Mesoporous carbon for polymer electrolyte fuel cell electrodes

A.K. Sahu, P. Sridhar AND S. Pitchumani

Abstract | This article features the importance of mesoporous carbon as a constituent in the gas diffusion layer for easy reactant permeation and water removal in polymer electrolyte fuel cells. The utility of mesoporous carbon as catalyst support to enhance Pt utilization is also crucial in order to reduce Pt usage to meet both cost and Pt availability constraints. We attempt to provide an overview of the strategy and benefit of using mesoporous carbon to meet the specific requirements of emerging technological applications, such as fuel cells.

1. Introduction

Being energy efficient, environmentally benign and minimal noise, fuel cells are widely considered as 21st century energy-conversion devices for portable, mobile and stationary power applications as they generate electricity from hydrogen (H_2) and oxygen (O_2) exhausting only water[1]. Among various types of fuel cells, polymer electrolyte fuel cells (PEFCs) are the most promising power sources for a broad range of applications due to their quick start-up capability under ambient conditions. In recent years, although ground-breaking progress has been made for PEFCs in terms of membranes, bipolar-plate materials as well as the system design, a key performance limitation called the mass transport loss, originates from gas diffusion layer (GDL) owing to the blockage of available pore space by liquid water resulting flooding in the constituent components and limits reactant transport to active reaction sites in the electrode. The GDL, therefore, plays a crucial role in water management which dictates a delicate balance between membrane hydration and water removal from the catalyst layer (CL) and GDL especially when PEFCs is operating with hydrogen-air system at high current density region[1,2]. The surface area and pore size are central for optimal distribution of reactant gases and liquid water at the solid-liquid-gas interface to attain best performance of the PEFC. To address this issue, besides activated carbon, the other graphitic carbon nano-materials, such as carbon nanotubes, carbon nanofibers, graphitic porous carbon are the subject of continuing research and development[3–8]. Among several technical issues in PEFCs, yet another most important issue is the enhancement of catalytic activity of catalysts such as Pt on high surface area carbon support[9–14]. In this regard, a great deal of research effort has been devoted to the development of high performance catalysts, which include investigations of Pt based alloy compositions of electrocatalysts and optimization of particle size of catalysts[15]. In addition, considering the commercialization of fuel cell systems, lowering the amount of expensive catalysts by increasing the utilization of catalysts is an important issue. Nano structured high surface area graphitic carbon material has wide applications in adsorbents, catalyst supports, electrode materials, and energy storage media over amorphous carbon because of its well developed crystalline structure, high electronic conductivity, good thermal stability, and satisfactory oxidation resistance[13,16–25]. However, synthesis of graphitic carbon with high surface area has been a great challenge, and exploration of an economic method suitable for large-scale production is still an important issue. Although carbon nanotube (CNT)

CSIR–Central Electrochemical Research Institute (CECRI)—Madras Unit, CSIR Complex, Chennai 600113, India
spmanicecri@gmail.com

support materials offer both mechanical robustness and durability, the use of CNT is limited due to lack of control of the particle size to meet desired performance expectation of the PEFC[26–30]. To date, efforts in improving the PEFC performance have been focused on maximizing catalyst utilization by controlling particle size of the catalyst on the carbon support, dispersing the platinum nano particles on the support uniformly and enhancing proton transport using a polymer solution within the catalyst layer[31–33].

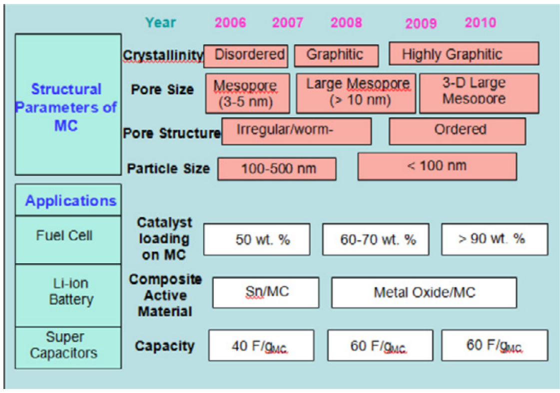
Great efforts have been made to develop new carbon nanomaterials with a higher surface area and/or a higher electrical conductivity other than carbon black and explore their feasibility as a catalyst support for fuel cells. Such materials with an amorphous framework include activated carbon, carbon microbeads, ordered nanoporous carbon arrays[34–36]. Those with a graphitic carbon framework include carbon nanotubes, carbon nanohorns, carbon nanofibers, carbon nanocages and graphitic porous carbon[37–41]. However, they still suffer from some deficiencies. Notably, the amorphous mesoporous carbon has a very high surface area ($\sim$500 m^2 g^{-1} or above) but low electrical conductivity, and the graphitic nanostructured carbon possesses high electrical conductivity but a low surface area ($\sim$ 300 m^2 g^{-1} or less). Additionally, most of these materials, especially those graphitic carbons, have limitations in terms of large-scale and economical production because of the harsh synthetic conditions used and low production yields. Moreover, microporous nature of aforementioned carbon restricts the optimal distribution of reactant at the GDL interfaces. Besides high surface area, distribution of micropores (pore size $<$2 nm) and mesopores (pore size 2–50 nm) in the carbon is central for optimal distribution of reactant gas and liquid water at the solid-liquid-gas interface of PEFCs. Ordered mesoporous materials have received enormous attention owing to their high surface area, regular frameworks, tunable pore sizes with narrow pore size distribution leading to multiple potential applications[42,43]. Mesoporous carbon (MC) is one of the most promising materials, possesses remarkable functional properties and excellent chemical/thermal stability, which makes it suitable for applications in catalysis,[44,45] adsorbents,[46] sensor,[47] electrode materials[48–51] and energy storage devices[52]. The technical evolution of MCs for energy related applications are summarized in Fig. 1. MC materials, comprising regular arrays of uniform mesopores are highly attractive from the viewpoint of pore structure and pore sizes that provide improved mass transport, electron transport and easy removal of product water from the PEFCs[53–55]. The present review is focused on recent advances of order mesoporous carbon (OMC) and its fuel cell applications both in GDL and CL. The various synthesis parameters and their impact on structural features of OMC are discussed, followed by a summary of recent progress in the synthesis of OMC relevant to fuel cell technology. Recent reports on the application of OMC for effective fuel cell catalysts are also discussed. Finally, a summary of this review and future perspectives on the application of OMC in energy conversion and storage devices are suggested.

2. Mesoporous carbon as gas-diffusion layer

Proper water management in PEFC is central to avoid cathode flooding by removing excess liquid water generated at the cathode and for easy access of reactant gases to the active catalyst layer[56]. The GDL typically has a dual-layer structure[57], the first layer is a fibrous macroporous carbon paper or carbon cloth that serves as a current collector-cum-physical support for the electrode. The second is a thin layer consisting of carbon black and a hydrophobic agent which helps easy gas diffusion to the active catalyst layer with proper water management depending on its structure[58–62]. Overall, GDL plays an important role in water management of a PEFC, which dictates a delicate balance between membrane hydration and water removal from the GDL[63–65]. In addition to various aforesaid physical parameters of the GDL, pore structure and pore size distribution are seminal for easy gas permeability and determine the limiting load current-density of the PEFCs, especially when air is used as oxidant[57]. Extensive studies have been conducted to investigate the effects of carbon types, such as Vulcan XC-72R, pearl black, acetylene black and ketjen black[66–68], PTFE content[69,70] and pore-forming agents[71,72] on PEFC performance. Jordan et al.[3] prepared the GDLs with different carbon blacks with varying porous structure and found that the acetylene black delivers a better PEFC performance compared to other types of carbon. This was attributed to higher pore volume and smaller pore size of acetylene black that facilitates gas diffusion and reduces the amount of water accumulation inside the GDLs.

Porous structures that can be of inorganic, organic, and inorganic-organic composite materials are of scientific and technological importance because of the ability of the pore wall to interact with atoms, ions, molecules to load or capture liquid and gas molecules, and solid particles. The tailorable pore size and pore wall make porous materials highly attractive in frontier research.

Figure 1: Technical evolution of mesoporous carbon for energy devices



In the past decade, significant breakthroughs in design and processing of novel porous materials for emerging applications, such as energy conversion and storage, environmentally friendly catalysis, sensors, drug delivery, medical diagnosis, and photonics are accomplished. The emergence of such new technological applications requires a higher level of control over the porous properties of porous structures[73]. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified into three categories, namely micropore, mesopore, and macropore with pore sizes less than 2 nm, between 2 and 50 nm, and larger than 50 nm, respectively. Since Kresege et al successfully synthesized mesoporous silica in 1992[74], the synthesis of MCs using this inorganic materials as a hard template has been described widely. The method has been proved to be effective for preparing MCs with large surface area, controlled pore structure with developed porosity. Ordered mesoporous carbon (OMC) materials with tunable pore sizes and pore structures prepared from hard template methods that include: (i) forming a composite by filling the nano-channels of hard template (usually SBA-15, MCM-48 and colloidal silica) with appropriate carbon precursors, (ii) carbonization of the composite at high temperature, and (iii) removal of templates with aqueous NaOH or HF[75–84]. Accordingly, the resultant porous carbon happens to be the structural replica of the hard template used[85–91]. In this process, an additional step is mandatory to prepare silica hard templates prior to the multistep template synthesis making it a long and complicated process[36]. Mesoporous carbon was also reported using surfactant-stabilized silica particles prepared from an aqueous Ludox HS-40 silica sol[92]. However, pores were not distributed in an orderly fashion and not interconnected to each other. As an alternative, many researchers have focused on synthesis of MC materials by direct one-step method without the hard template route[93] that can eliminate the preformed template and tedious infiltration steps. Although, these classes of MCs show some irregularly interconnected pores and relatively wider pore size distribution, their synthesis is simple and mesoporous structures can be controlled by varying the molar ratio of the respective precursors[94–99]. Amphiphilic triblock copolymers (PEO-PPO-PEO), which are commercially available as Pluronics or Synperonics, have been proven to be versatile and efficient structure directing agent for the fabrication of ordered mesoporous carbons[100,101]. Since the reactant distributions and proper water management in PEFC strongly depend on the porous structure of carbon materials in a GDL layer, it is of interest to learn about this behaviour as a function of pore structure. The nature and kind of structure directing agent plays a crucial role in tuning the geometry of pore structure while preparing the MCs. Synthesis of MC has been reported with a specific surface area of 370 m^2/g, pore diameter of 6.7 nm and pore volume of 0.45 cm^3/g by co-assembly of a tri-block copolymer, namely pluronic-F127, as a structure directing agent, and a mixture of phloroglucinol and formaldehyde as carbon precursor[101]. A peak power density of 0.53 W/cm^2 at a load current-density of 1.1 A/cm^2 is achieved for the PEFC employing electrodes with GDL of MC compared to the peak power density of 0.47 W/cm^2 at a load current-density of 0.93 A/cm^2 for the PEFC employing electrodes with GDL of commercial Vulcan XC-72R carbon, while operating at 70°C with H_2 and air feeds at atmospheric pressure. The mesoporous GDL with favourable surface area and pore size distribution helps ameliorating the liquid water flux through the GDL with minimum flooding and improves oxygen diffusion to the catalyst layer during the fuel cell operation.

3. Mesoporous carbon as catalyst support

State-of-the-art electro catalysts for PEFCs rely on large quantities of platinum to achieve acceptable performance. This presents a significant hurdle to market acceptance of fuel cell powered vehicles due to high cost and limited Pt availability. A commercially viable electro catalyst will require almost an order-of-magnitude reduction in Pt usage to meet both cost and Pt availability constraints. The US Department of Energy (DOE) has set targets for electro catalyst performance for the year 2010 and these include a mass activity of at least 0.44 A/mgPt (current status 0.28 A/mgPt), and a loss in electrochemical surface area after accelerated aging of ut most 40% (current status 90%). Three possibilities to reach these targets and reduce the Pt burden of PEFCs are[1] optimization of Pt cluster sizes for maximum mass activity, optimization of catalyst structure and chemistry to enhance durability, and Pt based alloys or less expensive, more abundant non-platinum based materials[102,103]. Reduction of Pt usage can change fuel cells to a more popular power source with low environmental load. To achieve these targets, the interplay between maximizing Pt dispersion and size-specific reactivity needs to be investigated fundamentally. As catalyst supports for fuel cell applications, carbon materials should satisfy several requirements[2,104] such as a large surface area for finely dispersing catalytic metal particles, high electrical conductivity for providing electrical pathways, highly developed meso-porosity for facile diffusion of reactants and by-products, and electrochemical stability for long-term operation. The commercially available porous carbon supports, such as carbon black and activated carbon, usually exhibit a large surface area, however, their pore structures are primarily microporous. The microporous structures are unfavorable for the transport of reactants while using in GDL; in the case of support materials, the catalyst particles are buried in the micropores and are inaccessible to fuels[105,106]. These Pt particles are not involved in the electrochemical reactions as they are not participating in the triple-phase boundaries (gas-electrolyte-electrode) which is essential for PEFC. In view of the above, synthesis of several types of nano structured carbon materials, such as carbon nanotube (CNT), carbon nanofiber (CNF) and ordered mesoporous carbon (OMC)[107–112] are reported as an attractive support materials for effective Pt utilization. Among them, the OMC, which is constructed of regular arrays of uniform mesopores, is highly intriguing from the viewpoint of mesostructures, large surface area and high pore volume, which may enable the solving of problems inherent in microporous carbon supports. The ordered mesoporous structures of OMC as support materials are expected to be advantageous for the utilization of catalyst particles as well as for efficient diffusion and transport of reactants and by-products in the application of fuel cells as also discussed in the earlier section.

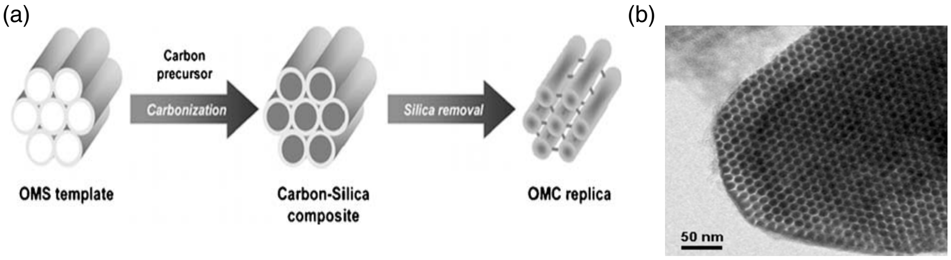
Beginning with the discovery of surfactant templated mesoporous materials in 1992, many new synthetic strategies have been realized[113]. Preformed templates, self-assembling systems, and a variety of spontaneous processes have been used to induce porous structure in the range between 1 nm and 10 mm length scale in extended inorganic systems. The nature of the templates used to induce pores is highly varied. For example, small amine molecules control the micropore (2 nm) formation in zeolites, while surfactant assemblies and more recently block copolymers control the formation of mesoporous (2–50 nm) inorganic materials[114,115].

Mesoporous carbon materials may be classified into two categories based on synthesis parameters and final structures as follows[109–112,116–122]. (i) Ordered Mesoporous Carbon (OMC): OMC is synthesized by nanocasting ordered mesoporous silica (OMS) templates or by directly templating triblock copolymer structure-directing species. The resulting OMC has uniform mesopores and such mesopores are periodically arranged to exhibit distinct X-ray diffraction lines. (ii) Mesoporous carbon with irregular pore structure: several methods have been reported to synthesize this class of mesoporous carbon. Template based approach using silica-gel or silica-sol and aerosol-assisted methods have been used to produce mesoporous carbon. Although this class of mesoporous carbon shows mesoporosity, in most cases, the mesopores are isolated or irregularly interconnected and the distribution of pore sizes is relatively wider than those of OMC. The idea of synthesizing mesoporous carbon materials via template-based methods was first realized by Knox et al., who they used a silica-gel as the template[117]. In 1999, Ryoo and coworkers applied this approach to the OMS template, which in turn led to the synthesis of OMC[90]. This later turned out to be a breakthrough in both ordered mesoporous materials and porous carbon materials. Since then, significant progress in OMC has been achieved[75,76,109–112], and OMC with various mesostructures, pore diameters, particle morphologies and framework microstructures are currently available. Applications of OMC as a catalyst support have been explored in diverse areas, such as adsorbents for bulky biomolecules and dyes, electrode materials for fuel cells and Li-ion batteries. The synthesis strategy of OMC by a nanocasting process is described in Fig. 2. In the first step, an ordered mesoporous silica (OMS) template with a specific pore topology is selected. A carbon precursor such as sucrose, furfuryl alcohol, phenolic resin, acetylene gas, naphthene, acrylonitrile, pyrrole and mesophase pitch is infiltrated into the pores of the OMS template. The carbon source is then polymerized and converted to a rigid carbon structure by pyrolyzing in a non-oxidizing atmosphere (under vacuum or flow of an inert gas such as N_2 or Ar) to result in silica-carbon composite. In the final step, the mesoporous carbon replica is obtained by treating the composite in an ethanol-water solution of HF or NaOH to remove the silica template.

In order to successfully synthesize OMC, the OMS templates should have three-dimensionally interconnected pore topology, so that the carbon structures formed within the silica pores have network structures and the final templated porous carbon structures exhibit three-dimensionally interconnected, ordered pore structures upon the removal of the silica templates. Another important condition for the synthesis of OMC is that the carbonization of the carbon precursor should be confined exclusively within the mesopores of the OMS templates to ensure the sufficient filling of silica mesopores with carbon structures. For this purpose, the carbon source should be converted to a cross-linked polymer before the pyrolysis reaction takes place. To prepare ordered graphitic mesoporous carbon, some unconventional carbon precursors such as mesophase pitch, polyvinyl chloride, naphthalene, anthracene, pyrene and polypyrrole have been employed to infiltrate the pores of mesoporous templates[123–126]. However, infiltration and polymerization using these liquid carbon precursors are time consuming because repeated infiltration and polymerization are required in order to obtain an ordered carbon replica.

More importantly, the physicochemical characteristics of OMC can be tailored by the control of synthesis parameters, which include the mesostructure and particle size of the OMS templates, type and amount of carbon precursor, addition of heteroelements other than carbon, and carbonization temperature. For example, the BET surface area of OMC can be changed from 200 to 2000 $m^2\ g^{-1}$ by the choice of carbon precursor and variation of the detailed synthetic conditions. Hence, the application of OMC as alternatives for currently available carbon supports is quite promising. In the following, the recent advances in the synthesis of OMC relevant to fuel cell applications are described. In an earlier period of development, the pore wall structure of reported OMC was amorphous although it exhibited periodicity on the mesoscale. However, for many applications including fuel cells, porous carbon materials with graphitic nature on the atomic scale are highly desirable. Ryoo and coworkers first synthesized OMC with graphitic frameworks, denoted as CMK-nG, through in situ conversion of various aromatic compounds to a mesophase pitch inside the OMS template by carbonization under high pressure using a specially designed autoclave[83]. The frameworks of the resulting OMC were composed of discoid graphene sheets, which self-aligned perpendicular to the template walls during the synthesis. Pinnavaia group also synthesized OMC with graphitic wall structures by using aromatic precursors such as naphthalene, anthracene and pyrene, and demonstrated that the synthesized OMC exhibit higher electrical conductivity, compared to the OMC constructed with amorphous frameworks[125]. Zhao group prepared graphitic OMC via a melt-impregnation method using a cheap mesophase pitch as the carbon precursor[123]. Alternatively, Fuertes and Alvarez prepared graphitic OMC by using poly (vinyl chloride) as the carbon precursor[124]. The OMC obtained in this way has a certain graphitic order and good electrical conductivity (0.3 S cm^{-1}), which is two orders larger than that of a non-graphitic carbon. Schüth and co-workers reported the synthesis of OMC via vapor-phase oxidative polymerization of pyrrole at room temperature using ferric chloride as the oxidant[126]. Fuertes and Centeno also prepared the OMC using pyrrole as the precursor[127]. The pyrrole precursor was impregnated into the pores of the OMS template via a liquid-phase incipient wetness method. The pyrrole-derived OMC synthesized by both laboratories exhibited graphitic structural order on the atomic scale. Although the OMC with graphitic structures exhibited enhanced electrical conductivity, compared to amorphous OMC, the BET surface area of such OMC gradually decreases with increase in graphitic nature. As mentioned above, for fuel cell applications, both the BET surface area and electric conductivity should be high. Thus, the optimum point, where the surface area and electric conductivity can maximize the single cell performance when OMC is used as electrodes for PEFCs, should be investigated. With several applications in mind, the synthetic efforts to prepare OMC doped with heteroatoms such as nitrogen, boron and phosphorous have been

Figure 2: (a) Schematic representation of the synthesis procedures for OMC from an OMS template (MCM-48, SBA 15 etc.). (b) Representative TEM image of OMC with a hexagonal mesostructure.



reported. Xia and Mokaya reported N-doped OMC with graphitic pore walls via chemical vapor deposition of acetonitrile[128]. Schüth and coworkers synthesized OMC containing nitrogen by using polyacrylonitrile (PAN) as the carbon source, and 2, 29-azobisisobutyronitrile as a radical initiator[129]. The Schüth group and Fuertes and Centeno used pyrrole as the precursor to prepare nitrogen-containing mesoporous carbon structures[126,127]. Considering the production process, the nanocasting procedure for OMC synthesis is rather long and complex, which may limit its widespread applications. In this regard, several methods for the simple preparation of OMC have been developed. Yu's group[89] and Hyeon's group[130] reported the direct synthesis of OMC using as-synthesized OMS materials. In their synthesis, surfactant molecules present in the as synthesized OMS were directly converted to carbon structures, thus saving the process time and energy required for the synthesis of OMC. The Hyeon group prepared mesoporous carbon by the carbonization of triblock copolymer/phenol-resin/silica nanocomposites[131]. The composites were simply prepared from the sol-gel polymerization of silica in the presence of a Pluronic-P123 triblock copolymer with phenol and formaldehyde. Dai and co-workers reported the preparation of highly ordered carbon thin films by carbonization of nano composite between resorcinol-formaldehyde (RF) resin and polystyrene-block-poly(4-vinylpyridine) (PS-P4VP)[94]. Through the carbonization under N_2 atmosphere, the RF resin was converted to a rigid carbon structure while the PS-P4VP template was decomposed. The resulting mesopores were oriented perpendicular to the film surface. Nishiyama and coworkers reported the preparation of highly ordered carbon thin films from nanocomposites composed of thermosetting polymeric carbon precursors, RF and triethyl orthoacetate and a thermally decomposable surfactant, triblock copolymer Pluronic F127[95]. The Zhao group also reported the synthesis of highly ordered mesoporous carbon films with hexagonal and cubic mesostructures by using Pluronic triblock copolymers as templates, and a soluble low molecular weight polymer of phenol and formaldehyde as precursors[99]. The same group synthesized OMC in powder form, which is more favorable for industrial production than the films, by performing the direct assembly of a Pluronic triblock copolymer and resol in an aqueous media[98,132]. Many reports are also available for synthesis of a mesoporous carbon with large pore diameter by a soft colloidal template route and its investigation on electrocatalytic activity[133,134]. The soft colloidal template route control the porosity of mesoporous carbon by tuning the geometry of the colloidal silica template via a variation of the aniline/cetyltrimethylammonium bromide (CTAB) ratio in the colloidal composition.

Ryoo and coworkers initially applied OMC materials for fuel cell electrocatalyst wherein uniform Pt nanoparticles are highly dispersed via incipient wetness impregnation of the Pt precursor (H_2PtCl_6) and subsequent reduction with H_2 gas[83]. The particle size of the resulting Pt catalyst supported on carbon was controlled below 3 nm, even though the Pt loading was as high as 50 wt. %. The resultant catalysts exhibited superior electrocatalytic mass activity toward oxygen reduction in a half-cell configuration, compared to the Pt particles supported on conventional porous carbon such as carbon black, activated carbon and activated carbon fiber. Ding et al. reported different approaches for the preparation of OMC supported catalysts[135]. For the cathode catalyst, Pt particles were pre-formed within the mesopores of the silica template, prior to the formation of the carbon structure, whereas, in previous examples, the Pt particles were supported after the synthesis of OMC. From the above, it is understood that various parameters such as metal particle size, surface area, pore diameter and ordering of the pores determine the final electrocatalytic activity.

Synthesis of OMCs with a large pore size of $\sim$23 nm and thick pore wall (11.5–12.4 nm) is also reported by considering two kinds of high-molecular-weight amphiphilic diblock copolymers poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS) and poly- (ethylene oxide)-*b*-poly (methyl methacrylate) (PEO-*b*- PMMA) via a versatile atom transfer radical polymerization (ATRP) technology [136]. All of these copolymer templates are laboratory-made, but it is difficult to vary the pore size by using individual copolymer templates. Although great success has been achieved in effectively tuning the pore size of mesoporous silica in a wide range by addition of small organic molecules such as trimethylbenzene (TMB)[137–139] but no work has been done to rationally adjust the pore sizes of OMCs.

To improve the performance of a catalyst, modifications of both surface chemistry and pore structure, may be required. To increase the number of surface functional groups on carbon materials, carbon is usually subjected to post treatments including oxidation, polymer coating and grafting[140–142]. In many cases the oxygen-containing groups behave as weak acids or bases, which possess ion exchange properties. The acidic groups, such as carboxyl, phenolic hydroxyl, lactone and quinone are introduced to the activated carbon treated with different oxidizing solutions[143–145]. Functional groups lead to change in the surface chemistry of the carbon support, which helps improved properties when it is used as catalyst support or adsorbent[146–148]. Oxidative treatment generally involves dry or wet oxidation, plasma treatment, and electrochemical modifications. In the case of dry oxidation, gaseous oxidizing agents like oxygen, ozone and carbon dioxide are often used. Wet chemical oxidation involves the use of nitric acid, sulfuric acid, phosphoric acid, alone or in combination with hydrogen peroxide, sodium hypochlorite, permanganate, chromate or dichromate of potassium, transition metal nitrates, etc.,[149–152]. Saha et al. oxidized porous activated carbon with nitric acid and distilled water at a ratio of 1:1 (v/v) for 6 h at 90°C, producing samples with weakly acidic functional groups[49]. Pradhan et al. functionalized activated carbon with surface oxygen complexes through reaction with different oxidants like HNO_3 (1 M), H_2O_2 (30%), and saturated solution of $(NH_4)_2S_2O_8$ in 4 M H_2SO_4[150]. They found that the nitric acid treatment is the most effective one in terms of modifying the surface area and the porosity of the activated carbon. By comparing the chemically modified activated carbon with nitric acid and hypochlorite, Vinke et al. found that nitric acid oxidation was the most effective, resulting in the highest amount of acidic surface groups, whereas hypochlorite appeared to be a much weaker oxidant[140]. Recently, Ryoo and his coworkers reported the surface modification of CMK-1 and CMK-5 by oxidation with concentrated HNO_3 at 110 °C for 15 min. The study also suggests that the pore structure of CMK-5 was destroyed in the presence of H_2O_2 (30%) by oxidation, reflecting the high-reactivity of CMK-5 carbon towards H_2O_2[152]. In this study, the oxidation behavior of OMCs has been investigated to find out the conditions at which high-amount of surface groups can be obtained, while maintaining the structural order. In order to check the reactivity of the surface groups, such chemically modified OMC was further subjected to functionalization by an esterification reaction. The chemically modified OMCs were characterized by various means in order to understand the surface and the structure evolution of OMC under nitric acid oxidation.

As a route to lower inter particle resistance between carbon particles, a new synthetic scheme has also been developed, where the surfaces of the OMC particles were selectively covered with a conducting polymer, polypyrrole (PPy)[153]. The PPy in the interfacial spaces between the OMC particles can be considered as an electrical bridge interconnecting the carbon particles. The resulting PPy-OMC composite maintained regular mesopore structure and a high surface area of the OMC. The PPy-OMC exhibited lower resistance than the pristine OMC. The Pt loaded PPy-OMC catalyst exhibited 50% enhanced power density compared to the commercial Pt catalyst in a PEFC.

4. Summary and perspectives

This overview presents the recent advances in the synthetic efforts of OMC as an innovative material relevant to fuel cell applications with examples as a constituent of the gas diffusion layer and as a catalyst support. The performance of OMC supported catalysts depends on the several factors, such as particle size, pore structure and crystallinity of the OMC as well as the preparation method. However, in most cases, OMC supported catalysts and gas-diffusion layers exhibited enhanced electrochemical properties in half-cell reactions (methanol oxidation or oxygen reduction) or in single cell configurations, compared to the commercial catalysts, which were attributed to the unique pore structure of OMC. For fuel cells, the catalyst preparation method using an OMC support should be developed, which could support metal (Pt or Pt/Ru) nanocatalysts with a high loading level while maintaining the particle size below 3 nm. Although the applications of OMC are still in infancy and there are several issues to be solved, intensive and interdisciplinary efforts are currently being conducted. The enhanced performance demonstrated in electrochemical energy devices by the use of OMC materials suggest their promise as innovative materials for such applications, which would eventually lead to their commercialization in the near future. Although the scope of the present review is limited to fuel cells, the applications of OMC in other electrochemical energy devices such as Li-ion batteries and electric double layer capacitors (EDLCs) are also promising.

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Dr. Akhila Kumar Sahu, Scientist, at Central Electrochemical Research Institute-Madras Unit, CSIR Madras Complex, Chennai, obtained his Ph.D. degree in Chemistry from the University of Madras in 2009. He was a Senior Research Fellow in National Aerospace Laboratories, Bangalore, during the period 2002–2005. In 2005, he joined Central Electrochemical Research Institute as a Senior Research Fellow and became Research Associate in the same institute during 2006-2008 and devoted his research work in the field of Fuel Cell Technologies. He has about 16 research publications in peer reviewed journals and 3 international patents to his credit. His present research activities include development of composite membranes for PEFCs operation at elevated temperature and reduced relative humidity, new membrane materials for mitigating methanol cross-over in DMFCs, new carbon materials for preparation of catalysts and as gas-diffusion layer electrodes for PEFCs.

Dr. Parthasarathi Sridhar, Scientist, Central Electrochemical Research Institute (CECRI) - Madras Unit, CSIR Madras Complex, Chennai is engaged in the development of PEM-based Fuel Cell Technologies. He obtained his Ph.D. degree from Indian Institute of Science, Bangalore in 1981. After serving CECRI, Karaikudi for a brief period, he joined the R&D Center, Southern Petrochemical Industries Corporation Ltd., Tuticorin and developed several important processes (1984-1990). During 1990-2004, he worked at SPIC Science Foundation, Chennai to develop PEMFC Technology. He was associated in establishing PEFC test facilities at various laboratories in India and abroad. He has 14 patents and 40 publications in international journals to his credit and so far, guided three students to their Ph. D. degree.

Dr. S. Pitchumani, has been a Material Electrochemist since 1983 at CECRI after earning Ph.D. degree (1980) from University of Madras followed by a post doctoral training at Fritz Haber Institut der MPG, Berlin, W.Germany (1981–1983). He is currently the Head of CECRI – Madras Unit at Chennai and his research area includes Materials development for electrochemical energy conversion and storage processes and systems. He has to his credit 100 research papers, 15 patents including 4 international patents and commercialised 4 electrochemical products. He has led successfully several R&D programmes at CECRI and mentored 10 Ph.D. thesis and number of post graduate dissertation work in Chemistry and Chemical Engineering. He had been a visiting Scientist at Karl Winnaker Institut der DECHEMA, Frankfurt, Germany under INSA-DFG exchange programme in 1998.