

Review

# The role of carbon in fuel cells<sup>☆</sup>

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## Abstract

Carbon possesses unique electrical and structural properties that make it an ideal material for use in fuel cell construction. In alkaline, phosphoric acid and proton-exchange membrane fuel cells (PEMFCs), carbon is used in fabricating the bipolar plate and the gas-diffusion layer. It can also act as a support for the active metal in the catalyst layer. Various forms of carbon – from graphite and carbon blacks to composite materials – have been chosen for fuel-cell components. The development of carbon nanotubes and the emergence of nanotechnology in recent years has therefore opened up new avenues of materials development for the low-temperature fuel cells, particularly the hydrogen PEMFC and the direct methanol PEMFC. Carbon nanotubes and aerogels are also being investigated for use as catalyst support, and this could lead to the production of more stable, high activity catalysts, with low platinum loadings ( $<0.1 \text{ mg cm}^{-2}$ ) and therefore low cost. Carbon can also be used as a fuel in high-temperature fuel cells based on solid oxide, alkaline or molten carbonate technology. In the direct carbon fuel cell (DCFC), the energy of combustion of carbon is converted to electrical power with a thermodynamic efficiency close to 100%. The DCFC could therefore help to extend the use of fossil fuels for power generation as society moves towards a more sustainable energy future.

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*Keywords:* Proton-exchange membrane fuel cells; Carbon components; Catalyst support; Direct carbon fuel cell

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<sup>☆</sup> This review is one of a series dealing with the role of carbon in electrochemical energy storage. The review covering the role of carbon in graphite and carbon powders for electrochemical applications is also published in this issue, *J. Power Sources*, volume 156, issue 2, pages 142–150. Publication of the series will continue in future issues of *J. Power Sources*.

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## 1. Introduction

### 1.1. The structure of carbon

Carbon is unique amongst the chemical elements in that it can exist in various solid forms, or allotropes. The softest, naturally occurring form is graphite, which can exist in both hexagonal and rhombic forms. In graphite, the atoms are arranged in a two-dimensional, sheet-like, polymeric structure. Each sheet may be regarded as a fused system of hexagons. The parallel layers of hexagons are weakly linked by van der Waals forces and are about 0.335 nm apart. Only three of the valence electrons in the carbon atoms are involved in forming  $sp^2$  hybrid bonds and this means that the fourth electron forms a  $\pi$  bond. Because  $\pi$  electrons are mobile, graphite is a good electrical conductor, which is an important feature for fuel-cell applications. The  $\pi$  electrons within graphite can also react with other elements without disrupting the layer structure. Some reacting atoms, molecules or ions can intercalate between the layers, and cause either an increase or a decrease in the electrical conductivity.

#### 1.1.1. Carbon black

Heating virtually any carbon-containing material in an inert, oxygen-free environment produces a material known as ‘carbon black’. For example, soot is a carbon black and is obtained when a carbon compound is heated in air with a limited supply of oxygen. Carbon black, once regarded simply as an amorphous form of carbon, usually consists of near-spherical particles of graphite, typically below 50 nm in diameter that may coalesce into particle aggregates and agglomerates of around 250 nm in diameter. The particles have para-crystallite structures [1], in which an assembly of parallel layers form non-discrete 3D groupings. The individual graphitic layers are the basic building blocks of carbon black particles. Each crystallite consists of several ‘turbostratic’ layers with an interplanar spacing, of 0.35–0.38 nm. The morphology and particle size distribution of carbon black is dependent on the source material and the process of its thermal decomposition. Particle size and distribution determine directly the surface area and are probably the most important properties of carbon black in terms of end-use applications. Under the electron microscope, some carbon blacks prepared by pyrolysis at very high temperatures ( $>2500^\circ\text{C}$ ) appear to be amorphous, and are termed ‘hard carbons’. Others readily graphitize when heated to such high temperatures and the layered structure is easily visible. Common, high surface area, carbon blacks suitable for fuel-cell applications can be obtained from Cabot Corporation (Vulcan XC-72R, Black Pearls BP 2000), Ketjen Black International, Chevron (Shawinigan), Erachem and Denka.

Carbon black can be treated either chemically (e.g., by adding  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$  to the carbon precursor) or with steam

and/or  $\text{CO}_2$  at 800–1100  $^\circ\text{C}$  and high pressure, to ‘activate’ the microstructure. Wood, coal, lignite, coconut shells and peat are all important raw materials for producing activated carbon. Although the particle sizes of activated carbons are relatively large (typically 20–30  $\mu\text{m}$ ), the process of activation increases the microporosity (i.e., the proportion of pores that are  $<2$  nm), and also the BET surface area (typically to 800–1200  $\text{m}^2 \text{g}^{-1}$  depending on the degree of activation). Activated carbon has been used as a support for industrial precious metal catalysts for many years, and has been a natural choice for supporting the electrocatalysts in phosphoric acid (PAFC), alkaline (AFC) and proton-exchange membrane (PEMFC) fuel cells.

#### 1.1.2. Diamond

The other well-known and natural allotrope of carbon is diamond, which can also exist in two forms or polymorphs. The most common is the cubic close-packed structure in which each carbon atom utilises  $sp^3$  hybrid orbitals to form four, strong, covalent bonds. These are not easily broken and give rise to the hardness and extremely high melting point of diamond. The other form of diamond is Lonsdaleite, a two-layer hexagonal structure that was first discovered in a meteorite crater in 1967 [2].

#### 1.1.3. Fullerenes

In between the ordered graphite and diamond structures, other allotropes have now been identified. Some of these have been found in the natural world, e.g., the carbon spherules discovered in the Murchison meteorite, but many others have been synthesised in the laboratory. In 1985, Kroto and Smalley discovered buckminsterfullerene, an allotrope that was to open up a whole new area of carbon chemistry [3]. Nicknamed the ‘buckyball’, since the molecular structure (an icosahedron) resembles that of the ball used in Association Football, it consists of a cage of 60 carbon atoms made up of 20 six-membered rings and 12 five-membered rings [4]. Each carbon atom is at a corner where two six-membered rings and one five-membered ring come together. Separate 60-atom cages are held together by weak forces with the result that buckminsterfullerene will dissolve easily in solvents such as benzene. This enables the material to be isolated and its chemistry explored. Since its discovery, buckminsterfullerene has been found to occur occasionally in nature. Other fullerenes with different sizes of carbon cages have also been synthesised, e.g.,  $\text{C}_{140}$ ,  $\text{C}_{260}$  and  $\text{C}_{960}$ .

#### 1.1.4. Carbon nanotubes

In 1991, Iijima [5] confirmed the structure of the now familiar carbon nanotube and this provided a seminal breakthrough in the science of nanomaterials. Carbon nanotubes can be synthesised in the laboratory and show remarkable mechanical, thermal conductivity and electrical properties. They consist of layers of graphite (graphene) rolled into the form of cylinders that are

often closed at both ends. Both single- and multi-walled nanotubes exist, with diameters of a few nanometers and lengths of the order of 1 mm. An interesting property of both fullerenes and carbon nanotubes is their ability to entrap atoms of other elements within their molecular structure. In this respect hydrogen storage in carbon nanotubes is of particular interest to fuel cell developers. More recently, workers at the Australian National University reported a new graphitic foam structure for carbon [6] that is made up of clusters of about 6 nm in width. Each cluster consists of about 4000 atoms linked together in graphite-like sheets that are given a convex hyperbolic curvature by the inclusion of heptagons among the regular hexagon pattern. This form of carbon was prepared by laser ablation in an atmosphere of inert argon, and is the lowest density form of carbon so far produced by any means; the density is in the range 4–40 mg cm<sup>-3</sup>. The carbon has a mixture of sp<sup>3</sup> and sp<sup>2</sup> bonds with the sp<sup>3</sup>/sp<sup>2</sup> ratio varying from 15 to 40%. The foam has a high surface area, typically above 400 m<sup>2</sup> g<sup>-1</sup>, and exhibits ferromagnetic properties at low temperatures [7] probably because the curved nature of the graphite sheets gives rise to localised, unpaired, electron spins.

Many forms of carbon therefore exist between the two extreme structures of graphite and diamond. Of particular importance to the developers of fuel cells is the wide variety of electronic properties that exist between the different allotropes. Some exhibit superconductivity, some exhibit unusual magnetic susceptibility, and some exhibit electrical properties that range from metallic to semi-conductor behaviour [8].

#### 1.1.5. Carbon fibres

Although not an allotrope, carbon fibres are an industrially important form of carbon that have been produced for many years by the controlled decomposition and graphitisation of organic carbon-rich polymers. The most common precursor is polyacrylonitrile (PAN), as it yields excellent high strength fibres, but pitch and cellulose can also be used. Variation of the graphitisation process produces either high strength fibres (at temperatures of ~2600 °C) or high modulus fibres (at ~3000 °C), with other types in between. Once formed, the carbon fibre has a surface treatment applied to improve matrix bonding and chemical sizing that serves to protect it during handling. The filament diameter of most types of carbon fibre is 5–15 μm. The fibres exhibit very high tensile and compressive strength, and have a high resistance to corrosion, creep and fatigue. For these reasons, the fibres are widely used in the automotive and aerospace industries. Carbon fibre is an important ingredient of carbon composite materials, which are now finding use in fuel cell construction, particularly in new bipolar plates, and as gas-diffusion layers in which the fibres are woven to form a type of carbon cloth.

#### 1.2. Carbon in fuel cells

The attractive features of carbon in electrochemical applications include its high electrical conductivity, acceptable chemical stability and low cost. Carbon can feature in fuel-cell systems

in several ways, namely:

- as part of the structure of the fuel cell and stack (e.g., bipolar plate or as the gas-diffusion layer in a PEMFC);
- as an electrocatalyst or an electrocatalyst support;
- as a reacting species in hydrocarbon-fuelled systems;
- as a potential means of storing hydrogen;
- as a fuel in its own right, in the direct carbon fuel cell (DCFC).

This paper aims to provide a topical summary of the role of carbon in fuel-cell design. To this extent, it provides a review of carbon as a structural element of fuel cells and focuses on recent work on carbon bipolar plate and electrode designs, as well as supports for catalysts. The use of carbon in hydrogen storage is not covered since this is a very active area of research in its own right. The role of carbon in hydrocarbon-fuelled systems is also not discussed, but a brief review is made of the direct carbon fuel cell, which is an area of topical research.

## 2. Carbon as a structural component in fuel cells

Early PAFC stacks employed bipolar plates that consisted of a single sheet of graphite with gas channels machined on each side. Machined graphite has also been widely used for the bipolar flow-field plates of PEMFCs. This approach has two disadvantages, namely: (i) the plates have to be reasonably thick to maintain mechanical integrity; (ii) machining channels in a graphite plate is an expensive although feasible method of manufacture. Thinner plates would increase the power density of the stack and reduce the weight, which are important aspects for transport applications. Thinner plates can be made by building up the carbon material in layers, and this approach is adopted in the construction of ribbed substrate plates for PAFCs; two identical porous plates with ribbed channels made of a carbon composite material are separated by a thin impervious carbon plate [9]. This method of construction has a particular advantage for the PAFC in that phosphoric acid can be stored in the porous ribbed substrates, where it acts as a reservoir for the electrolyte and helps to increase cell lifetime.

Although early alkaline fuel cells (AFCs) invariably used metal interconnects [10], some development of carbon bipolar plates has been reported [11,12]. Even though metals do offer prospects of more compact and lightweight designs, carbon continues to be the preferred material for bipolar plates in PEMFCs. When metal bipolar plates are employed in PEMFC stacks, they can be coated with dispersed carbon to provide corrosion resistance and good electrical conductivity [13].

Several layers normally make up the membrane electrode assembly (MEA) of a PEMFC (see Fig. 1). The MEA consists of the electrolyte and the two electrocatalysts of carbon-supported Pt or Pt-alloy. Porous gas-diffusion layers (GDLs) are located on the back of the catalyst layers and are made of carbon paper or woven carbon cloth. The GDLs provide not only structural support for the electrodes, but also the means of current collection and a diffuse path by which the oxidant or fuel gases can reach the catalysts whilst simultaneously contacting the electrolyte.

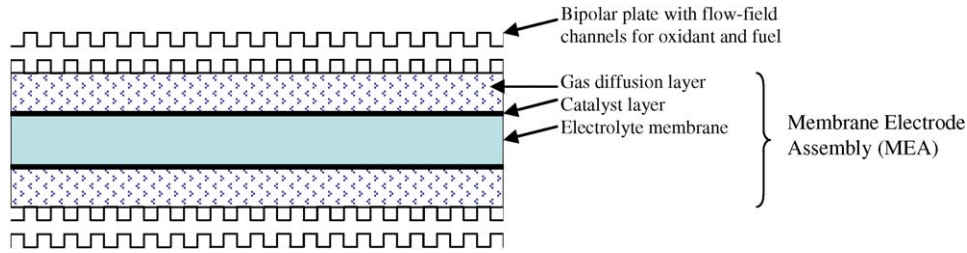


Fig. 1. Basic structure of a low-temperature fuel cell showing a simple configuration of bipolar plate.

### 2.1. Carbon bipolar plates

The bipolar flow-field plate is the main hardware component of the PEMFC, and its variant the direct methanol fuel cell (DMFC). This has to fulfil several requirements, namely:

- good electrical conductivity;
- non-porous and leak-free conduit for the reacting gases;
- provision for distribution of the fuel and oxidant gases and water and product gas removal;
- provision for stack cooling, by water or air;
- good thermal conductivity to achieve stack cooling and satisfactory temperature distribution between cells;
- construction to high tolerance in large volumes;
- acceptable corrosion resistance;
- good mechanical stability at low thickness;
- low weight, especially for transport applications;
- low cost.

Carbon meets many of these needs and has been proven by developers over many years. Nevertheless, the development of low-cost, non-porous, carbon materials continues to be a challenge and the bipolar plate remains one of the most costly components in a PEMFC system.

The design of bipolar plates for PEMFCs is dependent on the cell architecture, on the fuel to be used, and on the method of stack cooling (e.g., water or air-cooling). To date, most of the fuel cells have employed a traditional plate-frame architecture so that the cells are planar and gas flow distribution to the cells is provided by the bipolar plate. The bipolar plate therefore incorporates gas channels machined or etched into the surface. These supply the fuel and oxidant gases and also provide a means for removing water from the cells. Some alternative designs of plate have been suggested [14] for non-planar cell architecture and may provide higher volumetric power densities, whilst maintaining low contact resistance and good structural integrity.

Carbon bipolar plates for PEMFC applications have been traditionally made by machining graphite sheets that have been impregnated with polymer resin, but this is a very expensive process. In order to reduce costs, developers are turning to either metal or carbon composite materials. Metals have the advantage in that they can be made very thin and can be formed by stamping, which is a low cost process. Plates can also be fabricated by moulding carbon composite materials, another low cost option compared with machined graphite. Carbon composites have been used industrially for several decades and generally com-

prise carbon fibres to provide strength reinforcement for organic polymers such as polyethylene and polyvinyl chloride, or epoxy resins. For PEMFC bipolar plates, several composite materials have been investigated, including carbon-carbon composites, graphite/polymer mixtures, carbon-fibre/epoxy resin and carbon cloths impregnated with polymer and various conducting fillers [16–27].

The polymer or resin used to bind the carbon in composite plate material is usually thermoplastic or thermosetting, which implies that the plates can be fabricated either by injection moulding [19,21] or by hot pressing [28], respectively. To meet the required electronic conductivity, manufacturers have been using quite high loadings of carbon in the composite material, typically 60–90% by volume [23]. Unfortunately, this makes the plates brittle, resulting in high scrap rates and an inability to make thin plates, required for high stack power densities.

The form of carbon used in the composite also significantly influences the properties of the final material. In the case of carbon blacks in polyvinyl chloride, for example, the surface area and mesoporous volume are found to affect significantly the rheology and conductivity of the composite [29]. To enable low loadings of carbon to be used, researchers have been developing specific forms of carbon for use in composite materials [18,25,30–32]. In producing the composite material, the proportion of carbon filler to polymer is found to affect not only the electronic conductivity but also the mechanical properties such as the flexural strength, density, water absorption and gas permeability of the final plate. Good mechanical properties are afforded by keeping the carbon content low and the polymer content relatively high. Heinzl et al. [23], for example, have shown that additive loadings of 50 wt.% can achieve bulk conductivities of  $50 \text{ S cm}^{-1}$  for injection-moulded material. They have also reported conductivities of up to  $150 \text{ S cm}^{-1}$  for some samples although the nature of the carbon additives was not disclosed.

Work at Oak Ridge National Laboratory [26], on the other hand, has shown that successful composites can be made by suspending carbon fibres (typically  $10 \mu\text{m}$  in diameter by  $>100 \mu\text{m}$  in length, e.g., Amoco DKD-x mesophase pitch carbon fibres) in an aqueous phenolic resin base (Durez<sup>®</sup>). The fibre-to-phenolic ratio is 4:3 and with a vacuum-molding process produces a material that contains 18 vol% fibres and can then be hot pressed in a mould at  $150^\circ\text{C}$  to produce the required shape of bipolar plate. The process is low cost—the materials cost is estimated at US\$ 0.12 per plate, and the batch processing cost US\$ 0.25 per plate. Unfortunately, this material is relatively porous and to

seal the surfaces and ends, a chemical vapour infiltration (CVI) step has to be added to the preparation. This is a simple, low-cost procedure (US\$ 1 per plate) in which the pre-formed plates are placed in a furnace held at 1400–1500 °C and methane, or another gaseous hydrocarbon, is allowed to flow over the component under reduced pressure. The hydrocarbon pyrolyses and deposits carbon over the exposed fibres of the pre-form, and when sufficient carbon has been deposited, the surface becomes hermetically sealed. This carbon also adds strength and improves the electrical conductivity of the finished plate; values of 200–300 S cm<sup>-1</sup> have been measured (the US DOE target is 100 S cm<sup>-1</sup> for composite bipolar plates). Even with the CVI step, the plates can be made at a cost that is expected to meet the US DOE long-term target of US\$ 10 kW<sup>-1</sup> at volumes exceeding 100,000 units annually. The developments at Oak Ridge Laboratory have been licensed to Porvair to fabricate commercial quantities of bipolar plates for the industry, and plates are now being supplied to several fuel cell developers such as Plug Power and Honeywell.

An alternative to injection moulding and slurry moulding carbon composites is that of compression moulding. Described by Ruge and Buchi [15], this consists of mixing graphite and thermoplastic polymer granules and supplying the mixture to a mould that is then closed, and pressure applied. The mould is heated to the glass transition temperature of the polymer, at which point the materials mix and flow into the mould. The process allows much higher loadings of carbon to be used than in injection moulding and, although not as fast, may offer good commercial prospects.

Huang et al. [33] have reported a carbon composite of graphite particles, thermoplastic fibres and carbon or glass fibres that is prepared by a wet-lay process to yield highly formable sheets. The material can be hot pressed and the authors claim the plates contain 65% graphite and have a bulk conductivity over 200 S cm<sup>-1</sup>. Because the CVI process is not needed, the cost of preparing these plates should be low. It is clear, however, that much work is required to optimise carbon composite materials for fuel-cell applications, to ensure that they meet the performance targets for conductivity, physical properties and lifetime within operating stacks.

Special mention should be made of a new design of bipolar plate developed by Morgan Fuel Cells, known as the Biomimetic™ plate [34]. This is unusual in two respects. First, the term biomimetic refers to the design of flow-field pattern. This takes its inspiration from the design of flow channels in biological systems such as leaves and lungs. The aim is to achieve a more uniform distribution of reactants than that achieved in the traditional serpentine path of most bipolar plates. The effect of better distribution of reactants and reducing mass flow losses is to increase the cell performance by some 16%, and this is expected to increase as the technology improves. The biomimetic™ plate has several other positive attributes:

- a low pressure drop which reduces parasitic power on air blowers and fuel pumps by between 30 and 60% compared with a traditional serpentine flow path;
- increased power density with a standard MEA;

- a plate thickness that can be reduced for the same power output;
- a reduced risk of ‘hot spots’ due to more even current density distribution.

The second feature of the Morgan bipolar plate is that it is not made of a moulded or pressed carbon composite. Rather, a high-precision grit-blasting technique (ElectroEtch®) is used to etch away carbon to form the flow channels. Not only does this provide a short time for rapid prototyping, but also it offers the prospect of low-cost, volume production for the developing fuel-cell industry. Morgan Fuel Cells are now working on improved flow-field designs and on tailoring the designs to marry with gas-diffusion layers.

## 2.2. Gas-diffusion layer

The GDL or gas-diffusion electrode forms an essential component of the PAFC and PEMFC. Because the electrocatalyst in these two types of fuel cell is expensive platinum or platinum alloy, it is essential that the metal is utilised as fully as possible. The supported catalyst is therefore in the form of a thin layer of material (usually less than 10 μm in thickness) close to the polymer electrolyte surface. An additional layer behind the catalyst layer is usually needed to provide further support for the catalyst, and to improve gas distribution and water management in the cell. This layer has to be porous to the reacting gases, have good electronic conductivity, and be hydrophobic so that liquid product water does not saturate the material and reduce the permeability of gases. Unlike the bipolar plate, the gas-diffusion layer needs to be malleable and the material of choice for the PEMFC is usually carbon fibre paper or cloth, typically 0.2–0.5 mm in thickness [35,36]. This macroporous support layer is coated with a thin layer of carbon black which is mixed with dispersed hydrophobic resin, typically PTFE, to render it hydrophobic. This can, however, reduce the electronic conductivity of the GDL, and in the case of the PAFC can reduce the three-phase boundary by restricting diffusion of the liquid electrolyte to the catalyst [37]. Work by Hara et al. [38] showed that improved performance of the GDL in a PAFC could be obtained by separating the functions of the gas network and the electrolyte network. The technique used was to cover the surface of the carbon black particles with a thin film of polythene that was subsequently fluorinated to produce a hydrophobic coating. This gave a higher thermal stability than the usual application of PTFE.

A gas-diffusion layer is also an important component of the AFC. For these fuel cells, the GDLs are usually made by a rolling procedure similar to that used in paper making. The activated carbon/PTFE mixture is rolled onto a current collector made from planar nickel mesh. By using GDL and double-layer electrode structures, the Pt loading in the AFC can be reduced to 0.3 mg cm<sup>-2</sup> [39].

The structure of the porous GDL is governed by the type of carbon and by the hydrophobic resin that is used in its preparation. These, in turn, impact on the performance of the PEMFC. The most widely used carbons have been an oil furnace car-

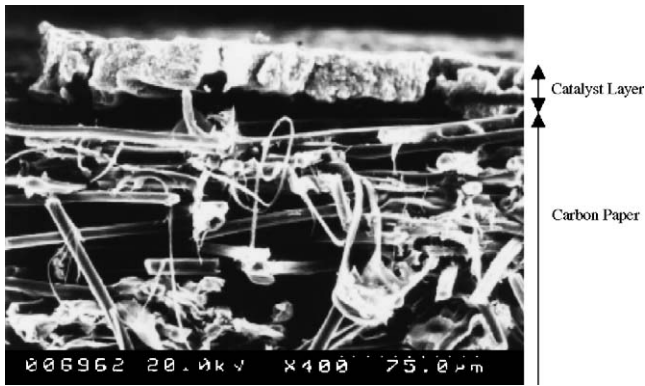


Fig. 2. Scanning electron micrograph of the cross-section of the interfacial region between the catalyst layer and the carbon paper GDL [44].

bon (Vulcan XC-72R) and acetylene carbon black. Jordan et al. [40] have shown that acetylene black carbon with a low pore volume and an optimised thickness, gave a better performance in PEMFCs than Vulcan XC-72R carbon. By contrast, Neergat and Shukla [41] have found that Ketjen black carbon with a high surface area gave better performance than acetylene black or Vulcan XC-72R in a PEM DMFC. In a study by Antolini et al. [42], Vulcan XC-72R was shown to be inferior to Shawinigan carbon when used for the GDL on the cathode side of the PEMFC, particularly at high current densities. The improvement was found to increase with increase in oxygen pressure.

The amount of hydrophobic resin used to coat the carbon in the GDL is also important. High resin content, higher sinter temperatures during sample preparation, or a combination of the two leads to better hydrophobicity but at the expense of electrical conductivity [43]. Lim and Wang [44] showed that a 10 wt.% loading of resin on a carbon cloth GDL enables a higher power to be achieved from a PEMFC than a higher resin loading (40 wt.%). This is attributed to the resin, at high concentrations, blocking micropores in the carbon surface and thereby contributing to significantly increased polarisation. A micrograph of the GDL prepared by Lim and Wang [44] is given in Fig. 2. The catalyst layer has a uniform thickness of some 25  $\mu\text{m}$  on top of wet-proofed carbon paper. Graphite fibres intermixed with tetrafluoroethylene–hexafluoro-propylene copolymer (FEP) resin are seen below the catalyst layer and provide a non-woven carbon paper GDL substrate. The marked

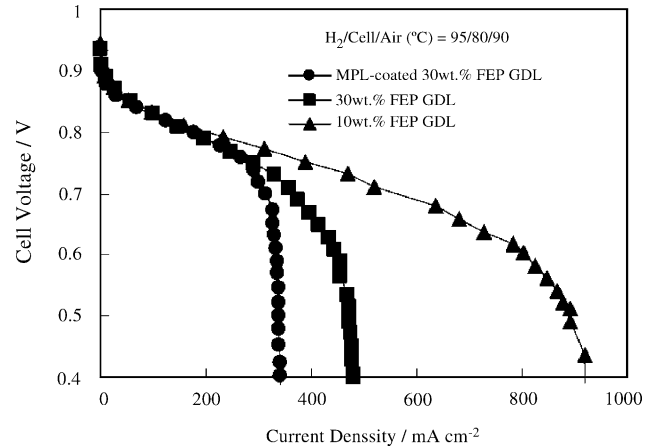


Fig. 3. Voltage–current curves obtained at 80 °C in 30 psi H<sub>2</sub>/air from MEAs with three different types of cathode GDL under an air stoichiometry of 2.1 (at 1 A cm<sup>-2</sup> equivalent): (●) microporous layer-coated and 30 wt.% FEP-impregnated cathode GDL; (■) 30 wt.% FEP-impregnated cathode GDL; (▲) 10 wt.% FEP-impregnated cathode GDL. Anode and cathode humidification temperature is 95 and 90 °C, respectively. Pt loading is 0.22 mg cm<sup>-2</sup> on both electrodes [44].

effect of resin loading on power density is demonstrated in Fig. 3.

Imazato et al. [45] have also shown that the amount of hydrophobic resin binder affects the performance of PEM DMFCs. They found that although the electrical resistance of the electrode rises as the ratio of resin rises, there is no direct relationship with the impedance of the DMFC. In addition, as the proportion of binder increases, so does the propensity for the GDL to crack and become more porous. Oedegard et al. [46] have compared the performance of carbon paper and carbon cloth and found that the latter is to be preferred for DMFCs on account of its higher porosity. Performance also increased in changing from one type of E-TEK carbon cloth, with a pore size from about 50  $\mu\text{m}$ , to another in which the pore size was 200–300  $\mu\text{m}$ . Fig. 4 shows the effect of coating the carbon with PTFE, and Oedegard found that a PTFE loading of 30 wt.% gave the most stable cell voltages.

As developers seek to create MEAs using materials other than fluoro-sulfonate ionomers, so the specifications for the GDL change. In a move to create thinner GDLs, Glora et al. [47] have investigated the use of resorcinol–formaldehyde aerogel

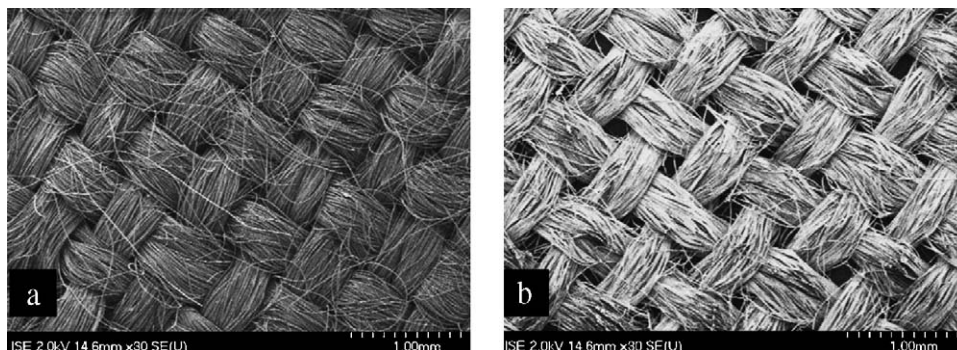


Fig. 4. Scanning electron micrographs of (a) untreated and (b) 15 wt.% Teflon-treated carbon cloth diffusion layers [46].

films reinforced with carbon fibres. More recently, Nishikawa et al. [48] also developed GDLs for novel organic–inorganic hybrid electrolytes. They mixed Triton and PTFE dispersions with carbon black and coated the mixture on to carbon paper that had been wet-proofed with tetrafluoroethylene–hexafluoropropylene copolymer. A nano-hybrid electrolyte was prepared by a sol–gel method and formed over the GDL. Addition of uncatalysed carbon black to the cathode GDL was found to enhance the performance at high current densities.

With more emphasis being placed on increasing the temperature of operation of the PEMFC, so that hydrogen with a lower purity can be used and more use can be made of the exhaust heat from the cell, developers are investigating alternative proton-conducting materials. Examples are inorganic salts (e.g., zirconium phosphate or silica) or composite materials made of normal sulfonated fluoropolymer in which inorganic nanoparticles have been synthesised. It is to be expected that such materials will have additional demands on the GDL. For example Higuchi et al. [49] have recently investigated the use of a proton-conducting, borosiloxane electrolyte, fuel cell and have found that the best performance in terms of cathode polarisation was obtained with a GDL that contained a mixture of borosiloxane ionomer and carbon black in the ratio of 1.5:1 by weight. Application of alternative carbon materials for GDLs is also evident in a recent paper by Huang et al. [50] who have investigated the use of carbon nanotubes as a secondary catalyst support in metal–air batteries. These reports indicate that much work still remains to be carried out in optimising the structure of the GDL for PEMFCs, in line with reducing material costs and increasing operating temperatures.

### 3. Carbon as a catalyst support

#### 3.1. Requirements for fuel cell catalysts

Carbon has been used for many years as a support for industrial precious metal catalysts [51], and activated carbon, carbon black, graphite and graphitised materials have all been applied in various catalytic processes. Compared with other widely used catalyst supports such as alumina and MgO, carbon is chemically stable in both highly acidic and basic media. It can also be burnt off when the time comes to recover the active precious metal, and therefore offers a sound environmental and ecological advantage. For fuel cells the electronic conducting properties of carbon means that the three-phase boundary (electrode–electrolyte–reactant) can be extended out into the electrode, with significant performance benefits.

In a fuel cell, the electrocatalysts serve the purpose of generating electrical power by reduction of oxygen at the cathode, and oxidation of fuel at the anode. In the PEMFC, AFC and PAFC, the catalysts are usually Pt-based and supported on carbon black of high surface area. The catalyst layers must be relatively thin so as to minimise losses due to (a) the rate of proton diffusion within the catalyst layer and (b) the rate of mass transfer of the chemical reactants and products to and from the active sites. The latter can contribute to a marked overpotential or polarisation of the electrodes that can limit cell performance, particularly at

high current densities. To minimise the thickness of the catalyst layer, the metal loading in fuel-cell applications is typically 40 wt.% or greater, in contrast to normal industrial supported metal catalysts which are usually under 5 wt.%.

In the PEMFC the three-phase boundary is extended by incorporating a soluble form of the proton-conducting electrolyte into the catalyst layer. This can be done by mixing a solution of the electrolyte material (e.g., Nafion<sup>TM</sup>) with the carbon black to form a slurry. The Pt-group metal is then precipitated out into the slurry, usually by chemical reduction, to form an ‘ink’ that can be painted or screen-printed directly on to the electrolyte or the gas-diffusion layer. This method of catalyst preparation yields a highly dispersed form of Pt metal in the form of very small crystalline particles (typically around 5 nm) with a metal surface area above 60 m<sup>2</sup> g<sup>-1</sup>, even when the Pt loading in the catalyst layer is as high as 70% [52].

#### 3.2. Anode and cathode electrocatalysts

Requirements for the anode and the cathode electrocatalysts in fuel cells depend on the type of cell and the nature of the fuel. Highly-dispersed platinum on carbon black (furnace black) has normally been used for the PAFC. Experience shows that in this type of cell the carbon cathode is subject to degradation and loss of carbon by an electrochemical oxidation mechanism [53,54]. The degradation of PEMFC cathodes has not, until recently, been such a concern because of the relatively low operating temperature. As developers seek to raise the operating temperature, however, cathode degradation could become more important. To illustrate this, Stevens and Dahn [55] measured the weight loss on heating catalyst samples in air. The samples comprised Pt (5–80 wt.%) on BP 2000 carbon of high surface area. For the base carbon heated in air at 195 °C, no weight loss was detected even after 3000 h. With Pt/C samples, however, significant weight loss occurs arising presumably from the catalysed combustion of carbon with oxygen. This weight loss increased as the temperature was raised from 125 to 195 °C and also as the Pt loading was increased. TEM images indicated that the weight loss was primarily from the carbon and that the Pt particles did not sinter or agglomerate during exposure to air at high temperatures.

The PEMFC anode catalyst, when operating on pure hydrogen, is relatively stable but is poisoned by sulfur and CO that originate from the fuel. The lower the operating temperature, the more severe is the poisoning effect. The PAFC tolerates up to around 2% CO in the fuel stream whereas the PEMFC can withstand only ppm levels. Much work has consequently been reported on improving the CO tolerance of PEMFC anodes, for example by alloying the Pt with Ru or Mo, and by incorporating other promoters [56].

#### 3.3. Catalysts on different forms of carbons

Although the carbon support serves to disperse the active metal, the literature on comparing different forms of carbon in fuel-cell electrocatalysts is quite sparse. Most developers have tended to stay with just a few well-characterised forms of carbon

black, even though it is recognised that the form of carbon can affect the dispersion of the Pt particles [56–59]. Antolini et al. [57], for example, have shown that metal–carbon interactions occur in carbon-supported catalysts, and that Ru can enhance the interaction between Pt and carbon. Such interactions appear to affect mainly the dispersion of the metal, with little influence on the final PEMFC performance. Indeed, the metal particle size in PEMFC electrocatalysts appears to have only a small effect on fuel-cell performance especially at low current densities. On the other hand, the morphology of the carbon supporting particles does influence cell performance and Van Nguyen et al. [58] have demonstrated that at high current densities, where liquid water and gas transport processes dominate, catalysts that contain carbon-supported Pt particles give enhanced fuel-cell performance compared with unsupported platinum black. Hall et al. [59] have also investigated platinum black and carbon-supported platinum with varying amounts of carbon support, but for DMFC applications. It was found that metal–carbon support interactions do influence the oxidation of both CO and methanol, and that the nanostructure of the catalyst and its influence on methanol oxidation are also related.

#### 3.4. Application of nanotechnology

It is to be expected that the nanostructure of the catalyst will influence its performance and stability. The usual method of preparing PEMFC catalysts is to impregnate an aqueous slurry of highly dispersed carbon-black powder with a Pt precursor

such as  $(\text{H}_2\text{Cl}_6\text{Pt})$  or  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ , and then precipitate the metal by chemical reduction. The method is easy, gives a high yield, and is very reproducible. It can also be applied to Pd as well as Pt catalysts [60]. The field is, however, wide open to develop improved methods of preparing both the carbon and the catalytic metal particles. Carbon nanotubes are increasingly becoming proposed as catalyst support material [61–63] and new methods of depositing Pt and Pt-alloy catalysts are also being developed, e.g., application of techniques such as sonochemistry and microwave irradiation. Already some catalysts prepared by the newer techniques are exhibiting much improved performance in hydrogen and PEM DMFCs.

Bonennemann et al. [64] introduced a method of synthesising carbon-supported Pt-alloy powders from organoaluminium-stabilised bimetallic colloids in which the metal particles were typically  $<2$  nm. Researchers [65,66] have also prepared Pt–Ru and other catalysts on a carbon nanofibres by decomposing single-source molecular precursors. Deivaraj and Lee [67] have produced carbon-supported Pt–Ru nanoparticles by three different methods, namely: (i) the simultaneous chemical reduction of  $\text{H}_2\text{PtCl}_6$  and  $\text{RuCl}_3$  by  $\text{NaBH}_4$  at room temperature; (ii) ethanol under reflux; (iii) the thermal decomposition of a single-source molecular precursor  $[(\text{bipy})_3\text{Ru}](\text{PtCl}_6)$ . All three routes yield catalysts that are more active than commercially available E-TEK (20 wt.%) Pt catalyst. The catalyst prepared from the single-source molecular precursor also displayed the highest tolerance to CO. More recently, Liu et al. [68] have obtained Pt nanoparticles for PEMFC catalysts by a simple microwave-

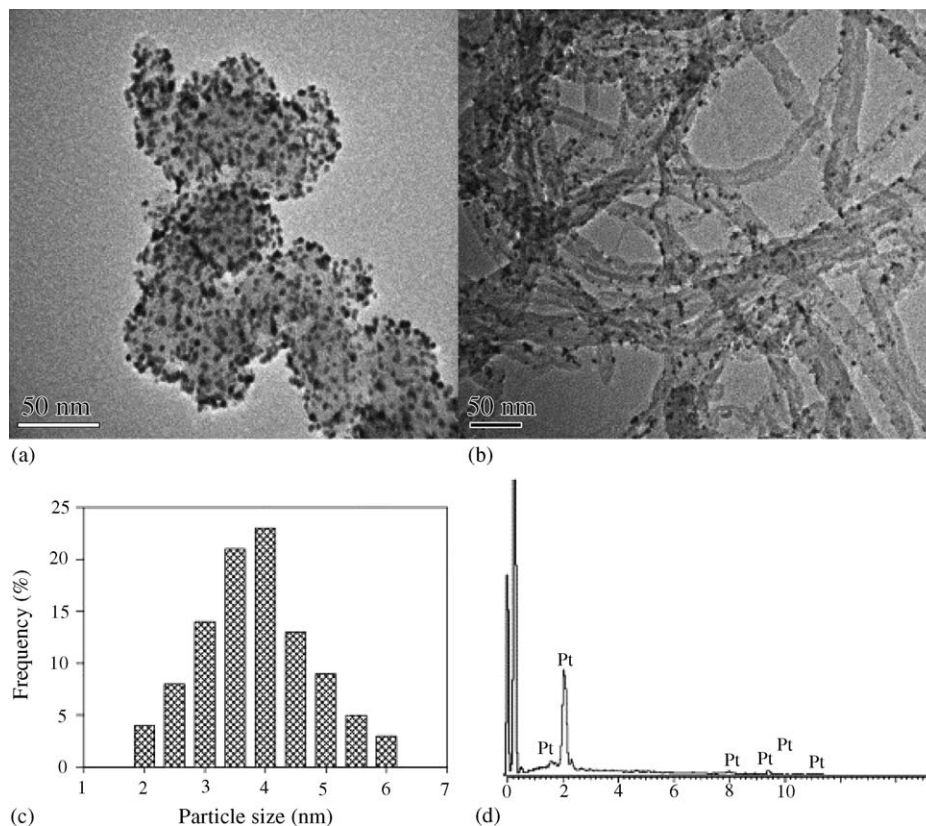


Fig. 5. TEM images of microwave-synthesised Pt nanoparticles supported on different carbons: (a) Vulcan XC-72 carbon; (b) carbon nanotubes (nominal Pt loading 20 wt.%); (c) particle-size distribution for Pt/Vulcan carbon; (d) EDX spectra of Vulcan carbon-supported Pt nanoparticles [68].



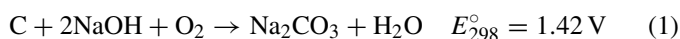
assisted polyol process in which an ethylene glycol solution of the metal precursor salt is refluxed at 393–443 K to decompose the glycol and generate reducing agents in situ for the reduction of metal ions to the element. As an example of the application of such nanotechnology, Fig. 5 shows micrographs of Pt nanoparticles deposited onto both Vulcan XC-72 and carbon nanotubes [68].

An ideal carbon support for PEMFC electrocatalysts would be one that combines good electrical conductivity with high surface area and with a pore structure that allows for filling of ionomer or polymer electrolyte to bring the catalyst particles close to the reactants and thus maximise the three-phase interface. A typical carbon black such as Vulcan XC-72 has a preponderance of small pores that cannot be filled with polymer molecules. By contrast, carbon aerogels have high mesoporosity, relatively low microporosity and high surface area that makes them attractive for this application.

Two groups have recently reported the preparation of catalysts using such carbon aerogels. Researchers in France [69] have employed two methods: (i) sol–gel reaction of formaldehyde and 2,4-dihydroxybenzoic acid, followed by deposition of Pt on the surface of the gel by ion-exchange from a precursor; (ii) the reaction of resorcinol and formaldehyde followed by drying and pyrolysis to produce a carbon powder that was subsequently impregnated with aqueous  $\text{H}_2\text{PtCl}_6$ . The Pt-doped aerogel showed high activity for oxygen reduction compared with BP 2000 and Vulcan XC-72 carbon catalysts. Smirnova et al. [70] in the USA have synthesised several carbon aerogels by means of aqueous condensation of resorcinol and formaldehyde, followed by drying and pyrolysis. In this procedure, however, supercritical  $\text{CO}_2$  is used to introduce Pt via an organometallic precursor. The Pt nanoparticles are then formed on the surface of the aerogel by a secondary pyrolysis step. Several supported Pt catalysts were prepared in this way and tested as cathode catalysts in PEMFCs. High power densities were reported for catalysts with low Pt loadings ( $0.1 \text{ mg cm}^{-2}$ ).

#### 4. Carbon as a fuel

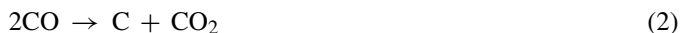
The concept of direct carbon conversion in fuel cells can be traced back at least to the work of Jacques in the 19th century [71]. He demonstrated, at the kW scale, the electrochemical oxidation of carbon in the form of rods made from baked coal. The electrolyte used was a mixture of potassium and sodium hydroxides, and the cell was run at 400–500 °C. Since the carbon was consumed rather than continuously supplied, and the hydroxides reacted to form carbonate according to Eq. (1), the system is really a battery rather than a fuel cell. Nevertheless, current densities as high as  $100 \text{ mA cm}^{-2}$  were reported for the earliest cells [71]. This early work of Jacques and others has been reviewed by Leibhafsky and Cairns [72].



Alkaline hydroxides will readily react with carbon (Eq. (1)) or carbon oxides to form carbonates, and this has proved to be a fundamental problem for all alkaline fuel cells, except where

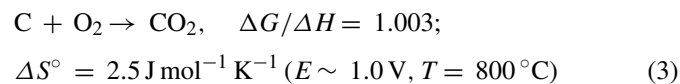
carbon is excluded from the system. The Bacon fuel cell, adopted by NASA for the space programme of the 1960s, worked well because pure hydrogen and oxygen were used as fuel and oxidant, respectively.

The use of carbon as an anode for a type of solid oxide fuel cell (i.e., employing zirconia electrolyte) was investigated by Gur and Huggins [73] and also by Nakagawa and Ishida [74]. Ihara et al. [75] have also examined the oxidation of carbon formed by the pyrolysis of methane on SOFC cermet anodes (Ni/YSZ and Ni/Gd-CeO<sub>2</sub>). In all of these studies, both  $\text{CO}_2$  and CO were produced from the anode exhaust. Thus, there was incomplete oxidation of carbon, even though the temperatures were as high as 935 °C in some cases. A novel approach to carbon oxidation with SOFC materials has been proposed by Horita et al. [76,77] in which the cermet anode is replaced with vanadium oxide/carbide. It was claimed that the latter provided an electronically conducting catalyst for the direct oxidation of carbon on its surface by the oxygen released from the zirconia electrolyte. The problem with this approach is that the carbon fuel does need to be in close contact with the anode material. This could be achieved if carbon is deposited from CO via the reverse Boudouard reaction



or by the decomposition of hydrocarbons on the surface. Another way of ensuring that carbon is close to the anode has been pursued by Cocks and LaViers at Duke University [78]. They have described a fuel cell in which carbon is dissolved in a molten metal (of the lanthanide or actinide series) to act as the electrolyte.

In 1979, Weaver et al. reported on fuel cells based on molten carbonate electrolytes and operating at 750 °C in which coal was used directly as the fuel [79]. Vutekakis et al. [80] also described a novel molten carbonate fuel cell in which coal is electrochemically oxidised. More recently work by Cooper and co-workers from Lawrence Livermore National Laboratory and other groups [81,82], has rekindled interest in the DCFC. Ironically, this is in response to the perceived need to decrease the use of carbon-containing fuels world-wide, so as to reduce greenhouse gas emissions. The argument is that the direct oxidation of carbon to  $\text{CO}_2$  in fuel cells can in theory proceed with very high conversion efficiency since the entropy change of the oxidation reaction is very small:

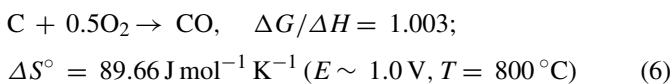


Unlike the carbon-fuelled SOFC where oxidation of carbon usually results in a mixture of both CO and  $\text{CO}_2$ , in the operating range of the molten carbonate electrolyte (700–900 °C) carbon is oxidised directly to  $\text{CO}_2$ , yielding four electrons per carbon atom. The anode and cathode half-cell reactions for the carbon fuel cell with a carbonate electrolyte are, respectively:



A further advantage of the DCFC is that, unlike most other fuel cell types in which both the anode reactants and products are gases, the cell potential is not dependent on the degree of conversion of the carbon. Thus, in theory up to 100% carbon conversion could be achieved in a single pass operation. Alternatively, if carbon is first converted to syngas (e.g., by gasification of coal with steam and oxygen), the syngas converted to hydrogen and the hydrogen used in fuel cells, then the energy and exergy losses in each conversion step can add up to a sizeable figure. In addition, the fuel cell efficiency would be limited by the need for less than 100% fuel utilisation to maintain a high Nernst potential [9,10].

The CO<sub>2</sub> produced by the DCFC would be relatively easy to capture, and ultimately sequester, since it is evolved from the anode side of the fuel cell rather than the cathode, and is therefore not mixed with oxygen-depleted air. This also makes the technology attractive from the point of view of minimising and dealing with greenhouse gas emissions. Nevertheless, simple conversion efficiency and the ability to capture the CO<sub>2</sub> released on oxidation of carbon are two of several issues that must be taken into account in a full analysis of the energy system. Also important are the practical difficulties and costs of the energy-conversion technologies, the transport and storage of fuel and the relative economic values of the different forms of energy. This has been recognised in some recent system studies. For example, Peelen et al. [81] have shown that if carbon can be oxidised to CO in a fuel cell, the conversion efficiency to electricity is very high on account of the high entropy change of the reaction:



The CO can then be shifted to high-value hydrogen for further use. This upgrading of fuel is brought about by burning low-grade fuel or by using solar power to provide the heat for the oxidation of carbon to CO. Solar thermal power can be used for preheating air and raising steam for coal gasification processes, to achieve similar ends [83]. Cooper [84] has also shown that a very high overall energy-conversion efficiency can be obtained for a system in which fuel oil is pyrolysed to carbon and hydrogen, the carbon then being oxidised to CO<sub>2</sub> in a DCFC, and the hydrogen oxidised to H<sub>2</sub>O in an SOFC. By recycling heat exhausted from the fuel cells to pyrolyse the fuel oil, conversion efficiencies of over 80% could be achieved. This approach avoids the entropy increase associated with gasification of heavy hydrocarbons such as fuel oil and coal, and could offer an attractive option for future electricity generation from high-carbon fuels.

Apart from these advantages, there are several challenges with developing DCFCs. These include the following:

- Transport of solid carbon into the fuel cell. An approach described recently by Cooper is to entrain small particles of carbon (~100 nm) in a flow of CO<sub>2</sub> to form a slurry in the fuel cell electrolyte melt.

- The fuel anode must be continuously polarised by ~20 mV during periods of standby or in areas of the cells remote from the current-collectors, to avoid oxidation of carbon to CO by the Boudouard reaction. This may require the anode pastes to be thin, and may limit the maximum generation efficiency. Cooper has found that 80% efficiency can be achieved at practical rates of fuel conversion.
- Sulfur emerges from the cell as toxic COS or COS<sub>2</sub>. The anode is not, however, poisoned, unlike Pt-containing catalysts in low-temperature fuel cells. Therefore, the presence of sulfur is not a limiting factor in cell performance.
- As with the MCFC, corrosion limits the choice of metal for the cell housing and current-collectors.
- Low-ash carbon, e.g., from cleaned coal, is necessary for a reasonable cell lifetime to be guaranteed. This could be expensive. Carbon produced by pyrolysis of liquid hydrocarbons and natural gas will have very low levels of contaminants, and should not limit the cell lifetime.

Of the various types of DCFCs, the most developed are those based on molten carbonates and molten hydroxide electrolytes.

#### 4.1. Carbon in molten carbonate fuel cells (MCFC)

The MCFC has been developed to a high degree of sophistication for running on fuels such as natural gas, which can be reformed internally due to the high operating temperatures (typically above 650 °C). Mixed alkali carbonates have a high conductivity and stability in the presence of CO<sub>2</sub> that also renders them very suitable for carbon and carbonaceous fuels. At MCFC temperatures, carbon is oxidised to CO<sub>2</sub> via half-cell reactions that may be represented by Eqs. (4) and (5). As with the conventional MCFC, the migrating ion is CO<sub>3</sub><sup>2-</sup> and although the reduction of oxygen at the MCFC cathode has been widely studied, the oxidation of carbon at the anode is not fully understood [84]. Selman [85] has suggested that the wetting behaviour of the carbon anode may be as important as the molecular mechanism for carbon oxidation.

The challenges to develop a practical carbon fuel cell using molten carbonate electrolyte have been build-up of ash in the electrolyte, low anode reaction rates, and the high cost of producing suitable carbon and its distribution in the fuel cells. The form of carbon has been found to be particularly influential on the performance of the DCFC. Cooper has shown that highly disordered carbon on the nanometre scale (2–30 nm), relative to graphite, produces high electrochemical reactivity [84]. Such disordered or ‘turbostratic’ carbon can be obtained by the controlled thermal decomposition of coal, petroleum or natural gas. The carbon structure has been found to influence the electrochemical reactivity, and although Cooper found that reaction rates did not correlate well with surface area, there was some correlation between the rates and the dimensions of the graphitic crystal structures (as measured normal and parallel to the basal plane) [86,87].

A tilted cell design of a DCFC developed by Cooper [84] at the Lawrence Livermore National Laboratory is given in Fig. 6. A conceptual approach of this design to an industrial

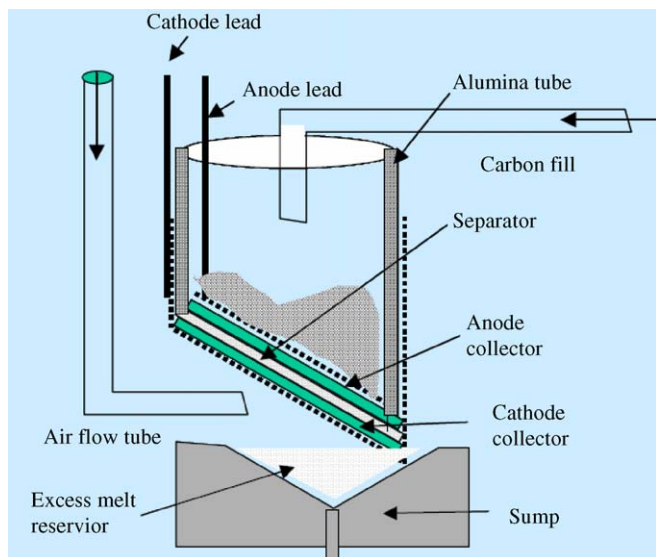


Fig. 6. Schematic of carbon fuel cell, tilted to allow exchange of melt between the cell and an underlying sump, to regulate wetting of the carbon [84].

scale unit is shown in Fig. 7. Preliminary estimates, based on the materials used in the laboratory prototype place the cost of this DCFC in the same order of magnitude as competing technologies such as coal-fired power plant, advanced gas turbines and internal-combustion engine generators [84]. Using a planar DCFC configuration with a nickel-felt air electrode, a zirconia fabric separator, a nickel-felt anode current-collector and graphite and stainless-steel construction, the cost of the cell is estimated to be below US\$ 500 kW<sup>-1</sup>.

Critical steps in the development of the technology for the conversion of fossil energy through carbonate-based DCFCs include: (1) extended duration tests of the cell at an engineering scale (1 kW) using a pneumatic feed of carbon fuel; (2) development of a scientific theory that will allow prediction of carbon electrochemical and chemical activity on the basis of pyrolysis; (3) development of electrolyte compositions to permit the conversion of high-sulfur fuels; (4) detailed investigation of processes such as pyrolysis, hydro-pyrolysis or solvent extraction for extracting the required form of low-ash carbon from fuels such as coal and lignite.

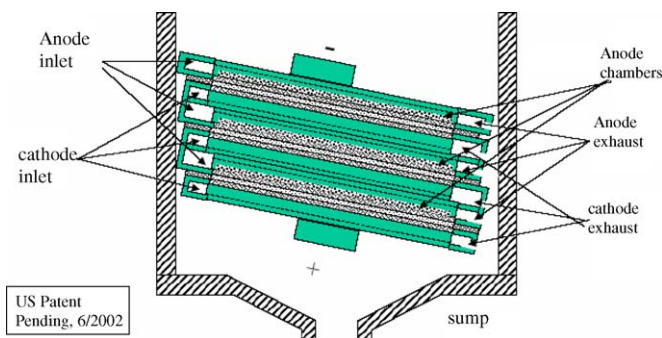


Fig. 7. A conceptual approach to industrial scale maintains orientation in a bipolar stack of rectangular cells. From Cooper [84].

#### 4.2. Carbon in alkaline fuel cells

The oxidation of carbon in molten alkaline hydroxides received little attention during the 20th century. Noting the perceived disadvantage that hydroxides readily form carbonates Zecevic et al. [88], have recently pointed out some advantages of molten alkaline electrolytes compared with molten carbonates, namely, higher ionic conductivity, higher anodic oxidation rates and lower anode overpotentials [89]. The last-mentioned offers the prospects of lower operating temperatures than molten carbonate systems and this allows low-cost materials such as low-carbon and 300-series stainless steels to be used.

The formation of carbonates by the reaction of carbon or carbon dioxide in alkali environments has been found by Goret and Tremillon [89] to be a function of the O<sup>2-</sup> ion concentration, and therefore of the water concentration. By maintaining a high water content in the molten electrolyte (by having a humid atmosphere around the melt), Zecevic et al. have shown that carbonate formation can be avoided. A high water content also significantly increases the ionic conductivity of the melt [90], and helps to reduce the corrosion rate of nickel, iron and chromium that are present in the other cell components.

#### 5. Conclusions

Carbon is a vital component of several types of fuel cell. For the AFC, PEM, DMFC and PAFC it can serve as a structural component, in the bipolar plate and gas-diffusion layers. It is also used as a catalyst support. As developers seek to reduce costs and improve performance and endurance, new forms of carbon, such as carbon fibres, composites and nanotubes, are being explored for these fuel cells.

Bipolar plates in low-temperature fuel cells were originally made of graphite on which the gas-flow channels were machined mechanically. Developers have generally moved away from this approach and now fabricate the plates either out of stamped metal that may be coated with a thin layer of carbon to reduce corrosion, or by moulding the plate using a carbon composite material. For the carbon composite approach, carbon-carbon composites, graphite-polymer mixtures, carbon-fibre-epoxy resin have all been employed and, depending on the material chosen, can either be injection moulded or compression moulded. Carbon composite materials are amenable to different flow-field designs and offer the prospects of rapid manufacturing and volume production.

Several forms of carbon can be used in fabricating the GDL and catalyst layer, particularly in PEMFCs and DMFCs. Again composite materials are more often used in the GDL and much research is evident in optimising the loading of polymer resin to make the GDL hydrophobic. Nanotechnology is enabling GDL materials to be developed that will have the required properties in the PEMFC as researchers seek to raise the operating temperature in pursuit of more robust systems.

Nanotechnology is also evident in the recent developments of catalysts for low-temperature fuel cells. Whilst much is reported on the preparation of highly dispersed Pt and Pt-alloy catalysts, it is also recognised that improvements can be made to the carbon

support structure. In this context, carbon nanotubes and specifically synthesised aerogels may prove to be better alternatives than the traditional carbon blacks of high surface area.

Carbon deposition is usually viewed as a problem in high-temperature fuel cells (SOFC and MCFC). Nevertheless, if it is in the right form, it can also be used as a fuel in these types of cell, and the thermodynamic conversion efficiency of chemical energy to electrical energy can approach 100%. Developers, particularly in the USA, are therefore revisiting the use of molten carbonate or molten hydroxide technology for direct carbon oxidation. Although there are technical issues associated with the preparation and reactivity of the carbon, if successfully developed, the direct carbon fuel cell could help to extend the use of fossil fuels for power generation as we move towards a more sustainable energy future.

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