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Chapter 13 Nanoporous materials for proton exchange membrane fuel cell applications

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Abstract

This chapter starts with a brief introduction to the PEMFC history and principles. We then highlight the requirements in porosity in catalyst electrodes, followed by the electrode structure design and porosity characterization. Recent advancements in catalysts and supports are discussed, especially the development of 3D electrodes from aligned 1D nanostructures. The challenge and opportunities for future research are finally addressed.

Keywords: PEMFC, catalyst, electrode, support, CNT, graphene, PtNi, nanoframe, nanowire, 1D

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13.1 Introduction

Hydrogen is a clean energy carrier that only produces water emissions and the fuel cell is a highly efficient energy conversion technology. Both combined have a great potential to help fight the world greenhouse gas emissions, reducing dependence on fossil fuels and contributing to economic growth. As an electrochemical device, the fuel cell can directly convert the chemical energy in fuels (e.g. hydrogen) to electricity, with by-products of heat and water. Since this is a one-step electrochemical reaction process, the electricity efficiency is high which can reach 60%, and there is no noise and emission produced. If the heat can also be integrated in application, e.g. in a combined heat and power (CHP) unit, the energy efficiency can potentially reach 85-95%. Therefore, the fuel cell technology has attracted a lot of effort and has been successfully applied in vehicles and buildings.

There are many types of fuel cells. Among them, the proton exchange membrane fuel cell (PEMFC) is the fastest developed fuel cell technology and attracts most attention. It also dominates the fuel cell market in recent decades. Compared with other fuel cells, the PEMFC operates at a relative low temperature (-20 to 80°C), with advantages of easy start up and shut down, high energy efficiency and flexible power scales.

The fuel cell was invented by Sir William Grove in 1839 [1], and the first practical PEMFC unit was invented by Grubb and Niedrach at General Electric (GE) in 1960s used in NASA's Gemini space program in mid-1960s. Despite their success in space programs, fuel cell systems were only limited to space missions and some special applications, where high cost could be tolerated. Only until late 1980s and early 1990s, Los Alamos National Lab (LANL) and Texas A&M University experimented with ways to reduce the amount of platinum required for PEMFCs, and fuel cells became a real option for wider application base. Also, in 1983 the Canadian company Ballard began research into fuel cells, and was to become a major player in the manufacture of stacks and systems for stationary and transport applications in later years. More stories about the fuel cell development in history can be found in Babir's book [2].

Fuel cells began to become commercial in a variety of applications in 2007. A large-scale residential CHP program in Japan helped stimulate commercial stationary PEMFC shipments. These units began to be installed in homes from 2009. Only until 2014, the 1st commercial fuel cell electric vehicle (FCEV), named as Mirai (Japanese for "future"), was unveiled by Toyota, which has been sold near 10 000 by 2019. However, there is still significant debate as to whether hydrogen fuel cells will be a realistic technology for use in automobiles or other vehicles.

A typical PEMFC consists of a proton conductive polymer electrolyte membrane (PEM) in the middle, two electrodes (anode and cathode), flow field plates (FFP) and current collectors at both sides (Figure 1). In fuel cell operation, at the anode side, hydrogen is split to protons and electrons. Protons transfer through PEM to the cathode side, and the electrons pass through the external circuit to the cathode (which can power the load if there is one). At the cathode side, the electrons and protons combine with oxygen to generate water. As by product, the heat generated will also be released with the excel fuel and with the water produced. The detailed reactions in PEMFCs are listed below in Eq. 1-3. In this chapter, we will only talk about the electrodes where porosity play a significant role and nanoporous materials reported for the PEMFC application.

Figure 1. Schematic of a proton exchange membrane fuel cell.

13.2 Porosity with PEMFC electrodes

Membrane electrode assemblies (MEAs) are the heart of PEMFCs, and both electrodes are the places where electrochemical reactions take place. To complete fuel cell reactions, there are transport networks needed within the electrode for transferring reactants (H_2 at the anode and O_2 /air at the cathode), electrons and protons to catalytic reaction sites, and repelling the generated water out of the cathode. The intersect place where the catalyst surface for electron moving, electrolyte phase for proton conducting and pores for gases and/or water transferring, is named as triple phase boundary (TPB). A typical TPB in the cathode is schematically illustrated in Figure 2. This concept has been widely used in the development of catalysts, support and electrode structure to help understand the complex interaction between catalyst and support particles, pore size distribution and ionic/electronic conductivity in the catalyst layer of electrodes.

Figure 2. Schematic illustration of triple phase boundary in cathodes.

For a functional electrode, a highly porous structure is necessary for the effective transport of gases and water to complete the fuel cell reactions to produce power. A high TPB interface is favored for achieving high performance. For a PEMFC operating at a current density of 1 A cm^{-2} , the over potential (or potential loss) at the anode is about 20 mV while at the cathode it is about 400 mV [3]. The higher over potential at the cathode is caused by the sluggish oxygen reduction reaction (ORR), the oxygen transport and water flooding in the porous micro-structure. Therefore, we will focus on the porous structure of the cathodes in the following sections.

The first PEMFC unit in the Gemini aircraft contained a high loading (4 mg cm^{-2}) of unsupported platinum (Pt) black adhered by polytetrafluoroethylene (PTFE) within the electrodes [4]. The great breakthrough in the PEMFC development from LANL in the 1980s was to extend the TPB zone by introducing proton conducting ionomer (Nafion®) and carbon supported platinum catalyst (Pt/C) into the electrodes, which significantly improved the catalyst utilization and reduced the Pt loading to less than 0.4 mg cm^{-2} as mostly used today. Beside of great progress in material science and electrocatalysis of PEMFCs [5], understanding characteristics and properties of the porous structures in the electrodes has also enabled the rapid advances in the research and development of this clean technology.

13.2.1 Porous structure

There are two layers in an electrode, i.e., catalyst layer (CL) and gas diffusion layer (GDL), or three layers if including a microporous layers (MPL) between the CL and GDL. The structure of a typical cathode is shown in Figure 3 [6]. The catalyst layer, a porous medium with randomly distributed hydrophobic and hydrophilic sites, is made of carbon supported platinum (Pt/C) catalyst and ionomer. The ORR occurs at the TPB zone in the CL and water is produced. The MPL provides improved electrical contact between the CL and the GDL, and helps avoid fast dry-out of PEM at low current densities or low humidity [7]. The MPL is comprised of carbon black and a hydrophobic agent of PTFE, and the later also serves as adhesive. The GDL is a textile sheet (or paper) that contains carbon fibres, a binder, and a hydrophobic agent such as PTFE. This substrate provides structural support to the MEA as well as providing transport pathways for the reactants and the produced water and electric collector [8].

The excess water condenses to form liquid that fills the pores in the CL and GDL, which is called flooding phenomenon. Flooding is believed to significantly limit the oxygen diffusion and affect the TPB interface, and hence the fuel cell performance is deteriorated. This is attributed to pore size jump at interface of the CL and GDL, $0.05 \text{ }\mu\text{m}$ versus $10 \text{ }\mu\text{m}$. Inserting a microporous layer (mean pore radius $0.5 \text{ }\mu\text{m}$) between the CL and GDL reduces both the droplet size and liquid saturation, and therefore improves the cell performance [6].

Figure 3. Structure of cathodes (a) with two layers (catalyst layer and gas diffusion layer) and (b) with three layers (catalyst layer, microporous layers and gas diffusion layer). Reproduced from Ref. [6] with permission of Elsevier, 2009.

The structural parameters of the CL, MPL, and GDL are summarized in Table 1 [4,9,10].

Table 1. Structural parameters of the CL, MPL and GDL

Parameters	Catalyst layer (CL)	Microporous layer (MPL)	Gas diffusion layer (GDL)
Porosity, %	20-40	50	70-80
Mean pore radius, μm	0.02-0.03	0.5	10
Thickness, μm	5-30	10-50	120-300

13.2.2 Diffusion principle in electrodes

As listed in Table 1, the pore size distribution of the electrode ranges from 20 nm to 10 μm , which includes both meso (2-50 nm in diameter) and macro (>50 nm) pores. The diffusion mechanism in a porous medium is determined by the Knudsen number, Kn , which is a ratio of the molecular mean free path, λ , to a representative physical length scale of the porous medium, l , as written in Eq. (4).

$$Kn = \frac{\lambda}{l} \quad (\text{Eq. 4})$$

where λ is a constant for a given gas under a condition of specific temperature and pressure, while l is mostly an average pore diameter.

If the molecular diffusion is dominated by collisions between the molecules and pore walls when $Kn > 1$, it is called as Knudsen diffusion. Adversely, the diffusion mainly occurs with collisions between the molecules when $Kn < 1$, which can be called bulk diffusion or molecular diffusion.[11]

Tortuosity, τ , affecting oxygen effective diffusivity, is defined as a ratio of the length of the shortest continuous path and the distance between any two points within the porous medium. Oxygen effective diffusivity, D^{eff} , is defined as a function of the porosity, ε , the tortuosity, τ , and oxygen diffusivity in the pore scale, D , which can be expressed by:

$$D^{\text{eff}} = \left(\frac{\varepsilon}{\tau}\right) D \quad (\text{Eq. 5})$$

Oxygen diffusivity in the pore scale can be approximated by Bosanquet's formula as the following:

$$D = [(D^{Kn})^{-1} + (D^{\text{bulk}})^{-1}]^{-1} \quad (\text{Eq. 6})$$

Here D^{Kn} and D^{bulk} represent Knudsen diffusivity and bulk diffusivity, respectively.

The experimental results show that the $\text{O}_2\text{-N}_2$ diffusion in the catalyst layers is dominated by the Knudsen effect [10].

The liquid water generated by the ORR at the cathode can significantly reduce the effective porosity under high current density conditions, and flooding is severe which limit oxygen transport. Capillary functions of the GDL and CL help removing water and result in lower saturation levels. In the GDL, the removal rate of liquid water due to capillarity-induced motion can be enhanced conspicuously by an increase in hydrophobicity at first, and this effect then diminishes gradually. On the contrary to the flooding, efficient retention of the liquid water generated from the cathode is also preferred. It can be used to alleviate the dependence on external humidification of air feed, because the electrolyte perfluorosulfonated ionomer requires to be kept humidity to attain reliable proton conductivity. A strategy has been suggested by using the MPL and multiple-layered CLs for the structural-driven retention of liquid water [11]. It was demonstrated that in the dual CLs, as compared with the inner catalyst layer, the outer catalyst layer significantly reduced the diffusion rate and thus promoted the structural-driven retention of liquid water.

13.2.3 Characterization of porous structure and diffusivity

Many experimental methods can be used to measure the porosity of porous materials, such as mercury porosimetry - mercury penetration, BET adsorption measurement - nitrogen adsorption and thermoporometry-calorimetric analysis of the solidification of a liquid filling the pores. From the experiment results, pore structural parameters of the specific surface area, the pore size distribution vs pore radius, and the cumulative pore volume can be calculated.

The microstructures can also be resolved with tomography methods, such as the focused ion beam (FIB) - scanning electron microscopy (SEM) tomography, X-ray computed tomography (XCT) and cryo-STEM-tomography. The FIB-SEM tomography is proceeded with several steps: i) the FIB ion milling is firstly performed with the cutting distance of 10-nm scale; ii) subsequently, the SEM analysis is conducted to generate a stack of images and then the stack is cropped to a volume; and iii) finally, the segmented images were assembled to create the three-dimensionally reconstructed CL for the detailed analysis. For example, the pore-scale analyses on diffusivity and tortuosity were performed for three-dimensional (3D) reconstruction of the dual-layered electrode for PEMFCs [11]. XCT is a non-destructive technique, which can be used to investigated the CL structure which enables reconstruction of 3D images for more comprehensive analysis than what is possible from 2D views. XCT instruments use X-rays to collect 2D radiographs at regularly spaced angles about a specified rotational axis to yield a tomography set which when processed yields a complete 3D rendering of the sample under study [12]. XCT can extract the structure information covering a wide range at nano, micro scales, and multilength scale of them combined. At the nano length scale, XCT has been used to extract the distributions of the pores and carbon support agglomerate diameters in the CL [13]. At the micro length scale, XCT was also used to examined the morphology and uniformity of fuel cell electrodes affected by fabrication methods.

The effective gas diffusion coefficient (EGDC) of the CL is a very important parameter, which affects the uniformity of oxygen reduction reaction through the whole CL, and the performance of PEM fuel cells. Except of calculating by Equation (5), effective gas diffusion coefficients

(EGDCs) of oxygen in the electrodes can also be directly measured in a cell based on oxygen "in-plane" diffusion which is parallel to the electrode surface [14], or "through-plane" diffusion which is perpendicular to the electrode surface [10].

13.2.4 Improvement

The CL is made of Pt/C catalyst and proton conducting ionomer, for which the thickness is determined mainly by the carbon content and the porosity is determined mainly by the ionomer content, while TPB zone in the CL depends on the distribution of Pt catalysts, the ionomer and porosity. In preparing the CL, when the catalyst ink is drying, the volume ratio of solid matter (about 3% in the catalyst ink) gradually increases and carbon aggregates form a network on the substrate. Some ionomer remained in the solvent gradually fills and buries the pores in the carbon network [15].

A binary solvent of dipropylene glycol (DPG) and water has been suggested to control the ionomer distribution and agglomerate size in the CL [16]. Because of the high affinity of DPG with the perfluorinated backbone of Nafion ionomer, the hydrodynamic diameter of the ionomer aggregates reduces from a micron to a nanosize with the increase of the DPG content. The increased homogeneity in the ionomer distribution is beneficial in enhancing proton transport in the CL at a low relative humidity (RH) condition. However, it leads to a performance loss at high RH conditions in terms of the mass transport property, which infers that a certain degree of inhomogeneity in the ionomer distribution is needed to prevent the pore clogging or narrowing. In pure DPG, the size of the ionomer aggregates (17 nm) is much smaller than that of the catalyst aggregates and fill up the mesopores (2–20 nm) in the catalyst aggregates as showed in Figure 4(a). In pure water, the ionomer aggregates are too bulky to cover the external surface of the catalyst aggregates; therefore, it rather forms isolated ionomer phases in the CL (Figure 4(c)). When the size of ionomer aggregates is comparable to that of the catalyst aggregates with the DPG content of 50%, the ionomer aggregates just cover the external surface of the catalyst aggregates, not significantly clogging or narrowing the mesopores in the catalyst aggregates (Figure 4(b)). In such an ionomer distribution, the ionomer phases can properly function as binder and proton conductor.

Figure 4. Suggested models to account for the ionomer distribution in the catalyst layer depending on the dimension of the ionomer aggregates in the dispersion: the ionomer aggregate size (D_{ion}) is (a) small, (b) similar and (c) larger than the catalyst particle aggregate size (D_{cat}). Reproduced from Ref. [16] with permission of American Chemical Society, 2018.

A catalyst layer was designed by introducing Nafion nanofibers to the conventional catalyst layer that contains Nafion ionomer, as shown in Figure 5 [17]. The Nafion nanofiber in the catalyst layer impacts properties of the proton conductivity, porosity, and electrochemical surface area (ECSA) of Pt. The addition of Nafion nanofibers significantly increases the proton conductivity of the catalyst layer up to $8.3 \times 10^{-1} \text{ S cm}^{-1}$ at 70°C and 100% relative humidity, which is 15.7 times higher than that of the catalyst layer with the same content of Nafion ionomer.

Figure 5. Scheme of a catalytic layer with hierarchical proton transport channels. Reproduced from Ref. [17] with permission of American Chemical Society, 2019.

Cathode catalyst layer with gradients of ionomer distribution for proton exchange membrane fuel cells was also suggested [18]. It is ideal that the ionomer loading in the CL near the membrane layer is higher to facilitate proton transport. A cathode catalyst layer with gradients of ionomer distribution consisting of two sub-layers with different loadings of short-side chain ionomer and Pt catalyst for each sub-layer was confirmed with improved fuel cell performance.

Pore forming agent addition has been considered to form controlled pores to assist the transport of oxygen through the CL. The CL sample with additional ethylene glycol as a secondary pore forming agent was confirming effectively improving the transport of oxygen through the CL [19].

A special design of ordered 3D electrodes from aligned 1D nanostructures is considered as the 3rd generation PEMFC electrodes, which will be discussed in details in section 13.5 within this chapter.

13.3 Nanoporous catalysts

The development of highly active and durable electrocatalysts for ORR is still a challenge for the PEMFC technology. The fuel cell power performance decreases as the Pt catalyst is deactivated due to Pt surface area loss. This has limited the Pt loading reduction for a fuel cell below the current $\sim 0.2 \text{ mg}_{\text{Pt}}/\text{cm}^2$ in the MEA [20]. A lower Pt loading is highly preferred for commercial applications. A low Pt loading of $0.025 \text{ mg}_{\text{Pt}}/\text{cm}^2$ in the MEA translates to about 2 g of Pt per vehicle (mid-size light duty vehicle), which is equal to or lower than the Pt amount used in an automotive catalytic converters of an internal combustion engine vehicle. Various strategies and considerable efforts have been devoted to improve the catalytic activities and stability, and reduce the overall cost of PEMFC catalysts. The common approaches include in finely controlling the physical (crystallite size and shape) and the chemical (alloying Pt with transition metals) structures of the Pt nanoparticles [21], as well as using platinum group metal free (PGM-free) catalysts [22].

13.3.1 Pt-based electrocatalysts

Up to today, the Pt-based electrocatalysts are still the only choice for PEMFCs in practical applications. As shown in Figure 6, Pt-based electrocatalysts can be classed into three main groups: pure platinum, platinum alloys and core-shell platinum structures, which show different trends of activity and stability in their controlling structure/geometry and electronic state [5].

Figure 6. Groupings of Pt-based electrocatalysts for ORR in PEMFCs. Reproduced from Ref. [5] with permission of the Royal Society of Chemistry, 2017.

It is well known that the exposed percentage of the catalyst surface available for catalytic activity is the reciprocal of particle size. This means that reducing the particle size to below 1 nm levels may lead to 100% Pt utilization. However, research revealed that the porous structure of the carbon support with a pore size at approximately 2 nm is a hindrance. That is, reduction of Pt particle size below 2 nm lowers its specific activity and results in the pocketing of the particles inside the porous structure of the carbon support, rendering them inaccessible for catalyst reaction. Also, the metal particle smaller than 1 nm displays a very strong interaction with the carbon support and deviates its normal behaviour, thereby reduces the participation in electroactivity [23]. Finally, extremely small Pt nanoparticles have a high surface energy and are thermodynamically unstable, so they tend to grow into larger particles during a long-term PEMFC operation following two proposed mechanisms: Pt dissolution and redeposition (Ostward ripening), and Pt migration and coalescence. The effective particle size of Pt based catalysts is confirmed to be between 2 and 5 nm, and only 20-50% of total Pt is available for catalytic reaction.

The commercial Pt/C catalysts prepared by conventional wet chemical methods usually show a broad size distribution (2–5 nm). This causes a low catalytic activity and high trend of Oswald ripening for a poor stability. To address this problem, some novel processes have been developed recently to prepare Pt nanoparticles with a narrow size distribution. For example, a supercritical deposition (SCD) approach has been used to prepare carbon-supported Pt nanoparticles [24]. Pt precursor dimethyl(1,5-cyclooctadiene)platinum(II) ($\text{Pt}(\text{cod})\text{me}_2$) was adsorbed onto Vulcan XC-72 under supercritical carbon dioxide (scCO_2) solutions at 13.2 MPa and 50°C, and then converted to its metal form via three different routes: thermal conversion in N_2 at ambient pressure (route 1), thermal conversion in scCO_2 (route 2), or chemical conversion in H_2 at ambient pressure (route 3). Pt nanoparticles with an average particle size of 1.7, 2.1 and 6 nm were obtained with the three routes, respectively, but the Pt/C electrocatalysts prepared using the SCD method were shown to be the most promising catalysts due to the small particle size, homogeneous dispersion, and narrow distribution.

Pt hollow nanospheres (HNSs) were also deposited on Vulcan XC-72R (VC) and explored as an electrocatalyst for the ORR in PEMFCs [25]. Pt HNSs were formed with a uniform size of ca. 18 nm, consisting of discrete Pt nanoparticles (NPs) with a crystallite size of ca. 2-3 nm. The unique nanostructure of the hollow mesoporous core and discrete (porous) shell of Pt crystallites finally led to a very high catalytic activity.

Combining Pt with other transitional metals to generate bimetallic/multimetallic nanocrystals with structures in forms of alloys, core–shells, yolk structure, nanoframe nanostructures is popular and considered as a highly potential method for reducing Pt usage. The atomic arrangements of these nanoparticles are described either as solid solution alloys or as

segregated structures, which can lead to differential catalytic enhancement mechanisms including the strain-induced d-band center shift and electronic ligand effect between the substrate and the overlayer [26,27]. Dealloying treatment is an effective method to modify the surface of PtM (M=Ni, Co, etc, transitional metals) alloy catalysts, which produces Pt-rich shell catalysts by dissolving a certain amount of the transitional metal. The rapid dealloying treatment did not cause any obvious agglomeration or other unfavorable morphology change, but can result in a significant refinement of morphology and enhancement of catalytic activities. However, it is not all the case that a perfect Pt shell structure is achieved, and the shell thickness is not truly uniform.[20]

To understand the influence mechanisms of the shell thickness on the catalyst performance, carbon supported hollow PtNi nanoparticles with different metal shell thicknesses and central cavity sizes were synthesized via a method involving the galvanic replacement (an electrochemical process in which the oxidation of the non-noble metal nanocrystallites provides electrons for the deposition of Pt^{2+} ions onto their outer surface) and the nanoscale Kirkendall effect (Figure 7) [28]. The ORR activity and the robustness of the porous hollow PtNi/C nanoparticles depended on the size of the central void and, to a less extent, on the Pt-rich shell thickness. These nanocatalysts combine opened porosity, compressed Pt lattice constant, and preferential crystallographic orientation, resulting in 6 and 9-fold enhancement in mass and specific activities toward the ORR, respectively, over standard Pt/C nanocrystallites of the same size.

Figure 7. Schematic illustration of the synthesis process of hollow Pt-rich nanoparticles. Reproduced from Ref. [28] with permission of American Chemical Society, 2015.

PtNi nanoframes

Porous PtNi nanoframes were synthesized by exploiting the structural evolution of PtNi bimetallic nanocrystals [29]. The process started from crystalline PtNi_3 polyhedra, which was transformed by interior erosion in solution into Pt_3Ni nanoframes (Figure 8). The surfaces of the unique structure offered three-dimensional molecular accessibility. The edges of the Pt-rich PtNi_3 polyhedra were maintained in the final Pt_3Ni nanoframes. Both the interior and exterior catalytic surfaces of this open-framework structure were composed of the nanosegregated Pt-skin structure, which exhibited enhanced ORR activity. The Pt_3Ni nanoframe catalysts showed 36 and 22 times enhancement in mass activity and specific activity to Pt/C catalysts, respectively, during prolonged exposure to reaction conditions.

Figure 8. Schematic illustrations and corresponding TEM images of the samples obtained at four representative stages during the evolution process from polyhedra to nanoframes. (A) Initial solid PtNi_3 polyhedra. (B) PtNi intermediates. (C) Final hollow Pt_3Ni nanoframes. (D) Annealed Pt_3Ni nanoframes with $\text{Pt}(111)$ -skin-like surfaces dispersed on high-surface area carbon. Reproduced from Ref. [29] with permission of AAAS, 2014.

Single-crystal Pt nanowires

The stability of catalysts is one key factor in determining the fuel cell durability. As the most commonly used catalysts, the stability of Pt-based nanoparticles is still poor in PEMFC operation and cannot meet the requirements for practical applications [30]. Pt-based nanoparticles can degrade through a few mechanisms, including dissolution, aggregation and Oswald ripening, as well as detaching from the support, finally resulting in a low catalytic performance. The degradation processes of Pt-based nanoparticles were summarized by Meier et al. recently [31]. To overcome the challenges with the Pt-based nanoparticles, in past three decades, many new catalyst nanostructures have been developed. Chorkendorff et al. [32] compared various latest fuel cell catalysts reported based on their mass activities towards ORR in liquid half cell electrochemical measurement and in fuel cell testing, and it was found that ultrathin jagged Pt nanowires showed the highest catalytic activity, about 52 times higher than the Pt/C nanoparticle catalyst and with much better stability (Figure 9). Therefore, ultrathin jagged nanowires were considered as the next generation fuel cell catalysts and received lots of attention from fuel cell researchers and manufacturers.

Figure 9. Mass activity comparison of various latest fuel cell catalysts by liquid half cell electrochemical measurement and fuel cell testing. Reproduced from Ref. [32] with permission of AAAS, 2016.

Comparing with their zero-dimensional (0D) counterparts, one-dimensional (1D) metal nanostructures, in particular single crystal metal nanowires exhibit several advantages, such as high specific surface activity due to the preferential exposure of high active crystal facets, facilitating the electron transport by the path directing effects in catalyst layers, and good stability to alleviate the dissolution, Oswald ripening and aggregation because of the asymmetric structure [33]. A 1.5 kW PEMFC stack has been built using Pt nanowire/C as cathode catalysts and compared with conventional Pt/C nanoparticle catalysts [34], and the stability of the Pt nanowire catalysts in real-life context operation was evaluated using a 420 h dynamic drive cycle durability test. The TEM image and particle size histogram analyses were conducted to the cathode catalysts before and after the durability testing (Figure 10). The results depicted minimal changes observed with the Pt nanowires compared with severe Pt nanoparticle growth and aggregation for Pt/C after the durability testing. A comprehensive comparison of nanoparticles with 1D nanostructures for fuel cell applications could be found in the very recent review paper from our group [35].

Figure 10. TEM images and particle size histograms of the cathode PtNW/C and Pt/C before ((A) and (A')), (C) and (C')) and after ((B) and (B')), (D) and (D')) 420 h durability testing, respectively. Reproduced from Ref. [34] with permission of Elsevier, 2015.

However, it still remains a big challenge to translate the full extent of the superior performance of the latest generation of fuel cell catalysts, e.g. PtNi nanoframes and jagged Pt nanowires to PEMFC devices. There are two large difficulties to really apply them into practical fuel cell applications: i) Most preparation approaches still stay at laboratory level and difficult to be scaled up. For example, PtNi nanoframes and jagged Pt nanowires were both synthesized using organic solvent oleylamine (OAm) process. The synthesis yield of the reaction is low and the separation process is very sophisticated; and ii) novel catalysts have a much different morphology and cannot be just fabricated into electrodes using the conventional method optimized for spherical Pt/C nanoparticles (coating from the catalyst ink) which cannot turn the outstanding catalytic properties of novel catalysts to high performance devices. In fuel cells, the catalyst environment is severe and complex, not like the clean environment in the half cell measurement in liquid electrolytes [36,37]. So, new electrode structure platforms are really required to make them into high power performance fuel cell devices.

13.3.2 Platinum group metal - free (PGM-free) catalysts

To replace the precious Pt-based electrocatalysts for minimizing the cost, extensive study has been carried out to develop platinum group metal - free (PGM-free) catalysts. The enhancement of the ORR catalytic performance is achieved through the doped carbon materials and Fe/Co-based electrocatalysts, which could be considered as potential substitutes for Pt-based catalysts. However, up to today, the stability of these PGM-free electrocatalysts is still very poor under the acidic operation environment in PEMFCs [22].

Transition metal-nitrogen-carbon (M-N-C) materials have been reported on 1D, 2D and 3D morphologies. Fe-N supported on graphitic carbon nano-networks was synthesized as ORR catalysts [38], and the best performance was observed with the catalyst having the highest amount of Fe and Co and the highest amount of defects. This was attributed to the influence of Co on morphology, graphitization and level of disorder, and thus on the efficiency of nitrogen introduction in the carbon structure. M-N-C complexes were also synthesized using a high temperature pyrolysis method in the presence of iron and/or cobalt precursors [39]. The high temperature process led to in-situ graphitization of carbon, forming catalyst structures that consist of multilayer highly porous graphene encapsulating CNTs with an abundance of nitrogen and iron defects. This surface chemistry rendered the catalyst highly active towards the ORR, coupled with the robustness of the graphene-like morphology.

The catalytic activities of M-N-C electrocatalysts can be further improved by using S doping or single atom iron catalyst. S-doping Fe/N/C catalysts (denoted as Fe/N/C-SCN) were derived from Fe(SCN)₃, poly-m-phenylenediamine, and carbon black. The using of Fe(SCN)₃ as iron source led to a high level of S doping and surface area, enhancing ORR activity (showing 23 A g⁻¹ vs previous 11.5 A g⁻¹ at 0.80 V without S-doping) in 0.1 M H₂SO₄ solution. When the Fe/N/C-SCN was applied in a PEMFC as cathode catalyst, the maximal power density exceeded 1 W cm⁻² [40]. The single-atom iron catalyst supported on the nitrogen doped graphene (NG) (SA-Fe/NG) was synthesized by a surfactant assisted method, which provided the maximum atomic efficiency, and possessed the refined M-N-C configuration (M = Fe, Co, and Ni, etc.) and the strong interaction between the single atom (SA) and support [41]. The key to synthesize the SA-Fe/NG catalyst was the addition of surfactant F127, because it helped disperse the iron to easily form Fe-N_x moieties, and Fe doped F127 sheets strongly anchored on the g-C₃N₄ substrate so that the surface Fe clusters could be easily removed by acid etching. The SA-Fe/NG exhibited excellent ORR activity, and the onset and half-wave

potentials reached 0.9 V (vs. RHE) and 0.8 V in acidic medium, respectively. Figure 11 reveals that the formation of Fe-pyrrolic-N moieties is the origin of high-ORR activity of SA-Fe/NG, because an SA-Fe incorporation creates an Fe atom and eight C atom active sites next to pyrrolic N, leading to the increase of active sites in an order of magnitude.

Figure 11. DFT calculation studies on the origin of high-ORR activity of SA-Fe/NG. Computational models of Fe@pyrrolic N moieties for ORR, where both Fe atom and eight-carbon atoms next to pyrrolic N are the active sites marked by red letters. Reproduced from Ref. [41] with permission of National Academy of Sciences of the United States of America, 2018.

Another method recently reported is to use hydrophobic protic ionic liquids to modify porous M-N-C catalysts for PEMFC reactions. The first application was reported by Snyder et al. [42] for the modification of PtNi porous nanostructures and enhanced stability was recorded. Very recently, the positive effects of the IL modification were observed to M-N-C catalysts by both half-cell electrochemical measurement and PEMFC test [37,43]. The excellent oxygen solubility and diffusivity of ILs can help maximize the contribution of active catalyst sites within the mesopores of catalyst nanostructures, which are too small to be penetrated by the large polymer clusters of the proton conducting ionomer (e.g. Nafion), thus increase the catalyst utilization ratio in electrodes. Furthermore, the hydrophobicity of ILs can protect the catalyst surface from a direct contact with the acidic water in fuel cell operation preventing the fast leaching of transitional metals [37,44], and help limit the building up of generated water on the exterior of the catalyst, lowering its effect on the mass transport of reactant O_2 [45].

13.4 Nanoporous catalyst support

It is widely accepted that the structure of the carbon support is an important factor affecting the performance of the Pt/C electrocatalyst. It determines the accessibility of the reactants to the catalytic site and also the removal of the generated water. The most commonly used catalyst support is still carbon black today, even after more than 30 years' fast development of fuel cell electrocatalysis technologies.

13.4.1 Carbon Black

The use of carbon supports for catalysts in 1980s is a big breakthrough in the development of PEMFCs. It allowed Pt loadings to be significantly reduced from 4 to $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The carbon support enables the use of extremely small Pt nanoparticles (2-5 nm) to improve the catalytic activities, helps the dispersion and reduces Oswald ripening and agglomeration of Pt nanoparticles, as well as provides electron transport path for the poorly electroconductive Pt nanoparticles. Furthermore, the carbon also forms a porous catalyst layer structure (typically 40-60% porosity) facilitating the reactant transport. Together with the low cost, good chemical stability, high surface area, and excellent affinity for supporting metallic nanoparticles, carbon supports were then widely employed in PEMFCs.

To improve the distribution of catalyst nanoparticles, high surface area carbon black support is preferred in early years, as it can provides a large number of available nucleation sites to

decrease the average Pt particle size. The most commonly used carbon blacks are Vulcan XC-72 (Cabot) and Ketjen Black (TKK) today, and the BET specific surface areas reported are ca. 890 m²/g for Ketjen Black and 228 m²/g for Vulcan XC-72, respectively [46]. Although the very detailed structures of carbon nanoparticles vary from one to another type, their main morphology and pore are very similar. The primary carbon particles are about 30 nm in diameter. It is porous materials consisting of a pseudospherical arrangement of quasi-graphitic microcrystallites a few layers thick filling of less than 2 nm micropores. The primary carbon particles have a propensity to aggregate to form agglomerates of 100–300 nm, within which mesopores of 2–20 nm exist. These agglomerates coalesce into chainlike aggregates with a continuous network of pores greater than 20 nm formed in the interstices. The mesopores within agglomerates and larger pores between aggregates of agglomerates are often referred to as primary and secondary pores, respectively. The microstructures of carbon black particles: turbostratic crystalline domain, primary carbon particle, agglomerate, and aggregate, showing micro-, meso-, and macropores are schematically shown in Figure 12.

Figure 12. The hierarchy of carbon particles and pores. Reproduced from Ref. [46] with permission of American Chemical Society, 2010.

When being fabricated into electrodes, the aggregates of carbon particles are largely preserved in the structure of the catalyst layer, so that the <2 nm micropores, primary and secondary pores are all remained. However, not all these pores are useful when carbon black is used as catalyst support for Pt nanoparticle catalysts in fuel cells. In the catalyst preparation under fuel cell context, Pt deposition rarely happens into the micropores less than 2 nm, so their contribution is usually not discussed. Since the size of proton conducting ionomer micelles is larger (>40 nm), the primary pores (2-20 nm) in carbon black are inaccessible to ionomer which is required for building proton transfer network in the catalyst layer. It is found ionomer is mostly distributed on the surface of secondary pores, covering the intraagglomerate pores below 20 nm. In this case, the dominated primary pores are useless for carbon black to be used as catalyst support. Therefore, catalyst supports are preferred with a high surface area mainly contributed from pores larger than 20 nm, which are necessary for ionomer to be reached to form TPB thus contributing to fuel cell reactions. Furthermore, carbon black is electrochemically unstable at a high voltage over 1.0 V, which usually happens in the startup steps in PEMFCs. The corrosion of the carbon support finally results in disintegration of catalyst layer and decreases the fuel cell power performance. Consequently, other carbonaceous materials were widely considered as catalyst support, including carbon nanotubes (CNTs), ordered mesoporous carbons (OMCs), colloid imprinted carbons (CICs), porous carbon nanofibers and graphene. Comparing with carbon black, these materials can potentially provide higher surface area with accessible pores in the catalyst layer while with a better stability in fuel cell operation.

13.4.2 Carbon nanotubes (CNTs) and graphene

Compare with carbon black, CNTs show a much higher electronic conductivity and corrosion resistance due to the high degree of sp² hybridization. Multi-walled CNTs (MWCNTs) also exhibit a higher electronic conductivity than single wall CNTs (SWCNTs), and are therefore mostly investigated for PEMFC applications. However, in catalyst preparation process, the

high percentage of sp² hybridization also results in very few functional groups on the surface, makes Pt deposition on CNTs very challenging. Therefore, CNTs must first be functionalized, such as by refluxing in strong acid (e.g. HNO₃/H₂SO₄) solutions to create hydroxyl and carboxylic acid surface groups [47]. However, this lowers the CNT electronic conductivity and makes them more susceptible to oxidation in PEMFC operation. Researches then focused on nitrogen-doped CNTs to improve Pt deposition and catalytic activity. It is also reported a strong bond can be formed between the doped nitrogen and Pt leading to an enhanced stability. Pt nanoparticles, short nanorods and nanowires have all been demonstrated on nitrogen-doped CNTs for fuel cell applications with enhanced catalytic performance and stability reported (Figure 13) [48-50].

Figure 13. TEM images and size distribution histograms (inserts) of Pt nanoparticles deposited on CNTs. The scale bar is 20 nm in (a). Reproduced from Ref. [48] with permission of American Chemical Society, 2007. Reproduced from Ref. [50] with permission of Elsevier, 2020. Reproduced from Ref. [49] with permission of American Chemical Society, 2011.

However, despite many advantages offered by CNTs, their application to fuel cells still faces several big challenges. The specific surface area of MWCNTs is relatively lower and the size of the inner pores is also not large enough for the access of proton conducting ionomer. Furthermore, the large aspect ratio of CNTs makes the supported catalysts difficult to be fabricated into practical electrodes with the conventional process used for Pt/C nanoparticle electrodes. The obtained electrodes usually have a very loose structure providing poor mechanical durability for a long-term fuel cell operation.

In this case, the opened structure of SWCNTs, graphene nanosheets were explored for catalyst support applications in recent years [51]. Graphene has aroused interest as potential support owing to the similar advantages of high electron transfer rate, large surface area and high conductivity. Graphene is an atomically thin sheet of hexagonally arranged carbon atoms. The 2D planar structure allows both the edge planes and basal planes to interact with the catalyst nanoparticles. Similar to CNTs, the incorporation of nitrogen to form nitrogen-doped graphene is also considered as a very effective way to provide anchoring sites for the deposition of catalyst nanoparticles. Graphene oxide (GO), as graphene's oxidised counterpart, has also drawn a lot of interest and attention as catalyst support. Oxygen groups with GO create defect sites on surface as well as edge planes, which can act as nucleation centres and anchoring sites for the growth of metal nanoparticles. However, the conductivity of GO is much lower (two to three orders of magnitude) compared to graphene, and they need to be reduced to remove most oxygen groups to achieve a good electrical conductivity. The biggest challenge with the graphene supported catalysts is also caused by their 2D planar structure, which leads to a high trend to stack and form agglomerates in fabricating into practical fuel cell electrodes. This change dramatically reduces the porosity of catalyst layer, blocks the transfer of reactants and water and reduces the catalyst utilization, making the fuel cell very difficult to achieve high current density in operation [52,53].

13.4.3 Mesoporous carbons (MCs)

Ordered mesoporous carbon (OMC) materials have pore sizes of 2–50 nm providing high surface area and conductivity. They are usually prepared by using ordered mesoporous silica templates or by templating triblock copolymer structures. OMCs possess mono-dispersed mesospheres connected three-dimensionally facilitating diffusion of the reactants and by-products, making them also very attractive materials as catalyst supports. It is very important to achieve larger pore diameters in the OMCs to improve the accessibility of electrolyte ionomer and reduce proton transport limited currents. It is reported that the increase in the pore size of carbon aerogel support from 16 to 20 nm allows significantly increase cell performance and maximum power density of the PEMFCs [54]. This requirement of large pores makes the hard templating approach very challengeable for synthesizing OMC for fuel cell applications, because this approach usually constrains the OMC pore diameters to <7 nm due to the big difficulty to increase the wall thickness (which eventually becomes the OMC pore diameter) of the silica template while still maintaining the desired porosity.

To prepare mesoporous carbon with controlled diameter and length, colloid imprinted carbon (CIC) approach has been adopted to develop catalyst support (Figure 14(a)) [55]. This synthesis is based on the unique physical properties of a naphthalene-based mesophase pitch precursor. SiO₂ colloids coated on the pitch surface can be imprinted into its volume by heating to temperatures within its softening range. Importantly, they were able to show that the depth of imprinting of the SiO₂ colloids can be controlled based on the imprinting temperature that is used. By subsequently carbonizing the silica/pitch composite and removing the SiO₂ colloids by refluxing in NaOH, a porous colloid imprinted carbon powder is generated, with pore diameters equal to the size of the SiO₂ colloids that are used and pore lengths controlled by the imprinting temperature. For CIC supports with relatively large pores (26 nm) facilitating mass transport to the Pt nanoparticles inside these pores, the ORR activity of the supported Pt nanoparticles was demonstrated independent of their location down within the CIC pores [56]. Work from Birss' group also indicated that carbon wall thickness in CIC materials had big influence on the ORR activity of Pt/CIC catalysts, and this can also be well controlled by SiO₂ colloid size (Figure 14) [57].

Figure 14. 2D cartoon showing (a) the origin of the range of wall thicknesses for CIC-26, CIC-50 and CIC-80 (number designated to the pore diameter in nm); (b) how the CIC wall thickness will increase as the silica colloid diameter increases (after removal of SiO_2); (c) shows that the disordered packing of the 12 nm colloids results in thicker walls than expected for CIC-15. Reproduced from Ref. [57] with permission of MDPI, 2015.

13.4.4 Nanoporous carbon fibre

Carbon nanofibers are regarded as a promising conducting material because their 1D structure acts as efficient pathways for the electrons transporting through freely. Its scale-up controlled producing is also made available taking advantage of the recent development in electrospinning as an easy, reliable, and cost-effective technique to prepare fibers with thin diameter into nanometer size. The recent focus on this technology is to increase the special surface area to work as a proper catalyst support. Nanoporous carbon fibre is usually prepared by electrospinning the solution mixture of carbon precursor polymer (CPP) and thermally decomposable polymer (TDP) followed by carbonization, and the porosity can be tuned by varying the ratio of TDP to CPP [58,59]. However, similar to CNTs, how to fabricate these 1D carbon fibres into a robust fuel cell electrode still remains as a big challenge.

13.5 Ordered 3D electrodes from aligned 1D nanostructures

The porosity in the conventional Pt/C nanoparticle electrodes is formed randomly. This results in a very low catalyst utilisation and very difficult to achieve a high current density operation in practical PEMFC applications. The development of aligned nanostructured catalyst electrodes is regarded as the most promising approach to address this challenge of conventional electrodes to boost fuel cell performance. With well-designed porosities, the electrodes with aligned 1D nanostructures can provide a super-high degree of active site exposure with significantly improved mass transfer performance. An ideal electrode model was designed by Middelmann in 2002 (Figure 15) [60]. It is expected this unique structure can be built with a

vertically oriented catalyst-coated electron conductor, vertically oriented proton conductor and vertically oriented through-hole structure. Based on this understanding, in recent decades, various aligned 1D nanostructure electrodes have been reported based on catalyst coated aligned nanotubes or even self-standing aligned 1D nanostructured catalysts.

Figure 15. Schematic diagram for the ideal electrode. Reproduced from Ref. [60] with permission of Elsevier, 2002.

13.5.1 Nanostructured thin film (NSTF) catalyst layer

One significant development of ordered electrodes from 1D nanostructures is nanostructured thin film (NSTF) catalysts from 3M Co. and they have been reviewed in many papers [61,62]. The preparation of MEAs from the NSTF catalysts is a vacuum based roll-to-roll coating process achieved within a vacuum roll-coater. The catalyst layer consists of a thin layer of polycrystalline thin film of PtCoMn (or PtNi) catalyst (0.05/0.1 mg_{Pt}/cm₂ at anode and cathode, respectively) coated by magnetron sputter on aligned electroconductive PR-149 polymer whiskers with an average cross-sectional size of 55 nm x 30 nm less than 1 μm tall. The catalyst coated whiskers have a distribution density of 30-40 per square micrometer, forming nanosized hydrophilic pores between the walls of catalysts. The total catalyst layer thickness is ca. 1 μm which is more than 10 times thinner than equivalently loader Pt/C nanoparticle electrodes. The thin catalyst layer effectively enhances the proton and electron transfer. Within this catalyst layer, the catalyst covers the entire surface of the support and the nanosized hydrophilic pores are typically flooded with water during operation which facilitates proton transport due to electrostatic interactions with the surface charges of the pore walls. Therefore, the NSTF catalyst layer mitigates the requirement of proton conducting ionomer for which the degradation is considered as one main challenge to improve the PEMFC durability. However, the large size of catalyst structure results in a low electrochemical surface area (ECSA) in the range of 10 to 25 m²/g which is small compared to high surface area Pt/C catalysts, although this could be partially compensated by the 10 fold gain in specific activity to achieve reasonable mass activity. Another very major consequence of the extreme thin NSTF catalyst layer is the flooding issues. At a given current density, the water generation rate per unit thickness on the cathode is 20 to 30 times higher for an electrode proportionately thinner. This brings in a big challenge for water management strategies. These issues finally limit this promising NSTF technology to be really put into practical application.

Similar work has been conducted with other electric conductive polymers, e.g. such as aligned polypyrrole (PPy) and polyaniline (PANI) nanowires. The deposition of the catalyst layer using physical vapor deposition (magnetron sputtering) also leads to the same thin film nanostructured catalyst. An improvement of this work was conducted by Sun's group to decorate Pt nanoparticles on aligned PPy nanowires directly in-situ grown on the GDL [63]. The PPy nanowires were grown under the existing of ionomer which doped into the matrix of PPy molecular chains. Pt ions were then deposited onto nanowire surface driven by the electrostatic interactions between Pt cations and sulfonate groups of ionomer. Finally, Pt ions

were reduced to form Pt nanoparticles using hydrogen at 250°C. The achieved Pt nanoparticles had an average size of 4.3 nm with well-defined spherical nano-crystallines uniformly distributed on the surface of the PPy nanowires. The unique electrode structure finally recorded a cathode mass specific power density of 11.97 W mg_{Pt cathode}⁻¹.

13.5.2 Pt nanoparticles supported on aligned nanotubes

Considerable efforts have also been devoted to the construction of electrodes based on vertically aligned CNTs and TiO₂ nanotubes. These structures possess similar advantages to the NSTF catalyst layer, including the vertically oriented structure and continuous straight pore structure.

Aligned CNTs have a high electronic conductivity and enhanced mass transportation in practical electrodes. A typical fabrication process for the electrode from Pt decorated aligned CNTs is shown in Figure 16(a). In general, aligned CNTs are grown on substrate surface (stainless steel, SiO₂, quartz, Al foil, etc.) with catalysts (e.g. Fe or FeCo), then the top part of CNTs were decorated with Pt nanoparticles by chemical or physical methods followed by surface coating with proton conducting ionomer, finally the substrate with Pt decorated aligned CNTs is decal transferred onto PEM by hot pressing. Hatanaka et al. [64] reported the aligned CNT structure grown on PEM for fuel cell applications in 2006, and the process was further improved by other groups to prepare thin CNTs and uniformly distributed Pt nanoparticles. Tian et al. [65] grew aligned CNTs with the average length of about 1.3 μm and a diameter of about 10 nm using plasma enhanced chemical vapor deposition (PECVD) technique (Figure 16(b)), and then physical sputtering was used to deposit Pt nanoparticles. With a Pt loading of 0.035 mg cm⁻², the MEA from the Pt/aligned CNTs exhibited a comparable power performance to the conventional Pt/C one with a Pt loading of 0.4 mg cm⁻² in H₂/O₂ PEMFC (Figure 16(c)). However, with the physical sputtering method, it's very difficult to achieve a high Pt loading without aggregation in practical electrodes. In Birmingham, we combined the aligned CNTs with 1D Pt nanostructure to overcome this obstacle [50]. Aligned CNTs were grown on carbon paper GDLs using PECVD technique and then activated using active screen plasma nitriding to achieve aligned N-CNTs. Pt nanorods were then grown on N-CNT surfaces rather than Pt nanoparticles. A Pt loading of 0.2 mg cm⁻² was achieved, showing a better power density and durability then the electrode with Pt/C nanoparticle catalysts at 0.4 mg_{Pt}⁻².

Figure 16. (a) Schematic diagram for the fabrication of a MEA based on Pt/aligned CNTs. (b) Cross-sectional SEM image of Pt/aligned CNTs on Al foil. (c) Polarization curves of the MEA based on Pt/aligned CNTs with a Pt loading of 0.035 mg cm⁻² and a conventional MEA with

the Pt loading of 0.4 mg cm^{-2} in H_2/O_2 PEMFC. Reproduced from Ref. [65] with permission of Wiley, 2011.

Although better than the active carbon support, the CNT still suffers from a poor tolerance to the electrochemical corrosion at a high potential in PEMFC operation. Therefore, porous metal oxide nanostructures, aligned 1D TiO_2 nanostructures were explored for the application [66]. Different to carbon materials, TiO_2 possesses a high corrosion resistance to oxidation and special interaction with metal catalysts as catalyst supports. Aligned TiO_2 nanotubes were prepared by electrochemical anodic oxidation followed by wet chemical reduction or PVD to decorate catalyst nanoparticles, which is very similar to the catalyst decoration onto the aligned CNTs. A main challenge with TiO_2 as the catalyst support is the relatively poor electronic conductivity. As a consequence, the treatment by the reducing gases or by surface carbon coating has been researched to improve the electrical conductivity of aligned TiO_2 nanotubes as catalyst supports for PEMFC applications [67,68].

13.5.3 Electrodes from aligned single crystal Pt nanowires

The outstanding catalytic activity and stability of single crystal Pt nanowires make them ideal catalysts for PEMFC applications. Compared with polyol [69] and oleylamine [70] process using organic solvents and operated at high temperature, formic acid reduction approach is a green chemical process and can be conducted in aqueous solution at nearly room temperature to grow single crystal nanowires [48,71]. Taking the advantages of this simple method, our group developed an approach to fabricate gas diffusion electrodes (GDEs) by in-situ growing aligned single crystal Pt nanowires on the GDL [72,73]. A 3D nanostructured electrode was formed with the catalyst layer consisting of a monolayer array of single crystal Pt nanowires with a diameter of 4 nm and length of 100-150 nm. Different from the NSTF catalyst, no regular pores formed due to the really thin Pt nanowires. It is a highly open 3D structure within the catalyst layer, together with the relative hydrophobic Pt surface (*cf.* PtCoMn and PtNi in the NSTF catalysts), the produced water is still easily to be repelled out and not accumulated to form continuous channels for ion transfer. This means the degradation induced by local water flooding and accelerated catalyst decay in the NSTF catalyst are mitigated here. However, proton conducting ionomer is thus still required to build ion transfer network to achieve high power performance [74]. As the electrode with a monolayer array of Pt nanowires within the catalyst layer, a uniform distribution of the nanowires is key to achieve PEMFCs with high power performance. This is determined not only by the Pt nanowire loading [75] and the GDL surface structure [76], but also the surface wettability in the nanowire growth. To make the surface wettable to the aqueous reaction solution in the formic acid reducing process, a few techniques were deployed to increase the surface activity, including building composite microporous layer (MPL) from various carbon black to control the surface active sites [76], optimizing reaction temperature to improve the wettability in reaction [77], introducing Pd nanoseeds to inducing the distribution of Pt nanowires [78], and modify the GDL surface by active screen plasma nitriding (ASPN) [79,80]. Among various technologies, ASPN has been confirmed as a very effective technology. It can introduce various functional groups, e.g. C-N, C=N and O-H onto the support surface, increasing the surface activities and facilitating the formation of Pt nuclei thus enabling a uniform distribution of aligned Pt nanowires (Figure 17(a) to 17(c)). Furthermore, the ASPN process introduces N-doping to the support surface, which confines the Pt atoms in reaction to form tiny nuclei, resulting in the growth of ultrathin Pt-nanowires with diameters of about 3.0 nm (Figure 17(d) to 17(f)). The reduced diameter leads to an increased ECSA and less agglomerates with an enhanced catalyst utilization, finally resulting in an improved power performance.

Figure 17. Images of Pt-nanowires grown on the plasma activated GDLs. (a–c) SEM images of a 3D nano-architected catalyst layer with aligned Pt nanowires in-situ grown on the activated GDL support surface, at three different magnifications. (d–f) TEM and HR-TEM images of Pt-nanowires in the nano-architected catalyst layer. (f) shows a HR-TEM image of the part specified by the white square in (e), indicating the single-crystal nanowires with the growth direction along the $\langle 111 \rangle$ axis. Reproduced from Ref. [79] with permission of Springer Nature, 2014.

Compared with GDE method, catalyst coated membrane (CCM) or decal approaches have a good potential to fabricate MEAs with higher power performance due to the better contact between the catalyst layer with PEM [2]. Sui's group reported half MEAs made with aligned Pt nanowires grown on the inert PEM and decal substrates using the same formic acid reduction method by introducing a thin carbon powder matrix as a functional layer [81,82]. They also studied the carbon loading and proton conducting ionomer in the matrix, and Pt loading to optimize the electrode power performance [83,84]. With the decal method [85], they also introduced a very small amount of Pt/C catalysts ($5 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$) as crystal seeds to control the growth of Pt nanowires [86]. The optimal cathode with a total Pt loading of 0.205 mg cm^{-2} ($5 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ with Pt/C and $0.2 \text{ mg}_{\text{Pt}} \text{cm}^{-2}$ with the aligned Pt nanowires) showed a 110% higher specific current density than that of the commercial GDE with a Pt loading of 0.40 mg cm^{-2} , demonstrating a good potential of this approach.

13.5.4 Electrodes from aligned Pt-based nanotubes

Pt-based nanotubes also owe similar advantages to nanowires and suffer less from dissolution, aggregation and Ostwald ripening compared to Pt nanoparticles. Furthermore, nanotubes have a potential to provide a high surface area with their porous structure and be easier prepared at alloy form for enhanced catalytic activities.

With a sacrificial template of porous anodized aluminum oxide (AAO), Pt is deposited onto the inside wall of AAO pores using atomic layer deposition (ALD) or electron beam evaporation (EBE) technique, and was then decal transferred to PEM surface by hot pressing followed by removing the AAO template to obtained half MEA with aligned Pt nanotubes [87,88]. With this approach, depending on the pore size of the AAO template, aligned Pt nanotubes with an

external diameter of around 150-180 nm and 20 nm thick Pt walls were achieved. It can also be conducted by deposit another less-precious metal, e.g. Cu into the porous AAO template followed by galvanic displacement reaction to prepare porous Pt alloy walls to increase the surface and mass specific activity. Morin et al. [89] used this method preparing a 2 μm thick catalyst layer consisting of an array of aligned nanotubes of 30 nm in diameter, with an average distance of 60 nm (about 32 billion nanotubes per cm^2). The wall of nanotubes was made of PtCu alloy nanoparticles of 3 nm in diameter. The specific activity obtained for such structure was demonstrated ten times higher than Pt/C catalyst ($2.2 \text{ mA cm}^{-2}_{\text{Pt}}$) in real operating conditions. Through a hydrothermal and PVD method, open-walled PtCo bimetallic nanotube arrays were also constructed for PEMFC applications [90]. Highly ordered Co-OH-CO₃ nanowire arrays (NWAs) were prepared as the template, then Pt layer was coated onto Co-OH-CO₃ NWAs by magnetron sputtering. Pt and Co were alloyed by thermal annealing, endowing the catalyst layer with extra electro activity, then the template was removed by acid wash. A catalyst layer with a thickness ca. 300 nm was achieved with aligned open-walled PtCo bimetallic nanotubes with a diameter ca. 100 nm and skin thickness estimated to be ca. 17 nm. Serving as the cathode, a 1.7 fold higher Pt-based specific power density ($14.38 \text{ kW g}_{\text{Pt}}^{-1}$) was obtained than the conventional CCM based on Pt/C electrocatalyst.

13.6 Perspective

The advance in materials synthesis and nanotechnology has led to exciting progress to PEMFC technologies, from the catalyst, support to electrode design. We have seen the successful applications of PEMFCs in practical applications and the commercial PEMFC-based vehicles. To move this clean technology to extensive commercial applications, some breakthroughs are necessary to really bring the current promising materials into high performance MEAs, in particular the novel electrode structure design.

Significant advancements have been achieved with the catalyst electrode design, from the earliest NSTF catalyst layer, to Pt nanoparticle decorated aligned CNTs and TiO₂ nanotubes, and to self-standing catalysts from aligned Pt nanowires and nanotubes. The extremely thin catalyst layer, together with the vertically oriented structure enabling better mass transportation in practical electrodes for a super-high degree of active site exposure and catalyst utilization. Outstanding catalytic performance and durability were observed, and the big potential was demonstrated for PEMFC applications.

The ultrathin jagged single crystal Pt nanowire has been demonstrated as the most promising catalyst materials up to now, and lots of research groups and fuel cell manufactures are working on it with an expectation to scale up the process for the development of next generation PEMFCs. A breakthrough is urgently required to fully transfer their superior performance to working electrodes to realize the dream of PEMFCs operating at a high power density with long-term durability. The concept of 3D electrodes from aligned nanowires fits the jagged Pt nanowires perfectly. The simplicity and green preparation process make the formic acid reduction to fabricate aligned Pt nanowire electrodes a promising approach for prepare high power performance MEAs by the roll-to-roll processing. More techniques are still required to precisely control the nanowire distribution to form well designed 3D structure to accurately tune the catalyst exposure and mass transfer behaviour within the catalyst layer. To further improve the 3D structured electrodes, a fundamental understanding of the structure-property relationship is necessary in particular with help from the numerical simulation techniques. Another major direction is to increase the ECSA of the aligned single crystal Pt nanowires, either by reducing the diameter to prepare ultrathin Pt nanowires, or to make jagged single crystal Pt nanowires.

The NSTF catalyst layer is one important approach for the development of ordered nanostructure electrodes. Combined with the PVD method, it has been confirmed as a

technique to fabricate MEAs based on a roll-to-roll process. A further development of this process is partially limited by the corrosion of support polymer material in long-term operation, the low ECSA, and the water flooding in high current density operation in PEMFCs. Electrodes from Pt nanoparticles decorated aligned 1D supports, including aligned CNTs, TiO₂ nanotubes and nanorods were hot topics in PEMFC research, and further breakthroughs are necessary to simplify the complex preparation process, as well as addressing the poor intrinsic conductivity of the metal oxide supports. The electrodes from the self-standing catalyst nanotubes are still limited by the large thickness of nanotubes and the complex process based on the template approach.

In addition to the research work on novel catalyst nanostructures and electrode fabrication techniques, the surface and structure modification of catalysts and electrodes were also studied in recent years, in particular the using of hydrophobic protic ILs. Although the enhancement mechanisms of the IL modification for catalysts in PEMFCs are still in debate, the positive effects have been confirmed. Especially, the positive effects from the surface protection and access to mesopores make the IL modification an ideally approach to modify low cost porous PGM-free catalysts (e.g. FeCN and CoCN deduced from MOFs) for PEMFC applications, which can help address the major challenge of the poor stability due to the corrosion in the acidic operation environment.

Proton conducting ionomer in the catalyst layer plays a significant role in controlling the porosity of the catalyst layer to improve the electrode performance. For 1D nanostructures and even aligned nanowires, the surface contact with ionomer could be much different from that with conventional Pt/C nanoparticles. A systematical study of the ionomer contact on various catalyst nanostructures, and monitoring the behavior of ionomer in fuel cell operation will provide invaluable reference for the design and development of next generation PEMFC electrodes.

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