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Review (Special Column on Electrocatalysis for Fuel Cells)

Nano-electrocatalyst materials for low temperature fuel cells: A review

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ABSTRACT

Low temperature fuel cells are an attractive technology for transportation and residential applications due to their quick start up and shut down capabilities. This review analyzed the current status of nanocatalysts for proton exchange membrane fuel cells and alkaline membrane fuel cells. The preparation process influences the performance of the nanocatalyst. Several synthesis methods are covered for noble and non-noble metal catalysts on various catalyst supports including carbon nanotubes, carbon nanofibers, nanowires, and graphenes. Ex situ and in situ characterization methods like scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and fuel cell testing of the nanocatalysts on various supports for both proton exchange and alkaline membrane fuel cells are discussed. The accelerated durability estimate of the nanocatalysts, predicted by measuring changes in the electrochemically active surface area using a voltage cycling method, is considered one of the most reliable and valuable method for establishing durability.

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1. Introduction

Unlike conventional power generating systems which rely on the thermal expansion of gases to drive electro-mechanical generators, fuel cells do not have moving parts except for blowers and controllers. Direct conversion avoids mechanical frictional losses and leads to increased fuel conversion efficiency. In addition, fuel cells are not limited by the thermodynamic constraints imposed by Carnot efficiency [1,2].

The choice of the electrolyte determines the range of operating temperature and physico-chemical properties of the other cell components (catalysts, electrodes, interconnectors and

current collectors) [3]. For example, a proton exchange membrane fuel cell (PEMFC) is typically operated below 100 °C and hence could be a potential system for automotive applications. In contrast, the molten carbonate fuel cell requires temperatures exceeding 800 °C which makes it slow to start up and it should be run continuously rather than intermittently. While low temperature fuel cells are better suited for periodic on and off usage patterns, the slow electrochemical kinetics at low temperature requires the use of catalysts to achieve the type of performance required for typical transportation applications.

Fig. 1 illustrates the schematic of a single PEMFC configuration and its main components including the bipolar plate, gas

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Fig. 1. Schematic diagram of a fuel cell showing the gas flow plates, gas diffusion layers, catalyst layers and electrolyte.

diffusion layer (GDL) electrode, electrocatalyst layer, polymer electrolyte membrane and sealant. The hydrogen oxidation reaction (HOR) occurs at the anode catalyst layer, while the oxygen reduction reaction (ORR) takes place at the cathode catalyst layer. Protons generated at the anode are transported through a humidified electrolyte membrane and they combined with pure oxygen (or oxygen from air) at the cathode to form water and heat. The membrane prevents electrons from passing through, so they move through an external circuit to drive the load. Nafion (DuPont™) is a commercially available electrolyte membrane for PEMFCs and it is based on a chemically stabilized perfluorosulfonic acid/PTFE (Poly-tetra-fluoro-ethylene) copolymer in acid form, which provides a relatively high ionic conductivity (e.g., 0.16 S cm^{-1} for $117 \text{ }\mu\text{m}$ thickness membrane) [4]. As seen in Fig. 1, the electrolyte is sandwiched with the electrocatalyst and GDL layers and the assembly is generally referred to as a membrane electrode assembly (MEA).

Since the 1960s, much progress has been made in PEMFC development in terms of increasing the stack conversion efficiency and reducing the overall system cost. However, there are several technical barriers which limit the commercial viability of PEMFCs. These include issues associated with hydrogen generation, storage and distribution, system cost and fuel cell reliability and durability [5]. Electrocatalysts such as platinum or other highly active materials play a critical role in the cost and durability of PEMFCs [6]. With the Pt-based anode and cathode catalysts used in PEMFCs, the cost of the electrocatalysts accounts for 35%–42% of the total cost of the PEMFC stacks [7]. Furthermore, the sensitivity of Pt-based catalysts to contamination, carbon corrosion and particle agglomeration has shifted the technical burden to a high purity hydrogen supply and the development of advanced support materials. A recent publication highlights the various approaches in developing Pt-based nanocatalysts with the focus to improve performance as well as durability [8]. The major objective of this review is to examine advanced nanomaterials and the synthesis techniques used to enhance electrocatalyst properties and electrochemical performance to promote cost-effective catalyst use in PEM and alkaline fuel cells. In particular, advanced electrocatalyst support nanomaterials, durable Pt nanocatalyst synthesis, advanced non-platinum electrocatalyst fabrication, core-shell nanocatalyst development and catalyst characterization (including the evaluation of catalyst degradation, analysis

of fuel cell performance and failure mode diagnosis) are discussed in detail.

2. Electrocatalyst support structures

The electrochemical activity of catalysts depends on the size of the catalyst particles and their dispersion on the support network. The ideal support material should have the following properties: high surface area, optimum pore size and distribution, good electrical conductivity, good physico-chemical stability, oxidative stability and cost effectiveness [9,10]. Commercially available carbon black-supported Pt catalyst (Pt/C) is widely used due to its simple synthesis process as well as the high surface area of the carbon particles. However, it is well known that a Pt/C catalyst shows a relatively low Pt utilization due to the poor mass transfer characteristics of carbon black. Carbon black is also sensitive to electrochemical oxidation under many fuel cell service conditions such as H_2 starvation, stack start-up/shut-down and a high cell potential, leading to carbon corrosion and Pt detachment from the support material [11]. Advanced support materials with nanostructures such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), nanowires (NWs) and graphenes are discussed and consolidated in the following sections.

2.1. Carbon nanotube supports

Significant progress has been made in CNT synthesis and property improvement since its first discovery by Iijima in 1991 [12]. CNTs have extraordinary mechanical and electrical properties and have been extensively applied in various research fields (including nanocomposite materials, nanoelectrode materials, field emitters and nanoscale sensors) [13,14]. There are many special issues of journals and books documenting the potential applications of CNTs [15–17]. CNTs can be classified into two main types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The common synthesis techniques of CNTs include arc discharge, laser ablation and chemical vapor deposition (CVD). The first two methods use a high energy input to release carbon atoms from precursors, whereas CVD applies catalytic decomposition from a precursor onto the surface of transition metal particles. This technique enables the scale-up to industrial level for high volume CNT production. Fig. 2(a) shows vertically aligned CNTs produced using a photo-thermal CVD technique by a Ti/Fe bilayer film as the catalyst, which was obtained by the research group of Shang *et al.* [18].

Prior to introducing the catalyst onto the CNT support, many non-covalent and covalent modification methods can be employed to functionalize the CNTs and create active sites around the inert CNT walls for improving catalyst dispersion and molecular interactions. To incorporate carboxyl, carbonyl and hydroxyl groups on the surface of the CNTs, a strong acid treatment (e.g., HNO_3 , $\text{HNO}_3 + \text{H}_2\text{SO}_4$) has been used [19]. A mild and facile method using citric acid prevents the degradation of the CNT nanostructure during the functionalization process [19,20]. In fact, citric acid functionalization of MWCNTs

Fig. 2. SEM images of different materials. (a) Vertically aligned CNTs using a photo-thermal CVD technique in different magnitudes (Reproduced with permission from Ref. [18]); (b) Nickel grown vertically aligned carbon nanofibers (VACNFs) (Reproduced with permission from Ref. [25]); (c) Typical nanostructure thin film (NSTF) catalysts as fabricated on a microstructured catalyst transfer substrate (Reproduced with permission from Ref. [22]); (d) Chemically reduced Pt (19 wt%) catalysts on pure graphene (Reproduced with permission from Ref. [33]).

prevents the damage of π -bonding arising from sp^2 hybridization.

2.2. Carbon nanofiber supports

CNFs (or carbon filaments) consist of graphite sheets aligned in exact directions that are determined by the catalyst selected for the growth process. Unlike conventional graphite materials and CNTs where the basal plane is exposed, CNFs only expose their edge region and this feature provides the catalyst support sites. Metal particles supported on CNFs have also been reported to have less susceptibility to carbon monoxide poisoning compared to traditional catalyst systems [21,22]. Similar to CNTs, CNFs also require functionalization before the introduction of metallic nanoparticles. For instance, Toebe *et al.* [23] suspended CNFs into dilute nitric acid (pH of 3) at 90 °C under an inert atmosphere to generate active sites and remove the metallic nickel catalyst. Tang *et al.* [24] reported an electrodeposition method to introduce Pt nanoparticles on graphitic CNFs from an acidic solution of H_2PtCl_6 by cyclic voltammetry (CV) in the potential range from +0.1 to -0.25 V vs. SCE at a sweep rate of 15 mV s⁻¹. Fig. 2(b) shows vertically aligned carbon nanofibers (VACNFs) grown by Sarac *et al.* [25] using ligand-stabilized Ni nanoparticle catalysts and plasma-enhanced CVD.

2.3. Carbon-ceramic support structures

These carbon-ceramic support structures are a promising type of silicate-containing electrodes for fuel cell applications and consist of electronically conducting carbon particles attached by a ceramic binder formed by a sol-gel process [26]. Carbon-supported Pt with a silicate (SiO_2) ceramic is most commonly used. The use of a carbon-ceramic support structure

with SiO_2 ceramic has been reported by Anderson *et al.* [27] for direct methanol fuel cells. According to their work, the electrocatalytic activity for methanol oxidation at colloidal-Pt-modified carbon-silica composite aerogels was increased by four orders of magnitude per gram of Pt over that at a native Pt-modified carbon powder. Jennie *et al.* [26] have used a sol-gel process using 20% Pt on Vulcan XC72 carbon black and tetra ethyl orthosilicate (TEOS) as the organosilane precursor. They reported that the process led to a homogeneous distribution of SiO_2 on the carbon supported Pt catalyst and a maximum in the active area of Pt occurred with 45% SiO_2 loading.

2.4. Mesoporous-carbon support structures

In fuel cell applications, carbon black is generally used as the catalyst support to improve the dispersion and utilization of the catalyst. Several properties of carbon materials such as pore size, particle morphology and size distribution need to be considered for the applications in PEM fuel cells [28]. The pore size of the carbon material generally determines the mass transport rate of gaseous and liquid reactants and products. Mesoporous carbon materials with a pore size in the range of 2–50 nm are commonly used as the catalyst support [28,29]. A technique known as template-assisted ultrasonic spray pyrolysis (TA-USP) was developed by Zhang *et al.* [28] to synthesize carbon materials with a large surface area and tunable pore size. Using this TA-USP aerosol process, a homogeneous mesoporous carbon powder with spherical solid or hollow particles were synthesized. Song *et al.* [30] studied the effect of pore morphology on the catalytic activity in two different mesoporous carbons: OMC-CMK-3 (ordered mesoporous carbon) and WMC (worm-like mesoporous carbon). It was found from their experiments that highly ordered OMC-CMK-3 provided Pt nanoparticles with more electrochemically active Pt sites and a higher electrochemical surface area.

2.5. Nanowire support substrates

Similar to CNTs, nanowires (also called nanowhiskers or nanorods) are one dimensional crystalline structures with a high aspect ratio and superior electrical, optical, mechanical and thermal properties. Nanowires (NW) can also be made from non-carbon materials (e.g., metals, semiconductors and inorganic compounds) and there is a broad choice of crystalline materials with compatible properties. For example, a 3M nanostructured thin film (NSTF) catalyst contains neither carbon nor an additional ionomer in the electrode layer and it is coated with a monolayer of oriented crystalline organic (pigment) nanowhiskers to increase the dispersion of Pt particles [22]. The organic whiskers have high thermal, chemical and electrochemical stability and encapsulate the catalyst particles, which eliminate issues that would exist with an unstable support. The NSTF nanostructure shown in Fig. 2(c) [22] illustrates the homogenous geometry of nanowhiskers. The major challenge in NW synthesis is to control their phase purity, crystal structure and dimension with a uniform environment. Physical techniques (e.g., lithography, patterning) are more

expensive and less versatile than chemical methods (such as CVD, metal-organic CVD, arc discharge and sol-gel). Nucleation and growth rate factors have direct impact on the quality of the NWs.

2.6. Graphene nanocatalyst support

Functionalized graphene sheets (FGSs) synthesized by a thermal expansion process using a high temperature treatment are used as high conductivity support materials [31,32]. The synthesis begins with the chemical oxidation of graphite flakes. The resulting graphite oxides are then split apart by a rapid thermal expansion process to yield single but wrinkled graphene sheets. To prepare Pt/FGS, a Pt precursor H_2PtCl_6 in acetone is added dropwise into the FGS powder under mild stirring. The graphene powder loaded with Pt precursor is incubated in the oven at 100 °C overnight, and then treated in H_2 at 300 °C for 2 h. The homogenous dispersion of the catalyst particles on the surface of the graphene layer is shown in Fig. 2(d) [33].

3. Nanocatalysts for PEM fuel cells

Investigations on materials which can electro-catalyze the ORR is a key topic in the field of fuel cell research. In particular, the performance of a low temperature PEM fuel cell is limited due to the sluggish ORR on Pt [34]. To improve the catalytic activity in PEM fuel cells, transition metals like Fe, Co, and Ni are alloyed with Pt. The high cost of platinum is a major concern for the mass production of PEM fuel cells, which are commonly used to power light duty vehicles [35]. Different methods have been adopted to reduce the Pt loadings in PEM fuel cells and at the same time increase the power density. Also, several non-platinum catalysts have recently been synthesized to reduce the cost of the fuel cells. These noble and non-noble metal catalysts used in PEM fuel cells are described below.

3.1. Noble metal nanocatalysts

In the early 1990s, binary Pt alloy systems such as PtNi, PtCo and PtCr were investigated at Texas A&M [36]. In this work, 20 wt% Pt on Vulcan carbon was alloyed with different metals at 900 °C. The test results showed 20–30 mV activity gains over Pt/C. The highest activity was recorded for a PtCr/C catalyst. Activation energies for Pt and Pt alloy catalysts were found to be comparable. Several other Pt-based binary alloy catalysts such as PtFe, PtMn and PtTi (with Pt:M = 50:50) on Pt-alloy/Vulcan support were investigated and 25% activity gains for PtTi, PtMn and PtFe were observed in comparison to the Pt/C baseline catalyst.

Due to the limited supply and high cost of Pt, reducing the Pt loading is a key requirement in the R&D of fuel cells. Several methods have been adopted to synthesize low Pt loading catalysts for PEM fuel cells. These are explained in Section 4. The US Department of Energy has set a 0.05 mg cm^{-2} Pt loading or even less requirement for 50 kW PEM fuel cell stacks [37]. Several works have been reported with different synthesis methods to

reduce Pt loadings. In 2010, a solution phase synthesis method was studied by Li *et al.* [38] to prepare a carbon supported Pt-Co alloy catalyst. In this work, organic precursors of Pt acetylacetonate and Co acetylacetonate were reduced in a high boiling point solvent of octyl ether in the presence of oleic acid and oleylamine to produce fine Pt-Co nanoparticles, which were subsequently deposited on a carbon support to obtain Pt-Co/C catalysts. Fuel cell tests showed that the heat-treated Pt-Co/C catalyst has higher activity towards the ORR than Pt/C at 0.9 V operating voltage. This was attributed to the smaller particle size and reduced lattice parameter.

Pt electrocatalysts supported on functionalized ordered mesoporous carbon (CMK-3) have been tested by Calvillo *et al.* [39] for low temperature PEM fuel cell applications. Pt/CMK-3 showed a better electrocatalytic performance than commercial Pt/C black (E-Tek), possibly due to effective hydrogen diffusion to the active catalyst sites through the ordered porous structure of the support.

Zhu *et al.* [40] studied a Cu@Pt/C core-shell nanocatalyst synthesized by a two-step reduction method. In this core-shell structure, the active metal was distributed only on the surface of the other transition metal which led to increased Pt utilization even with reduced Pt loading. Electrocatalytic activity measured by CV (cyclic voltammetry) showed a higher value for this core-shell structure compared to a regular Pt/C catalyst with same amount of Pt. Zhuang *et al.* [41] have synthesized and studied carbon supported Pt-Cu catalyst (Pt-Cu/C) with surface enriched Pt. The results of their electrochemical testing showed 3.7 times higher Pt mass activity for Pt-Cu/C for the ORR as compared to a commercial Pt/C catalyst. According to their report, this increased ORR activity of Pt-Cu/C was due to the reduction in surface blocking of oxygenated species caused by the moderated electronic properties of the surface Pt atoms. Moreira *et al.* [42] have synthesized a catalyst based on Pd. They prepared Pd/C and Pd/Vulcan catalysts using an impregnation method using Pd (II) acetyl acetonate dissolved in acetone. The fuel cell test showed that the Pd/Vulcan performed better than Pd/C. Bing *et al.* [43] synthesized carbon supported Ir-V nanocatalysts using IrCl_3 and NH_4VO_3 precursors. They found that the pH value for the synthesis of catalysts affected the catalytic performance and the maximum performance was reported for a loading of 0.4 mg cm^{-2} 40% Ir-10% V/C catalyst synthesized at pH 12. This gave a power density of 1008 mW cm^{-2} at 0.6 V and 70 °C. This is 50% higher than the commercial Pt/C catalyst.

3.2. Non-noble metal nanocatalysts

Due to the low availability and high cost of Pt, several other nanocatalysts based on non-noble metals were synthesized and tested in the recent past. Instead of using a minimized amount of an expensive catalyst like Pt, using a larger amount of a very cheap catalyst can have several advantages, even if it is less active [35]. Two main advantages are the reduction of cost and less impact on fuel cell performance with time. Some important non-noble metal catalyst works in the literature are summarized below. Further details on these non-noble PEMFC cata-

lysts are given elsewhere [35].

Zhang *et al.* [44] have synthesized a non-precious metal FeCoTETA/C catalyst by chelating Fe and Co with triethylenetetramine (TETA) in ethanol followed by pyrolyzing in an Ar atmosphere. TETA is a simple and cheap ligand. The electrochemical testing showed better ORR activity compared to Co-TETA/C.

4. Noble metal nanocatalyst synthesis for low temperature fuel cells

Because of the high cost and low availability of Pt, it is crucial to develop a cost-effective nanocatalyst synthetic technique that reduces Pt content but maintains its high electrochemically active surface area. There are two general techniques to prepare Pt and its associated catalysts on the nano-scale. Physical methods, such as plasma sputter, laser ablation or metal organic CVD benefit from the well-controlled metal deposition and growth environment. However, these techniques suffer from the high cost of the operating instruments, time-consuming procedure and challenge to scale up the process with high catalyst yields. Chemical methods such as colloidal, impregnation or microemulsion methods create Pt nanoparticles that are well disseminated on the advanced catalyst support structure in a simple and versatile manner.

There are numerous studies investigating the mechanism of nanoparticle growth, which starts with the nucleation stage and forms solid seeds [45–47]. To stabilize the particle size, the seeds should grow to a critical size where the volume to surface ratio is high enough and the Wulff Theorem under thermodynamic equilibrium conditions dominates the particle shape [45]. Pt has a face centered cubic (FCC) structure with a truncated octahedron equilibrium shape. The particles start growing in size after the solid seeds are formed and the process is due to seed collision by Brownian agitation and Ostwald ripening [46]. The following sub-sections discuss the various synthesis methods.

4.1. Chemical precipitation method

The chemical precipitation synthesis method has been widely used due to its simplicity. The combination of a reducing agent with the precursor solution forms the Pt nanoparticles. By controlling the process conditions (temperature, solution pH, ratio of Pt ion to reduction agent, reaction time and sonication frequency/magnetic stirring rate), the metal particle size can be manipulated. For example, alkaline solutions such as NaOH, Na₂CO₃ or Li₂CO₃ are used to adjust the pH value in the aqueous mixture of the Pt salts (H₂PtCl₆). Reetz *et al.* [47] reported PtO_x precipitation and used catalyst supports as the stabilizer to immobilize PtO_x according to the chemical reaction:

Shen *et al.* [48] studied the effect of pH on bridging PtCl₄²⁻ on amine functionalized multi-walled carbon nanotubes (NH₂-MWCNTs). After dispersing NH₂-MWCNTs in an aqueous solution and adjusting the pH to 3.5 with hydrochloric acid, K₂PtCl₄

was added and kept stirring overnight. It is reported that PtCl₄²⁻ adsorbed on the MWCNTs, and the reaction product was collected with a nylon membrane filter followed by a heat treatment with H₂ gas reduction at 300–600 °C. The effect of furnace temperature on catalyst particle growth was not substantial (2.1 nm at 300 °C and 2.6 nm at 600 °C), as shown in Fig. 3 [49]. One of the major drawbacks of the chemical reduction method is the non-uniformity of the nanoparticles (shape and size) due to the sensitivity of particle growth to environmental conditions.

4.2. Colloidal synthesis method

After preparing a Pt salt solution, a reducing agent (e.g. sodium borohydride) and a capping agent (surfactant) are added. The capping agent allows for particle size control and prevents the agglomeration of the catalyst. Bönemann *et al.* [50] applied tetraalkylammonium triethylborohydride (N(alk)₄⁺(B(et)₃H)⁻) as a reducing agent to reduce an anhydrous PtCl₂ platinum salt solution. Reducing agent droplets were added to the mixture and the Pt²⁺ ion reduction reaction occurs based on the chemical reaction

The tetraalkyl chloride surfactant suppresses Pt particle growth in the colloidal solution. Fig. 4(a) [51] shows a schematic of Pt nanoparticles protected by the surfactant chains and the TEM image of the Pt[N(octyl)₄Cl]₂ colloid precursor shown in Fig. 4(b) [51] confirmed the effect of the surfactant on Pt particle size control and the homogenous dispersion. The catalyst support substrate can be added to the colloid solution and the surfactant is removed by calcination of the remaining powder at 300 °C in air [52]. The catalyst powder was washed

Fig. 3. HRTEM images of Pt/MWCNTs formed by a heat treatment of PtCl₄²⁻/MWCNTs in H₂ atmosphere at 300 (a), 400 (b), 500 (c), and 600 °C (d) (Reproduced with permission from Ref. [49]).

Fig. 4. (a) Schematic of a platinum particle protected by tetraalkyl chloride surfactant chains; (b) TEM image of the $\text{Pt}[\text{N}(\text{octyl})_4\text{Cl}]_2$ colloid precursor (Reproduced with permission from Ref. [51]).

with ultrapure water in order to remove impurities (e.g., chlorides, bromides). To further control the Pt crystalline structure and reduce the fusion rate of the solid seeds to avoid agglomeration, organic co-solvents are introduced as the environment for the Pt reduction reaction. Our research group used tetraoctylammonium bromide [TOAB, $\text{N}(\text{C}_8\text{H}_{17})_4\text{Br}$] to extract Pt^{2+} from aqueous chloroplatinic acid into the non-aqueous medium [53]. After preparing Pt-thiol ligands by introducing dodecanethiol (DDT) to the organic mixture, functionalized MWCNTs were added and the Pt-thiol ligands self-assemble on the surface of the MWCNTs. The Pt reduction reaction follows after introducing sodium formate, which is a milder reducing agent. Fig. 5 [53] illustrates the scheme of these steps. The surfactant was further removed at 500 °C for 30 min. Bimetallic and other colloidal catalyst alloys can be prepared by co-reduction using similar methods. The colloidal synthetic techniques have the benefits of a well-controlled Pt nanoparticle size and crystalline structure, and these methods also give a stable colloidal solution that last for several months without any decantation of the platinum particles. However, this technique requires additional steps to remove the capping agent (surfactant) and ensure the purity of the Pt nanoparticles.

4.3. Sol-gel synthesis method

The sol-gel technique starts with the formation of a liquid solution with suspended particles (a sol) that is aged and dried

Fig. 5. Schematic of Pt/MWCNT nanocatalyst synthesis via two phase transfer and a self-assembled monolayer (Reproduced with permission from Ref. [53]).

to form a semi-solid suspension of particles in a liquid (a gel). This is followed by calcination. A mesoporous solid or powder is the final product. Generally, there are four distinct steps in the sol-gel technique: (1) gel formation, (2) aging to allow fine-tuning of gel properties, (3) gel solvent removal and (4) calcination. The pore size distribution and volume are controlled during the aging and calcination stages by adjusting the experimental parameters (reaction time, temperature, heating rate and liquid composition). Prefabricated nanoparticles can be incorporated into the mesoporous solids by adding these particles into the sol-gel mixture and metal salts can be added during the gel formation or after the formation of the mesoporous structure [54]. Liu *et al.* [55] prepared carbon xerogels (CX) by the resorcinol-formaldehyde sol-gel method and Pt catalyst was precipitated onto the carbon powder. The Pt/CX was filtered and thoroughly washed with DI water, followed by 100 °C vacuum drying. Fig. 6 shows the dispersion of the Pt nanoparticles on CX and the Vulcan XC-72R carbon black support. A major disadvantage associated with this technique is the burning of the catalytic nanoparticles in the structure or pores, which may make them inaccessible to reactants and reduce catalyst utilization.

4.4. Impregnation method

Impregnation is one of the widely used methods to prepare metal catalyst particles on large surface area carbon supports. Chloride salts are commonly used as the precursor for impregnation, which is followed by a reduction stage with reducing agents (such as $\text{Na}_2\text{S}_2\text{O}_3$, NaBH_4 , N_2H_4 , formic acid and H_2 gas phase). In this technique, the Pt precursor salt and reducing agent are directly mixed into the aqueous solvent, which avoids the use of organic solvents. However, Pt particles can easily agglomerate in an aqueous solvent and the high surface tension of the liquid solution can cause fragile supports (e.g., aerogels) to collapse [56]. Fig. 7 demonstrates the schematic of using a super critical fluid (SCF) as processing solvent to synthesize supported nanoparticles via deposition or impregnation [56].

4.5. Microemulsion method

Most metal precursors are inorganic salts and are soluble in water. The reduction of the particle growth rate and particle shape control is achieved by mixing a small part of the aqueous metal salt into an organic solvent to form a water-in-oil struc-

Fig. 6. TEM image of Pt/CX (a) and Pt/Vulcan XC-72R carbon black (b) (Reproduced with permission from Ref. [55]).

Fig. 7. Schematic representation of supported nanoparticle synthesis using a super critical fluid as processing solvent via deposition or impregnation routes (Reproduced with permission from Ref. [56]).

ture (microemulsion). The inherent hydrophobicity of the organic chain acts as the protection chain to prevent particle agglomeration when the reducing agent is added. The micelle-encapsulated nanoparticle defines the crystalline structure of the metal catalyst. The size of the water-in-oil droplets is controlled by the amount of water content and surfactant chain length. Lin *et al.* [57] created micelle-encapsulated MWCNTs with sodium dodecyl sulfate (SDS) as the catalyst support, shown in Fig. 8. The Pt/MWCNTs with 4 nm Pt particle size showed superior performance stability with a power density degradation of only 30% after completing 1500 potential cycles between 0.1 to 1.2 V, as compared to 70% power reduction with a commercial Pt/C catalyst fabrication by microemulsion technique. However, due to the use of expensive surfactants and organic solvents, the process is expensive, and also most of these solvents are environmentally not benign.

4.6. Microwave-assisted polyol method

The polyol method is very promising for the preparation of Pt nanoparticles. In this method, nanoparticles are synthesized by the reduction of metal salts in ethylene glycol [58,59]. The main advantage is that the reduction can be performed without the addition of a surfactant, and also the solvent used (ethylene glycol) is inexpensive. Conventionally, the reduction reaction is activated by temperature by heating the reaction mixture at temperatures higher than 120 °C. To synthesize a Pt/C catalyst,

Fig. 8. Schematic representation of SDS-MWCNT micelles (Reproduced with permission from Ref. [57]).

Liu *et al.* [60] refluxed a polyol solution with the metal salt at 120–170 °C and decomposed ethylene glycol to reduce the metal ions. Recently, Lebegue *et al.* [61] developed a microwave-assisted method to synthesize a well-dispersed Pt/C catalyst with a high electrochemical surface area. This method of synthesis using microwave impulsion resulted in a highly active Pt/C catalyst for the ORR. Microwave assisted heating led to improved monodispersity and morphological control compared to samples heated conventionally. Also, the synthesis of catalysts with very small (< 3 nm) nanoparticles is possible with short pulses of microwave irradiation to induce nucleation.

4.7. Other synthesis methods

Many other techniques such as electrodeposition, spray pyrolysis and vapor deposition have also been reported for synthesizing nanocatalysts. Their benefits and drawbacks are consolidated in Table 1. Among these, spray pyrolysis is the only easy method for scale-up. The readers are advised to refer to the references for more details [62–68].

5. Nanocatalysts for alkaline fuel cell applications

5.1. Noble metal nanocatalysts for alkaline fuel cells

In order to ensure the direct four electron transfer reaction

Table 1

Catalyst synthesis techniques: electrodeposition, spray pyrolysis and vapor deposition.

Technique	Benefits	Drawbacks
Electrodeposition	Pt nanoparticle can be directly deposited on the substrates (e.g., GDL) and control 2D or 3D growth with underpotential deposition and current pulse deposition	Challenging to control the charging voltage. High volume of Pt salts is used in solution than what is actually deposited on the substrates
Spray pyrolysis	Easy to dope films and from alloy; no requirements for high purity substrate and vacuum. This method is also less sensitive to operating environments. The major advantage is the simplicity in scaling up	Stable agents like polyethylene glycol (PEG) is required to prevent particle agglomeration during solvent evaporation stage
Vapor deposition	Well controlled alloy composition in source precursors. The catalyst directly forms and deposits on the electrode substrates (GDL)	Pt or associated catalyst particle is affected by sublimation temperature, vapor pressure, and mass transfer kinetics. The precursors are also highly toxic and difficult to work with

for the cathodic reduction of oxygen, the focus was mainly on developing Pt or Pt-alloy electrocatalysts in alkaline fuel cells [69]. It is worth noting that the PtAu/C ($1.6 \text{ mW cm}^{-2} \text{ mg}^{-1}$) is more active than the PtBi/C ($1.25 \text{ mW cm}^{-2} \text{ mg}^{-1}$) catalyst for glucose (0.3 mol/L) electro-oxidation in alkaline medium. In a recent study, Pt crystallites with an average particle size of 50–100 nm were deposited by the galvanic displacement of the Ni layer. Electrodes containing Pt loading of $16.5 \mu\text{g cm}^{-2}$ were found to be more active than Pt toward the electro-oxidation of borohydride, methanol and ethanol in the alkaline media [70]. Extensive research was carried out for improving the catalytic activity by using coconut shell carbon supported bimetallic electrocatalysts by A.K. Shukla's group in the 1980s and 1990s [71]. Zhiani *et al.* [72] have consolidated the performance of various noble metal catalysts published in the literature under different conditions in alkaline media. It is interesting to note that the Tafel slope values are in the range of 50 to 120 mV per decade for oxygen reduction. A very recent publication by Lai *et al.* [73] dealt with synthesizing Ag nanoparticles (2–10 nm) on carbon nanofibers for oxygen reduction in 0.1 mol/L KOH aqueous solution using the rotating disk/rotating ring disk electrode (RDE/RRDE) technique. The electrocatalytic results revealed that all the Ag/CNF systems exhibited high activity in the ORR matching the theoretical four electron pathway, and the mass activity (119 mA mg^{-1}), exceeded that of the commercial Pt/C catalyst (98 mA mg^{-1}).

5.2. Non-noble metal nanocatalysts for alkaline fuel cells

Research activity for non-noble metal catalysts has increased due to the limited availability and high cost of Pt for use as the catalyst for large scale fuel cell applications. Transition metal-nitrogen containing MN_4 macrocycles, particularly metallophthalocyanines and metalloporphyrins, are the most promising non-noble metal catalysts. They have been investigated intensively since the pioneering research work of Jasinski [74]. These macrocyclic compounds are especially interesting because of their cost advantage compared to platinum-based nanocatalysts. Since the work of Jasinski in the mid-60s, several review articles on O_2 reduction using MN_4 macrocycle-based electrodes have been published [75,76]. Also, the ability of some MN_4 macrocycles to reduce O_2 via the four electron pathway has led to enormous research activity on these catalysts [77–79].

Even with numerous publications, it is difficult to make definite conclusions about the exact catalytic mechanism on these catalysts. Similarly, information about particular MN_4 macrocyclic complexes that reduce oxygen via the direct four electron pathway or producing H_2O_2 can be contradictory. In any event, the literature makes it possible to choose catalyst materials for different environments and applications. In several cases, the central metal ion has been considered as the driving force for the ORR and the mechanism of the ORR depends on the nature of the metal center in these complexes. For monomeric iron and manganese phthalocyanines, it has been found that at low overpotentials, the four electron reduction is favored while many other MN_4 -macrocycles with a different central metal ion

(Ni, Co and Cu) promote oxygen reduction mostly via the two electron pathway, and therefore, they are not suitable as the fuel cell cathode catalyst [80]. In contrast to most simple monomeric MN_4 macrocycles, the polymerized forms of these complexes can catalyze the ORR in a different way from their monomeric structure. For example, polymerized Fe phthalocyanines only promote the two electron reduction whereas its monomer catalyzed the ORR via the four electron pathway to water as mentioned above.

Opposite effects have been recognized for Co phthalocyanine and its polymeric form [81,82]. There are, of course, always exceptions in the research results of different scientific working groups, which is caused by the so named “co-facial MN_4 macrocycle” effect, where the molecular arrangement of the metal complex refers to the situation in which the metal ions of the two independent macrocycles exist face-to-face with each other due to π - π stacking or by providing special synthetic procedures [83]. For this case, two metal central ions in the MN_4 macrocycles have been proposed to act in concert to achieve the electro-reduction of oxygen via the four-electron pathway [84]. Some authors have proposed that the splitting of the $\text{O}=\text{O}$ bond takes place because of the formation of a peroxo dimer on the two metal active sites (so called dual-site mechanism), which is possible in the case of polymerized metallo-macrocycles or the formation of cofacial MN_4 macrocycles. Other authors have suggested that MN_4 macrocycles will catalyze the ORR via the dual-site mechanism where oxygen coordinates to the metal active center and to the N atom on the macrocyclic ligand [85]. This leads to the importance of nitrogen ligands. There is a general agreement in the literature that besides the transition metal, the nitrogen ligands in the MN_4 macrocycle play an important role in their stability and activity, although the active site and exact mechanism are uncertain [86]. However, the number of simple MN_4 -metallomacrocyclic complexes for direct four electron ORR is limited.

5.2.1. Metallomacrocycles supported on carbon nanomaterials

To employ MN_4 -macrocycles on fuel cell electrodes, they can be supported on carbon nanotubes or graphene. The modification of carbon materials with MN_4 macrocycles enables the transformation of two-electron reduction metallomacrocyclic complexes into hybrid materials with the capability to reduce oxygen to water via the direct four electron transfer pathway [87–89]. Tammeveski's group has recently reported that iron porphyrine and cobalt phthalocyanine supported on MWCNTs afforded the electro-reduction of oxygen via direct four-electron transfer in 0.1 mol/L KOH solution [90]. Catalyst supports including carbon nanotubes, carbon nanofibers, graphene, Ketjen Black and Vulcan carbon have been employed for different MN_4 macrocyclic complexes in numerous studies in the field of ORR electrocatalysis [88,91–93].

5.2.2. Metallomacrocycles supported on carbon hybrid materials

MN_4 macrocycle materials in tetrahydrofuran (THF) and their impregnation on CNTs ($\text{MN}_4\text{:CNT} = 2\text{:}1$) are carried out by ultrasonication to form a homogeneous dispersion. Then, the

Fig. 9. Chemical structure of MN₄ and schematic representation of the hybrid catalysts (Reproduced with permission from Ref. [89]).

THF solvent is evaporated under a nitrogen stream. A schematic representation of some hybrid catalysts systems is shown in Fig. 9 [89]. To prepare the dispersion for rotating disc electrode studies, the catalyst ink solutions are prepared by sonicating 3 mg of hybrid catalyst powder in 0.75 mL of ethanol and 75 μ L of Nafion or Tokuyama AS-4 ionomer solution (0.5 wt% in alcohol) [89]. The stability tests have shown that long term stability is a major problem in using MN₄ macrocycles in fuel cells. It has been found that pyrolysis in an inert atmosphere increased both the catalytic activity and stability of the metallomacrocyclic catalyst materials [94]. Since the pioneering study of Jahnke *et al.* [95], who reported the effect of the heat treatment, numerous research efforts have been made to find and optimize the conditions of pyrolysis as well as to clarify the exact structure of the catalytic center with the electrocatalytic activity for the ORR [96]. The choice of temperature for the heat treatment depends on the specific MN₄-macrocycle. Temperatures used for the pyrolysis of MN₄-macrocycles in an inert atmosphere vary from 500 to 1000 $^{\circ}$ C, but it has been found that most macrocycles achieve the highest activity at

temperatures from 500 to 800 $^{\circ}$ C. Typical RDE (Rotating Disk Electrode) polarization curves of heat-treated MN₄-macrocycle-modified carbon catalysts are presented in Fig. 10 [97].

5.2.3. Alkaline fuel cell performance with metal phthalocyanines

We have developed Co- and Fe-phthalocyanines (CoPc and FePc) based-cathodes and evaluated the alkaline fuel cell using a Tokuyama membrane (# A201). As can be seen from the Fig. 11 [98], the Tanaka Pt/C catalyst showed the highest performance (~ 120 mW cm⁻²). CoPc/MWCNT performed almost (power density 100 mW cm⁻²) as well as the E-TEK catalyst-based MEAs. However, the FePc/MWCNTs based MEA only showed about 60 mW cm⁻² under identical operating conditions.

6. Nanocatalyst characterization techniques

The characterization of nanocatalysts is carried out both under ex situ as well as in situ conditions. The following sections describe typical characterization methods like electron

Fig. 10. Rotating disk electrode data at 1900 rpm for the oxygen reduction reaction for cobalt phthalocyanine/MWCNT annealed at 400 and 800 $^{\circ}$ C in O₂-saturated 0.1 mol/L KOH (Reproduced with permission from Ref. [97]).

Fig. 11. Fuel cell performance of MEAs with various metallomacrocycle/MWCNT catalysts along with commercial catalysts based cathodes using the Tokuyama's A201 anion exchange membrane (Reproduced with permission from Ref. [98]).

microscopy, XRD, BET method, CV, and fuel cell performance.

6.1. Catalyst morphology analysis by electron microscopy

SEM images show topographical and elemental information due to their superb resolution. They help to determine the chemical composition and structural changes of the fuel cell material under different operating conditions. The SEM primary imaging method operates by the collection of the secondary electrons released by the sample. The SEM scans its electron beam line by line over the sample instead of forming a real image. The TEM has the advantage of increased magnification and resolution, and it can provide the “inside” image of the sample rather than the surface. TEM builds an image by way of differential contrast and it forms black and white images. TEM has a spatial resolution on the order of a few Angstroms, and it is mainly used to analyze the structure, composition and properties of a specimen.

6.2. Catalyst composition and phase analysis

X-ray diffraction (XRD) is a non-destructive technique to characterize materials in terms of chemical composition and crystallographic structure. X-ray diffraction takes place from lattice planes based on Bragg's Law. By scanning a range of angles of reflection, a pattern of peaks with different intensities is identified. Planes with high electron density have strong intensity and reflect strongly. Fig. 12 shows the XRD pattern of a graphitic carbon nanofiber (GCNF) supported Pt-Ru alloy synthesized by Steigerwalt *et al.* [99]. It shows the composite pattern of the catalyst's Pt-Ru peaks consistent with the FCC structure (111). Electron diffraction (ED) is a collective elastic scattering phenomenon where the electrons are scattered by atoms in a regular array in a crystal. When an incoming electron wave interacts with the atoms, secondary waves are generated and interfere with each other and they form diffraction patterns. ED has the benefit of the strong interaction of electrons with the sample because the electrons are scattered by the positive potential inside the electron cloud, whereas X-rays interact with the electron cloud. ED is a valuable tool in crys-

Fig. 12. XRD scan of a Pt-Ru/graphitic carbon nanofiber composition (Reproduced with permission from Ref. [99]).

tallography and it can provide information about the crystal symmetry of active catalytic components. Fig. 13 shows the TEM bright field images and electron diffraction patterns of electrodeposited Ni and Co nanowires in nanochannel membrane filters from Ohgai *et al.* [100]. According to the TEM bright field images, the shape of the nanowires was almost cylindrical and the electron diffraction patterns are composed of spots, which suggest that the nanowire consists of a crystalline phase with a preferential orientation.

6.3. Measurements of the catalyst physical surface area and electrochemical active surface area

In 1938, Brunauer, Emmett, and Teller [101] developed the BET method to estimate the catalyst surface area. The BET method is based on the surface area of adsorbed gas molecules. By measuring the amount of gas adsorbed by the sample at equilibrium, the surface area of the sample can be determined. N₂ is mostly used to measure the BET surface. Ar or Kr may also be used if the surface area is small. The electrochemical active surface area (ESA) of a Pt-associated catalyst can be measured by the electrochemical hydrogen adsorption/desorption approach. The CV method is based on the formation of a hydrogen monolayer electrochemically adsorbed on the catalyst surface [102]. Fig. 14 [51] shows a typical CV of Pt/C in H₂SO₄ solution. Two well-resolved peaks on the cathodic sweep in the low potential area (region A) corresponded to hydrogen deposition on the electrode surface. The electrochemical active surface area

Fig. 13. TEM bright field images and electron diffraction patterns of Ni ((a) and (c) respectively) and Co ((b) and (d) respectively) nanowires electrodeposited in nanochannel membrane filters (Reproduced with permission from Ref. [100]).

Fig. 14. Electrochemical characterization of a Pt(40 wt%)/Vulcan XC-72 catalyst in N_2 -saturated 0.5 mol/L H_2SO_4 electrolyte with a scan rate of 20 mV s^{-1} (Reproduced with permission from Ref. [51]).

S_{ESA} ($m^2\text{ g}^{-1}$) can be estimated by the equation

$$S_{ESA} = Q(\mu\text{C cm}^{-2}) / [\text{Catalyst loading} (\text{mg cm}^{-2}) \cdot 210(\mu\text{C cm}^{-2})] \quad (3)$$

where S_{ESA} is the electrochemical surface area of catalyst, Q is the charge density and 210 is a global charge of the adsorption of a hydrogen monolayer on a polycrystalline Pt surface. It is worthwhile to note that the hydrogen peaks can be used not only to measure the active surface area of a catalyst but also as an indicator to qualitatively estimate the purity of the Pt/C catalyst.

6.4. Catalyst surface and composition

XPS employs X-ray tubes with aluminum or magnesium anodes. It can be used to study the electrons in both valence band and core states because the X-rays have sufficient energy to ionize the core levels in all elements. XPS is used to identify the atoms at the surface by comparing the observed lines with either calculated core level binding energy or experimental spec-

tra from standards. XPS analysis can provide information about the elemental surface composition of the catalyst, the oxidation state of an atom, the chemical environment, and so forth. Fig. 15 shows the XPS spectra of a Pt-associated catalyst alloy and core-shell catalysts reported by Gao *et al.* [103]. The metal Pt $4f_{7/2}$ lines for $Ru@Pt_1Pd_1/C$, $Ru@Pt_2Pd_1/C$ and $Ru@Pt_1Pd_2/C$ occur at 71.26, 71.34, and 71.14 eV, respectively, whereas the metal Pt $4f_{5/2}$ lines are at 74.55, 74.65, and 74.49 eV respectively. The Pt binding energies of the $Ru@Pt_xPd_y/C$ core-shell catalysts are higher than those of Pt_2Pd_1/C , indicating an interaction between Ru and Pt_xPd_y . The percentages of Pt in the zero valence state for $Ru@Pt_1Pd_2/C$, $Ru@Pt_1Pd_1/C$ and $Ru@Pt_2Pd_1/C$ are higher than that in Pt_2Pd_1/C (71.2%), and are 74.6%, 75.8%, and 80.4%, respectively, and increased with the increase of Pt content.

Electrons scattered within the excitation volume of a specimen deposit energy in many atoms and the atom releases distinct quantum energy when they return to the ground state. If the excited atom ejects an inner-shell electron, an outer-shell electron fills that vacancy and emits an X-ray having energy equal to the difference between the two electron shells. Detection of the X-rays emitted by the specimen during the electron-beam excitation is known as the energy dispersive spectroscopy (EDS). EDS is generally associated with SEM or TEM analysis and provides further information about the chemical composition for selected regions of the surface. The EDS technique has been extensively used in metal alloy catalyst characterization to determine the relative amounts of individual metal species in the catalyst. Fig. 16 shows a broad area EDS spectrum of a Pt-Ru alloy catalyst deposited on a graphitic carbon nanofiber [99]. The relative intensity of the appropriate pairs of Pt and Ru emissions give the Pt/Ru stoichiometry and atomic ratio. The Cu emission was attributed to the copper grid of the sample holder and the Si emission was derived from trace amounts of the carbon nanofiber growth support.

Fig. 15. XPS spectra of Pt (a–d), Pd (e), and Ru (f) nanocatalysts (Reproduced with permission from Ref. [103]).

Fig. 16. Broad area EDS spectrum of Pt-Ru/graphitic carbon nanofiber (Reproduced with permission from Ref. [99]).

6.5. Half-cell electrode performance

Even though *ex situ* methods are very important process control tools, *in situ* methods are needed for understanding the nanocatalysts under actual fuel cell operating conditions in acidic and alkaline media. Catalyst properties such as reduction current by the rotating disk electrode, electrochemically active surface area by cyclic voltammetry, structural deformation and particle size growth, electrochemical impedance, oxidation and/or dissolution and durability (accelerated cycling) by voltage cycling and also actual single electrode performance (both for fuel oxidation and oxidant reduction) can be determined by *in situ* methods. These characterization techniques also focus on measuring the effect of the other components of the fuel cell on the catalysts. The *in situ* characterization of the nanocatalysts can be conducted by assembling and studying the three electrode half cells or single cell fuel cells. Galvanostatic or potentiostatic polarization methods can be used to characterize nanocatalysts at various RH conditions and temperatures using dissolved oxygen in the electrolyte with oxygen blanket in half cells in acidic or alkaline media. In addition, the following *in situ* techniques can be used to characterize the nanoelectrocatalysts.

7. Electrochemical performance and durability of nano-electrocatalysts

Nano-electrocatalysts are evaluated both by *ex situ* and *in situ* methods for performance as well as durability. The following sub-sections describe nanocatalyst characterization in the MEA for fuel cell performance and durability by accelerated methods.

7.1. Fuel cell performance of nano-electrocatalysts

Polarization curves are one of the most common methods to measure the performance of a PEMFC. It is a non-destructive test which generates a chart that plots the relationship between current density and voltage. This test can be very effective for assessing the real world performance of a fully assembled system as it includes the interactions between individual components. Unfortunately, this also means that the reduced perfor-

mance of a cell cannot be clearly attributed to a particular failing component. Polarization curves can be compared through thousands of cycles and a simple quantitative measure of performance degradation over time can be made [104].

As described in section 6.3, the electrochemically active surface area (ESA) and Pt loading are two other important performance measures. Increasing the ESA improves performance by creating a larger surface area where chemical reactions can take place. The Pt loading refers to the weight as well as the distribution and is usually expressed in terms of $\mu\text{g cm}^{-2}$. Higher Pt loadings with the same catalyst material will create a thicker layer of the porous catalyst material and will thus increase the ESA, which will increase the performance in a fuel cell. Pt is a rare and expensive metal, so it is important to minimize the amount of Pt required. Reduction of the Pt loading while maintaining the same performance is an area of active research.

7.2. Durability evaluation of nano-electrocatalysts

Durability in PEMFCs is usually an expression of the ability to maintain performance over time. A fuel cell that is highly durable will be able to maintain initial performance characteristics after long periods of intermittent or continuous use. Durability can also refer to the ability of the system to maintain performance after uncommon events such as mechanical shock, extreme high or low temperature, or varied humidity conditions. Current US Department of Energy targets for transportation applications include 5000 h of operation, which is the equivalent of 150000 miles travelled. There are several known degradation mechanisms of nanocatalysts, which are actively researched. The dominant form of degradation in the catalyst layer is platinum particle dissolution. Many deposition techniques rely on suspending the Pt particles in an ionomer solution, which is then deposited uniformly on the membrane. Dissolution causes Pt particles to diffuse, through a mechanism known as Ostwald ripening, and form agglomerates with neighboring particles (Fig. 17). These particles have also been observed to migrate into the membrane to form a band of Pt particles. These processes cause a reduction in the electrochemically active surface area and gradually reduce the performance of a PEMFC [105].

Fig. 17. Schematic illustration of Pt nanoparticle growth through (a) Ostwald ripening and (b) particle agglomeration (Reproduced with permission from Ref. [105]).

Fig. 18. (a–c) Cyclic voltammograms of different Pt/MWCNT cathode materials and (d) the corresponding changes in the electrochemically active surface area with potential cycling (Reproduced with permission from Ref. [53]).

Other sources of performance loss include substrate degradation and adsorption of contaminants from external sources. Pt particles are dispersed on a highly porous carbon black or another material. This support material must be highly electronically conductive, maintain a high surface area, and be hydrophobic. Corrosion of the carbon substrate can lead to reduced conductivity. This is especially problematic in pure carbon substrates, which are susceptible to corrosion at the operating conditions typically found in PEMFCs. High temperatures increase the oxidation rate of the carbon support. The substrate can also be subjected to physical stresses during the freeze-thaw cycles. Adsorption of external contaminants such as carbon monoxide is particularly important when reformed hydrogen is used as the fuel [106]. Contamination can also come from the byproducts of corrosion in various other components of the fuel cell. There are several methods for measuring the degradation of the nanocatalyst. One of the most common methods is the use of CV. This method uses a potentiostat/galvanostat and a function generator to simulate load changing and generally scans from 1.0 to 0.4 V. These CV scans give a qualitative measurement of the ESA, which can be compared across cycles to give some insight into the nature of the changes within the cell such as corrosion or increasing particle size [104,107]. Fig. 18 [53] shows the CV data as well as the estimated ESA with cycle number for Pt/MWCNTs in PEMFCs.

Direct measurement of catalyst layer degradation can be performed using electron microscopy. Images produced either by SEM or TEM have high enough resolution to show platinum agglomeration. Particle size distributions can be generated from these images. The initial images can be compared to images taken thousands of cycles later and compared. Studies using this technique have shown that agglomeration and detachment are among the primary causes of catalyst degradation.

8. Conclusions

Electrocatalysts are the key in the performance, durability, reliability and cost that limit the commercial viability of fuel cells. This review brought together synthesis and characterization methods for nanocatalysts for proton exchange membrane fuel cells and alkaline membrane fuel cells. To improve catalyst utilization and reduce catalyst loading (and cost), various catalyst support materials are explored in the literature, but the commercial catalysts still employ Vulcan XC or another spherical carbon due to their simple synthesis process and relatively lower costs. Numerous synthesis methods for nanocatalyst preparation such as chemical, colloidal, sol-gel, impregnation, microemulsion methods, and electrodeposition, spray pyrolysis and vapor deposition are well documented in the literature. All the methods have advantages and disadvantages related to the performance and durability of the nanocatalysts. The review also discussed the durability evaluation of nanocatalysts as one of the reliable *in situ* accelerated test methods.

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Graphical Abstract

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Nano-electrocatalyst materials for low temperature fuel cells: A review

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Low temperature fuel cells have gained momentum for transportation and portable applications due to their higher power density and ability to start instantaneously. This review gave the current status of their nanocatalyst materials.

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