed by exposing this membrane to a reductant, such as $NaBH_4$. As shown in Figure 19.13, a dense and porous platinum film can be formed using this chemical deposition technique.
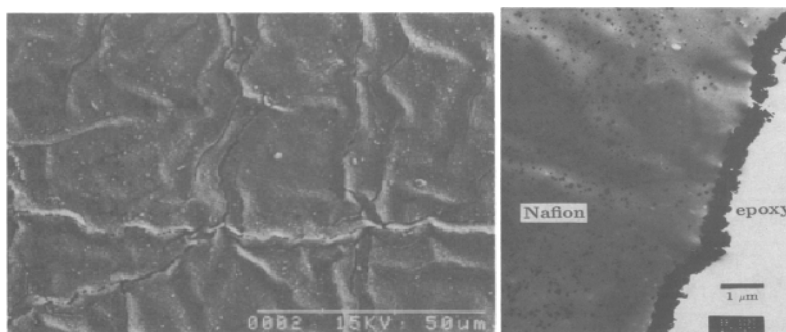
Figure 19.13. SEM top view and TEM side view of a non-equilibrium impregnation-reduction electrode. Deposition conditions: 0.6 mM $Pt(NH_3)_4Cl_2$, 1 mM $NaBH_4$, 40 minutes impregnation time, 2 hours reduction time, 50 °C [3]. (Reprinted by permission of ECS—The Electrochemical Society, from Liu R, Her W-H, Fedkiw PS. *In situ* electrode formation on a Nafion membrane by chemical platinization.)

A unique advantage of electrodes fabricated by chemical techniques is improved proton conductivity due to sufficient contact between the Nafion membrane and the catalyst layer. The disadvantages are poor mass transportation through the catalyst layer and lower platinum activity, caused by large particle size.

Ion-beam Assisted Deposition (IBAD) Electrode. The ion-beam assisted deposition (IBAD) technique has been previously used for a wide range of applications [69], and the detailed methodology can be found in [70]. Dual IBAD is a vacuum-deposition process that combines physical vapor deposition (PVD) with ion-beam bombardment. A vapor of coating atoms is generated with an

electron-beam evaporator and deposited on the substrate. Ions are simultaneously extracted from the plasma and accelerated into the growing PVD film at energy levels of several hundred to several thousand electron volts (500–2000 eV). Two ion beams are used in the dual IBAD approach: one is to roughen the substrate and the other is to embed the target atoms (such as Pt). Saha et al. [71, 72] prepared a series of ultra-low pure Pt-based electrodes (with Pt loading of 0.04–0.12 mg Pt/cm^2, the corresponding film thicknesses ranged between 250 and 750 Å) by the dual IBAD method on the surface of a commercially available GDL (LT1400, E-TEK). These electrodes were compared with a conventional E-TEK electrode having a total MEA Pt loading of 1 mg Pt/cm^2. The results showed that a mass specific power density of 0.297 g Pt/kW may be possible at 0.65 V if using a dual IBAD electrode containing a 250 Å deposit with a total catalyst loading of 0.08 mg Pt/cm^2. This activity is superior to that of the conventional MEA with a total loading of 1 mg Pt/cm^2. Furthermore, the dual IBAD method also has an advantage in terms of mass manufacturability of the PEMFC electrodes. However, in comparison with the performance target of 0.8–0.9 W/cm^2 at 0.65 V, this technique could give a performance of only 0.27–0.43 W/cm^2, mainly due to high mass transport losses.

19.3.2.2 Gradient Configuration Catalyst Layer

Most of the catalyst layers described above have uniform structures and compositions over the whole catalyst layer. However, current distribution measurements (or current mapping) and the corresponding mathematical models indicate that current density is strongly dependent on the relative position on the MEA; in other words, different locations across the MEA can give different current densities or reaction rates. This is mainly due to the non-uniform distribution of the reactant concentrations along the flowfield channels. It is understandable that the electrochemical reaction consumption of the reactant, as well as product water accumulation along the MEA in-plane direction, lead to a gradual decrease in reactant concentration from fuel cell inlet to outlet. In this non-uniform reactant distribution, the configuration of flowfield channels plays an important role. Along the MEA through-plane direction, the electrochemical reaction prefers to occur at zones close to the membrane in the catalyst layer. Therefore, in order to ensure an efficient electrochemical reaction and sufficient utilization of the catalyst, a decreasing gradient distribution of the catalyst from the membrane side to the GDL side would be favorable. With respect to this, some "fine gradient" electrodes with non-uniform structure and composition in the in-plane direction or through-plane direction have been explored.

In-plane Catalyst Gradient Electrode

A non-uniform electrode was introduced in 1989 [73]. In this electrode, the electrocatalyst concentration increased along the direction parallel to the electrode substrate. It is expected that the effect of increased catalyst loading in the direction of gas flow could balance the effect of diminishing reactants in the gas stream. In this way, the reaction rate could be substantially uniform across the electrode surface. Prasanna et al. [74] employed the catalyst-gradient method for single fuel cell fabrication, and found that it was an effective way to reduce Pt loading without

any loss in fuel cell performance. Various gradient electrodes have been designed, as shown in Figure 19.14 (a). The corresponding cell performance is also given in Figure 19.14 (b). It can be seen that with the same catalyst loading (0.3 mg/cm^2), the gradient electrode displays much better performance than does the non-gradient electrode, particularly in the high current density range. The disadvantage is that the fabrication of a non-uniform electrode is much more complicated than that of a uniform electrode.
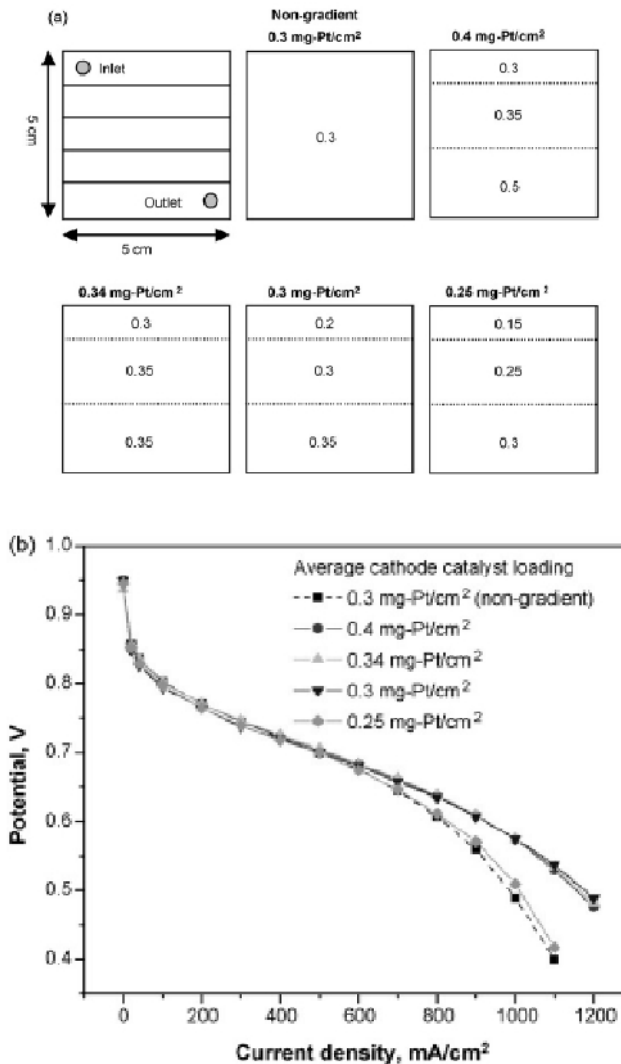
Figure 19.14. (a) Distribution of the cathode catalyst loading in a gradient electrode, (b) cell performance of non-gradient and gradient electrodes [74]. (Reprinted from Journal of Power Sources, 166(1), Prasanna M, Cho EA, Kim H-J, Oh I-H, Lim T-H, Hong S-A, Performance of proton-exchange membrane fuel cells using the catalyst-gradient electrode technique, 53–8, ©2007, with permission from Elsevier.)

Through-plane Catalyst Gradient Electrode

An electrode with the catalyst gradient along the through-plane direction contains a series of catalyst layers from the GDL side to the membrane. Each catalyst layer has its own catalyst loading that differs from the others'. A typical example is a PTFE-bonded or ionomer-bonded catalyst layer with an additional sputtered Pt layer on the top surface of the CL or membrane. The objectives of this method are to reduce the thickness of the supporting catalyst layer and increase the catalyst concentration in the layer adjacent to the membrane. The catalyst through-plane gradient configuration is also beneficial in terms of catalyst utilization improvement. For example, Ticianelli et al. [5, 75, 76] made this kind of electrode by sputtering a 50 nm Pt layer on a PTFE-bonded layer and testing its performance. They found that with a highly concentrated Pt localized in the layer near the membrane, the activation as well as the ohmic losses within the catalyst layer were diminished and the power density was improved significantly. Similar conclusions were also obtained by Mukerjee et al. [77].

Other Composition Gradient Electrodes

Besides the catalyst gradient in the catalyst layer, other components such as the hydrophobic agent (PTFE) and proton conductive polymer (Nafion) may also need to be adjusted in order to optimize gas/water transportation and electron/proton transfer. It can be expected that the catalyst layer adjacent to the gas diffusion layer side should be more hydrophobic to ensure much more of the reactants penetrates the inside of the electrode. While near the membrane side, more proton conductive polymer is needed to ensure a continuous network for proton conduction. Therefore, a non-uniform catalyst layer with a decreasing PTFE loading and an increasing Nafion content along the through-plane direction from GDL to membrane should be more efficient.

Song et al. [78] presented a multi-layer agglomerate model for the performance analysis of a non-uniform catalyst layer. The catalyst layer is assumed to be composed of several sub-layers with different material properties, such as agglomerate size, agglomerate porosity or sub-layer porosity, and so on. The effects of different material property combinations in these sub-layers on the whole catalyst layer performance were studied numerically. The results showed that the performance of the catalyst layer was strongly dependent on the properties of the sub-layer adjacent to the membrane. Furthermore, decreasing agglomerate sizes, increasing agglomerate porosities, or decreasing sub-layer porosities along the direction from the side of the gas diffusion layer to the side of the membrane will also improve the performance of the whole catalyst layer.

Non-uniformity in an electrode is also developed according to the configuration of the flowfield channels [79]. The MEA area that is in contact with the landing areas of the flowfield plate has no catalyst, and only the channel area is coated with catalyst. In this way, it is possible to reduce the quantity of expensive electrocatalyst material while maintaining the same cell performance.

Although a non-uniform catalyst layer can improve fuel cell performance to some extent, the preparation process is complicated and difficult to control. Therefore, this kind of catalyst layer is not suitable for mass production.

19.4 Preparation of the MEA

The MEA, which is composed of anode, membrane, and cathode, is a key unit in PEM fuel cells. The MEA is normally prepared by sandwiching a membrane between an anode and cathode under hot pressing. Before hot pressing, the membrane usually needs to be pre-treated in order to remove impurities and completely protonate the membrane. In practice, the membrane is treated in 3% $H_2O_2(aq)$ and then in 1 M $H_2SO_4(aq)$ for 1 hour each at 60–80 °C, followed by careful washing with double-distilled water.

The hot-pressing process (also called MEA bonding) is a simple way to assemble the anode, cathode, and proton exchange membrane together, and ensures interfacial contact between the electrode and the membrane. The bonding conditions of the hot-pressing process, such as the bonding temperature, pressure, and time, play an important role in obtaining high-performance MEAs. For example, the glass transition temperature of Nafion is about 125 °C, which restricts the hot-pressing temperature. However, at temperatures much lower than the glass transition temperature of the membrane, the Nafion resin in both the catalyst layer and the membrane will not melt, so ionomeric contact with the catalyst and between the catalyst layer and the membrane will become a problem, resulting in poor catalyst utilization and higher ionic resistance. On the other hand, if a much higher bonding temperature is used, the membrane may lose its water retention properties, the ionomer acidic group may degrade, and the catalyst layer may be partially delaminated from the membrane. Therefore, an optimal temperature value exists for hot pressing. As for the hot-pressing pressure, the choice is strongly dependent on the electrode's mechanical strength, porosity, and thickness. The porosity of the electrode decreases with increasing bonding pressure, which limits mass transport. Moreover, the carbon fibers are prone to being crushed under a very high pressure. However, high pressure can result in a thinner catalyst layer, favoring mass transport. Therefore, the choice of bonding pressure should also be optimized. Hot-pressing time is another important parameter affecting the contact between the membrane and the electrode, as well as the porosity of the electrode. It seems that as the hot-pressing time increases, the ionic conductivity and three-phase reaction area in the catalyst layer first increase and then decrease, resulting in a reduction in the porosity and mass transport rates [80]. Normally, hot pressing is conducted in a temperature range of 120–160 °C, and a time period of 30–300 seconds.

It is worth noting that the hot-pressing process is not necessary for some kinds of MEAs. For example, when a CCM is used in a fuel cell, the CCM can be put directly between two pieces of GDL and assembled into the fuel cell hardware.

19.5 Summary and Outlook

This chapter has addressed the fabrication technologies for catalyst inks, catalyst layers, and MEAs. Due to the electrochemical reactions taking place in the three-phase areas of fuel cell catalyst layers, the proton conductor, electron conductor, and reactants must meet together at all active catalyst sites. Passages for proton,

electron, gas, and water transport must co-exist at the same time in a catalyst layer. The preparation procedures for catalyst inks, catalyst layers, as well as MEAs have a strong effect upon the formation of such passages. There is no doubt that high fuel cell performance is primarily determined by how the catalyst ink, catalyst layer, and MEA are prepared.

During the development of PEMFCs, many kinds of catalyst layers have been designed and accordingly, many techniques have also been developed to fabricate these catalyst layers. It is still difficult to make fair comparisons among the techniques developed. Besides the fabrication method, electrode performance also strongly depends on its components and the materials used in the catalyst ink, catalyst layer, and MEA. Therefore, the greatest challenge in achieving efficient and cost-effective electrodes for fuel cell commercialization remains to achieve a breakthrough in materials exploration, such as catalyst and membrane materials.

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