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Carbon nanotube architectures as catalyst supports for proton exchange membrane fuel cells

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Abstract

Catalyst support materials exhibit great influence on the performance and durability of proton exchange membrane (PEM) fuel cells. This minireview article summarises recent developments into carbon nanotube-based support materials for PEM fuel cells, including the membrane electrode assembly (MEA). The advantages of using CNTs to promote catalyst performance and stability, a perspective on research directions and strategies to improve fuel cell performance and durability are discussed. It is hoped that this mini-review will act as a conduit for future developments in catalyst supports and MEA design for PEM fuel cells.

Keywords

fuel, cells, supports, architectures, carbon, nanotube, membrane, catalyst, exchange, proton

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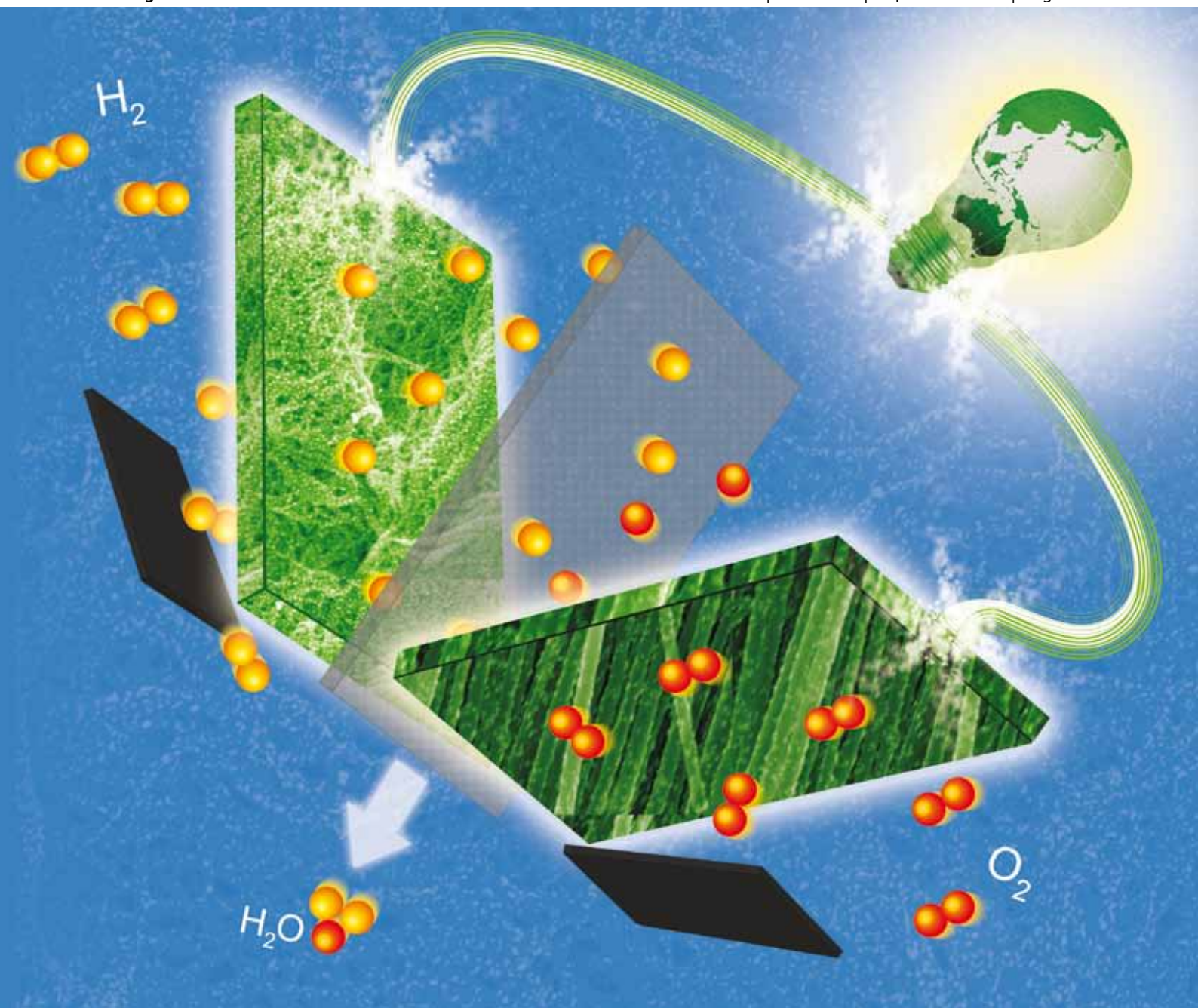
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Carbon nanotube architectures as catalyst supports for proton exchange membrane fuel cells

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Catalyst support materials exhibit great influence on the performance and durability of proton exchange membrane (PEM) fuel cells. This minireview article summarises recent developments into carbon nanotube-based support materials for PEM fuel cells, including the membrane electrode assembly (MEA). The advantages of using CNTs to promote catalyst performance and stability, a perspective on research directions and strategies to improve fuel cell performance and durability are discussed. It is hoped that this minireview will act as a conduit for future developments in catalyst supports and MEA design for PEM fuel cells.

1. Introduction

The world's energy demands are currently met by fossil fuels and whilst they are unsustainable in the long-term, alternative *renewable* energy technologies are not yet capable of meeting these demands. This issue is further hampered by the significant economic cost of their implementation. A promising future power source that is particularly useful for mobile applications are proton exchange membrane (PEM) fuel cells. Their main advantages over other forms of power sources for portable device applications include: (1) rapid start-up and shut down, (2) theoretical ability to produce higher power density outputs, and (3) construction from all-solid-state components (*i.e.* no liquid electrolyte is packaged).

A critical area of activity in PEM fuel cell research involves the development of suitable electrocatalytic electrodes for incorporation into the membrane electrode assembly (MEA). The ideal electrode must possess high specific surface area and be decorated with well-dispersed electrocatalyst. This design is necessary because the catalytic reduction of oxygen (cathode) and the catalytic oxidation of hydrogen/methanol (anode) are both

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surface processes.[1] However, the current high cost of the electrocatalyst (due mainly to the exclusive use of Platinum, Pt)[2,3] and the inherent lack of stability of Pt when supported on Carbon-black (Pt/C, the typical commercial material used as a catalyst support)[4,5] pose major barriers to PEM fuel cell commercialisation.

In addition, the most widely used Carbon-black based electrocatalyst, Vulcan XC 72R, leads to low Pt utilisation due to its structural density,[6] and is known to undergo electrochemical oxidation during long-term fuel cell operation. Platinum particles detach from the electrode support and aggregate into larger cluster sizes, which reduce the effective Pt surface area, resulting in significant reductions in fuel cell performance. It is well known that catalytic activity is highly dependent not only on the size and dispersion of the active material on the support,[7] but also the degree of their interaction.[8–10] Consequently, research into the development of more efficient supports to prevent detachment and/or aggregation of the catalyst has become an area of significant activity.[11–13]

Indeed, a suitable support for an electrocatalyst should posses the following properties: (a) high surface area, (b) good electrical properties, and (c) high electrochemical stability under PEM fuel cell operating conditions. Carbon nanotubes (CNTs) potentially match these requirements including a wide electrochemical potential window, good chemical stability and large surface area which make them attractive as electrode material candidates.[14]

Broader context

The world's energy demands are currently met by fossil fuels and whilst they are unsustainable in the long-term, alternative, renewable technologies are not yet capable of meeting these demands. Proton exchange membrane (PEM) fuel cells are one promising future power source that are particularly useful for mobile applications, with many advantages over other power sources. Before becoming commercially viable, a critical area of activity involves the development of suitable electrocatalytic electrodes for the fabrication of the membrane electrode assembly (MEA). These catalytic support materials are critical components directly influencing the overall fuel cell performance and durability. One such promising material is carbon nanotubes. This minireview discusses not only the advantages of using carbon nanotube architectures as the support materials but also a perspective on current research directions and strategies to improve PEM fuel cell performance and stability *via* the approach development for catalyst deposition and novel MEA design.

Effective use of these attributes as a new class of support material[15–17] should lead to significant increases in catalyst utilisation and therefore improvements in electrocatalytic activity.

Indeed, enhancement in electrocatalytic performance using nanostructured CNT supports has recently been reported.[18,19]

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Andrew I. Minett

CNT-based electrodes have been shown to provide enhanced electron transfer characteristics with electrochemical activity known to take place at the edge-plane sites, on the tube surface, on the tube ends and at defects.[20,21] However, it is apparent that a large amount of research activity is required before we can really make the most out of the properties of CNTs in PEM fuel cell applications. In this short overview, we will explore the progress that has already been made to this end. We will review the use of carbon nanotubes, both from as-received CNT powder and from pre-formed architectures, as PEM electrocatalyst supports. The techniques to load metal catalysts onto these architectures will also be compared. Finally, we will discuss our perspective on what needs to be done in the near future.

2. Carbon nanotube powders

Carbon nanotubes (CNTs) have attracted great interest in fuel cell applications as a promising support for metal catalysts, due to their unique chemical stability and higher surface to volume ratio compared with carbon black.[14,22] Initial research into both single-wall (SWNT) and multi-wall carbon nanotubes (MWNT) were directly used for catalyst deposition from as-received or purified soot.[16–22] However, recent studies have shown that the functionality of CNTs also play a key role in achieving high and stable catalyst loading levels.[28–32]

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Jun Chen

2.1. Carbon nanotubes (SWNTs and MWNTs)

SWNT and MWNT soot have been widely investigated as supports in the dispersion and stabilisation of Pt or Pt-metal alloy electrocatalysts for PEM fuel cells.[22–44] Typically, MWNT have higher conduction than SWNT due to the larger outer shell which is considered to be conductive relevant, whilst the latter usually provide greater surface area in preparation of supported Pt catalysts. For instance, investigations into support/catalyst interactions have shown increased catalytic activity in both SWNT and MWNT systems. Yang and co-workers[45] prepared Pt decorated SWNT and MWNT using Pt nanoparticles with an average size of 3.5 nm in diameter. Electrochemical characterisation revealed an electrochemically active surface area and electrocatalytic activity of Pt catalysts to be higher on SWNT (114.7 m^2 g^{-1} Pt) compared to those supported on MWNT (93.6 m^2 g^{-1} Pt). Recently, we investigated the effect of supports on the electrochemical performance of Pt catalyst toward PEM fuel cell evaluation (Fig. 1). In our studies, we prepared Pt on SWNT and carbon black using a microwave-assisted polyol method. Subsequent characterisation indicated that the electrocatalytic activity and fuel cell performance of the Pt catalyst are support-dependent with higher electrochemical active surface area as well as greater power density (340 mW cm^{-2} at 0.6 V) obtained on Pt/SWNT than on Pt/C (200 mW cm^{-2} at 0.6 V).[38]

Due to the versatility of carbon chemistry, many of the methods used to prepare Pt/C are directly transferable to CNT supports. Synthetic techniques include; conventional impregnation,[23–26] precipitation,[34,35] colloidal,[36,37] microwave-assisted polyol,[38–40] electrochemical deposition,[41,42] ion-exchange,[43] and sputter deposition processes.[51] Recent advances in the development of these synthesis methods have resulted in improved control of the deposition, size and distribution of the Pt nanoparticles, directly improving the electrocatalytic activity of the catalysts.[23,24] Li et al.[24] investigated the impact of the synthetic approach and support material on Pt dispersions. In their experiments, impregnation, precipitation and the colloidal method were used to prepare CNT and Vulcan XC 72 carbon black supported Pt nanoparticles (Fig. 2). They found the colloidal method to be more effective than the other two methods in terms of dispersion uniformity for either CNT or carbon black being decorated with ~2 nm Pt nanoparticles. In comparison, nanoparticle agglomeration, larger particle sizes (9.8 nm and 4.8 nm for impregnation and precipitation respectively) with broad distributions of nanoparticles being observed for the impregnation and precipitation processes.
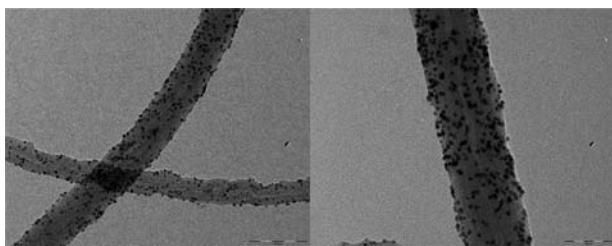

Fig. 1 Scanning electron microscopy images of Pt nanoparticle loaded multi-wall carbon nanotubes.
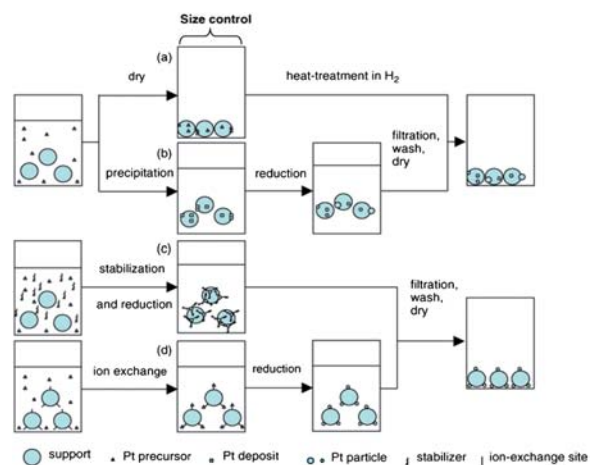

Fig. 2 Synthesis strategies of (a) impregnation, (b) precipitation, (c) colloidal, and (d) ion exchange methods. *Reprinted from ref. 31 with permission from Elsevier.*

Recently, a microwave-assisted polyol process was employed for the preparation of Pt/CNT catalysts,[38–40] highlighting the advantages of using this method for fast, simple and uniform deposition of nanoparticles using energy efficient microwave heating. Liu et al.[39] prepared highly dispersed Pt nanoparticles on CNTs with a nanoparticle size of 3.6 ± 0.3 nm. In addition, Day et al.[42] developed an electrochemical method to prepare nanoparticles on as-received SWNT surfaces. This method involves applying a potential between the SWNT network as a working electrode and the reference electrode. In their investigations, they demonstrated control over the number density and distribution on the CNT surface as a function of deposition potential and time. Other methods such as sputter coating or ion-exchange have also proved attractive to prepare uniform-dispersion of Pt/CNTs.[43,44]

2.2. Functionalised CNTs

Pristine CNTs are chemically inert and generally do not provide enough surface charge for metal nanoparticle deposition. Typically, this lack of anchor points results in adsorption dominate functionalisation of the nanoparticles, leading to aggregation and low loading levels on the substrates.[26,35] Therefore, it is vital for the CNTs to be functionalised before preparation as fuel cell electrocatalysts,[28–32] to increase surface nucleation sites for the nanoparticle deposition. The most widely investigated methods for functionalisation of CNTs can be separated into two categories: covalent modification[28–32,46–48] and noncovalent modification.[49,50] The covalent surface modification of CNT involves a permanent change to the surface hybridisation such that covalent bonds form with another molecule. Non-covalent modification is usually a physical adsorption process which does not lead to the formation of a chemical bond between the CNT surface and a molecule.

The most widely investigated covalent functionalisation method firstly involves conventional chemical surface oxidation. This typically involves harsh pre-treatment of the CNTs by refluxing in one or a mixture of strong acids such as concentrated HNO$_3$, H$_2$SO$_4$, and HCl or strong oxidizing reagents such as

H_2O_2, $KMnO_4$ to produce functionalities such as carboxyl (–COOH), hydroxyl (–OH) and carbonyl (>C=O) groups. Such species have been demonstrated as suitable anchoring sites for platinum metal particles on CNT supports.[29–32,46] More uniform distribution and higher loading levels of Pt nanoparticles (up to 30 wt%) could be obtained on functionalised CNT support compared with those prepared on pristine or as-received CNT soot under identical conditions (<10 wt%).[46]

Since harsh treatment with such concentrated acid mixtures causes structural damage and degradation of electrical conductivity during the oxidation process, new gentler functionalisation methods were investigated. Guo and Li[47,49] demonstrated a milder electrochemical pre-treatment method without causing serve damage to the CNT, whilst introducing the required carboxyl (–COOH), hydroxyl (–OH) and carbonyl (>C=O) groups. The subsequent electrochemical deposition lead to 5 nm Pt nanoparticles formed on the CNT supports.[46,48]

Recently, many other effective covalent modification methods have also been investigated. For example, Guo and co-workers[28] described a method to functionalize the CNT surface by using ionic liquids (IL) (Fig. 3). In their experiments, COOH-functionalized CNTs were further reacted with amine-terminated methylimidazoles in the presence of a coupling agent (N,N′-dicyclohexylcarbodiimide, DCC) which lead to the formation of amide bonds between the IL and CNT surface. The imidazolium group which is a common cation in ILs, can serve as the linker to couple the counter-anion $PtCl_4^{2-}$. The subsequent reduction was carried out using ascorbic acid as the reducing agent. They reported higher electrochemically active surface areas of the as-prepared Pt catalysts on IL functionalised CNTs (67.6 m^2 g^{-1}) compared with those supported on the polyelectrolyte functionalized CNTs (52.9 m^2 g^{-1}) and E-TEK catalyst (51.7 m^2 g^{-1}).

Non-covalent functionalization of CNT has attracted a great deal interest in synthesis of Pt/CNT catalyst since this method not only yields a high density and homogeneous distribution of
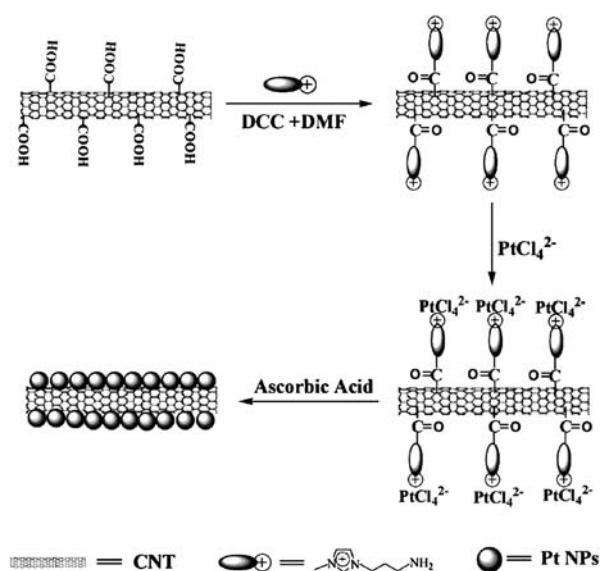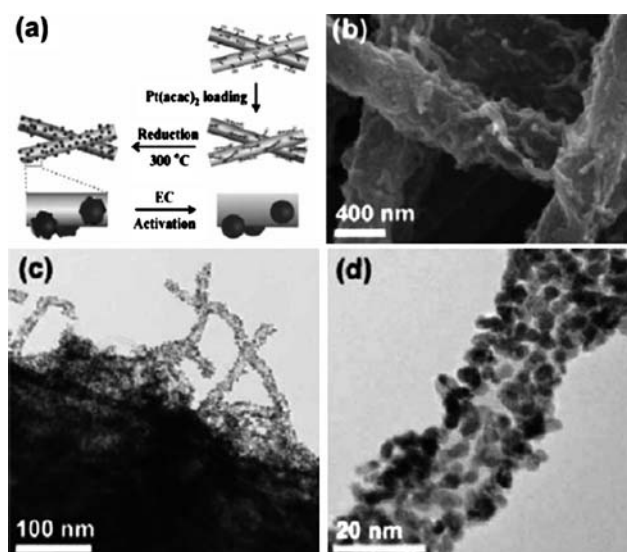

Fig. 4 Schematic of PDDA functionalization of MWNTs and the formation of Pt/MWNTs. *Reprinted from ref. 49 with permission from Institute of Physics.*

functional groups on CNT surface but also maintains the intrinsic properties of the support.[49–56] Wang et al.[49,53,56] investigated a highly effective polyelectrolyte functionalization of multi-walled carbon nanotubes with diallyldimethylammonium chloride (PDDA) (Fig. 4). The π–π interaction between PDDA and MWNT leads to strong adsorption of the positively charged PDDA on the MWNT which could serve as a linker between the MWNTs and negatively charged Pt precursors. The subsequent reduction of the Pt precursors yielded high density Pt nanoparticles (40–60 wt%) with an average particle size of 1.8 ± 0.4 nm uniformly distributed on the MWNT. In the case of Pt on conventional acid treated CNT, much larger 5 ± 2 nm particles and aggregates were observed.[49]

3. Carbon nanotube architectures

In spite of the significant amount of research on carbon nanotube soot for PEM fuel cells, there are a number of fundamental impediments to the commercialisation of these materials. The key impediment is the loss of catalytic stability in CNT supported catalysts during the assembly of a MEA. This assembly often results in a loss of available catalytic surface area. In order to improve the catalytic performance and increase the utilisation of the catalysts, researchers have recently started to investigate alternative approaches, such as utilising CNT-based nanostructured architectures (templates and/or substrates) as catalyst supports. Traditional CNT membrane electrode assemblies have involved the decoration of CNT soot with catalytic particles followed by membrane formation through drop casting or pellet pressing. Typical membranes formed include Nafion-CNT melt pressed papers,[57] CNT-Nafion ball-milled films,[58] and CNT-polymer films.[59] Unfortunately these assemblies typically have an uncontrolled structure and are not optimised for FC membranes. The most significant oversight for these materials is the waste of platinum buried deep within the structure, which is inaccessible during the operation of the device.

Fig. 3 Schematic of the synthesis process of CNTs/IS-ILs/Pt hybids. DMF represents N,N-dimethylformamide.[26] *Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.*

3.1. CNT bucky paper and gas diffusion layer (GDL)

Carbon nanotube/amorphous carbon (CNT/AC) "Bucky" papers are produced by the filtration of a CNT dispersion into a mechanically durable architecture.[60–63] The advantage of bucky papers lie in the ease of production, lateral conductivity and durability. Adaptation of bucky papers for FCs can occur through two pathways; decoration of CNTs with Pt during the soot phase; or decoration of the pre-formed architecture with Pt. This second method has the advantage of conserving Pt as the metal is only decorated at the most accessible sites within the structure (Fig. 5).

Zhu *et al.* demonstrated high platinum utilisation using a bucky paper electrode of 0.5 g_{Pt} kW^{-1} whilst maintaining a current density of 760 mA cm^{-2} by using such an architecturally-based decoration technique. Bucky papers have also shown significant promise as materials for GDLs within PEMFCs. Tang *et al.* demonstrated a clear improvement in the performance of the GDL when switching from a porous woven carbon fibre cloth to a bucky paper.[64,65] Soehn *et al.* postulate that the use of a bucky paper electrode can create a defined boundary of catalytic loading, due to the hydrophobicity of the substrate, leading to a decreased catalyst loss through diffusion and water drag.[65] Despite the durability of these materials, research into bucky papers as functional FC electrodes is limited due to a lack of achievable morphological control.

The focus on gaining more active surface area in order to increase PEM performance has led to the development of 3-dimensional (3D) porous materials as catalyst supports. One of the most common forms of these 3D supports are CNTs grown on a porous carbon fibre support (Fig. 6).[58,64–74]

Many of these porous carbon supports double in function as the GDL for the FC membrane electrode assemblies (MEA).[65,75–77] The deposition of MWNTs onto GDLs provide several specific advantages to the system, including; increasing the surface area and the number of triple contacts (gas|electrolyte|electrode). Methanol oxidation has been observed in such systems with loadings as low as 0.4 mg Pt cm^{-2}. The key advantage from these forms of materials is the electronic connection between the catalyst particles and the external electrical circuit (Fig. 6).[70–72] There are, however, a number of additional advantages to using such 3D supports, including; minimising the number of processing steps; the ability to tailor the porosity of the material; and increased electrochemically active surface area. Preliminary work on these
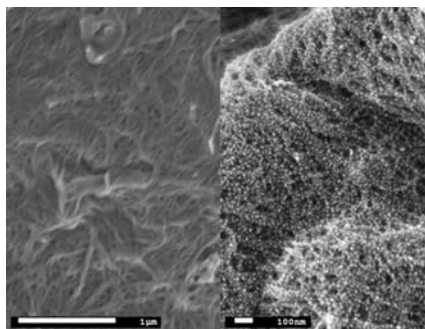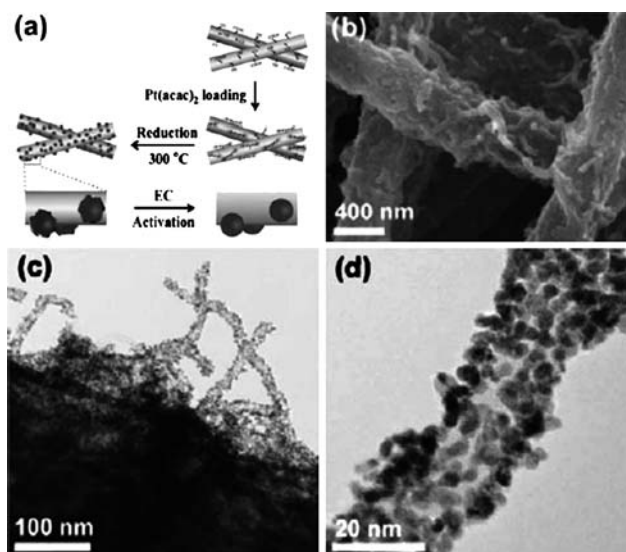

Fig. 6 (a) Scheme of Pt loading on a CNF mat. (b) SEM and (c)–(d)TEM images of Pt nanoparticles loaded on a 3D architecture oft-MWCNTs anchored CNF composite mat. Ref. 69 – *Reproduced by permission of The Royal Society of Chemistry (RSC).*

materials by Wang *et al.* utilised such structures as MEAs through hot pressing with Nafion.[78]

Although the performance of these devices was comparatively poor, there remained significant scope for improvement in the materials through decreasing the CNT and catalyst particle diameters. Xuyen *et al.* demonstrated that current density of a carbon nanotube/nanofibre (CNT/CNF) composite was 1.7 times higher than the previously reported benchmark, using 2.9 nm Pt particles (compared to the 25 nm particles initially utilised by Yan *et al.*).[69] This improvement in catalytic performance is quite similar to that of Saha *et al.* who demonstrated a 56% improvement in platinum mass activity by using such a composite structure (from 62 mA mg_{Pt}^{-1} to 146.4 mA mg_{Pt}^{-1}). Addition of nitrogen atoms into the CNT backbone also has a significant effect on the performance of the electrode, with an improvement in ORR current density from 29 mA cm^{-2} for a CNT/CNF composite to 80 mA cm^{-2} for an N-CNT/CNF composite.

3.2. Advanced 3D nanostructured CNT architectures

Vertically aligned CNTs (VACNT) have been intensely studied as electrode materials due to the high surface area:volume ratio, conductivity and regular pore structure these materials possess. One of the limiting factors in adapting VACNTs to fuel cell technologies has been the difficulties in getting the catalytic particles into the fine pore structure. Gong *et al.* has recently overcome this limitation using nitrogen doped VACNTs which function as oxygen reduction catalysts without the need for metallic particles.[79] Tang *et al.* demonstrated a four-fold improvement in electrocatalytic current using a VACNT network compared to a graphite electrode.[73,74] This improvement is attributed to higher catalytic utilisation compared to a flat electrode surface.

Fig. 5 SEM image of a bucky paper (a) prior to, and (b) after Pt decoration for use as FC electrodes.

Additionally, iron-containing VACNTs were shown to function as ORR catalysts *via* the formation of Fe–N–C junctions in the material by Dahn and Liu.[81] For conventional catalytic systems however, it is required that the VACNT be given some lateral connectivity. This connectivity is achieved through the deposition of a thin polymer layer giving the forest flexibility and durability for electrode use.[82] An alternative method for the preparation of VACNTs is through an anodised aluminium oxide template. This method has the advantages of producing a stable, controllable pore size distribution though the electrode (Fig. 7).[80] The methanol oxidation current for an AAO-VACNT material was 73 mA cm^{-2} with a large negative shift in potential for the reaction compared to a Pt microdisk. One key advantage of using a templating method in the production of VACNTs is the change in macro porosity, as shown in Fig. 7, allowing for greater electrolyte diffusion into the electrode structure.

Recently, we demonstrated a novel free-standing, sandwich-structured MEA (Fig. 8). This ACNT/Nafion/ACNT structure with nano-Pt (0.142 mg cm^{-2}) was created *via* the attachment of *two sets* of aligned CNT array electrode structures to opposite sides of a Nafion PEM membrane exhibits significantly improved performance compared to commercially available Pt/CB catalysts used in PEM fuel cell applications. The single PEM fuel cell using nano-Pt-loaded ACNT/Nafion/ACNT, displayed improved performance with a current density of 605.88 mA cm^{-2} and a power density of 397.23 mW cm^{-2} at a potential of 0.65 V. This was more than two times higher than the values obtained using Pt/CB electrodes under the same operating conditions. This novel structure appears to offer a prospective future platform
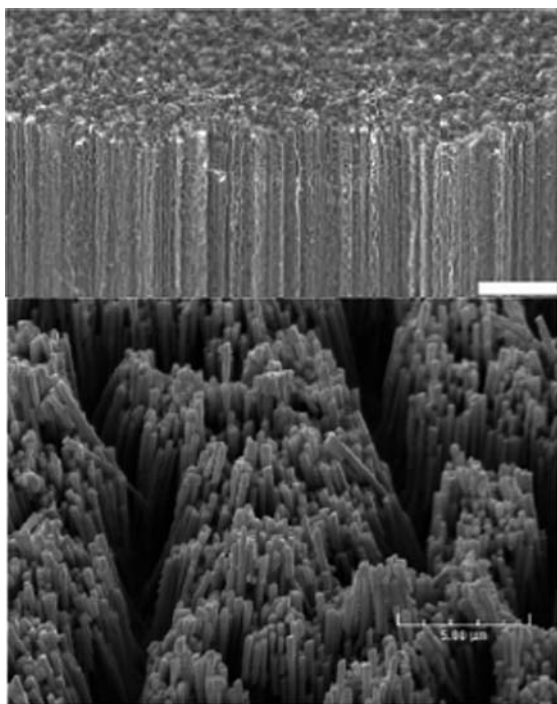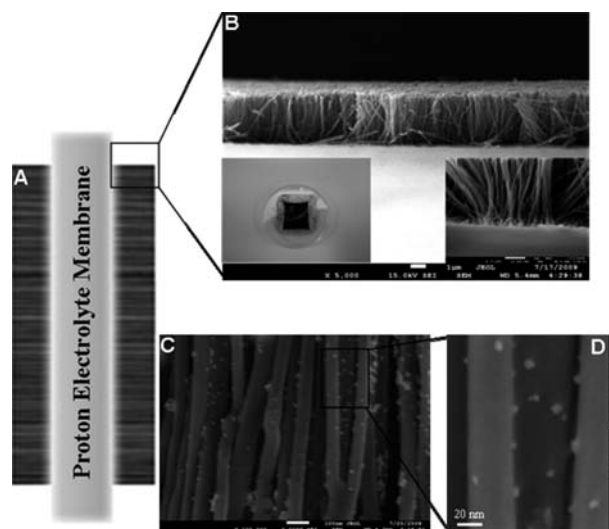
Fig. 8 Images of nano-Pt-loaded ACNT/Nafion membrane electrode; (A) designed structure of the ACNT/Nafion membrane electrode; (B) SEM image of the aligned CNT array on the Nafion membrane (the right insert shows an SEM image of the cross-section of ACNT/Nafion membrane electrode; the left insert depicts the whole nano-Pt-loaded ACNT/Nafion membrane array as tested in a single-cell arrangement; (C) & (D) SEM images of nano-Pt on aligned CNTs after single-cell test.[83] – *Reproduced by permission of The Royal Society of Chemistry (RSC).*

technology, lowering Pt levels in fuel cells and directly increasing overall fuel cell performance.[83]

A next evolution in design of the GDL or MEA will involve entangled CNT networks removed from any underlying carbon fibre layer and control of macroporosity through templating during production or tailored pore sizes. Indeed such free-standing architectures already exist, however they have yet to be applied as fuel cell electrodes.[84,85] In addition, recent work has demonstrated the ability to rapidly decorate an array of 3D structures (Fig. 9), including these free-standing architectures, fibres and bucky papers, quickly and cheaply using microwave polyol processes. This process has been reported to produce highly stable particles which do not appear to agglomerate over preliminary fuel cell tests.[39] In essence, this presents a excellent opportunity for the study of a new range of 3D CNT architectures in the near future.

Conclusion

In conclusion, considerable progress has been made over the last few years in exploring several forms and architectures of carbon nanotubes either as catalyst support materials or as packaged membrane electrode assembly (MEA) components of PEM fuel cells. Carbon nanotubes, when appropriately processed, function well in PEM fuel cells because of their high surface area, good conductivity, controllable porosity and appropriate electrochemical stability under fuel cell operating conditions. Many researchers have shown that significant improvement on catalytic performance can be achieved owing to the increased stability of catalyst nanoparticles deposited on CNT-based support materials. Typically, a metal nanoparticle-decorated carbon nanotube soot is prepared (deposited *via* chemical or electrochemical

Fig. 7 (a) SEM image of VACNTs containing nitrogen as grown on a quartz substrate (scale bar is 2 μm); *from ref. 79. Reprinted with permission from AAAS.* (b) Pt-CNT composite array from an AAO template. *Reprinted from ref. 80 with permission from Elsevier.*

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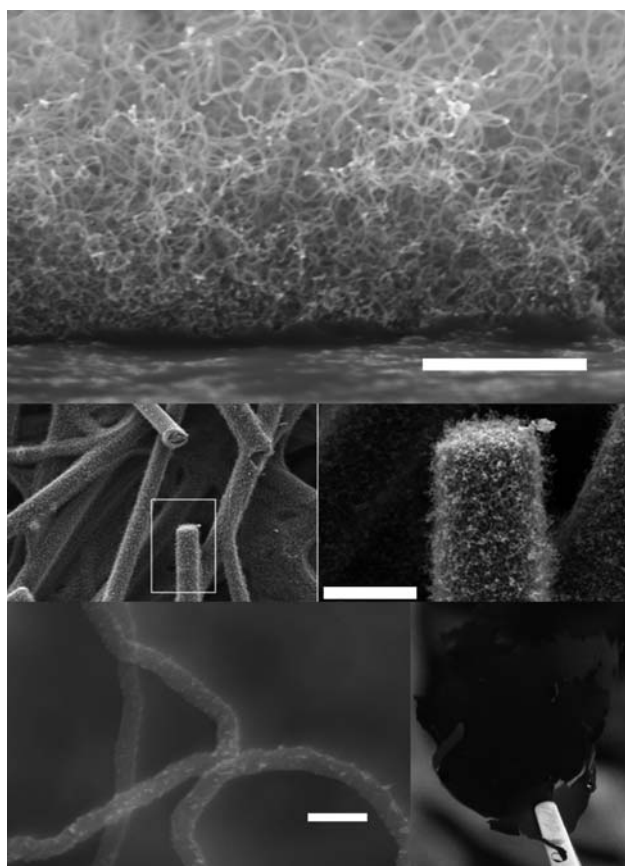*Energy Environ. Sci.*, 2010, **3**, 1286–1293 | 1291

Fig. 9 SEM images of (a) free-standing entangled CNT architecture (scale bar = 5 μm); (b) structure shown in (a), produced on a carbon fibre mat; (c) enlarged carbon fibre-CNT composite (scale bar = 100 μm); (d) platinum loaded entangled CNT free-standing material (scale bar = 100 nm); and optical image (e) of the free-standing entangled CNT material.

process) prior to fabrication of membrane electrodes. A more recent exciting development is the direct deposition of metal catalyst onto several forms of pre-fabricated free-standing 3D carbon nanotube architectures. This latter process allows catalyst decoration only to the active area exposed to the fuels, thus improving efficiency and reducing the cost of electrode manufacture. The resulting architecture also functions as the gas diffusion layer, minimising the number of components required for the fuel cell device. This results in a further improvement in the overall fuel cell performance (increased power density). In both methods, surface functionalisation has been shown to play a key role in improving the overriding problem of substrate-metal interaction, thereby preventing catalyst migration and re-aggregation (and in some cases, further improving electrode durability).

We envisage that there is still wide scope for improvement in the development of CNT-based catalyst support materials. Furthermore, catalyst adsorption can be further improved *via* more effective functionalisation protocols. More importantly, the MEA must be carefully designed. However, we believe that it is the dynamic development of all the MEA components combined together and how it is incorporated into a functioning device, that will contribute to the greatest improvement in overall fuel cell performance. If this area continues to develop apace, we can expect a potentially very useful and commercially viable technology to overcome some of the challenges we currently face in the alternative energy sector.

Acknowledgements

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