Application of carbon nanotubes in polymer electrolyte based fuel cells

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Abstract
Polymer electrolyte based fuel cells (PEFCs) are always in the forefront of fuel cell revolution. Recently a wide variety of application of carbon nanotubes (CNTs) in PEFC components has been exploited. The impetus is to improve the PEFC performance by taking advantages of CNTs’ extraordinary physical, chemical and electronic properties. Herein, we briefly review these efforts with an attempt to obtain a better understanding on the role of CNTs in PEFCs, and this article is structured as the following: the contribution of CNTs is first addressed in terms of improving the mechanical strength and proton conductivity of polymer electrolyte membrane; their role in electrocatalysis is then discussed with respect to facilitating the utilization of noble metal catalysts (platinum) and exploring the platinum-free catalysts; the consideration of CNTs as hydrogen storage materials is also highlighted. Based on the literatures studied, CNTs demonstrate great potential as multifunctional materials in improving PEFC performance.

Keywords: polymer electrolyte based fuel cell; carbon nanotube; polymer electrolyte membrane; electrocatalysis; hydrogen storage
Introduction

With the ever-growing concerns about the environment pollutions and the exhaustion of energy resources, and the commercialization of fuel cell automobiles, there is an urgent need for the development of reliable, high performance fuel cells that are operable at low temperature. As such, polymer electrolyte-based fuel cells (PEFCs), which can be operated at around 100 °C, have attracted particular attention recently. PEFCs are also distinguishable because they can provide high power density with a short start-up time. PEFCs include proton exchange membrane fuel cells (PEMFCs) using hydrogen gas as the fuel source and direct methanol fuel cells (DMFCs) which generate power using liquid methanol as the fuel source. Owing to their advantageous features, PEFCs have been considered as the promising power sources for portable, automobile, and stationary applications [1-4]. Despite the tremendous development of PEFCs, challenges are still there, hampering the large scaled commercialization of PEFCs. The first barrier is their high cost. For instant, the cost target of the US Department of Energy (US D.O.E.) for PEMFC stack is 30 $ per kW by 2015, which is less than one third of its current cost (110 $ per kW) [5]. High loading of the noble metal catalysts on the electrodes and the use of perfluorosulfonic acid membrane are among the main contributors to the current high cost. The durability of fuel cell is another property needing to be improved. The major modes of failures are the breakdown of polymer electrolyte membrane (PEM) and the loss in active surface area of metal catalysts with operating time. To find a suitable material that is capable of adsorbing and releasing large quantities of hydrogen at ambient temperature and
pressure easily and reliably represents another challenge. Undoubtedly, the success in overcoming these barriers will witness the proliferation of PEFCs.

On the other hand, carbon nanotubes (CNTs) have set themselves apart as a new kind of materials due to their distinct properties. Recently, a number of investigations have been carried out to incorporate CNTs into the components of fuel cells to improve the performance and lower the cost. CNTs have high strength and toughness to weight characteristics, which stimulate researchers to employ them as reinforcing fillers to improve the mechanical strength of PEM; their high surface area and thermal conductivity make them useful as electrocatalyst supports; they can also be applied in gas diffusion layers and current collectors because of their high electrical conductivity; their layered graphene tubular structure enables them to be a potential candidate for hydrogen storage. In this article, we will briefly review the recent communications, mainly published in 2005 and after, and discuss the results obtained; this may help us obtain a better understanding on the multifunctional role of CNTs and improve the fuel cell performance by taking advantage of the unique properties of CNTs.

1. Application of CNTs in PEM

PEM is one of the key components in PEFCs, which not only restrict the performance of fuel cell but also the overall cost. An ideal PEM should be proton conductive, facilitating the transport of proton from anode to cathode; but yet electron insulating, avoiding the occurrence of electrical short circuiting. It should also have low permeability to the feeding fuels, such as hydrogen and methanol, and high chemical stability to withstand the harsh chemical conditions that the fuel cell is undergoing under operation. Additionally, it needs to be mechanically strong enough to withstand
the stress of fabrication and the dimension change (swelling and contraction) due to the change of water content as well. Owing to the presence of sulfonic acid groups, perfluorosulfonate ionomer, such as Nafion (see Fig 1 for its chemical structure), possesses high proton conductivity. And it is also relatively mechanically and chemically stable. Therefore, it seems to match most of the requirements as a PEM material, and is a promising candidate. Indeed, its applications in fuel cells have been explored extensively in the past few years.

1.1 Improvement of mechanical properties

The strength of the sp² carbon-carbon bonds gives CNTs amazing mechanical properties. The Young's modulus of the best nanotubes can be as high as 1000 GPa which is approximately 5 fold higher than steel; the tensile strength of nanotubes can be up to 63 GPa, around 50 fold higher than steel. These properties, coupled with their lightness, endow CNTs great potential to be applied as reinforcing fillers to improve the mechanical strength of host matrices [6]. On the other hand, Nafion membranes merely have a moderate mechanical stability, especially at high temperature [7,8]. This may incur problems in the fabrication of membrane; furthermore, when the fuel cell is in operation, the swelling and contraction of Nafion membrane initiated by the variation in hydration level may change the dimension of membrane and affect the fuel cell performance and working life. As a matter of fact, the breakdown of PEM is one of the major modes of failures of fuel cell systems. To hurdle these obstacles, great efforts have been devoted to improving the mechanical strength of Nafion by incorporating CNTs [9].
Liu et al reported that the incorporation of 1 wt% CNTs into Nafion could decrease the dimensional change of membrane, whilst maintain the proton conductivity [10]. Based on this work, they subsequently proposed a sandwich structured electrolyte membrane with a platinum (Pt)/CNT/Nafion layer interpolated between two plain Nafion layers [11]. The beauties of this design are (i) as a catalyst, Pt can facilitate the recombination of H₂ and O₂ that permeate from electrodes in the electrolyte layer and produce H₂O, and thus this layer has the self-humidifying function; (ii) as reinforcing fillers, CNTs can improve the mechanical strength of the membrane; (iii) as electrical insulators, the two Nafion layers can remove the worries about the happening of short circuiting between two electrodes. Thomassion et al also demonstrated that the incorporation of 2 wt % carboxyl acid group decorated multi-walled carbon nanotubes (MWCNTs) into Nafion could increase the Young’s modulus up to 160%, but still maintain the similar level of ionic conductivity with respect to pure Nafion membrane [12]. By blending 3 wt % H₂O₂/NaOH oxidized MWCNTs into Nafion membrane, the tensile strength increased from 18.5 MPa to 28.6 MPa and the elongation at break increased from 112 % to 142 % [13].

It is worth stressing that care must been taken when CNTs are used to reinforce Nafion membrane that is going to be applied as ionic conductive membrane in fuel cell. This is correlated with another distinct property of CNTs—excellent electrical conductivity. If the quantity of CNTs involved is sufficiently high, the membrane will become electron conductive and completely lose its function as the electron barrier. It seems 2-3 wt. % can be the safe threshold value [12,13], but this can really truly serve as the referenced number and the true value for any specific system can only be established by trials and errors, because the development of electron conductive
network by CNTs in polymer matrix is also controlled by the aspect ratio of CNTs, their intrinsically electrical property, their dispersion and orientation state in polymer matrix, their interactions with the matrix at the interfaces, and the phase separation effect of a third phase, if applied [14].

1.2 Effect on proton conductivity

The proton conductive ability of polymer electrolyte layer is one of the key parameters that govern the performance of fuel cell. As such, the effect of incorporation of CNTs on the proton conductivity of Nafion has become the research topic of many researchers.

Cele et al found that the introduction of HNO$_3$-oxidized 1 wt. % MWCNTs or hexadecylamine-functionalized MWCNTs into Nafion decreased its ionic conductivity by a small amount, particularly, in the case of amine functionalized MWCNTs, which might be ascribed to the presence of amine surfactant chains on the tubes’ outer layer and the poor dispersion of CNTs in Nafion [7]. By covalently grafting hydrophilic layers composed of poly (oxyalkylene)diamines and tetraethyl orthosilicate-reinforced polysiloxane in a layer-by-layer manner, MWCNTs were functionalized with polysiloxane, which were then blended with Nafion to form a proton-conducting membrane [15]. The proton conductivity of these membranes kept stable up to 130°C; unlike pure Nafion, the proton conductivity of which dropped significantly when the temperature was over 100°C. The authors ascribed this to the stronger binding of water inside the membrane, particularly the stronger bonding of water on –CH$_2$CH$_2$O- and –SO$_3$-NH$_3^+$ linkages. This finding is exciting, since the proton conductivity of Nafion increases exponentially with increasing temperature and it is likely that fuel cell performance will be improved by operating at elevated
temperatures. Another bonus of operation at elevated temperatures is its beneficial effect on electrode kinetics, promoting the carbon monoxide (CO) tolerance of electrocatalyst and lowering the loading of precious metal, for instant, Pt [16]. Nafion is conductive to proton in that its sulfonic acid groups provide the active sites for the hopping of proton upon hydration [17]. Hence, the increase of sulfonic acid group concentration could, in principle, increase the proton conductivity of Nafion. By mixing the sulfonic acid functionalized single walled carbon nanotubes (SWCNTs) and Nafion, followed by heat-cast at 70°C, a decorated Nafion membrane was prepared and it was observed that the proton conductivity was enhanced by one order of magnitude [8].

Despite its excellent ionic conductivity, Nafion is costly and can only work efficiently with a high level of humidity [18]. These limitations are the driving forces for exploring other cheaper ionic conductors that may be used to replace Nafion [19-21]. Kannan et al implanted 2-aminoethylphosphonic acid functionalized MWCNTs into polybenzimidazole membrane and observed that the proton conductivity of membrane was improved by 50% (from 0.07 S cm\(^{-1}\) to 0.11 S cm\(^{-1}\)) [22]. By the solution casting method, Zhou et al manufactured a series of composite membranes consisting of sulfonated MWCNTs and sulfonated poly (ether sulfone ether ketone ketone) [23]. It was reported that the introduction of sulfonated MWCNTs could increase the proton conductivity from 2.94×10\(^{-3}\) S cm\(^{-1}\) to 4.39×10\(^{-3}\) S cm\(^{-1}\), depending on the quantity of MWCNTs involved; while the reverse trend was observed for raw MWCNTs, where the proton conductivity dropped a bit on the blending of MWCNTs. Irrespective of these efforts, Nafion is still preferred in terms of ionic conductivity, which is generally 10 fold higher than these proposed polymers [12,13,15,24,25].
2. Application of CNTs as catalyst supports

One dominant obstacle to the commercialization of fuel cells is their high cost. Even though Pt is used currently as the benchmark catalyst, it has to be ultimately eliminated from the catalyst layer considering the very low abundance of Pt on the earth crust \((3.7 \times 10^{-6} \%)\) and its fluctuating cost \([26]\). It has been estimated that the fuel cell electrode encompassing the carbon backing layer and Pt precious metal represents about 40% of the total cost of a fuel cell system \([27]\). Thus, there is a clear demand and urgency to reduce the quantity of Pt applied, which is intimately related to reducing a major cost contributor of fuel cells.

As innovative catalyst supports, CNTs have drawn a great deal of attention due to their unique geometric shape, excellent mechanical and thermal properties, high electric conductivity, large surface areas, and fascinating chemical stability. As compared with the most widely used Vulcan XC-72R carbon black (CB) support that has an electronic conductivity of 4.0 S cm\(^{-1}\) and specific surface area of 237 m\(^2\) g\(^{-1}\) \([28]\), CNT has extremely higher electronic conductivities of 104 S cm\(^{-1}\) and significantly high specific surface areas of 200-900 m\(^2\) g\(^{-1}\) \([29]\). Furthermore, Vulcan XC-72R has a large ratio of micropores that are smaller than 2 nm, whereas the CNT has no micropores smaller than 2 nm. For the Vulcan XC-72R support, the Pt nanoparticles may sink into the micropores and become inaccessible for triple-phase-boundary formation, reducing the Pt utilization \([30]\); for the CNT support, however, no Pt particles may sink in the micropores and be wasted \([31]\). Additionally, Vulcan XC-72 undergoes corrosion, particularly sensitive to peroxide species environment, resulting in the aggregation and dissociation of Pt nanoparticles \([32]\); whilst the
chemical inertness of CNTs can offer another bonus on this issue [33]. Therefore, in the past few years, continuous efforts have been devoted to increasing the utilization efficiency of Pt and reducing Pt loading by taking advantage of the unique properties of CNTs.

2.1 Improvement of the utilization of Pt catalysts

2.1.1 Commercial Pt black catalysts

Girishkumar et al demonstrated that SWCNTs could serve as an excellent support to anchor Pt black particles and carry out electrochemical oxidation and reduction reactions effectively, similar to the existing commercial CB support [34]. Films of SWCNTs and commercial Pt black were sequentially cast on a carbon fiber electrode (CFE) using a simple electrophoretic deposition procedure. Electrochemical impedance spectroscopy revealed that the CNT-based electrodes exhibited an order of magnitude lower charge-transfer reaction resistance for the hydrogen evolution reaction than did the commercial CB-based electrodes, 44 Ω vs. 496 Ω. The PEM assembly fabricated using the CFE/SWCNT/Pt electrodes (as depicted in Fig 2) was evaluated using a fuel cell testing unit operating with H₂ and O₂ as input fuels at 60 °C. The maximum power density obtained using CFE/SWCNT/Pt electrodes as both the anode and the cathode was 20% higher than that using the CFE/CB/Pt electrodes. By using a thin film rotating disk electrode, Kongkan et al evaluated the oxygen reduction reaction at Pt black particle/SWCNTs catalysts [35]. Compared with a commercial Pt/CB catalyst, Pt/SWCNT films cast on a rotating disk electrode exhibited a lower onset potential, i.e. 10 mV shift, for oxygen reduction. What is more, in durability tests, SWCNT exhibits a greater stability to anchor Pt particles; this is because SWCNTs can minimize the Pt aggregation effect during long term usage.
2.1.2 Pt catalysts produced by chemical reduction of hexachloroplatinic acid (H$_2$PtCl$_6$)

_Ethylene glycol (EG) reduction_

EG is one of the most popular agents that are employed to reduce H$_2$PtCl$_6$ to obtain Pt particles. Li et al developed a partially oriented MWCNT film for PEMFC usage [36]. Pt/MWCNTs were prepared by EG reduction of H$_2$PtCl$_6$; the obtained catalysts were then filtrated with nylon. This obtained film was subsequently transferred to a Nafion membrane by a hot-press method. A PEMFC with the oriented CNT film as the cathode achieved higher single-cell performance than those with CB and a disordered CNT-film-based cathode in 0-0.2 A cm$^{-2}$ current density range. This was proposed to be associated with the aligned arrangement of CNTs, which is favourable for the improvement of fuel cell performance in that (i) the electrical conductivity of CNTs is much higher in axial direction than in radical direction, and there is no energy loss when electron transfer along the tubes; (ii) higher gas permeability is expected with the oriented CNT film, promoting fuel utilization; (iii) an oriented film may exhibit superhydrophobicity, facilitating water removal within the electrode and improving mass transport in PEMFCs. Using an analogous filtration method, Tang et al prepared a thin 1.3 µm catalyst layer with Pt nanoparticles (2.1 nm) supported on 360 µm long MWNTs (Pt/MWNT) [37]. When this catalyst layer was incorporated into the cathode (see Fig 3), a peak power density of 431 mW/cm$^2$ (at a current density of 1.15 A/cm$^2$) was achieved in a H$_2$/O$_2$ fuel cell operating at 70$^\circ$C. The merit of this technique is no additional ionomer (e.g. Nafion) is applied in the catalyst layer, since such a thin catalyst layer allows for a higher surface area to volume ratio, giving smaller travelling distances for protons to percolate to the catalyst surface sites from the PEM.
As stated previously, in a general polyol process, CNTs are first subjected to oxidation pretreatment using a strong acid, such as HNO$_3$ or a mixture of HNO$_3$/H$_2$SO$_4$, so as to remove impurities and generate sufficient amounts of functional groups, e.g. –OH, –COOH, –CO, etc. on the surfaces. These surface functional groups have stronger attraction forces toward metal ions than bare CNT surfaces and some even have ion exchange capabilities, such as carboxylic acid groups. Therefore, they are believed to work as metal-anchoring sites and facilitate metal nuclei formation and electrocatalysts deposition [38]. Yue et al developed a reduction route for the direct immobilization of Pt nanoparticles on nitrogen-containing carbon nanotubes (NCNTs) without the necessity of pre-surface modification on CNTs [39]. NCNTs with nitrogen content of 3–5% were synthesized at 700 °C by the chemical vapor deposition (CVD) process. Pt nanoparticles with diameters ranging from 3-9 nm were supported on NCNTs by the EG reduction. The Pt/NCNTs catalyst demonstrated better electrocatalytic activity over Pt/CNTs catalyst for methanol oxidation according to the cyclic voltammetry analyses. This can be interpreted by the good dispersion of Pt nanoparticles on the NCNTs due to the N-participation as well as the homogeneous n-type or metallic behaviour of NCNTs.

It is also recognized that the dispersion state of CNTs in solution affects the deposition of metal catalysts. When suspended in solution, pristine CNTs like to form large bundles due to the strong van der Waals interactions between them. Such a bundling effect leads to a poor dispersion of metal particles on CNTs and limits the overall electrocatalytic activity. To increase the active surface area of CNTs and facilitate the diffusion of reactant species, Kongkanand et al suggested to wrap and disperse CNTs with poly(sodium 4-styrenesulfonate) first, and then deposit Pt
particles on polymer wrapped CNTs by the EG reduction of PtCl$_6^{2-}$ [40]. The obtained CNT supported Pt showed 10 fold high peak current than the commercial CB supported Pt in the oxidation of methanol at the comparable Pt loading (30 wt. % Pt).

**Hydrogen (H$_2$) reduction**

Suitable Pt particles are required in fuel cell applications; this can be attributed to the structure sensitive nature of the chemical reaction and the fact that particles with different sizes will have different dominant crystal planes and hence the different intercrystallite distances, which may influence the adsorption of feeding fuels. To deposit small Pt particles on CNTs, CNTs were first functionalized with aryl diazonium salt and then treated with concentrated H$_2$SO$_4$, the experimental procedure is diagrammatically shown in Fig 4 [41]. These attached sulfonic acid groups provided active sites for Pt ion (PtCl$_6^{2-}$) adsorption; after the reduction with H$_2$ at 600°C, Pt particles with the diameters of 2-2.5nm were uniformly deposited on CNTs. The small size of Pt nanoparticles can be attributed to the presence of bulky functional groups on CNTs which act as molecular sites for the Pt ion adsorption and also avoid nonuniform Pt deposition on the CNT surface. A membrane and electrode assembly (MEA) with a Pt/CNT electrode as cathode and an E-TEK Pt/Vulcan XC-72 electrode as anode offered better performance than a conventional E-TEK MEA.

By H$_2$ reduction of H$_2$PtCl$_6$, Kaempgen et al deposited Pt particles on SWCNTs and developed a SWCNT network based multifunctional electrode [42,43]. With respect to the commercially available amorphous carbon based electrode, the conductivity of this electrode was increased by more than two orders of magnitude (2000 S cm$^{-1}$ vs. 2 S cm$^{-1}$), whereas the thickness and mass were decreased by more than one order of magnitude (10-20 µm vs. 400 µm and 0.7 mg cm$^{-2}$ vs. 24 mg cm$^{-2}$, respectively).
Although the performance of this electrode in H₂/O₂ fuel cell is still inferior to the commercial amorphous carbon electrode, this technique does pave ways to make highly conductive but extremely thin and light gas diffusion electrodes by using CNT networks.

The incorporation of nitrogen also contributes to the improvement of catalyst performance. NCNTs were synthesized by impregnating polyvinylpyrrolidone inside the alumina membrane template and subsequent carbonization of the polymer. Pt particles were then dispersed onto the nanotubes by the H₂ reduction of H₂PtCl₆. The NCNT supported electrodes showed a ten fold increase in the catalytic activity in methanol oxidation compared with the commercial E-TEK electrode; the peak current density values were 13.3 mA cm⁻² and 1.3 mA cm⁻², respectively [44]. The authors believed that the nitrogen functional group on the CNT surface intensifies the electron withdrawing effect against Pt and the decreased electron density of Pt facilitates the oxidation of methanol.

Sodium borohydride (NaBH₄) reduction

NaBH₄ offers another option as a reducing agent to reduce H₂PtCl₆. Reddy et al prepared SWCNT supported Pt catalysts by the reduction of H₂PtCl₆ with NaBH₄-NaOH [45]. Pt particles with a size of about 3-5 nm were uniformly deposited on SWCNTs. Again, prior to the metal deposition, SWCNTs were treated with HNO₃ to obtain anchoring sites for metal precursor salt. The PEMFC with both the anode and cathode containing 50 wt % Pt/SWNT and 50 wt % Pt/C nanocomposite gives a better current density (at 540 mV) of 485 mA cm⁻² and power density of 262 mW cm⁻² than E-TEK/E-TEK one (258 mA cm⁻² and 139 mW cm⁻² respectively). To improve
the utilization of noble Pt catalysts in PEFCs, Du et al modified Pt/CNT catalysts by tethering sulfonic acid groups onto the surface of CNT supports by thermal decomposition of ammonium sulphate, \( (NH_4)_2SO_4 \), and in situ radical polymerization of 4-styrenesulfonate [46]. The electrodes with the Pt/CNT catalysts sulfonated by the in situ radical polymerization of 4-styrenesulfonate exhibited better performance than those with the unsulfonated counterparts, mainly resulting from the easier access of protons and the well dispersed distribution of Pt catalysts. The electrodes with the Pt/CNT catalysts sulfonated by the thermal decomposition of \( (NH_4)_2SO_4 \), however, did not yield the expected performance as in the case of CB supported Pt catalysts, presumably due to the significant agglomeration of Pt particles on the CNT surface at high temperatures. This result indicates, for the Pt/CNT-based PEFCs, the sulfonation of CNTs can be an efficient approach to improve performance and reduce cost. However, the introduction of sulfonic acid group will unavoidably increase the hydrophilicity of CNTs and decrease their electrical conductivity, affecting the water management and electron transport property. To balance these effects and achieve an optimum overall performance, an optimum sulfonation degree should be targeted.

### 2.1.3 Pt-alloy catalysts

Pt-based electrocatalysts display the significant activity and necessary stability in the harsh environment of the PEFCs. However, the hydrogen-rich feeding gas in PEMFCs, produced by reforming or partial oxidation of hydrocarbons, usually contains CO as well; for DMFCs, the partial oxidation of methanol can also result in the presence of CO. The existence of CO will create troubles for the Pt catalyst based full cell systems, as CO can adsorb strongly on the Pt surface and block the active sites from adsorbing fuels (H\(_2\) or methanol), deteriorating the performance of
electrode. One possible solution for this CO poisoning problem involves the use of CO-tolerant electrocatalysts formed by alloying Pt with a second transition metal (e.g. Ruthenium, Ru, Molybdenum, Mo) [47,48]. Among all the binary alloys, the Pt-Ru has shown the most promising performance for both the hydrogen oxidation reaction in the presence of CO and the oxidation of methanol. This is because Ru can form oxygenated species at a lower potential than Pt and promote the oxidation of CO to CO$_2$ [49].

By H$_2$ reduction of H$_2$PtCl$_6$ and ruthenium chloride (RuCl$_3$), Carmo et al prepared MWCNT, SWCNT, and CB (Vulcan XC 72) supported Pt-Ru catalysts [50]. When the feeding H$_2$ in PEMFCs was mixed with 100 ppm CO, Pt-Ru catalysts that were supported on both CNTs and CBs still exhibited good performance, demonstrating high CO tolerance. The power densities accomplished on a single DMFC exceeded 100 mW cm$^{-2}$ at 90 °C and 0.3 MPa and the activity of the anodes followed the descending sequence of Pt-Ru/MWNT, Pt-Ru/CB, and Pt-Ru/SWNT. Similarly, Pt-Ru/MWCNTs catalyst was prepared by the NaBH$_4$ reduction of H$_2$PtCl$_6$ and RuCl$_3$.

When the anode and cathode of DMFCs was fabricated using Pt-Ru/MWNT and 1:1 Pt/MWNT+Pt/C electrocatalyst, respectively, a maximum power density of 39.3 mW cm$^{-2}$ at 80 °C (with a methanol flow rate of 1 ml/min) was obtained [51]. Using the same reducing agent, Prabhumet al also synthesized Pt-Ru/MWCNTs catalysts [52]. In a single DMFC, the power density yielded using MWCNT supported Pt-Ru was 35-39% higher than that using CB (Vulcan XC-72) supported Pt-Ru. They attributed this to the influence of supporting materials on the crystalline nature of Pt and proposed that the distinctive Pt crystallite phases, i.e., Pt (110), on the Pt-Ru particles supported on the MWCNTs is likely to be the reason for enhancing the activity of the
methanol oxidation. Li et al compared the catalytic performance of Pt-Ru loaded SWCNTs, DWCNTs, MWCNTs in DMFCs [53]. Pt-Ru/CNTs were prepared by the EG reduction of \( \text{H}_2\text{PtCl}_6 \) and \( \text{RuCl}_3 \), the obtained catalysts were then filtrated with nylon and transferred to a Nafion membrane by a hot-press method, as illustrated in Fig 5. The Pt–Ru/DWNTs catalyst showed the highest performance for methanol oxidation reaction in rotating disk electrode experiments and as an anode catalyst in DMFC single cell tests. It is notable that the DMFC single cell with Pt–Ru/DWNTs (50 wt %, 0.34 mg Pt-Ru/cm\(^2\)) produces a 68% enhancement of power density, and at the same time, an 83% reduction of Pt–Ru electrode loading when compared to Pt–Ru/C (40 wt %, 2.0 mg Pt-Ru/cm\(^2\)). The reason underlying this is still not fully understood and the authors tentatively associated this with the unique properties of DWCNTs such as electrical conductivity, surface area, and diameter etc, with respect to other types of CNTs.

One challenge facing the preparation of Pt-Ru alloy based catalysts is to obtain the proper atomic ratio of Pt and Ru, since Pt and Ru ions or salts can not be reduced with the same rate at the same pH. For example, the pH value for Pt deposition can be as high as 12, but Ru salts will precipitate under this condition. Jeng et al succeeded in preparing Pt-Ru/CNTs catalysts with the desired atomic ratio of Pt and Ru (1:1) by creating a deposition environment on the CNT surfaces near the isoelectric point [54]; at this specific point, the composition of formed Pt-Ru catalyst can be controlled by tailoring the composition of metal ions in the deposition solution. When the synthesized catalyst was used as an anode catalyst in a single cell DMFC operating at 60°C, a maximum power density of 62 mW cm\(^{-2}\) was obtained around 0.21 V with a current density of 300 mA cm\(^{-2}\).
2.2 Application of CNTs in the exploration of Pt-free catalysts

Apart from the improvement of Pt utilization efficiency, the entire replacement of Pt with other cheaper catalysts provides another alternative approach to reduce the prohibitive price of fuel cell system.

Molybdenum (Mo) is cheaper and more abundant than Pt, and more important molybdenum carbide (Mo$_2$C) possesses similar electronic states as Pt. Based on these facts, Mo$_2$C/CNTs has been suggested as the anode catalyst by Nakamura et al [55,56]. Ultraviolet light was first applied to create defects on CNTs; after adsorption on CNTs, molybdenum dioxo acetyl acetonate was reduced with H$_2$ and carburized in CH$_4$. In contrast to Pt-based electrodes, these Mo$_2$C/CNT electrodes need to work at a much higher overvoltage. Although their activity may be further improved, at current stage, they still can not compete with Pt catalysts.

Transition metal-nitrogen-carbon nanotube (TM/N/CNT) catalyst is another focus of recent research. The active site for oxygen reduction reaction on such kind of catalyst containing iron is proposed to comprise iron and nitrogen and can be expressed by the formula FeN$_x$ ($x = 2, 4$) [57]. Using ferrocene as an iron additive catalyst and ammonia as the N-dopant, Yang et al prepared vertically aligned CNTs with built-in FeN$_x$ sites by CVD process [58]. The obtained CNTs exhibited catalytic activity in an O$_2$-saturated acidic electrolyte, analogous to the conditions on the cathode of PEFCs. X-ray absorption spectroscopy revealed that the active site is composed of a divalent iron coordinated with four nitrogens in a slightly distorted squareplanar configuration. Prehn et al produced NCNTs in a CVD method by adding acetonitrile as nitrogen
source and found that these obtained NCNTs exhibited rather low catalytic activity in oxygen reduction reaction [59]. However, by impregnating CNTs with iron-tetramethoxyphenylporphyrin chloride and then heating, the electocatalytic activity was enhanced greatly, reflecting the beneficial effect of iron. According to density functional theory, Titov et al conducted the ab initio studies on the energetics and the geometries of the metal-nitrogen sites in CNTs [60]. The results showed that the iron atom binding energy in both Fe-2N and Fe-4N configurations is much higher than that on pristine CNTs, suggesting that N stabilizes Fe on CNTs. For Fe-2N configurations, the binding energy is generally lower than that in Fe-4N configurations. In the case of Fe-4N configurations, theoretical results showed that the pyridinic configurations are energetically preferred over pyrrolic configurations. The results also illustrated the preferable incorporation of Fe-4N sites into large-diameter CNTs with regard to small-diameter ones. These results suggested the iron atoms are embedded into the surface of CNTs. However, it needs to be pointed out that the role of metal in the oxygen reduction reaction is still a controversial issue.

Matter et al synthesized [61] NCNTs by the pyrolysis of acetonitrile at 900 °C using iron/nickel particles supported on alumina as catalysts. The most active catalysts in oxygen reduction reaction were prepared over alumina impregnated with up to 2 wt % iron, but the catalysts that were prepared by the acetonitrile pyrolysis over alumina without any metal doping still had significant activity. The lack of correlation between iron content and activity makes them suggest that an iron phase formed during the heat treatment is not the primary source of the oxygen reduction reaction activity. Similarly, by pyrolyzing a suitable polymer precursor, including poly(phenylacetylene), poly(4-vinylpyridine), poly(3-methylpyrrole), poly(2-
methyl-1-vinylimidazole), and poly(p-pyridazine-3,6-diyl), within the cylindrical and uniform-sized pores of an alumina membrane, Rao et al synthesized NCNTs without the involvement of any metal particles [62]. All obtained NCNTs exhibited a certain extent of catalytic activity, demonstrating that the present of metal phase is not a prerequisite to obtain catalytic activity. They further studied the effect of N content in carbon lattice on the electrocatalytic activity, and found poly (2-methyl-1-vinylimidazole) gave the optimum catalytic performance. As the surface N content in the obtained CNTs using the aforementioned polymers is 0, 4.3, 5.6, 8.4 and 10.7 atom %, respectively. They concluded that there exists an optimum N concentration (8.4 atom %), and ascribed this to a higher density of pyridinic-type nitrogen active sites. Analogously, NCNTs were prepared by the pyrolysis of acetonitrile over cobalt catalysts at different temperatures. A detailed analysis of the Co 2p spectra and N 1s spectra of NCNTs indicated that a very small amount of cobalt nitride was likely to be present in the sample. On the other hand, the authors did not observe any voltammetric peak that would correspond to the oxidation of metallic cobalt or reduction of cobalt oxide on the surface of the CNTs. Transmission electron microscopy studies of the NCNTs showed that the cobalt particles are covered by at least a few graphene layers, indicating that the cobalt nanoparticles are not accessible by the electrolyte. Based on these facts, the authors suggested that cobalt is not part of the active sites. The experimental results also revealed that the NCNT samples prepared at 550 °C exhibited higher activity in contrast to the samples prepared at 750 °C, which could be attributed to higher amount of pyridinic groups presented in the former samples [63].
Despite these arguments regarding the virtual role of metal in the oxygen reduction reaction, there seems to be consensus in literatures that pyridine-type nitrogen can be considered to be responsible for the high catalytic activity; this is somewhat in agreement with the N 1s X-ray photoelectron spectra on NCNTs, where three principle types of nitrogen coordination, namely pyridinic, pyrolic, and quaternary, can be identified [64,65]. In terms of electrocatalytic activity, TM /N/CNT catalysts remain too low to be considered for real fuel cell applications, in general only about one tenth of the activity of Pt-based catalysts [66].

As discussed above, it is an efficient and effective way to decrease the Pt loading by dispersing Pt particles on CNTs to increase Pt utilization efficiency. In general, small particle size and uniform dispersion will result in high electrocatalytic activity; the incorporation of nitrogen into CNTs can also impose a positive effect. Additionally, both the type of CNTs and their arranged manner on substrate have a role to play with respect to the catalytical activity.

3. Application of CNTs in hydrogen storage

Developing safe, cost-effective, and practical means of storing hydrogen is crucial for the advancement of fuel cell technologies [67], because hydrogen has a much higher per unit mass energy density than typical hydrocarbon fuel, but a poorer per unit volume energy density [68]. This high occupied space will create problems for mobile applications, and the US D.O.E. has set up the criteria with respect to the hydrogen storage density (9 wt.%, in 2015) for the practical applications of fuel-cell powered vehicles [5]. CNTs have been viewed as a possible solution to the storage of hydrogen
in fuel cell-powered vehicles due to their low density, high strength, and hydrogen adsorption characteristics.

Hydrogen can be adsorbed by CNTs in a physisorption manner, that is to say, hydrogen is trapped inside the cylindrical structure of the nanotubes or in the interstitial sites between nanotubes. By studying the H\textsubscript{2} adsorption in the (4,4) armchair SWCNTs with density function theory method, Mahdavian pointed out the efficient hydrogen storage in CNTs requires the control of tube size, pressure, and temperature [69]. Chen et al established a continuum mechanics model to study the hydrogen storage in SWCNTs, MWCNTs and the bundle of SWCNTs [70]. The results also indicated the importance of tube size in affecting hydrogen storage and the authors concluded that tiny CNTs can not achieve the goals of hydrogen storage without fracture, see the 2nd column in Table 1; small CNTs are strained during hydrogen storage (the 3rd column); medium CNTs can achieve the above goals without the strain and do not self collapse (the 4th column); and large CNTs may self collapse upon the release of hydrogen (the 5th column).

Doping of certain metal ions was also predicted to be beneficial for the hydrogen storage in CNTs. A first-principles study suggested that one SWCNT coated with single titanium (Ti) atom can bind up to four hydrogen molecules and at high Ti coverage, a SWCNT can absorb up to 8 wt. % hydrogen [71]. Similarly, density-functional calculations of the adsorption of molecular hydrogen on the external surface of a (4,4) CNT, undoped and doped with lithium (Li), have been carried out by Cabria et al [72]. The calculations predicated that the physisorption binding energy of hydrogen on Li-doped CNTs is almost doubled when compared with that on pure
CNTs, 54-84 meV/molecule vs. 147-173 meV/molecule. The analysis of the charge density showed the origin of this increase: the charge transfer from the Li atom to the CNT induces a larger electron density of the surface region near the Li impurity, which enhances the interaction between the hydrogen molecule and the Li-doped surface, resulting in the enhancement of hydrogen storage ability. To further increase the adsorption of hydrogen, Tylianakis et al built up a nice 3D carbon nanostructure model with large surface area and tunable pore size [73]. The model consisted of parallel graphene layers at variable distance, stabilized by CNTs placed vertically to the graphene planes (see Fig 6). In this architecture, CNTs supported the graphene layers like pillars and assembled a 3D block reducing the empty space between the graphene layers by filling it with CNTs. When this material was doped with Li ions, it could store up to 41 g H$_2$/L under ambient conditions, only slightly lower than the volumetric capacity (45 g H$_2$/L) required to be matched in 2010 by the US D.O.E.

In the above mentioned studies, the interaction between H$_2$ and CNTs is dominated by weak van der Waals forces, and thus only a limited quantity of hydrogen can be stored. As such, chemisorption of hydrogen on CNTs has been suggested, where the molecular hydrogen is dissociated with the aid of catalyst and the resulting atomic hydrogen subsequently forms bond with the unsaturated carbon bonds along the tube. Obviously, this method offers safety benefit because the hydrogen atoms are bonded to carbon atoms, rather than freely floating as a potentially explosive gas. By applying an atomic hydrogen beam to SWCNT thin film, new C-H bonds were created, and such C-H bonds could be completely broken by heating to 600°C, reflecting the reversible nature of this process [74]. The authors demonstrated an approximately 65±15 at % hydrogenation of carbon atoms in the SWCNTs, which is equivalent to
5.1± 1.2 wt % hydrogen capacity. This result is marvellous, but challenges still exist. The stored hydrogen could be released by breaking the C-H bond at above 600°C, but two cycles of hydrogenation and de-hydrogenation appeared to cause defects in the tubes. Not to mention, ideally, the hydrogen should be released at 50 to 100 °C. Adding metal catalysts and adjusting the radius of the tubes are potential solutions.

The theoretical and experimental studies indicate CNTs hold a great promise for future mobile hydrogen storage. So far, however, no practical product is envisionable, even at laboratory scale. To turn such a potential into a reality, it is essential for physicist, chemist and engineer to come together and cooperate with each other.

4. Summary

The overall performance of PEFCs is controlled by different processes like diffusion of the feeding fuel to the electrolyte-catalyst interface, electrochemical reaction at the catalyst-electrolyte interface, transport of charges by the current collector, proton transport across the membrane, and the hydration of electrolyte membrane etc. As illustrated, CNTs have demonstrated great performance in PEFC components. When blended with Nafion to make PEM, CNTs can improve the mechanical strength of the membrane; if functionalized with sulfonic acid group, they can improve the proton conductivity as well. Pt/CNTs and Pt-Ru/CNTs exhibit higher electrocatalytic activity than the CB supported counterparts; the doping of nitrogen also has a beneficial role to play with respect to catalytic activity; CNTs have also been adopted to explore Pt-free catalysts, e.g. TM/N/CNTs. New CNT based modelling structures show high hydrogen storage ability, which almost meets the requirement set by the US D.O.E.
Even though CNTs have been proved to be valuable in improving the PEFC performance, few challenges still need to be overcome before the widespread use of CNTs in PEFCs. One challenge arises from the inhomogeneous nature of as-grown CNTs. Regardless of the growth methods, the obtained CNTs are always with scattering helicity, number of layers, diameter, length and topological defects. This, in turn, will affect their electrical properties, chemical stability and interactions with other species, leading to the difficulty in predicting and manipulating their performance in PEFCs. CNT purity is another concern. Depending on the growth method and growing conditions, as-grown CNTs are usually accompanied with impurities, such as amorphous carbon, graphite particles and metal particles. The knowledge on how these impurities can affect the PEFC performance is still not fully established. Additionally, so far only limited data is available regarding the toxicity of CNTs, and still not much is known about their impact on biological systems including humans.

In brief, the research efforts, made so far, have lead to the successful incorporation of CNTs into PMFC components; the outcome is the improved performance of PEFCs in many aspects. This indeed raises the hope for the proliferation of PEFCs by combining the virtues of fuel cells with CNTs, and it is likely that the further advances in CNT growth and purification techniques will accelerate this procedure.

**Acknowledgement**

We would like to thank Dr. Martin Blissett for his useful discussions.
Table 1 Behaviour of different carbon nanotubes to achieve the goals of hydrogen storage (62 kg $\text{H}_2$/m$^3$ and 6.5 wt. %) [70]

<table>
<thead>
<tr>
<th></th>
<th>Fracture</th>
<th>Strained</th>
<th>No strain or self collapse</th>
<th>Self collapse</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Single-wall CNTs</strong></td>
<td>(7,7) and down</td>
<td>(8,8) to (18,18)</td>
<td>(19,19) to (30,30)</td>
<td>(31,31) and up</td>
</tr>
<tr>
<td></td>
<td>&lt;0.47 nm</td>
<td>0.54-1.2 nm</td>
<td>1.3-2.0 nm</td>
<td>&gt;2.1 nm</td>
</tr>
<tr>
<td><strong>Bundle of single-wall CNTs</strong></td>
<td>(7,7) and down</td>
<td>(8,8) to (21,21)</td>
<td>(22,22) to (30,30)</td>
<td>(31,31) and up</td>
</tr>
<tr>
<td></td>
<td>&lt;0.47 nm</td>
<td>0.54-1.4 nm</td>
<td>1.5-2.0 nm</td>
<td>&gt;2.1 nm</td>
</tr>
<tr>
<td><strong>Double-wall CNTs (inner tube)</strong></td>
<td>(11,11) and down</td>
<td>(12,12) to (31,31)</td>
<td>(32,32) to (36,36)</td>
<td>(37,37) and up</td>
</tr>
<tr>
<td></td>
<td>&lt;0.75 nm</td>
<td>0.81-2.1 nm</td>
<td>2.2-2.4 nm</td>
<td>&gt;2.5 nm</td>
</tr>
<tr>
<td><strong>Triple-wall CNTs (innermost tube)</strong></td>
<td>(16,16) and down</td>
<td>(17,17) to (41,41)</td>
<td>-</td>
<td>(42,42) and up</td>
</tr>
<tr>
<td></td>
<td>&lt;1.1 nm</td>
<td>1.2-2.8 nm</td>
<td>-</td>
<td>&gt;2.8 nm</td>
</tr>
</tbody>
</table>
References


Figure Captions:

**Fig 1** Chemical structure of Nafion

**Fig 2** SWCNT-based PEM assembly for a H\textsubscript{2}/O\textsubscript{2}-based fuel cell [34]

**Fig 3** Schematic of the fuel cell architecture. E-TEK 20 wt % Pt/XC-72 is used in the catalyst layer of anode. The cathode contains the thin film Pt/MWNT in the catalyst layer. The Nafion NRE-212 is used as a PEM. The assembly of the carbon backing layer and microporous layer on both anode and cathode are SGL Carbon Group products (GDL 25CC) [37].

**Fig 4** Scheme for Pt deposition on CNTs on carbon paper [41]

**Fig 5** Schematic illustration of Pt−Ru/CNTs-film-based membrane electrode assembly for DMFC [53]

**Fig 6** Snapshot from the GCMC simulations of Li doped pillared structure at 77 K and 3 bar. Hydrogen molecules are represented in green while Li atoms are in purple [73]
Fig. 1

Fig. 2

Fig. 3