Ultra-low loading of platinum in proton exchange membrane-based fuel cells: a brief review

Aristatil Ganesan¹ · Mani Narayanasamy¹

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Abstract

This review report summarizes different synthesis methods of PEM-based fuel cell catalysts with a focus on ultra-low loading of Pt catalysts. It also demonstrates fuel cell performances with ultra-low loading of Pt catalysts which have been reported so far, and suggests a combination method of synthesis for an efficient fuel cell performance at a low loading of Pt catalyst. Here, maximum mass-specific power density (MSPD) values are calculated from various reported performance values and are discussed, and compared with the Department of Energy (DOE) 2020 target values.

Keywords Fuel cell · Ultra-low loading · MSPD values

Introduction

The fuel cell is recognized as a noble product of the twenty-first century, as it has high potential to replace batteries, IC engines, and power grids by the virtues of efficiency and durability. Now, a great challenge is ahead to reduce the cost of fuel cells to make them available as normal commodities. Proton exchange membrane fuel cells (PEMFCs) will be a part of the modern power technology in the future. It is noted that PEMFCs have already been in the commercial market for widespread applications including automobiles, stationary power, portable power pack, and logistics [1–3].

As leading automobile manufacturers have started sales of fuel cell electric vehicles (FCEV), fuel cells are penetrating the commercial market with exponential growth. Increased sales at decreased cost are a sale economy and to achieve this, the cost of every component of the PEMFC should be considered (Fig. 1).

Regrettably, expensive platinum group metal (PGM) catalysts block the commercial sales/volume. PGMs (plus application) cost contribute to the total cost of FC stack from 21% (1000 FC systems/year) to 45% (500,000 systems/year) [5] as expected. Since PGMs are expensive, the PGMs loading should be reduced from current (target) levels. As

PGMs play a critical role in both hydrogen oxidation reaction (anode–HOR) and oxygen reduction reaction (cathode–ORR) of the fuel cell, the challenge is ahead in the PEMFC community to address PGM cost issues for its use in both anode and cathode of the fuel cell.

Since PEMFCs will be in the automotive market, this drives long-term cost analysis and catalyst requirements. Nevertheless, the market spaces for PEMFCs are being extended to portable power, backup power, materials handling, stationary power pack, and buses. In addition to huge market availability for PEMFC automobiles, there is another market available for PEMFCs, as mentioned above. Catalyst developers are encouraged to keep in mind the above discussion, to focus and develop next-generation catalysts which have huge commercial opportunities. According to DOE 2020, the loading target of PGM is $0.0250.025 \text{ mgcm}^{-2}$ and $<0.1 \text{ mgcm}^{-2}$ for the anode and cathode, respectively. Nevertheless, a still lower loading of about 0.0625 mgcm^{-2} is required for PEMFC vehicles to stand along with IC engine vehicles [6].

Literature

Many research groups are working on Pt alloy catalysts such as PtCo; PtNi; PtCoMn; WSnMo; PtRu; PtAgRu; PtAuRu; PtRhRu; and Pt–Ru–W₂C to replace Pt/C [7–10]. By providing high surface area carbon supports, Pt content could be reduced with high Pt utilization [11, 12]. Using

✉ Aristatil Ganesan
arisamutha@gmail.com

¹ Ingsman Energy and Fuel Cell Research Organization
Private Limited, Chennai 600096, India

Fig. 1 Component cost breakdown at a production volume of 500,000 units/yr for the FC stack [4]

the plasma sputtering technique [13], the total Pt loading in both anode and cathode is reduced to $20 \mu\text{gcm}^{-2}$. By this method, uniform dispersion of Pt as clusters with size less than 2 nm is achieved with high catalyst utilization.

Most researchers have made an attempt to reduce Pt loading by providing novel catalyst supports such as multiwalled CNT and single-walled CNT [14]. Binary alloys of Pt, Pt–Cu [15], Pt–Co [16–19], Pt–Ni [17, 18], Pt–Cr [17] revealed 2–3 times higher mass-specific activity than Pt/C, which is due to alloy effects and ligand effects. A ternary alloy of PtFeNi and PtFeCo [19] showed excellent ORR activity, but in some cases presents Pt particles aggregation. A bimetallic alloy of Pd–Pt on hollow core mesoporous shell carbon (PtPd/HCMSC) demonstrated enhanced ORR activity and stability [20, 21]. Recently, a core shell of PtCo@Pt offered low loading of catalyst, but it had a disadvantage of base metal cobalt (Co) leaching (dissolution) from bulk to surface [22]. Wang et al. [21] investigated PtNi alloy as a high-performing catalyst for automotive applications with a low loading of Pt: 0.125 mgcm^{-2} which satisfied the DOE 2020 target.

Pt–Ni alloy catalyst synthesized by direct current magnetron sputtering involves Pt sputtering on synthesized PtNi/C substrate which forms multilayered Pt-skin surface, with superior ORR activity. This catalyst involves the mature technology of synthesis with improved performance compared to Pt/C. Though this catalyst presents superior performance, it involves careful preparation of Pt target material for sputtering (costly), preparation of PtNi by chemical reduction, thermal decomposition, and acid treatment with final heat treatment. Materials' preparation involves many steps and needs careful optimization for getting a reasonable

yield of catalyst. Durability studies were not conducted at the MEA level as it is specified by DOE.

Kongkanand et al. investigated [22] PtCo on high surface area carbon (HSC), which demonstrates a less degree of PtCo particle coalescence after the stability test. Also, HSC is favored for start-up performance and long-term durability. The dissolution of Pt and Co was resolved by developing a deposition model [23]. DOE has updated its cost estimation for an automotive fuel cell by 15%, i.e., \$45/kW, because of the development of catalyst, PtCo/HSC. This catalyst system would reduce the total cost of the system to 14% or \$7.5/kW [22]. These catalysts (PtNi/PtCo) cost about \$15.20/g for cathode (Pt 0.100 mgcm^{-2}) and \$10.86/g for Anode (Pt 0.025 mgcm^{-2}) [1]. Chen et al. investigated Pt₃Ni nanoframes and demonstrated high mass activity with durability, but MEA performance at high current density was challenging [23]. The shape-controlled synthesis of Pt–Pd and Ru–Rh catalyst showed high mass activity and it offers a commercially efficient scale-up method. This catalyst has issues with performance at the MEA level and stability [24]. In addition to catalyst support modification, and alloying of Pt, for Pt content reduction, a proper MEA fabrication methodology is to be identified for low Pt loading. This review provides intensive guidance for researchers working on low Pt loading catalyst for fuel cells.

Most promising methods for the preparation of electrodes

Though there are several methods such as physical vapor deposition, chemical vapor deposition, sputter deposition, galvanic replacement reaction (Pd nanocrystals with different shapes) [24] hydrothermal synthesis [25] electrodeposition (hetero-structured nanotube dual catalyst) [26] electrospinning [27] and molten salt method [28], electrodeposition [29] are available for catalyst synthesis and coating, only very few methods are practically feasible for producing nanoparticles of a catalyst and its efficacy for coating on electrodes.

Electrodeposition

The need and necessity for nanostructured energy materials with high surface area, and for its efficient application in energy conversion devices, can be achieved only with the electrochemical synthesis route. Electrodeposition technique proves to be the best method for the following reasons [30, 31].

1. Electrode potential, deposition potentials, current densities, and bath concentrations could be controlled for the synthesis of homogenous nanostructured materials.

Hence by varying deposition parameters, one can synthesize thin catalyst film, with desired stoichiometry, thickness, and microstructure.

- Particle size, desired surface morphology, catalyst loading, thickness, and microstructure can be easily achieved using various control parameters involved in electroplating.
- Electrochemical reactions proceeded at ambient temperature and pressure, as high thermodynamic efficiency during plating is maintained.
- Environmentally friendly.
- Synthesis can be started with low-cost chemicals as precursor materials.
- One-pot single-step synthesis of the final product is possible by avoiding a number of steps.
- Any metal or alloy can be easily doped into desired nanostructured materials.
- The required nanostructured energy materials can be directly grown on the electrode surface by electrochemical method, and it provides good adhesion, large surface area, and electrical conductivity. And hence, this method is found suitable for construction of energy devices with high efficiency and with low cost.
- By this method, materials with poor electrical conductivity of metal oxide used as catalyst supports can be easily incorporated into advanced energy materials and will facilitate fast electron transport mechanism. Therefore, electrical conductivity of catalyst supports can be enhanced by the electrodeposition method.
- The electrochemical synthesis route eliminates the complexity of mixing catalyst powders with carbon black and polymer binder in fabricating electrodes for fuel cells in a short time [29].

Experiment: [29]

There are two modes of electrodeposition, viz, pulse and direct current (DC) deposition. Pulse deposition results in a high concentration of metal ions at the vicinity of the electrode surface, during ON time, and no coating during OFF time, this creates homogenous mixing of electrolyte and uniform coating with different surface morphologies [32] on the working electrode. Also, it offers efficient mass transfer kinetics by varying pulse parameters, ON time, OFF time, and peak current density. In each pulse, there is a periodic switching of current between ON time and OFF time (no current) when plating occurs. A typical pulse diagram is as shown in Fig. 2 [33].

The basic pulse mathematics needs to be known for understanding the terms involved in the pulse cycle. In a pulsed current deposition, duty cycle (γ) is the total time of a cycle in percentage [34], and its reciprocal is frequency ($1/T$).

Fig. 2 Typical waveform of a pulse deposition mode of electroplating

$$\begin{aligned} \text{Duty cycle} &= \frac{T_{\text{on}}}{T_{\text{on}} + T_{\text{off}}} = T_{\text{on}} \times f \text{ or Frequency}(f) \\ &= \frac{1}{T_{\text{on}} + T_{\text{off}}} = \frac{1}{T} \end{aligned}$$

The average current density (I_A) is defined as:

$$I_A = \text{Peak current } (I_p) \times \text{Duty cycle } (\gamma)$$

In DC deposition, the formation of negative charge cloud around the cathode would hinder the movement of ions, but in the case of pulse electrodeposition (PED), the charge cloud will get discharged and permits metal ions to migrate to form a coating on working electrode. In the electrolyte bath solution, there is a scarcity of metal ions in peak current density areas when compared to low current density regions. In PED, during T_{off} , metal ions migrated into regions where there is a lack of metal ions in bath. During T_{on} , the metal ions are readily available for plating on the electrode. Peak current (I_p) will increase the density of adatoms and nucleation rate during T_{on} and form fine-grained microstructure. The distortions during T_{off} may result in re-nucleation, which is due to the removal of impurities. At low duty cycle, higher I_p is required for medium deposition rate, and the duty cycle is to be maintained as a minimal range 33–50%. During T_{on} , there is a lack of uniformity of current distribution at higher I_p , irrespective of waveform employed during plating, and T_{off} time influences additives' mass transfer in the electrolyte. For plating of alloys, usually, high-frequency pulses are preferred for homogenous coating and desired composition. By manipulating T_{on} and T_{off} , the composition of alloy can be modified by producing multilayered deposits [25].

Chemical precipitation method [35]

A thin nanocatalyst layer is formed by the reduction of reducing agent in the precursor solution. The desired particle size of the catalyst can be achieved by varying parameters, such as temperature, pH, the ratio of reducing ion to Pt,

reaction time, and stirring rate. The main disadvantage of this method is producing irregular particle size and shape, and resulting in the inhomogeneous layer. This formation is due to various growth kinetics and conditions, and thus it is least used for catalyst synthesis.

Colloidal method [36]

By this method, colloidal dispersion is formed by stabilizer and the precursor. The suitable support material is added and by which colloid deposition occurs on the support surface. In the final stage, the decomposition of colloid results in the formation of catalyst. The common colloidal particles formed by the precursors, H_2PtCl_6 and RuCl_3 , and reduced with reducing agent. The stabilizers and reducing agents present in the final product will have to be removed by thermal treatment. This method involves various steps to be followed for the catalyst synthesis.

Sol-gel synthesis method [37]

This method allows forming solid particles suspended in liquid solution (sol) and upon subsequent aging, and drying to form a semi-solid suspension in a liquid (gel). And subsequent calcination results in a mesoporous solid or powder formed on the substrate. Pore size distribution on the catalyst layer can be varied by various experimental parameters. The disadvantage associated with this technique is catalytic burning in pores, makes them inaccessible to reactants, and resulting in low catalyst utilization.

Impregnation method [38]

This method uses high surface area carbon supports for the formation of catalyst. In this method, chloride Pt salt directly mixed with reducing agents, $\text{Na}_2\text{S}_2\text{O}_3$, NaBH_4 , N_2H_4 , formic acid, and H_2 gas in an aqueous solvent. This method results in Pt agglomeration and weak support due to the high surface tension of the liquid solution [56].

Microemulsion method [39]

The water-soluble inorganic salt was used as a metal precursor in the solution. Here the particle growth rate, size, and shape are being decided by a proper proportion of metal salt and organic solvent and the resulting solution forms water-in-oil structure (microemulsion). The hydrophobic property of organic molecules protects the metal particle as an insulation layer and prevents agglomeration when the reducing agent is added. That is a surfactant-assisted synthesis of catalyst which forms suitable catalyst support with the protection layer. The main drawback of this method is the

use of expensive chemicals and not being environmentally friendly [39].

Microwave-assisted polyol method [40] [41]

Here, Pt metal salts are reduced in ethylene glycol, and the reduction reaction occurs at a temperature above 120°C . Microwave-assisted heating could produce more active ORR catalyst than the conventional heat treatment. Microwave heating produces uniform dispersion and greater morphological control over particle size ($< 3\text{ nm}$). The main advantage of this method is that it has no surfactant addition and uses an inexpensive solvent like ethylene glycol. The disadvantage associated with this method is that it is time consuming.

Chemical vapor deposition (CVD) [42]

This method uses the required precursors in the gas phase using external heat energy plasma sources in an enclosed media-assisted chamber. The thin solid film formed on the substrate by decomposition reaction of precursors. The impurities produced during reaction is removed by the flowing media gas into the chamber. This method is most widely used for the synthesis of advanced materials like CNT and graphene. This method involves a huge cost for instruments and process.

Spray technique [43]

Spray painting involves printing techniques for coating catalyst directly on the substrate, and it involves inkjet printing, casting, sonic method, etc. The advantage of printing technique is that we can coat a large area of the electrode, irrespective of surface (conductive or non-conductive) of the substrate. After coating, the coated surface is allowed for evaporation of the solvent. Though many advantages are provided by this technique, it has a large influence on practical applicability and mass production, so catalyst utilization is very low.

Atomic layer deposition (ALD) [44]

This method is under the sub class of CVD. Here gas phase molecules are used sequentially to deposit atoms on the substrate. The precursors involved react on surface one at a time, in sequential order. The substrate is exposed to different exposures at different time and forms uniform nano-coating on the substrate. This method involves four steps to complete the whole process: (1) exposure to precursor first, (2) purging of the reaction chamber, (3) exposure to second reactant precursor, and (4) a further purge of the reaction chamber. During step 1 and 2, the precursors react with the substrate at all available reactive sites. The unused precursors

and impurities are removed by purging the inert gas. During the third stage, the adsorbed precursor on the substrate starts reacting with reactant precursor to eliminate ligands of the first precursor for forming target material, while the residues formed in step 3 are eliminated in step 4 of inert gas purging which complete one cycle; likewise many cycles are repeated to achieve desired thickness of the target material.

Key features to consider when preparing the electrodes

In emerging hydrogen economy, fuel cell technology developments need to be redressed in cost effectiveness and benchmark performance as directed by DOE US and operation under long life cycles.

There are many ways to reduce the cost of fuel cells without sacrificing performance and are [45–50] listed below:

1. reduction of precious metal loading.
2. Nanostructured thin-film (NSTF) development for catalyst layer.
3. Particle size reduction for electrocatalyst.
4. Developing non-precious metal/alloy.
5. Developing novel catalyst preparation methods.
6. Using novel MEA fabrication methods to adopt for advanced catalyst and membrane materials.
7. Adopting new techniques to promote triple-phase boundaries and mitigate mass transfer limitation.
8. Attempt to develop carbonaceous and non-carbonaceous catalyst support materials to achieve peak performance at low-cost investment.

In addition to various useful applications of PEMFC, still, it has to go a long way in terms of catalyst for successful commercialization, like cost, efficiency, and cycle stability. Even now, Pt/Pt-based materials hold its strong position in functioning as an efficient catalyst for PEMFC and DMFC, as it exhibits superior catalytic activity, electrochemical stability, high exchange current density, and excellent work function [50–53].

Due to the lack of Pt resources in earth's crust, they are a costlier and limited supply for industries. In regard to PEMFC automotive applications, the present resources of Pt are not sufficient to fulfill the requirements, and the obtained ORR activity is also not up to the benchmark performance [51]. Because of these reasons, researchers are now focussed mainly on synthesizing ultra-fine nanoparticles of Pt, alloying with other metals, and ultra-low loading of Pt on highly porous, high surface area metal oxide/composite support to reduce the cost without sacrificing the performance [52]. Usually, conductive porous membranes are used as catalyst support materials for PEMFC and DMFC, but the use of metal catalyst support shows higher stability, and activity when compared to unsupported catalyst.

The typical characteristics of catalyst support are as follows:

- High surface area.
- Ability to maximize triple-phase boundary through their mesoporous structure.
- Good metal–catalyst support interaction.
- High electrical conductivity.
- Good water management.
- Increased resistance to corrosion.
- Ease of catalyst recovery [54].

Support material, in addition to increasing catalytic activity and durability, also determines the particle size of a metal catalyst. Hence, the choice of support material should be chosen, in such a way that it supports performance, behavior, long cycles of operation, and cheaper cost of catalyst.

The following steps should be considered for developing a new catalyst system,

- Developing non-precious metal catalyst.
- Choice of suitable catalyst support materials.

The metals other than Pt group are palladium, ruthenium, rhodium, iridium, and osmium. The availability of these metals is scarce compared to Pt. Hence by incorporating all the above points and alloying with non-Pt group metals, the loading of precious metal could be reduced with higher performance [55]. The essential properties of support materials discussed above are important to achieve better performance of fuel cell at a cheaper cost.

Stability

The major issue with PEMFC catalyst is long-term durability. During the continuous operation of PEMFC, catalytic agglomeration, and electrochemical corrosion of carbon-based support result in deterioration of catalyst activity [53]. By choosing the correct catalyst support, one can eliminate the agglomeration of catalyst, and corrosion of support. With the existing carbon black support, the electrochemical corrosion triggers at above 0.9 V which results in the catalyst getting detached from support, and agglomerates. It will create a lack of diffusion of fuel/oxidant reactants and reduces overall fuel cell performance, and life. These issues force us to find a solution for long cyclic stability of PEMFC by choosing proper support, which has strong electrochemical stability under acid/alkaline medium.

The most widely used support materials are carbon black with various grades from various companies based on quality in terms of porosity and surface area. Since from last decade, the researcher's focus is on nanostructured catalyst supports, as they deliver faster charge transfer, surface area,

Table 1 Summary of different synthesis methods as discussed in “Most promising methods for the preparation of electrodes” to “Atomic layer deposition (ALD)”

Synthesis methods	Advantages	Disadvantages	Commercial viability
Electrodeposition	One step method, short time required, avoid complicated synthesis methods, high purity and particle size, less fatigue and cheap fabrication method	External power supply is required	Good
Chemical precipitation method	Involves no bigger instruments or devices	Long-term process, involves careful attention in preparation	Good
Colloidal method	Involves no bigger instruments or devices	Many more steps involved, long time is required, stabilizers and reducing agents have to be removed	Moderate
Sol–gel synthesis method	Wet method, involves no bigger instruments or devices	Less mass transfer and low utilization of catalyst	Moderate
Microemulsion method	Simple method	Expensive chemicals and their activity is not environmentally friendly	Moderate
Microwave-assisted polyol method	Simple and most commonly used method	Takes a long time to complete a reaction	Moderate
Chemical vapor deposition (CVD)	More precision and accuracy, high purity of materials	Costly chemicals, expensive instruments, highly operator oriented	Moderate
Spray technique	Easy method, direct application of nano-materials, tunable to desired catalyst loading	High amount of catalyst loading, time consuming, operator oriented, agglomeration of particles, less catalyst utilization	Moderate
Atomic layer deposition (ALD)	High accuracy method, more precision, desired particle size or in atom level, ultra-low loading of catalyst with high performance of devices	Very expensive instruments, need more control over operations, costly chemicals	Moderate

Table 2 Development criteria for automotive fuel cell electrocatalysts [51] Reproduced with permission from Publishers: Nature, Order Number: 4638121383737 Title: Electrocatalyst approaches and challenges for automotive fuel cells, Mark K. Debe

Performance	<p>Must meet beginning-of-life performance targets at full and quarter power</p> <p>Must meet end-of-life performance targets after 5000 h or 10 years operation</p> <p>Must meet performance, durability and cost targets and have less than 0.125 mg PGM per cm²</p> <p>Corrosion resistance of both Pt and the support must withstand tens of thousands of start-up/shut-down events</p> <p>Must have low sensitivity to wide changes in relative humidity</p> <p>Must withstand hundreds of thousands of load cycles</p> <p>Must have adequate cool start, cold start and freeze tolerance</p> <p>Must enable rapid break-in and conditioning (the period needed to achieve peak performance)</p>
Materials	<p>Must have high robustness, meaning tolerance of off-nominal conditions and extreme-load transient events</p> <p>Must produce minimal H₂O₂ production from incomplete ORR</p> <p>Must have high tolerance to external and internal impurities (for example, Cl₂) and ability to fully recover</p> <p>Must have statistically significant durability, meaning individual MEA lifetimes must enable over 99.9% of stacks to reach 5000-h lifetimes</p> <p>Electrodes must be designed for cost-effective Pt recycling</p> <p>Environmental impact of manufacturing should be minimal at hundreds of millions of square meters per year</p>
Process	<p>Environmental impact must be low over the total life cycle of the MEAs</p> <p>Manufacturing rates will need to approach several MEAs per second</p> <p>MEA manufacturing quality must achieve over 99.9% failure-free stacks at beginning of life (one faulty MEA in 30,000 for just 1% stack failures).</p> <p>Proven high-volume manufacturing methods and infrastructure will be required</p> <p>Catalyst-independent processes will be preferred, to enable easy insertion of new-generation materials</p>

and improved catalytic activity. They are broadly classified into carbonaceous and non-carbonaceous supports.

Carbonaceous type includes different types of modified carbon materials such as mesoporous carbon, carbon nanotubes (CNTs), nanodiamonds, carbon nanofibers (CNF), and

graphene [36, 54–61]. This nanostructured modified carbon offers high surface area, high electrical conductivity, and good stability in acid and alkaline environments. High crystallinity of carbon nanomaterials, such as CNT and CNF, exhibits stability and good activity [62].

However, under repeated cycles of fuel cell operation, carbon materials such as carbon black face serious problems of corrosion. Though there is considerable decrement of corrosion rate with higher graphitic carbon materials such as carbon nanotubes, carbon nanofibers, they do not prevent carbon oxidation [63]. To achieve high corrosion/oxidation resistant, stability, and durability; metal oxides are preferred as a good catalyst support material instead of carbon [52, 64]. Metal oxides offer [62, 64]:

high electrochemical stability,
mechanical stability,
porosity,
high surface area,
cycling stability and durability [62, 63].

Debe et al. derived development criteria for automotive fuel cell electrocatalysts as given in Tables 1 and 2. They proposed that increased surface area of catalyst will improve the activity of the outer Pt layer [65]. Nanostructured thin-film (NSTF) catalysts will give high surface area for efficient

Fig. 3 Fuel cell performances with different anode catalyst loading, and comparison with literature values (as per data in Table 3)

Table 3 Ultra-low loading of anode catalyst

Sl. no	Anode mgcm ⁻²	Cathode mgcm ⁻²	Power Wcm ⁻²	Experiment conditions	References
1	0.0442	0.546	0.561	Back pressure 1 bar (anode/cathode)	[74]
2	0.005	0.005	0.132	H ₂ /O ₂ No bp	[75]
3	0.04	0.04	0.43	Back pressure 4 bar (anode/cathode) H ₂ /air	[76]
4	0.05	0.05	0.714	Back pressure 2.7 bar (anode/cathode)	[77]
5	0.013	0.4	0.619	H ₂ /O ₂ No bp	[78]
6	0.08	0.08	0.4	H ₂ /O ₂ No bp	[79]
7	0.03	0.03	0.07	Back pressure 1.5 bar (anode/cathode)	[80]
8	0.01	0.01	0.4	Back pressure 3.8 bar (anode/cathode)	[13]
9	0.05	0.1	0.720	H ₂ /O ₂ No bp	[81]
10	0.035	0.5	0.7	Back pressure 1.5 bar (anode/cathode)	[82]
11	0.0021 0.02145	0.05 0.05	0.016 0.024	H ₂ /O ₂ No bp	[83]
12	0.15	0.022	0.614	Back pressure 1.72 bar (anode/cathode)	[84]
13	0.029	0.029	2.5	Back pressure 3 bar (anode/cathode)	[85]
14	0.04	0.12	0.66	Back pressure 3 bar (anode/cathode)	[86]
15	0.035	0.035	1.02	Back pressure 2.06 bar (anode/cathode)	[87]
16	0.1	0.029	0.3	H ₂ /air No bp	[88]
17	0.059	0.055	0.45	H ₂ /air No bp	
18	0.015	0.04	0.55	Back pressure 2 bar (anode/cathode) H ₂ /air	[89]
20	0.06	0.4	0.254	H ₂ /O ₂ No bp	[90]
21	0.18	0.5	0.864	H ₂ /O ₂ No bp	[91]
22	0.025	0.1 (PtCo)	1.09	Back pressure 2.5 bar (anode/cathode) h ₂ /air	[4]
23	0.05	0.05	0.25	H ₂ /O ₂ No bp	[92]
24	0.04	0.04	0.033	Dry H ₂ /O ₂ No bp	[93]
25	0.014	0.3	0.7	Back pressure 2 bar (anode/cathode)	[94]
26	0.16	0.16	0.38	Back pressure 4 bar (anode/cathode) H ₂ /air	[76]

Bp back pressure

activity for the catalyst. NSTF electrocatalysts offer area-specific activity [66, 67] of the catalyst, catalyst utilization, stability [68, 69], and performance with ultra-low PGM loadings [70].

Problems associated with ultra-low loading

During continuous operation of fuel cell, there will be a loss in ECSA due to dissolution, agglomeration, and Ostwald ripening. So, catalyst stability and durability are being decided by ECSA loss before and after operation of specified hours. Most recent catalyst systems with ultra-low loading present very high mass activity ($30\times$ higher mass activity vs. Pt/C), but they fail at high current density targets. For example, core-shell (Pt@Pd/C) catalysts exhibit higher mass activity but undergo some degree of base metal dissolution [71]. So, new catalyst development with the focus on ultra-low loading of precious metal and stability at high current densities (HCD) is required even though they exhibit higher mass activity.

Requirements of cathode catalysts

PGM alloy shows high performance at the beginning and offers higher ohmic/mass transport losses during continuous operation. During long cycling, a conventional Pt/C lost its performance by degradation (dissolution, agglomeration, and Ostwald ripening). And PGM alloy contaminates ionomer by the dissolution of ions and results in additional performance loss at high current densities. Hence, a novel cathode catalyst layer is required for high performance and durability. As pointed out earlier, most Pt alloy catalysts with high mass activity show high performance at low current densities, but suffer from performance loss at high current densities due to base metal or support dissolution, and it is progressive when operating under voltage cycling. Hence, a novel cathode catalyst layer design is proposed to get rid of the above-discussed problems and to deliver stable performance/durability. Dustin Banham et al. [72] presents real-world requirements for the design of PEMFC catalysts.

Table 4 Ultra-low loading of catalyst (both anode and cathode) by various synthesis methods, MSPD and peak power

Catalyst synthesis method	Catalyst (anode/cathode)	MSPD $\text{mW}\mu\text{g}^{-1}$ Pt total (0.65 V)	Peak power Wcm^{-2}	References
Spraying	Pt	2.96	0.66	[86]
Sputter deposition	Pt	9.1	0.132	[75]
Plasma sputtering technique	Pt	20 (peak)	0.4	[13, 95]
	Pd@Pt	13	0.260	
		1.65		
Electrospraying	Pt	2.28 (0.5 V)	0.243	[96, 97]
	Pt	2.16 (peak)	0.150	
		0.128 (0.65)		
Electrospinning and electrospraying	Pt	0.04		[84]
		5.4 (peak)	1.06	
		3.21		
Ultrasonic spray technique	Pt	1.15	0.695	[98]
Spraying and sputtering	Pt	14.5 (peak)	1.02	[87]
		9.28		
Electrospinning	Pt	1.30	0.306	[88]
Hand painting or modified thin film	Pt	4.06	0.714	[77]
Inkjet	Pt	1.95	0.35	[80]
Electrodeposition	Pd@Pt and Pt/C	3.62 (Pt/pd as anode)	0.780	[89, 99]
	PtRu and Pt/C	3.92 (Pt/pd as cathode)	0.068	
	DMFC	0.14		
Dual ion beam-assisted deposition	Pt	3.3	0.43 @0.65 V	[76, 100]
	Pt	3.36	0.38	
Doctor blade	Pt	3.12	0.48	[101]
Piezo-electric printing	Pt	2.44	0.365	[102]
Electroless deposition	Pt	0.34	0.4	[103]
Atomic layer deposition		1.27	0.254	[90, 91]
		1.27	0.864	
Pt alloy–De alloy	Pt–Ni	8.76	1.09	[4]

Table 5 Various synthesis methods are shown: merits and demerits

Sl.no	Catalyst synthesis method	Merits	Demerits
1	Spraying	Easy method, direct application of nanomaterials, tunable to desired catalyst loading	Non-uniformity of catalyst loading, time consuming, operator oriented, agglomeration of particles, less catalyst utilization
2	Sputter deposition	Low loading of Pt could be done, possible to coat directly on GDL, membrane and non-catalyzed carbon layer (NCL), cheaper method, uniform dispersion/distribution of Pt particles	Poor bonding with substrate, short durability, chance of Pt dissolution and sintering results in multilayered Pt layer obstruct water transport
3	Plasma sputtering technique	Mass production feasibility This method allows to control particle size and also to create “sticking” defects and influence in catalytic activity Co-sputtering of Pt and carbon is possible with high utilization and efficiency	–
4	Electrospraying	Uniformity, catalyst utilization, large electrode size possible. Possible to coat on any substrate-like membrane or GDL. Depending on the operating conditions, aggregates or even single particles can reach the substrate generating a porous deposit with high roughness and fractal structure, higher Pt utilization	Needle alignment, careful optimization of catalyst ink, operator oriented and require individual skills, needs optimization of distance between target and nozzle
5	Electrospinning and electrospinning	Higher Pt utilization, produces unique nanoparticle/nanofiber electrodes for fuel cells	Complex experimental set up to align two needle system. Electrode pre-treatment is required
6	Ultrasonic spray technique	Any substrate, GDL, NCL or membrane Mass production, higher catalyst loading for HTPMEMFC and DMFC is possible through this technique	Careful optimization of nafion content is required Lower Pt utilization, difficult to achieve ultra-low loading (μg), loading uniformity
7	Spraying and sputtering	High Pt utilization, desired particle size, uniformity distribution	Careful optimization of two coating techniques are required as they have their own difficulty
8	Electrospinning	Superior catalyst utilization, right method for ionomer (proton/anion exchange membrane)/fabrication	Carrier polymer is required and to be optimized for electrospinning solution and cannot be removed after coating Time consuming for electrospinning solution preparation (48 h) Custom-built environmental chamber is required to maintain 40% RH Annealing of electrode under vacuum after coating
9	Hand painting or modified thin film	Higher Pt utilization, no cracking on catalyst layer as low hot pressing temperature. No need to add organic solvents and eliminate time consuming in slurry preparation and cost effective	Difficult to load in terms of microgram and maintain uniformity of Pt dispersion
10	Inkjet	High deposition control like the ultra-thin methods, high level uniformity, ultra-thin low loading is possible, transfer losses are significantly reduced and reproducibility	At some operational conditions, membrane deformation and surface cracks during the deposition process may occur, lower catalyst utilization, increased drying time, bubble formation in ink, ink viscosity has to be maintained
11	Electrodeposition	Higher Pt utilization, ultra-low loading is possible, easy formation of active sites with triple-phase boundary. Excellent uniformity, nanoparticle formation, easy and accurate control of the surface micro-structure, lower grain size, thin catalyst layer ($< \mu\text{m}$), produce novel electroactive materials, synthesis in a single step process, mass scale production and cost effective In general it is presumed that Cl ⁻ ions produced in process are known to poison Pt and reduce the catalytic activity, but it could be easily eliminated by changing deposition methods	Higher loading $> 4 \text{ mg cm}^{-2}$ might be difficult, external power supply is required

Table 5 (continued)

Sl.no	Catalyst synthesis method	Merits	Demerits
12	Dual ion beam-assisted deposition	Low loading of catalyst is possible with higher catalyst utilization, different morphologies with amorphous nature for better performance, uniformity of coating	System complexity and costlier method, operator oriented, need to be optimized for mass production
13	Doctor blade	Faster than hand painting, the machine spreader, highest precision of catalyst loading	Time-consuming process, not commercially viable method
14	Piezo-electric printing	High degree of precision and accuracy. Lower transfer loss, cost savings compared to other spray techniques	Membrane swelling from water and causes uneven printing surface, careful optimization in ink preparation
15	Electroless deposition	Suitable for Pt/Ru binary electrocatalyst, Pt atoms reduced on the surface of the Ru nanoparticles and exactly at the reaction site. Thus, an ultimate reduction of Pt loading can be achieved	Depends largely on surface morphology of substrate, solution concentration and other parameters (pH, temperature, storage etc.) has to be carefully maintained, causes particle agglomeration, non-uniform particle size distribution
16	Atomic layer deposition	High accuracy method, more precision, desired particle size or in atom level, ultra-low loading of catalyst with high performance of devices	Very expensive instruments, need more control over operations, costly chemicals
17	Pt alloy–De alloy	Mature technology, improved performance over Pt/C, enhanced membrane and MEA durability	Though these catalyst superior performance and cost effective, it offers complex catalyst synthesis process and long-term durability studies are underway

Requirements for PEMFC anode catalyst

Platinum is a superior catalyst for hydrogen oxidation reaction in the anode of the fuel cell, and it accounts for 50% of the fuel cell cost [72]. During the stack operation, if flow field in anode side is blocked, the current forces malfunctioning of the cell, and stack. Materials such as carbon, catalyst, water present in the anode layer oxidized to supply the necessary electrons. This is, in turn, leads to high anodic potential (> 1.5 V), and the deterioration of the anode catalyst layer. This implies that the requirement of a novel catalyst layer with strong support material which has electrochemical stability and durability. Nowadays, the catalyst research group must have a strategy to test their catalyst for fuel cell performance and durability at the MEA level. It will further require real-time stack testing and optimizing various parameters by incorporating interdependency of various materials involved in the system.

Maximum mass-specific power density (MSPD)

DOE has targeted maximum mass-specific power density (MSPD) values [73], which account for both low Pt Anode and low Pt cathode catalysts, as an index for performance with reference to Pt loading. DOE targets more than $5 \text{ mW } \mu\text{g}^{-1}_{\text{Pt total}}$ at cell voltages higher than 0.65 V [Department of Energy (DOE)]. This cost reduction to meet DOE target 2020 is possible if we could reduce Pt loading in MEAs to less $125 \text{ } \mu\text{g cm}^{-2}_{\text{MEA}}$. In general, it is classified into three regions: (1) $> 5 \text{ mW } \mu\text{g}^{-1}_{\text{Pt total}}$ (2) between 1 and $5 \text{ mW } \mu\text{g}^{-1}_{\text{Pt total}}$ (3) $< 1 \text{ mW } \mu\text{g}^{-1}_{\text{Pt total}}$.

The maximum MSPD value $8.76 \text{ mW } \mu\text{g}^{-1}_{\text{Pt total}}$ at 0.65 V is obtained by a proprietary catalyst, PtNi/PtCo, of General Motors and United Technologies Research Center (UTRC), and stack modeling performed by ANL [23] (Fig. 3).

Catalyst synthesis and deposition methods: MSPD values

Various catalyst synthesis methods are listed in Tables 4 and 5 with a primary focus on how an ultra-low loading of catalyst impacts the fuel cell performance by the influence of maximum mass-specific power density (MSPD) values. Each method has achieved maximum performance with low loading of catalyst within the boundary of its limitation.

Combination method of synthesis and coating

By comparing all synthesis methods (Fig. 4), it is found that the combination method of synthesis and coating (e.g., spraying and sputtering) has achieved increased MSPD values than the specific method of synthesis. It is also encouraged to note that the combination method of synthesis and

Fig. 4 Ultra-low loading of catalyst (both anode and cathode) by various synthesis methods and MSPD values compared with DOE 2020 target

coating may eliminate the limitation posed by a specific method.

In this review, for example, electrodeposition and plasma sputtering/spraying synthesis methods are recommended for developing an efficient catalyst system which would deliver good performance and stability, at high current density with long-term durability. Here the disadvantages posed by each method are overcome by other methods. Any catalyst synthesis and coating technique, which is being scaled up with high performance/durable catalyst layer, is now a superior priority. Hence, greater attention should be paid not only towards the alloy catalyst but also the catalyst preparation methods, and choice of catalyst support materials [64].

Table 4 shows various catalyst synthesis methods and respective MSPD values along with reference. Table 5 shows various synthesis methods and their merits and demerits.

Conclusion

Here a brief review of various catalyst synthesis methods and their efficacies is performed with a focus on ultra-low loading of catalyst. Also, the merits and demerits of various synthesis methods are discussed. The ultra-low loading in electrodes was discussed in terms of MSPD values, and is compared with DOE 2020 target values. The catalyst prepared by any combination of the method of synthesis which results in MSPD values more than $5 \text{ mW } \mu\text{g}^{-1}$ Pt total at $>0.65 \text{ V}$ will be the best catalyst to meet the target of DOE 2020.

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