



Review

# Fabrication methods for low-Pt-loading electrocatalysts in proton exchange membrane fuel cell systems

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## Abstract

While the use of a high level of platinum (Pt) loading in proton exchange membrane fuel cells (PEMFCs) can amplify the trade off toward higher performance and longer lifespan for these PEMFCs, the development of PEMFC electrocatalysts with low-Pt-loadings and high-Pt-utilization is critical. Such development strongly depends on the electrode fabrication method and the loaded substrate. This study presents some of the latest research into promising methods of reducing the Pt loading while increasing the Pt utilization of the electrocatalysts used in PEMFCs.

The application of the modified thin film method, despite its relatively higher Pt utilization, to micro-PEMFC applications has proven ineffective due to relatively higher Pt loadings.

Although electrocatalysts fabricated by the electrodeposition method achieved the highest Pt utilization, the application of this method to large-scale manufacturing is doubtful due to concerns regarding its scalability.

The advantage of the sputter method is its ability to deposit Pt directly onto various components of the membrane electrolyte assembly (MEA) with ultra-low-Pt-loadings. However, the low utilization and poor substrate adherence of the Pt remain challenges. Nevertheless, if these technical problems are overcome, this method appears to be the most promising technology for micro-systems and automotive application fields.

Other methods, such as dual IBAD method, electro-spray technique and Pt sols methods, exhibited relatively lower Pt loadings and higher Pt utilization. However, these methods require further research to evaluate their capabilities and improve their reproducibility.

Instead of the traditional carbon supports for electrocatalysts, nano-carbon supports such as nanotubes, powders, fibers and aerogels could be effectively used to reduce the Pt loadings.

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**Keywords:** Proton exchange membrane fuel cell; Low platinum loadings; Platinum electrocatalysts; Thin film method; Sputter deposition; Electrodeposition

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## 1. Introduction

Among the various types of fuel cells, proton exchange membrane fuel cells (PEMFCs) possess a series of highly advantageous features such as a low-operating temperature, sustained operation at high-current density, low weight, compactness, potential for low cost and volume, long stack life, fast start-ups and suitability for discontinuous operation [1–6]. These features have elevated PEMFCs as the most promising and attractive candidate for a wide variety of power applications ranging from portable and stationary power supplies to transportation. Therefore, fuel cell and automotive companies over the past few years have announced several new technologies or prototype vehicles adopting PEMFCs [7–12].

Recently, PEMFCs have begun to move from the demonstration phase to commercialization due to the impressive research effort in recent years. Nevertheless, several outstanding cost reduction problems and technological challenges remain to be solved [4].

Among the technological challenges in terms of PEMFC electrodes, the creating of an anode electrocatalyst tolerant to CO at levels of 50 ppm is deemed to be the most significant barrier, followed by a cathode electrocatalyst able to reduce the overpotential encountered under open circuit conditions and significantly enhance the exchange current density. The electrode fabrication cost can be reduced through several approaches such as reducing the platinum (Pt) loadings on both electrocatalysts and by achieving a more effective membrane electrolyte assembly (MEA).

The limited supply and high cost of the Pt used in PEMFC electrocatalysts necessitate a reduction in the Pt level [13,14]. In addition, the U.S. Department of Energy has set long-term goals for PEMFC performance in a 50 kW stack that included operation with cathode loadings of  $0.05 \text{ mg cm}^{-2}$  or less [15].

However, recent research has suggested that the lifespan or stability of PEMFCs is the most important factor, irrespective of the Pt loading per area. In other words, reducing the Pt loading in the electrocatalyst is not essential if the high-Pt-loading acts to increase the fuel cell lifespan, stability and effectiveness.

Nonetheless, the development of electrocatalysts with low-Pt-loadings remains important. The reduction of Pt loadings in electrocatalysts can be achieved through an enhancement of the Pt utilization by increasing the active Pt sites, thinning the active layer thickness ( $\leq 25 \mu\text{m}$ ) and introducing smaller, carbon-supported, nanometer-sized, Pt particles ( $< 10 \text{ nm}$ ) [16–18]. In addition, the electrode represents 40%, including 1.7% of Pt, of the total cost of PEMFCs [19]. Therefore such steps can substantially lower the MEA cost and reduce the weight and volume of PEMFCs [20]. The size of PEMFC is more impor-

tant when PEMFCs are applied to micro-system technology. Therefore, much of the research on the development of MEA has been devoted to improving the utilization efficiency of Pt electrocatalyst and reducing the Pt loadings [21–24].

The Pt loading of the cathode electrocatalyst is traditionally the same or more than that of the anode electrocatalyst due to different electrochemical kinetics at both electrode interfaces. In other words,  $\text{O}_2$  kinetics (at high potentials) and  $\text{O}_2$  diffusion (at low potentials) at the cathode are the primary limitation of the fuel cell performance. Therefore, increased Pt loading at the cathode is needed to increase the rate of  $\text{O}_2$  reduction (by increasing the available sites) and reduce the  $\text{O}_2$  diffusion resistances [12,15]. Therefore, research on reducing the Pt loading has focused more on the cathode electrocatalyst than the anode electrocatalyst. However, there is a limitation in increasing Pt utilization based on MEA when only considering the Pt loading on the cathode electrocatalysts.

Therefore, various Pt loaded supports (or substrates) for PEMFC components have recently been developed such as gas diffusion layer (GDL) of both electrodes, GDL-bonded noncatalyzed carbon layer (NCL), membrane (or Nafion), Nafion-bonded NCL, noncatalyzed carbon ink (NCI) and nano-carbon supports.

However, these advanced efforts have not yet been clearly investigated [25] and further research is thus required on PEMFC electrodes [13].

In this review, we introduce and discuss some of the latest research, limited to that published since 2000, into promising and/or potential methods of reducing the Pt loadings while increasing the Pt utilization in PEMFCs. The present review discusses the methods of fabricating lower Pt loadings at both electrodes using NCI, NCL, GDL, and membrane, as well as many kinds of combined substrates and other supports such as nano-carbons. This review also investigates the most effective location of Pt loading and the degree of Pt utilization and cell performance under those conditions. Therefore, this review provides useful information on the development of methods of lowering the Pt loadings in PEMFCs.

## 2. Pt electrocatalysts in PEMFC

### 2.1. Level of Pt loadings and Pt utilization

The first generation of PEMFCs introduced in the early 1990s used PTFE-bound, Pt-Black electrocatalysts [13,26] and exhibited excellent long-term performance at a high cost. These electrocatalyst layers generally featured expensive Pt loadings of  $4\text{--}10 \text{ mg cm}^{-2}$  of MEA which was prohibitive for commercialization [26,27]. At that time, it was considered that the Pt

loadings should be lowered to  $0.4 \text{ mg cm}^{-2}$  based on the cathode to support PEMFC commercialization [23,28]. Therefore, a considerable amount of research has been directed at reducing the Pt loading below this value.

In 1997, the Pt loading was decreased to  $<1 \text{ mg cm}^{-2}$  of MEA [29], primarily by substituting Pt-Black catalysts with higher surface area, carbon supported, Pt catalysts, and by using a perfluorosulfonic-ionomer binder in the thin-film catalyzed layers [21]. Due to these innovations in materials and processing technology, state-of-the-art fuel cells at that time yielded cell voltages which greatly surpassed those of the older PEMFCs. Two papers [30,31] presented reports on UTC Fuel Cells, which achieved  $0.68 \text{ V}$  at a current density of  $1.0 \text{ A cm}^{-2}$  at ambient pressure under conditions of  $65^\circ\text{C}$  cell temperature and fully humidified  $\text{H}_2/\text{air}$  at stoichiometric flows of 1.25/2.0. In this case, rather low-Pt-cathode loadings of  $0.4 \text{ mg cm}^{-2}$  were used and the Pt loadings on the anode were probably similar or lower [32].

While this represented a major development, and this Pt loading may be sufficient for PEMFC applications such as stationary and uninterrupted-power supply, it is still too high for other applications such as those in the mobile and automotive field, which require Pt loadings of less than  $0.2\text{--}0.4 \text{ mg cm}^{-2}$  of MEA or  $0.4 \text{ g kW}^{-1}$  [33]. Gasteiger et al. [34] have pointed out that with regard to the future requirements for PEMFC electrocatalysts for automotive application, the current state-of-the-art level (with  $\text{H}_2/\text{air}$  at  $80^\circ\text{C}$ ) of approximately  $0.7 \text{ W cm}^{-2}$  at  $0.68 \text{ V}$  (for 58% energy conversion), corresponding to  $0.85\text{--}1.1 \text{ g kW}^{-1}$ , needs to be improved to  $0.2 \text{ g kW}^{-1}$  at  $\geq 0.65 \text{ V}$  [35].

Meanwhile, the recent development of mobile applications is pushing for even further reductions in Pt loadings. As a result, the Pt loading has been reduced to  $<0.1 \text{ mg cm}^{-2}$  based on MEA [32,36,37]. Furthermore, Pt loadings as low as  $0.04 \text{ mg cm}^{-2}$  based on the cathode electrocatalysts have very recently been reported using novel methods featuring various advanced Pt loading methods and development of catalyst support materials [35,38]. As a consequence of these focused efforts, the catalyst cost may no longer be the major barrier to the commercialization of PEM fuel cells. However, most of these advanced methods have not yet achieved a commercially viable stage and various technical problems remain, such as catalytic activity, the MEA structure and long-term testing. In addition, the high cost of preparing low-Pt-loading electrocatalysts and scalability for mass-scale manufacturing also remain questionable.

## 2.2. General methods of fabricating low-Pt-loading and high-Pt-utilization electrocatalysts

Several ways of fabricating electrocatalysts have been shown to produce low-Pt-loadings and effective electrodes [13]. One such approach is the thin-film method [28] which fabricates a thin catalyzed layer on the membrane. It is evident throughout the report that the most common electrode design currently employed is the thin-film method. The MEAs prepared by the thin-film method have demonstrated high performance with low-Pt-loadings [21,26,39]. The thin-film, catalyzed layer increased

the active area from 22 to 45% [40] more than the older type. There are typically two methods of preparing a thin-film, catalyzed layer on the membrane. One is to use a “decals transfer” process, in which the catalyzed layer is cast onto a PTFE blank and then decalated onto the membrane [21,41]. The other method involves directly coating the catalyzed layer onto the membrane [39,41]. However, the second method has been shown to provide higher performance than the first method, since it provides a better ionic connection between the membrane and the ionomer in the catalyzed layer [26,42].

Thin film methods, however, suffering some of the following limitations of Pt utilization: problems with controlling the Pt particle size with Pt loading on carbon in excess of 40%, uniformity of deposition in large scale production and high cost due to several complex processes and/or steps involved [35]. To overcome these limitations, some modified thin film methods such as varying the choices of solvents and heat treatment have been reported [35,43].

The currently emerging methods include electrodeposition and sputter deposition. Sputtering is commonly employed to form catalyzed layers and is known to provide denser layers than the alternative evaporation methods do [44]. This method has been adapted for use in the window glass industry, and is cost competitive with other coating technologies. The sputtering of catalyzed layers consists of a vacuum evaporation process that removes portions of a coating material (the target) and deposits a thin and resilient film of the target material onto an adjacent substrate.

The other emerging method is the electrodeposition method. The patent [45] which first detailed this method involved fabricating electrodes featuring low-Pt-loadings, in which the Pt was electrodeposited onto a noncatalyzed carbon electrode in a commercial plating bath. This method [46–49] was able to produce electrodes featuring Pt loadings as low as  $0.05 \text{ mg cm}^{-2}$ .

Together with the aforementioned methods, new approaches such as the dual ion-beam assisted deposition [35], electroless deposition [50], electro-spray method [51], and direct Pt sols deposition [52] have been recently reported to be as effective as the traditional methods. In addition, nano-carbon supports such as nanotubes, powders, fibers and aerogels have also been investigated for use as catalyst support to reduce the Pt loadings.

In the following section, we review recent (since 2000) works in which the Pt loadings in electrocatalysts were effectively reduced. Table 1 summarizes these research efforts.

The table also lists the Pt utilizations calculated from the cell performances. While the conditions of the various cell performance tests are slightly different, the Pt utilizations were calculated at their best condition for their best performances.

## 3. Recent works on reducing Pt loadings and increasing Pt utilization in electrocatalysts

### 3.1. Modified thin-film methods

Most of the modified thin film methods to reduce the Pt loadings in PEMFC are related to the use of catalyzed carbon ink. In 2005, Xiong and Manthiram [43] published a paper which

Table 1  
Various methods reported since 2000 for reducing the Pt loadings and increasing the Pt utilization of electrocatalysts in PEMFCs

| Preparation methods               | Pt loaded supports or substrates (applied electrode) | Pt loading ( $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ )                       | Pt utilization ( $\text{g}_{\text{Pt}} \text{kW}^{-1}$ )  | Comments   | Reference | Referred earlier papers |
|-----------------------------------|--|---|---|--|-----------|-------------------------|
| Modified thin film                | NCI (both)   | 0.1 <sup>a</sup>  | 0.14 <sup>b,c</sup>   | Pt loading can be reduced to as low as $0.05 \text{ mg}_{\text{Pt}} \text{cm}^{-2}$ at both electrodes   | [43]      | [37]                    |
| Electrodeposition                 | NCL (cathode)  | 0.32 based on cathode<br>0.72 <sup>a</sup> (anode = 0.4)                    | 0.33 <sup>d</sup> based on cathode<br>0.75 <sup>d,c</sup>   | Possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode resulting in a $5 \mu\text{m}$ thick catalyzed layer                         | [55]      | [47,53]                 |
|                                   | Nafion-bonded NCL (cathode)                          | 0.50 based on cathode   | –   | Better performance than those of a conventional electrode with loadings of $0.1 \text{ mg}_{\text{Pt}} \text{cm}^{-2}$   | [56]      | –                       |
| Sputter deposition                | Membrane; Nafion 117 (both)                          | 0.04 <sup>a</sup>   | 1.21 <sup>e,c</sup> , 8 <sup>c</sup> (commercial)   | Performance is extremely sensitive to sputtered platinum thickness and membrane texture  | [32]      | –                       |
|                                   | GDL, membrane, MEA; NCI + membrane (both)            | 0.027 at one layer; 0.162 (six layers at MEA)                               | 0.26 <sup>f</sup> based on one layer; 1.59 <sup>f,c</sup>   | Of the three substrates, sputter-depositing Pt on the GDL showed the best performance  | [15]      | –                       |
|                                   | GDL (both)   | 0.054 (SGL), 0.107 (ETEK) (not clear whether based on one electrode or MEA) | 0.28 <sup>g</sup> (SGL), 0.53 <sup>g</sup> (ETEK) based on one electrode; 0.56 <sup>g,c</sup> (SGL); 1.06 <sup>g,c</sup> (ETEK) | Catalyzed layers sputter-deposited onto GDL are a very important factor to reduce the Pt loadings  | [59]      | –                       |
|                                   | MEA; NCI + membrane (anode)                          | 0.1 (three layers at anode); 0.4 <sup>a</sup> (cathode = 0.3)               | 0.51 <sup>h</sup> based on anode; 2.57 <sup>f,c</sup>   | Multi-layers of Pt sputter-deposited on the gas diffusion layer provide better performance than sputtering one Pt layer in the same loading                      | [20]      | –                       |
| Dual ion-beam assisted deposition | GDL (both)   | 0.04 at one electrode<br>0.08 <sup>a</sup>                                  | 0.297 <sup>i,c</sup>  | IBAD gas diffusion electrodes have the potential to create highly customized products, therefore also revolutionizing the micro-fuel cells market                | [35]      | –                       |
| Electroless deposition            | Carbon-supported Ru nanoparticles (anode)            | 0.017 (Pt), 0.18 (Ru) based on anode; Cathode (not clear)                   | 0.70 <sup>j</sup> $\text{g}_{\text{PtRu}} \text{kW}^{-1}$ based on anode  | Only a small degradation in performance was recorded after 1000 h of operation   | [50]      | [65]                    |
| Nano-carbons as catalysts         |  |   |   |  |           |                         |
| Electrodeposition                 | Amorphous supermicroporous carbons (cathode)         | 0.0175 based on cathode; 0.0575 <sup>a</sup> (anode = 0.4)                  | 0.1 <sup>k,c</sup>  | Further research on the improvement of Pt dispersion and on ASC supports prepared from different precursors are needed   | [38]      | –                       |
| Supercritical deposition          | Carbon aerogel (cathode)                             | 0.1 based on cathode; anode; PtRu (not clear)                               | 0.125 <sup>l</sup> based on cathode   | Better penetration of Nafion particles into the pores of the aerogel carbon support and better coverage of the membrane surface with a lower Pt content catalyst | [75]      | –                       |

<sup>a</sup> Remark: Pt loadings based on MEA.

<sup>b</sup> Performance condition:  $\text{H}_2/\text{O}_2$ ,  $80^\circ\text{C}$  at 2.6/2.7 atm of anode and cathode pressure.

<sup>c</sup> Remark: Pt utilization based on MEA.

<sup>d</sup> Performance condition:  $\text{H}_2/\text{O}_2$  at ambient pressure.

<sup>e</sup> Performance condition: Dry (non-humidified)  $\text{H}_2/\text{O}_2$ , room temperature at 1 atm.

<sup>f</sup> Performance condition:  $\text{H}_2/\text{air}$ ,  $70^\circ\text{C}$  at 1 atm.

<sup>g</sup> Performance condition:  $\text{H}_2/\text{O}_2$ , at ambient temperature and pressure.

<sup>h</sup> Performance condition:  $70^\circ\text{C}$  at backing pressure of 100 kPa.

<sup>i</sup> Performance condition:  $\text{H}_2/\text{air}$ ,  $80^\circ\text{C}$  at 50/60 psig of anode and cathode back pressure.

<sup>j</sup> Performance condition:  $\text{H}_2$  with 50 ppm of CO/4% air.

<sup>k</sup> Performance condition:  $\text{H}_2/\text{O}_2$ ,  $80^\circ\text{C}$  at 0.1 MPa.

<sup>l</sup> Performance condition:  $\text{H}_2/\text{air}$ ,  $60^\circ\text{C}$  at ambient pressure.

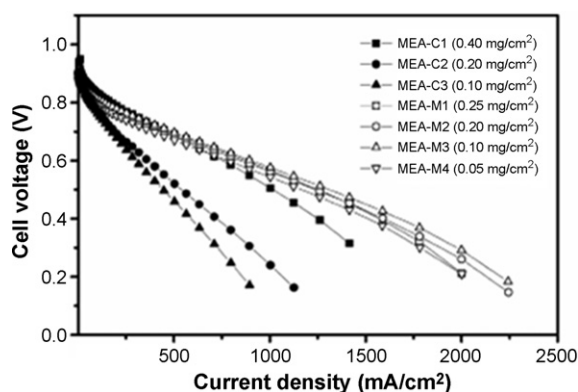


Fig. 1. Comparison of the electrochemical performances of MEAs with various Pt loadings. The weight/area values in the legend refer to the Pt loading. MEA-C1, MEA-C2, and MEA-C3 were prepared by the conventional method, and MEA-M1, MEA-M2, MEA-M3, and MEA-M4 by the modified thin film method. The data were collected with cell and humidifier temperatures of 80 °C and hydrogen and oxygen pressures of 2.6 and 2.7 atm, respectively [43].

described a modified thin-film method of fabricating MEAs with ultra-low-Pt loadings. The method involves mixing the catalyzed carbon with Nafion solution and water, i.e., the catalyzed carbon ink, without adding any additional organic solvent. According to the paper, this special catalyzed ink was coated on both sides of the Nafion and this MEA was heat-treated at lower temperatures (<100 °C). The performances of the MEAs fabricated by this method were evaluated as achieving higher Pt utilization efficiency and power density than the MEAs prepared by the traditional thin film method. The best performance was achieved at a Pt loading of 0.1 mg cm<sup>-2</sup> with a maximum power density of 714 mW cm<sup>-2</sup>, as shown in Fig. 1.

According to Xiong and Manthiram's paper [43], the improved performance of their MEAs was due to the characteristics of the preparation method. These include different hot-pressing temperature and pressure. Because the heating temperature for the elimination of the other additives is a relatively low 80 °C in this method, no obvious distortion or deformation of the painted area was observed in their study. In addition, they claimed that the higher electrochemical surface area of the MEAs prepared by this method might be due to the more intimate membrane/electrode interface achieved by directly depositing the catalyzed layer onto the membrane. A scanning electron microscopic analysis revealed that the thin catalyzed layers were more uniform, with better interfacial continuity bet the membrane and the electrodes, than those of the MEAs prepared by the traditional thin film method.

### 3.2. Electrodeposition method

Although basically similar to the thin film approach, the electrodeposition method might be more efficient in terms of Pt utilization, because the Pt is theoretically deposited at the most efficient contact zones for the ionic and electronic pathways of the substrate. Therefore, it is important to choose the Pt-deposited substrate such as the membrane and NCL.

In 1992, Taylor et al. [47], one of the first to report this approach, used pulse electrodeposition with Pt salt solutions

which relied on their diffusion through thin Nafion on a carbon support to enable electrodeposition in regions of ionic and electronic contact on the electrode surface [35]. Subsequent improvements to this approach have been reported by Antoine and Durand [53]. They impregnated carbon with H<sub>2</sub>PtCl<sub>6</sub> and applied an electrochemical, pulsed current to deposit Pt in the Nafion active layer. According to the paper, this process guarantees good ionic and electronic percolations (i.e., small ohmic drops), high-Pt-mass fractions (i.e., smaller active layer thickness and hence smaller diffusion limitations), and a narrow nanoparticle size distribution (2–4 nm) [35]. However, this process is strongly limited by diffusion of the Pt complex ion across the Nafion layer. In addition, the Cl<sup>-</sup> ions which are produced from the electrodeposition of Pt from H<sub>2</sub>PtCl<sub>6</sub> remain in the active layer and thereby poison the Pt and reduce its catalytic activity [54]. Therefore, based on the studies described above, in 2004, Kim et al. [55] described an advanced method in which Pt was deposited directly on the surface of the carbon blank electrode using a Pt plating bath containing 10 g L<sup>-1</sup> of H<sub>2</sub>PtCl<sub>6</sub> and 60 g L<sup>-1</sup> of HCl at room temperature. The blank carbon electrode [25] was loaded on the sample holder coupled with a copper plate which acted as a current collector. Pt gauze was used as the anode. A pulse generator was used to control both the pulse wave and the deposition current density. The current densities, duty cycle and charge density were varied in order to optimize the deposition rate. After electrodeposition, the electrodes were heat treated in air and H<sub>2</sub>. Then, the electrocatalyzed electrode was impregnated with 5 wt.% of Nafion solution. This Nafion-impregnated electrode and Nafion 112 were bonded together to form an MEA by hot pressing at 130 °C for 3 min at a pressure of 140 atm. According to their paper, when the cells were operated under ambient pressure, the MEA-equipped cell exhibited a current density of 1.6 A cm<sup>-2</sup> at 0.6 V with a Pt loading of 0.32 mg cm<sup>-2</sup> for the cathode. Furthermore, it was possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode, thereby achieving a 5-μm thick catalyzed layer with most of the Pt being in close contact with the membrane. They therefore proclaimed the results to be supportive of pulse electrodeposition as an attractive technique to replace the conventional, powder-type, MEA preparation methods and help achieve the industry goals of reducing the catalyst cost and increasing the PEMFC efficiency [55].

In a similar research direction, in 2005, Wei et al. [56] investigated the performance of electrodeposited Pt onto a Nafion-bonded carbon electrode for cathode reaction. Based on the results from the cyclic voltammetry showing loadings estimated at 0.50 mg cm<sup>-2</sup>, they claimed that the electrode performance was much better than that of a conventional electrode with loadings of 0.1 mg cm<sup>-2</sup>.

### 3.3. Sputter deposition methods

Sputter deposition is widely used for integrated circuit manufacturing and has been investigated as a preparation method for PEMFC electrocatalysts for more than a decade due to the following advantages:

- It allows the preparation of precise Pt content and thickness, as well as microstructure morphology [15] and much smaller Pt particle size which increases the Pt surface area, activity, and utilization.
- The method facilitates the fabrication of a nano-scale Pt layer with uniform distribution [57].
- The preparation process is simple and easy to scale-up.
- The process allows Pt deposition onto various PEMFC substrates such as GDL, membrane and NCL (or Nafion-bonded NCL).

Therefore, the sputter deposition technique has recently been recognized to have a great potential for reducing the Pt loadings of PEMFC electrocatalysts [20]. In 1997, Hirano et al. [58] firstly reported promising results with a thin layer of sputter-deposited Pt on wet-proofed, noncatalyzed GDL (equivalent to  $0.01 \text{ mg cm}^{-2}$ ) with similar results to those of a commercially available, conventional Pt/C ( $0.4 \text{ mg cm}^{-2}$ ) electrode [35]. Subsequently, the MEA performance of this method has been extensively evaluated by investigations on the choice of Pt-deposited components, MEA structure and sputter deposition condition.

In 2002, the effect of Pt loading directly onto Nafion was investigated by O'Hayre et al. [32]. They evaluated the ability of catalysts to reduce the Pt loading prepared by the direct sputtering of Pt onto the membrane. The MEAs used in their studies consisted solely of ultra-thin, sputtered Pt films deposited directly onto Nafion 117 membranes. No carbon inks, binding materials, Nafion solutions, or other agents were used in their construction. For the MEAs prepared in this way, cell polarization, electrochemical impedance spectroscopy, and cyclic voltammetry measurements were carried out to elucidate the connection between the sputtered Pt microstructure and the ultimate fuel cell performance.

According to these studies, the performance of the sputtered Pt fuel cells depends strongly on the thickness of the sputtered catalyzed layer. While Pt can be sputtered onto Nafion membranes to produce films up to several microns thick, it was found that films only 5–10 nm thick produced the best fuel cell performance. These ultra-thin films not only optimize the performance, but also result in ultra-low-Pt-loading in the range of  $0.01\text{--}0.02 \text{ mg cm}^{-2}$ . In addition, the performance of a sputter-deposited membrane with a Pt loading of  $0.04 \text{ mg cm}^{-2}$  based on MEA is comparable to that of a commercial MEA with a Pt loading of  $0.4 \text{ mg cm}^{-2}$ . At a maximum power output of 60% of the commercial MEA, it uses only 10% of the amount of Pt, as shown in Fig. 2.

Besides direct Pt sputtering onto the membrane, the following two methods have been reported for direct Pt sputtering onto the GDL.

In 2002, Huag et al. [15] reported their examination of the direct sputter deposition of Pt onto GDL, membrane, and NCL, for which GDL showed the best substrate performance. This result was ascribed to GDL's rough surface, which allows the generation of a greater Pt active area, and high porosity, which allows gas diffusion to and from the electrodes even after Pt deposition. They hypothesized that the deposition of a single Pt

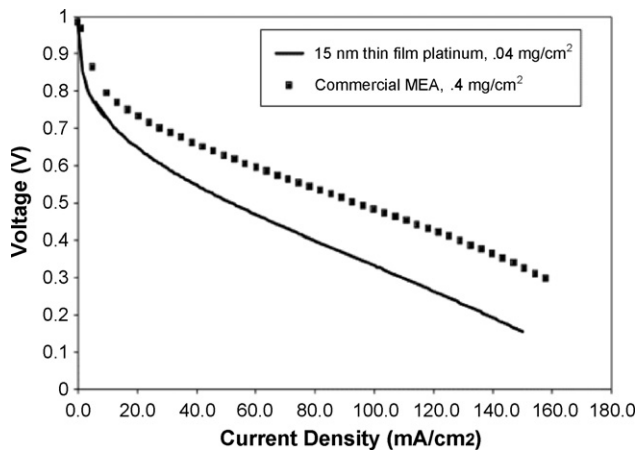


Fig. 2.  $I$ - $V$  curves comparing the performance of a commercial MEA, with a platinum loading of  $0.4 \text{ mg cm}^{-2}$ , to that of a thin film-sputtered platinum MEA with a platinum loading of  $0.04 \text{ mg cm}^{-2}$ . Cell measurements were taken at room temperature using dry (non-humidified)  $\text{H}_2/\text{O}_2$  at 1 atm [32].

layer creates alternating regions of active and inactive Pt. They claimed that Pt is only active as a catalyst when it is in contact with the electrolyte and a conductive support, whereas Pt not in contact with Nafion is inactive because of the impossibility of proton transport. The inherent roughness of the GDL increases this area of active Pt compared to the relative smoothness of the MEA and bare membrane.

They claimed, however, that the sputter deposition of multiple layers of Pt on the GDL showed no improvement in performance over an equivalent amount of Pt sputtered as a single layer. They postulated that this might be because the added Pt serves only to increase the layer of inactive Pt. Based on their experiments, they therefore concluded that the optimal performance of Pt sputter deposition was shown from the Pt-sputtered MEA containing a six-layered Pt + both dilute NCL with a current density of  $0.17 \text{ A cm}^{-2}$  at  $0.6 \text{ V}$ , as shown in Fig. 3.

In 2005, Gruber et al. [59] investigated the effect of Pt loadings onto GDL using sputter deposition. According to the paper,

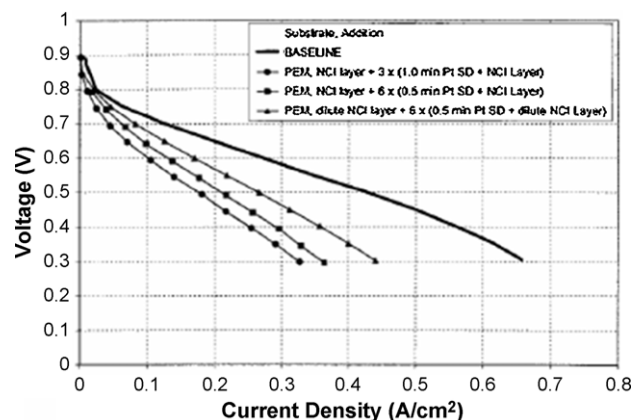


Fig. 3. Performance comparison of MEAs comprised of three and six layers (anode and cathode) using pure NCI.  $P = 1 \text{ atm}$ ,  $T = 70^\circ \text{C}$ . The Pt loadings and thicknesses of 1.0 min Pt SD layer:  $0.0407 \text{ mg cm}^{-2}$  and 5 nm; the Pt loadings and thicknesses of 0.5 min Pt SD layer:  $0.027 \text{ mg cm}^{-2}$  and 2.5 nm. The thicknesses of pure NCI:  $12 \mu\text{m}$ ; the thicknesses of dilute NCI:  $\sim 4 \mu\text{m}$  [15].

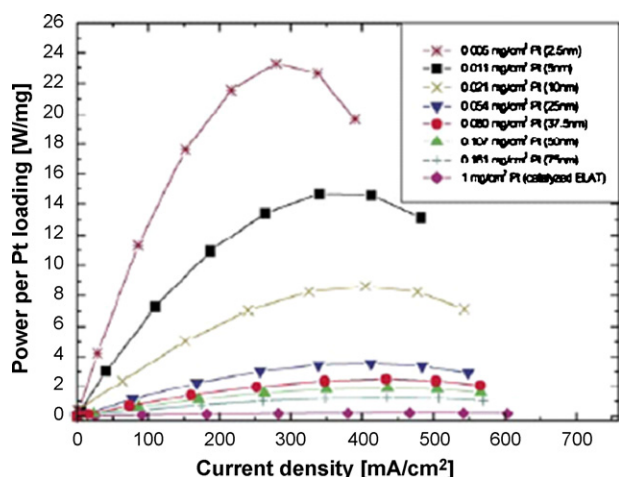


Fig. 4. Power per mg of Pt content vs. current density for different Pt loadings on E-TEK (21 °C, ambient pressure, and H<sub>2</sub>/O<sub>2</sub> operation) [59].

thin Pt layers were deposited on two types of GDLs (SIGRACET GDL-HM, SGL Carbon Group) and noncatalyzed ELAT (E-TEK Div., De Nora) from a Pt diode target using an RF power of 50 W and a pressure of 2 Pa at room temperature. Pt loaded GDLs and Nafion 115 were hot-bonded to form an MEA at a temperature of 140 °C. After evaluating the performances with two kinds of MEAs while feeding H<sub>2</sub>/O<sub>2</sub> at ambient temperature and pressure, the maximum power densities achieved with a 2.5-nm thick Pt layer (0.005 mg cm<sup>-2</sup>) were 124 mW cm<sup>-2</sup> for E-TEK and 132 mW cm<sup>-2</sup> for SGL, as shown in Fig. 4.

For the 5-nm thick Pt layer (0.011 mg cm<sup>-2</sup>), a maximum power density of 156 mW cm<sup>-2</sup> was observed for E-TEK, compared to 149 mW cm<sup>-2</sup> for SGL. For catalyzed layer thicknesses of 10 and 25 nm, the power densities for both GDL substrates were almost equal at about 184 and 191 mW cm<sup>-2</sup>, respectively. The best performances for the SGL and E-TEK samples were obtained at Pt loadings of 0.054 mg cm<sup>-2</sup> (191 mW cm<sup>-2</sup>, 285 mA cm<sup>-2</sup> at 0.6 V) and 0.107 mg cm<sup>-2</sup> (203 mW cm<sup>-2</sup>, 301 mA cm<sup>-2</sup> at 0.6 V), respectively. Therefore, the results of this paper confirmed that the sputter deposition of catalyzed layers onto porous electrodes was a very important factor to reduce the Pt loadings [59].

In 2006, Wan et al. [20] investigated the effect of Pt deposition on an anode electrocatalyst layer (Nafion + NCI layer) obtained by magnetron sputter deposition method. Similar to the method of Huag et al. [15], three layers of Pt were sputter-deposited on a Nafion + NCI layer, as shown in Fig. 5, to provide better performance, with an ultra-low-loading of about 0.10 mg cm<sup>-2</sup>, than sputtering one Pt layer in the same loading.

In this paper, they claimed that Pt utilization can be improved through the multi-nano, Pt electrocatalyst layer (or multi-dimensional) structure in MEA prepared by sputter deposition techniques.

Besides these works, many studies [16,60] have shown that low-Pt-loadings, e.g., below 0.1 mg cm<sup>-2</sup>, sputtered on PEMFC and DMFC allow remarkable power densities to be obtained. Furthermore, in 2006 Chang et al. [61] reported the performance of a Pt–Ru anode electrocatalyst prepared by sputtering method.

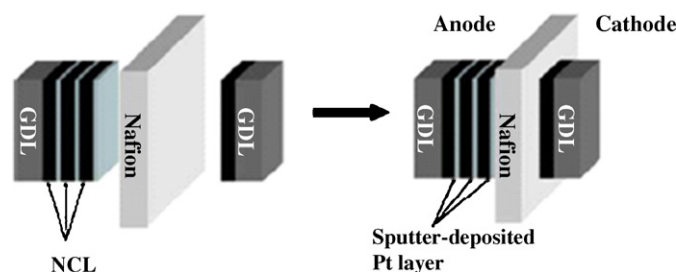


Fig. 5. Diagrams for the proposed catalyzed layer structure (anode) and MEA (NCL, Nafion-carbon ink layer) [20].

While the sputter deposition technique provides for a cheap, direct deposition method, the performance of such PEMFCs with the MEA (or GDL, NCL and membrane) prepared by sputter deposition methods still mostly falls behind that of conventional, ink-based fuel cells with higher Pt loadings. In addition, the most serious drawback of the sputter deposition method is well recognized to be its poor durability, i.e., physical weakness. In most cases, the deposition has relatively poor adherence to the substrate and there is a greater probability of dissolution and sintering [35]. Therefore, further research should be conducted to enhance the physical properties of components prepared by sputter deposition, such as multi-layered products, and to determine the optimum conditions of the sputter deposition method, such as bias voltage, RF power, sputtering-gas pressure and sputtering time, which influence the deposition rates of the microstructures on the substrates. Furthermore, studies on the optimum catalyst porosity and thickness are important because the smaller particle size of sputter-deposited Pt probably hinders water transport [58].

### 3.4. Dual ion-beam assisted deposition

In 2006, Saha et al. reported [35] an improved deposition methodology based on the ion deposition technique: a dual ion-beam assisted deposition (dual IBAD) method on the surface of a noncatalyzed GDL substrate. They claimed the dual IBAD to be an alternative technology to overcome many of the limitations of the aforementioned methods such as thin film, electrodeposition and sputter deposition. The dual IBAD process combines physical vapor deposition with ion-beam bombardment [44,62,63]. The results of a single cell test with their Pt-loaded GDL constructed by dual IBAD were 0.04 mg cm<sup>-2</sup> (for a total MEA loading of 0.08 mg cm<sup>-2</sup>) and 0.297 g kW<sup>-1</sup>. They claimed the electrode constituted a significantly different morphology, where low-density Pt deposits (largely amorphous) were formed with varying depths of penetration into the GDL, exhibiting a gradual change towards increasing crystalline character. However, the principal shortcoming of this method is its specific power density which is in the range of 0.27–0.43 W cm<sup>-2</sup> at 0.65 V. Nevertheless, they claimed that this lower area specific power density is due to the higher mass transport losses and that it could be mitigated using the more effective patterning of the electrode in the process.

### 3.5. Electroless deposition method

Using H<sub>2</sub> fuel with a CO level of over 50 ppm, the best available anode electrocatalysts are PtRu alloys, usually with a 1:1 Pt:Ru ratio. H<sub>2</sub> is oxidized on Pt, while Ru provides an O<sub>2</sub>-containing species to oxidize CO to CO<sub>2</sub>, thus reducing Pt poisoning [64]. In 2000, Brankovic et al. [65] claimed that electroless (or spontaneous) deposition of Pt on Ru could provide a simple method for well-controlled deposition of desired amounts of Pt on Ru nanoparticles that could lead to improved Pt/Ru electrocatalysts with considerably reduced Pt loadings.

Referring to this paper, in 2004, Sasaki et al. [50] investigated the long-term stability of the ultra-low-Pt-loading anode within the PtRu binary electrocatalyst. The electrocatalyst was synthesized by placing Pt atoms on the clean metallic surface of the carbon-supported Ru nanoparticles by the electroless deposition method using the following preparation procedures. A clean, treated Ru single crystal (0.3 μm) was transferred from the UHV chamber into an Ar-filled glove box and immersed in PtCl<sub>6</sub><sup>2-</sup> solution for a certain period of time. After immersing it in the solution, the crystal was thoroughly rinsed with 0.1 M H<sub>2</sub>SO<sub>4</sub> followed by ultra pure water and then protected by a water drop [65,66]. According to their paper, 1/8 of the anode electrocatalyst prepared by their method consisted of a monolayer of Pt on the surface of the carbon-supported Ru nanoparticles, and Pt was selectively deposited on the Ru nanoparticles, not on the carbon, because the metallic Ru surface acts as a reducing agent for Pt deposition. To obtain information on the electronic and structural properties of the anode electrocatalysts, measurements were made using X-ray absorption spectroscopy near the edge structure. Based on these results and other papers [65,67], they proposed a structural model for the active electrocatalyst, which included a cubo-octahedral model of the Ru particles with two-dimensional islands of Pt on its surface, as shown in Fig. 6. The Ru nanoparticles were supported on the high-surface area, Vulcan XC-72 carbon.

Fuel-cell tests offered the ultimate verification of the usefulness of the electrocatalyst made in this way, by determining its long-term stability under real operating conditions, such as H<sub>2</sub> or H<sub>2</sub> with 50 ppm of CO and 4% air. The tests were carried out using electrodes with an area of 50 cm<sup>2</sup> with an anode content of

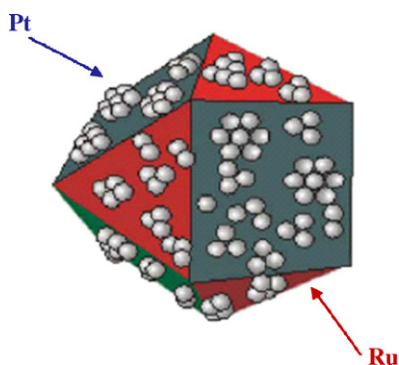


Fig. 6. A cubo-octahedral particle model for the electrocatalyst consisting of Ru particles with two-dimensional, Pt islands on its surface [50].

180 μg cm<sup>-2</sup> of Ru, and only 17 μg cm<sup>-2</sup> of Pt, a loading that was approximately 1/10 of the standard Pt loading for fuel cell electrodes. According to their paper, a cell voltage of about 0.7 V at a constant current of 0.4 A cm<sup>-2</sup> was maintained until 100 h. In their paper, however, the authors provided no clear explanation as to how such a small amount of Pt could maintain such large current densities, and how the Pt could remain on the surface of the Ru nanoparticles for a long time during operation at 80 C. However, they ascribed their results to a structure consisting of small Pt islands on the Ru surface. This structure seemed particularly suitable for the oxidation of H<sub>2</sub> with small concentrations of CO, since CO adsorption is weakened on Ru-supported Pt [50].

### 3.6. Other methods

In 2005, Benitez et al. [51] reported the electro-spray technique. The catalyzed ink was dispersed onto a carbon cloth using a Vega 2000 commercial airbrush. According to the paper, the electro-spray method consists of applying a voltage (3300–4000 V) between a capillary tube, in which the catalyzed ink is forced to flow, and the carbon cloth substrate. The high-electric field generates a mist of highly charged droplets when the solution emerges. During this process, the droplets are reduced in size by evaporation of the solvent and/or by “Coulomb explosion” (droplet subdivision resulting from the high-charge density). In order to force the catalyzed ink to pass through the capillary tube, a nitrogen-pressurized tank was used. After performance tests, they claimed that MEAs obtained by this method exhibited eight-fold increased power density than MEAs prepared by the spray technique. In addition, the power density obtained was twice that of a commercial E-TEK. However, this method is a variant of the modified thin film method, rather than a novel technique.

Khan et al. [52] reported another method in which Pt sols are directly deposited onto the membrane instead of traditional catalyzed ink. According to the paper, the Pt sols were prepared with a mixture of 0.1 M H<sub>2</sub>PtCl<sub>6(aq)</sub> and 0.1 M sodium citrate added to a methanol solution under reflux and stirring at 353 K. The reaction for Pt sols preparation was stopped by quenching to room temperature immediately, after which the solution turned black. In the method, no extra treatment is needed except the solvent evaporation. They claimed the Pt loading can be controlled to as low as 0.01 mg cm<sup>-2</sup> by varying the sol amount. In addition, the MEA fabricated by this method showed high-specific activity and comparable single cell performance with electrodes prepared from the traditional Pt/C electrocatalysts. However, this method might be applied to the electrodeposition and thin film methods.

### 3.7. Nano-carbon supports

Nano-carbon supports such as nanotubes, powders, fibers and aerogels are also being investigated for use as catalyst support for low-Pt-loadings. For example, the power density of PEMFC equipped with Pt loaded on carbon powder for the cathode GDL



was recently reported to be more than  $1200 \text{ mA cm}^{-2}$  at  $0.6 \text{ V}$  ( $85 \text{ C}$ ,  $\text{H}_2/\text{O}_2$ ,  $2/5 \text{ atm}$ ) at a Pt loading of  $0.4 \text{ mg cm}^{-2}$  [68]. This might be ascribed to the properties of nano-carbon catalyst supports being more stable and active for Pt loadings [69–71]. Therefore, various types of nano-carbon supports and low-Pt-loading methods have been investigated worldwide, some of which are presented below.

### 3.7.1. Carbon nanotubes

In 2005, Liu et al. [72] reported the studies on the Pt nanoparticles supported on carbon nanotubes prepared by a simple, microwave-assisted, polyol procedure. The polyol process, in which an ethylene glycol solution of the metal precursor salt is slowly heated to produce colloidal metal, has recently been extended to produce metal nanoparticles supported on carbon and  $\text{Al}_2\text{O}_3$  [73,74]. In the process, the polyol solution containing the metal salt is refluxed at  $393\text{--}443 \text{ K}$  to decompose ethylene glycol and thereby yield an in situ generated, reducing species for the reduction of the metal ions to their elemental states. Therefore, fine metal particles are produced and captured by a support material suspending in the solution. In these efforts, they claimed that the Pt nanoparticles in the cathode electrocatalyst were uniformly dispersed on carbon, with diameters of  $2\text{--}6 \text{ nm}$  and the low-Pt-loadings, and, furthermore, that the electrocatalysts showed high-electrocatalytic activity for  $\text{O}_2$  reduction as tested by a single PEM fuel cell [72].

### 3.7.2. Amorphous supermicroporous carbons

In 2005, Ismagilov et al. [38] investigated the use of amorphous supermicroporous carbons (ASC) as the supports for the low-Pt-loadings of the cathode. They claimed Pt loadings into ASC synthesized by electrodeposition method ranging from  $0.02$  to  $0.09 \text{ mg cm}^{-2}$ . In addition, their cathode electrocatalyst exhibited considerably better performance than commercial cathode (Pt/Vulcan XC-72R), even at a lower Pt loading, as shown in Fig. 7.

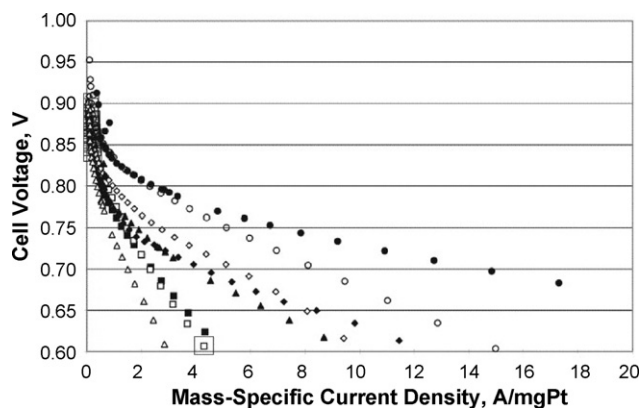


Fig. 7. Voltage vs. mass-specific current density for MEA with Pt cathodes with low-Pt-loading and a conventional anode consisting of 30 wt.% Pt/Ketjen Black of  $0.05 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ . Vulcan XC-72R: ( $\blacklozenge$ )  $0.0380 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ; ( $\diamond$ )  $0.0628 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ . Amorphous carbon ASC-1: ( $\bullet$ )  $0.0175 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ; ( $\circ$ )  $0.0592 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ . CNF: ( $\blacksquare$ )  $0.0400 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ; ( $\square$ )  $0.0639 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ . CNF: ( $\blacktriangle$ )  $0.0185 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ ; ( $\triangle$ )  $0.0914 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$  [38].

### 3.7.3. Carbon aerogel supports

In 2005, Smirnova et al. [75] published a paper on the performance of PEMFCs with carbon aerogel-supported Pt cathode catalysts. These supports are produced by the aqueous polycondensation of resorcinol with formaldehyde [76], followed by pyrolysis to form the porous carbon network structure. The metallic catalyst is introduced via organometallic precursors using supercritical carbon dioxide, followed by secondary pyrolysis to form Pt nanoparticles on the surface of the aerogel carbon support [77]. The  $20\text{-nm}$  electrocatalyst with a low-Pt-loading ( $0.1 \text{ mg cm}^{-2}$ ) showed the maximum power density of almost  $0.8 \text{ mW cm}^{-2}$  in air at ambient pressure. This may be due to the better penetration of the Nafion particles into the pores of the aerogel carbon support and better coverage of the membrane surface with a lower Pt content catalyst.

## 4. Conclusions

While a high-Pt-loading gives PEMFCs the advantages of longer lifespan with more stability and effectiveness, the development of electrocatalysts with low-Pt-loadings remains fundamentally important because such development will substantially lower the MEA cost and reduce the PEMFC weight and volume. Furthermore, higher Pt loadings do not necessarily mean higher power densities. The low-Pt-loadings and high-Pt-utilization strongly depend on the electrode fabrication technique, substrate loading, and electrode structure. Therefore, according to the various fields of PEMFC application, it is important to select the fabrication methods and related factors which hold the promise of increasing the efficiency. Table 2 summarizes the advantages and drawbacks of various fabrication methods to reduce the Pt loadings in PEMFCs.

In the modified thin film method, the relatively higher Pt loadings and higher Pt utilization may be primarily caused by the lack of any obvious distortion or deformation of the catalyzed layer and the formation of a more intimate membrane/electrode interface. However, the nature of this method limits the Pt loadings ( $<0.05 \text{ mg cm}^{-2}$ ) and ability to control the Pt particle size. Therefore, the use of this method in micro-applications is unlikely to be effective.

Electrocatalysts fabricated by the pulse electrodeposition method exhibited the highest Pt utilization because the Pt was deposited only onto the most active or effective substrate zones. However, this also represents a significant increase of Pt loadings compared to those of other methods. In addition, there are concerns regarding the method's scalability for mass scale manufacturing which suggest it may be difficult to apply this method to large-scale applications. Nevertheless, this method has great potential in terms of Pt loadings and utilization when using other catalysts supports such as ASC.

The sputter method has relatively more advantageous features and drawbacks, as listed in Table 2, which combine to give it significant potential that warrants further research effort. The most advantageous feature of the method is its capability for direct Pt deposition onto various MEA components, except for carbon electrode, such as GDL and membrane with ultra-low-Pt-loadings. However, challenges remain with the

Table 2  
Advantages and drawbacks of various methods of reducing the Pt loadings

| Preparation methods               | Advantages   | Drawbacks   |
|-----------------------------------|--|---|
| Modified thin film                | Relatively higher Pt utilization; no obvious distortion or deformation of the catalyzed layer due to low-hot-pressing temperature, 80 C, and pressure; without adding any additional organic solvent; more intimate membrane/electrode interface and interfacial continuity between them; more economical process                          | Relatively high-Pt-loadings; limits the Pt loading under 0.05 mg cm <sup>-2</sup> ; difficult to control the Pt particle size; uniformity of Pt deposition in large scale   |
| Electrodeposition                 | Relatively higher Pt utilization; deposition of Pt theoretically happens at solely active zone (ionic and electronic pathways of substrate) of membrane, and NCL diminishes inactive catalyst sites; possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode; most of Pt is in close contact with the membrane | Relatively higher Pt loadings; concerns on the scalability for mass scale manufacturing; complex processes and relatively high-Pt-loadings; Cl <sup>-</sup> ions produced in process are known to poison Pt and reduce the catalytic activity   |
| Sputter deposition                | Lowest Pt loadings; Allows the Pt deposition onto various substrates such as GDL, membrane and NCL (or Nafion-bonded NCL); denser Pt layers; possible to fabricate nano-scale; Pt layer with uniform distribution; simple and easy to scale-up; cheap direct deposition method   | Relatively lower Pt utilization; poor adherence of Pt to substrate; short durability, i.e., physical weakness; greater probability of dissolution and sintering of Pt; multi-Pt electrocatalyzed layer structure in MEA for higher performance; even smaller particle sized Pt probably hinders water transport |
| Dual ion-beam assisted deposition | Relatively lower Pt loadings and higher Pt utilization; significantly different morphology, largely amorphous for better performance; low-density Pt deposits  | Complex processes and/or steps involved; concerns on the scalability for mass scale manufacturing; low-specific power density   |
| Electroless deposition            | Effective for PtRu binary anode electrocatalyst  | Higher fabrication cost   |
| Nano-carbons as catalysts         | Relatively lower Pt loadings and higher Pt utilization   | Strongly dependent on Pt loading methods; high price of synthesis of nano-carbons   |

low-Pt-utilization, which is ascribed to the Pt deposition onto the substrate, including inactive zones, and poor adherence of Pt to the substrate. Nevertheless, if these various technical problems are overcome, this method holds the potential as the most promising technology for micro-systems and automotive application fields.

Other methods, such as dual IBAD method, electro-spray technique and Pt sols methods, exhibited relatively lower Pt loadings and higher Pt utilization. However, further research and careful evaluation are needed to confirm their reproducibility. The electroless deposition method used for the fabrication of Pt-based binary electrocatalysts, including the PtRu/C seems to be an effective approach.

Nano-carbons supports such as nanotubes, powders, fibers and aerogels could be effectively used to reduce the Pt loading of electrocatalysts in PEMFCs.

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