Applications of carbon nanotubes in polymer electrolyte membrane fuel cells

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Abstract | Carbonaceous materials play a vital role, in the performance of polymer electrolyte membrane fuel cells (PEMFC) irrespective of their use in cathode, anode and in bipolar plates. However, their use in composite electrolyte membrane has been only recognised recently especially after their functionalization to impart enhanced proton conductivity to the composite electrolyte. PEMFC development still has many material related challenges in terms of durability, degradation and more significantly cost reduction. Different methodologies have been adopted to deposit Pt electrocatalyst on CNTs and other carbonaceous materials, thus transforming them into the membrane electrode assembly. Functionalized carbon nanotubes with desired surface groups are found to be better for composite electrolytes since they increase the protonic conductivity along with increased mechanical stability. The use of CNTs doped with nitrogen indicates the possibility of total Pt removal from MEAs in the near future. Many of these recent advances in the application of carbon nanotubes and related materials in the functioning of polymer electrolyte fuel cells are discussed in this article providing an overview of their possible role and limitations.

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1. Introduction

Development of different types of carbonaceous materials is important for a variety of applications such as heterogeneous catalysts,[1] field emitters,[2] supercapacitors,[3,4] Li-ion batteries,[5,6] gas sensors,[7] nanoprobes,[8] actuators,[9,10] hydrogen storage[11–15], photo voltaic cells[16,17] and fuel cells. Although the use of carbon for these applications is ubiquitous the modern trend is to engineer carbon for special purposes to fulfil a set of application-specific criteria like surface area, particle size, pore size distribution and electronic conductivity, each tailored for optimum performance. For example, partially disordered graphitic carbon is considered to be better for reversible Li storage in batteries over other forms of carbon.[18]

Since the pioneering work by Ijima in 1991 carbon nanotubes (CNTs) have become the pinnacle of recent research among different carbonaceous materials due to their distinct characteristics such as inertness under various chemical environments, highest young's modulus, electrical conductivity, high surface area, light weight and easy interfacing capability with many inorganic and organic compounds.[19] Further, many recent reports have clearly illustrated that the unique electronic structure of CNTs helps in enhancing the catalytic activity of the supported metal in addition to providing mechanical integrity.[1]

Among the different energy related applications of CNTs, polymer electrolyte membrane fuel cell (PEMFC) represents one potential case for greening the world from a renewable energy point of view for our future needs. Indeed, PEMFCs are one of the important environment friendly options for electricity generation, if hydrogen is produced by solar technologies with out any carbon foot print. Fuel cells also do have higher efficiencies over commercial combustion engines especially if combined heat-power generation is targeted. Due to recent innovations in several nanostructured materials, fuel cells are considered more promising in the near future both for stationary and mobile applications. However, they still face many daunting challenges which need to overcome before realising practical applications in terms of inexpensive and durable materials as electrodes, electrolytes and other components.

2. Challenges of PEMFC and the role of carbon

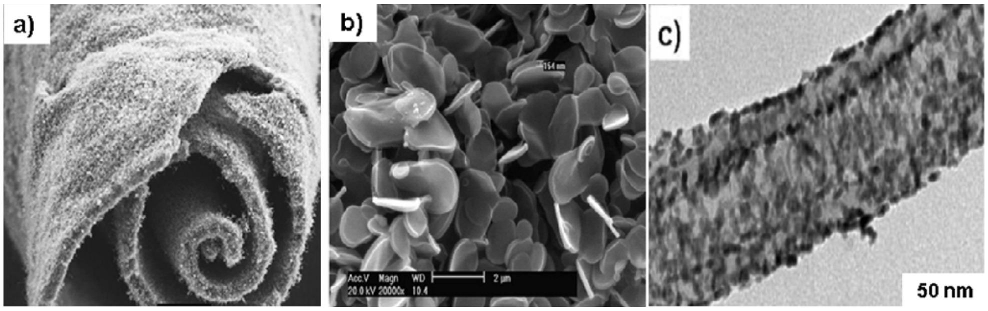
The commercialization of PEMFCs is mainly hampered by two key aspects, longevity or durability of some key components like membranes and electrodes and also the high cost of fuel cell systems. For example, the durability of a PEM fuel cell relies mainly on the performance of the membrane electrode assembly (MEA) of the stack, while the reduction in cost critically depends on enhancing the performance of the MEAs while minimizing the Pt content.[20] The major modes of failures are the breakdown of polymer electrolyte membrane and the loss in active surface area of the Pt electrocatalyst with time in addition to the corrosion of the support. The life time and cost as a function of performance is intimately linked with design, materials and operation strategies and various targets are often used by fuel cell researchers and funding agencies for comparison and also for measuring progress. The cost targets of the US Department of Energy (DOE) for PEM fuel cell stack is 30 $ per kW by 2015 which is way down from the current value of 110 $ per kW.[21] Most of this reduction has to be from the Pt catalyst, bipolar plate and PEM although total elimination of Pt has been recently indicated as a tangible possibility.[22] Development of different types of inexpensive carbon plays a critical role in accomplishing some of these objectives as it is well known that carbon with varying properties could be prepared to meet these technology-specific requirements. For example, the surface area of carbon can be varied from few meters to few thousand meters per gram although other useful properties like electrical conductivity vary dramatically some times in an adverse manner. Consequently, carbon has been extensively investigated by a huge number of groups as a support material in PEMFC.[23–28]

Earlier attempts to overcome these challenges by modifying carbon mainly include the use of three different forms of carbon, i.e., activated carbon, carbon black and graphite or graphitized materials, as the primary choice of support for catalyst materials in different types of fuel cells.[23] The preferred form of carbon in a fuel cell electrode including that in gas diffusion layers, is Vulcan XC-72, a kind of activated carbon, with moderate surface area (250 m^2/g) and good electrical conductivity, which is in stark contrast to the preference of activated carbon with a surface area of more than 3000 m^2/g for certain other applications, perhaps due to poor electrical conductivity and different pore size distribution. However, the mesopores in Vulcan XC-72 result in part, of the Pt nanoparticles getting buried deeply inside the pores and hence becoming inaccessible for the triple phase boundary (TPB) formation, which is essential for sustaining the electrode reactions in fuel cells. Further, Vulcan XC-72 undergoes corrosion (more rampant under peroxide intermediate formation conditions of fuel cell cathodes) resulting in the aggregation as well as dissolution of Pt nanoparticles. For example, many groups have found the influence of carbon corrosion in restricting the durability of MEAs as the size of the Pt particles double in approximately 200 hours of continuous operation.[24,30]

Attempts to improve the carbon support by different strategies have generated mixed results. Coin like hollow carbon (Figure 1) prepared by a simple solvothermal method has been used to support Pd electrocatalyst in methanol oxidation reaction with an improved mass activity of 2930 Ag^{-1} against 870 Ag^{-1} of Pd supported on Vulcan XC-72 Carbon.[25] Similarly, carbon nanofibers and even scrolls are also attempted as a support due to its ease of fabrication.[26–29]

Although all these improvements on carbon alone cannot solve most of the above challenges associated with fuel cells mainly in terms of durability and performance, CNTs with its unique properties can actually do alleviate some critical problems. For example, nitrogen or boron doped CNTs can replace Pt as an electrocatalyst and there is lot of excitement on developing these types of new nanostructured electrocatalysts. In this article we discuss current efforts on the use of CNTs in polymer electrolyte fuel cells in both electrodes and electrolytes illustrating their multifunctional role as catalyst layer, support and sometimes as a reinforcing component in polymer composite membranes. The impact of functionalized CNTs on the performance and durability of the MEAs in increasing the longevity and improved performance will be discussed in such manner to unravel their

Figure 1: (a) TEM image of carbon scrolls (b) SEM image of coin like hollow carbon and (c) TEM images of Pt deposited carbon nanofibers (25, 28).



potential in reducing the cost of the stack per kW. Besides discussing material applications and general procedures for functionalizing CNTs for PEMFC, the use of sulphonated CNTs in particular is also illustrated using both single walled and multiwalled carbon nanotubes.

3. Use of CNTs as electrode material for PEMFCs

Effective utilization of Pt nano particle is a key parameter in decreasing the cost of fuel cell stacks as very low Pt loading (few hundred microgram/cm^2) with out any change in performance is essential for progress in this area. This can be accomplished by the effective distribution of Pt on the supporting material with a high surface area as well as higher electrical conductivity.[30] For this purpose, a given support material for PEMFC electrodes should fulfil the following requirements.

1. High surface area,
2. Chemical stability under oxidative/reductive conditions,
3. Mechanical robustness under both open and closed circuit conditions and
4. Good electrical and thermal conductivity

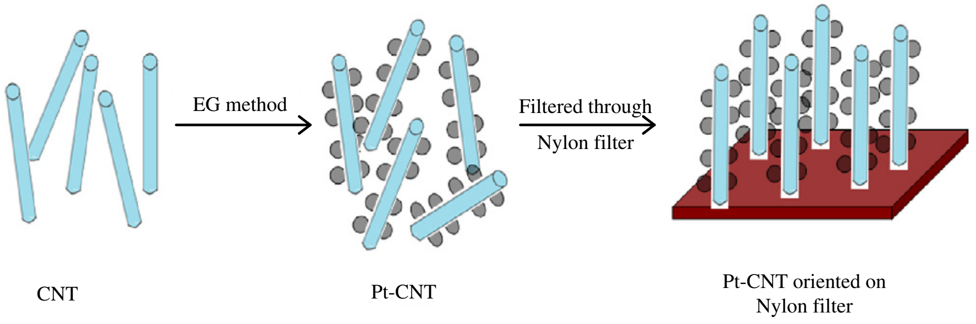
Many of these conditions are met exceptionally well with CNTs although CNT is not cheap at present for extensive applications. However, there are sufficient indications that CNT cost is likely to come down with increased production.[31,32]

One of the main problems associated with even commercial electrode formulations is the isolation of carbon particles by the use of Nafion as a binder in the catalyst layer. The insulating nature of binder can indeed block Pt particles associated with carbon from accessing the external circuit due to the lack of electrical network resulting in the decrease of Pt utilization further. Pt nanoparticles deposited on CNTs, however, are almost certain to have electrical contact with external circuit which eliminates these type of problems associated with the presence of a thin insulating layer of Nafion covering the carbon particles.[33] Hence a judicious use of CNTs could in fact overcome many of such issues that other forms of carbon based electrodes struggle to overcome in power source related applications.

3.1. *CNTs as cathode support material*

Poor kinetics of oxygen reduction reaction (ORR) sustained at the cathode of MEAs typically necessitates the use of higher Pt content in comparison with that in the anode. However, in many cases the use of CNTs has been shown to be profitable in terms of providing a better exchange current density towards ORR with out causing any detrimental mechanical behaviour as a support material for the electrocatalyst. For example, Yan *et al*,. have carried out pioneering work on the use of CNT in PEMFC electrodes especially in the cathode to improve Pt utilization.[33–36] Their initial study of depositing 4 nm Pt nanoparticles on CNTs has shown improved current and power density in all the regions (i.e., activation, ohmic and mass transport regions), presumably due to the intrinsic properties of CNTs to increase the oxygen reduction kinetics. This is in accordance with the findings of Britto et al, where CNT/metal electrodes show higher exchange current density than that on other metal/C electrodes.[37] Enhanced mass transport is also anticipated to be beneficial in the case of CNT based electrodes coupled with reduced ohmic loss, which is acceptable while comparing the electrical conductivity of CNTs, graphitic powders and other forms of conducting carbon. This has resulted in an enhanced Pt utilization of 58% against 34% of carbon based electrodes under favourable conditions. However, water clogging remains as a critical problem in the cathode which severely restricts the performance of PEMFC under high humidity conditions.[36]

Figure 2: (a) Scheme for the preparation of oriented Pt/CNT film based MEAs. (b) TEM image of Pt deposited CNT. (c) SEM image of the oriented CNTs on Nafion membrane (34).



Carbon nanotubes are generally hydrophobic in nature which helps in controlling gas diffusion properties. Oriented CNTs are shown to have increased hydrophobicity than that of disordered CNTs. Further the electronic conductivity is higher along the tubes than across the tube along with increased gas permeability which would help in better mass transport conditions.[38–39] Considering all these benefits associated with oriented CNTs Yan et al., have developed a unique method to orient the CNTs by a filtration method followed by transfer to the membrane (Figure 2). In this method, the surface of CNTs are introduced with functional groups such as –COOH by refluxing with Con.HNO_3/Con.H_2SO_4 mixture followed by *in situ* chemical reduction of Pt precursor solutions on them for the proper anchoring of Pt nanoparticles on the CNT surface. Subsequent to the chemical reactions the functionalized CNTs are filtered through a hydrophobic nylon membrane with precisely controlled pore size/distribution in CNTs standing up with the preferred orientation and length.

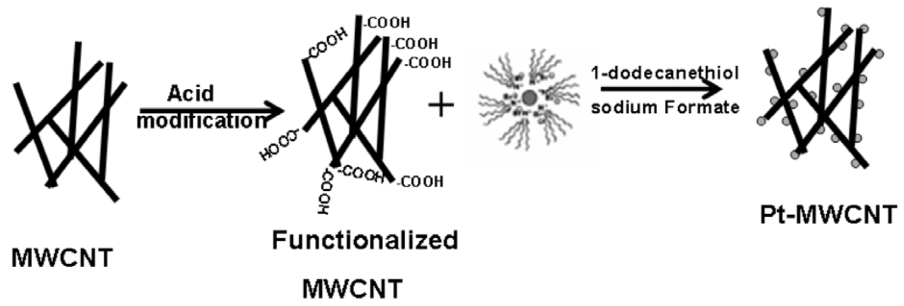
The use of this type of oriented CNTs results in better fuel cell performance than that of randomly aligned CNT based electrodes and Pt/C based electrodes. Table 1 illustrates this use of CNTs to enhance the fuel cell performance compared to that of commercial Pt/C catalysts.

Durability of a fuel cell stack is mainly restricted by the corrosion of carbon support under the operating conditions of the cathode especially due to the production of hydrogen peroxide as an intermediate. Several studies have established beyond doubt that Pt nanoparticles are expected to double in size with an operation time of around 200 hours.[36] In this regard, the use of CNTs which is known for their chemical inertness and remarkable mechanical strength can increase the endurance of a fuel cell MEA. More specifically, an attempt to prove the durability of CNTs carried out by a potentiostatic treatment for 168 hours for Pt supported on CNTs and Vulcan XC-72 reveals that CNTs have lesser surface oxides than that of Vulcan XC-72, concomitantly demonstrating 30% lower corrosion rates.[36] This is well supported by the histograms of Pt nanoparticles size distribution which confirms that the average particle size of 2.5 nm becomes 4.8 nm after 168 hours of operation while those Pt particles supported on CNTs show a slight increase in particle size despite majority of the particles remaining at 2.5 nm.[36]Further, after this prolonged oxidation treatment these Pt-CNTs show considerable ORR catalytic activity while Pt-C samples show a drastic decrease in the onset potential of ORR ($\sim$120 mV).

A more recent work by Lin et al., has attempted to reduce the cost of the fuel cell by reducing the particle size as well as increasing the Pt distribution by a wet chemical modification route (Figure 3).[39] By this method Pt nanoparticles of 1–3 nm are stabilized at the same time maintaining a uniform Pt distribution due to the anchoring groups present on the CNTs surface. Interestingly, fuel cell polarization plot with this catalyst shows a power density of 1100 $mWcm^{-2}$ against 800 $mWcm^{-2}$observed for a commercial catalyst. Further the activation loss observed at 50 $mAcm^{-2}$ is only 50 mV from the OCV for this surface modified process compared to that of 150 mV for unmodified CNTs. However, with carbon black it is much higher, which signifies the more efficient use of CNTs in the catalyst layer of PEMFCs.

A large number of reports are available on preparing CNT based electrodes especially to increase the Pt utilization by means of using different preparation conditions such as chemical reduction in a formaldehyde bath, and electrochemical

Figure 3: Scheme for the surface modification of MWCNTs and Pt nanoparticles deposition (39).



deposition of Pt on CNTs. Growing CNTs directly on the carbon paper support in order to reduce the ohmic resistance, and the modification of the reduction method to prepare smaller nanoparticles with narrow distribution on size have also been reported as an interesting alternative for Vulcan XC-72 based electrodes demonstrating performance better than that of Vulcan XC-72 based electrodes although durability and chemical stability aspects need to be rigorously evaluated.[40–49]

3.2. *Nitrogen doped CNTs as ORR catalysts to replace Pt*

Even though Pt is used currently as the benchmark catalyst for ORR, it has to be ultimately eliminated from the catalyst layer considering the very low abundance of Pt on the earth crust (3.7×10^{-6}%) and its fluctuating cost.[51] Interestingly, N_2 doped CNTs tend to give an option here although at present, it is only a partial solution.[52–54] For example, vertically aligned CNTs containing nitrogen have been reported to show better ORR catalytic activity than that of Pt as proved by the cyclic voltammetry and RRDE experiments. Despite the fact that these results are in alkaline medium, the possibility of N_2 doped CNTs to replace Pt as an electrocatalyst for the sluggish cathode oxygen reduction reaction has profound implications in making Pt free MEAs for PEMFC with out any change in performance. Further, N_2doped CNTs are also reported to be better support materials for Pt electrocatalysts on the cathode and anode of PEMFCs where some of the degradation issues can be prevented due to robust mechanical properties of CNTs.[54] More promising results on N_2 and B doped CNTs are expected to revolutionze this area in the near future.

3.3. *Use of CNTs as anode support*

Compared to the vast number of reports available on cathode support materials, only a few reports are available for anode supports mainly due the highly facile nature of the hydrogen oxidation reaction. However, the actual challenge in the anode is to obtain sustained performance using the reformed H_2 having considerable CO content. In this regard, catalyst systems (e.g., Pt-Ru) that show good activity towards methanol oxidation reaction are expected to have a better tolerance for CO and substantial efforts are rendered towards improving the support metal interaction. Since stronger metal support interactions would help the electron transfer between the metal and support during electrochemical reactions, the Pt nanoparticles deposited on CNTs tend to have increased catalytic activity than that of unsupported metal due to the unique electronic structure. Interesting improvements have been observed for methanol oxidation on Pt surfaces with and without the presence of CNTs like significant enhancement in the oxidation current of 50–60 mA/cm^2 for CNT/Pt electrode while unsupported Pt gives only 6 mA/cm^2. While this enhancement can have contribution from the increased surface area, the kinetic aspects demonstrate an unambiguous improvement in

Table 1: Increased performance of fuel cells by using CNTs in the cathode catalyst layer; data in the parenthesis represents the dispersion in particle size of the Pt catalyst.

S.No	Particle size (nm)	Pt Utilization(%)	Surface oxidation	Current density mA/cm^2	Reference
1	4 (2–10) Pt/CNT	58	Yes	153 at 0.8V	32
2	2.5 E-TEK	34	—	98 at 0.8V	
3	2.8 (2–5) Oriented Pt/CNT	—	Yes	220 at 0.8V	33

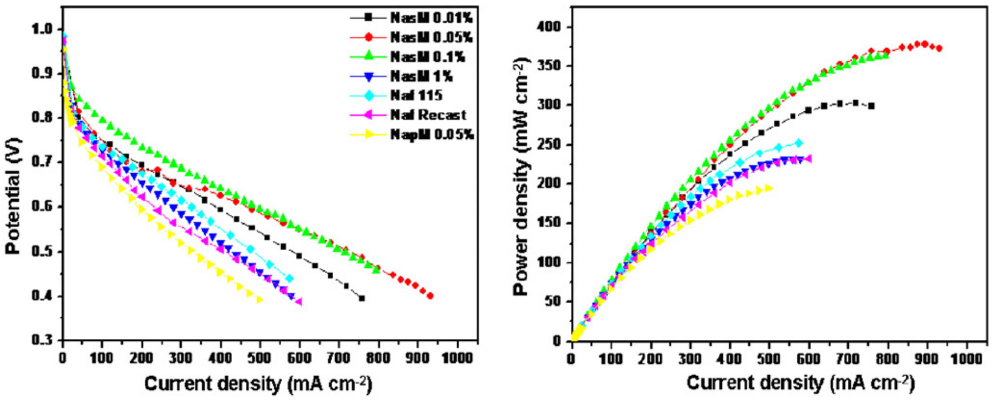


Figure 4: Polarization plots of showing the potential and power density variations with increasing current densities.

the catalytic activity of Pt that is supported on CNTs. The onset potential of methanol oxidation is shifted in case of CNT/Pt electrode associated with enhancement of the anodic current. Similar shift observed with Pt/Ru alloy system is attributed to the reduced work function of Ru ($\Phi_{Ru} = 4.52$ eV) in comparison with that of Pt ($\Phi_{Pt} = 5.36$ eV). Hence the shift observed in CNT/Pt can be ascribed to the reduced work function of CNT (($\Phi_{CNT} = 5$ eV).[54–61] In another report, Wu et al have shown the remarkable enhancement in CO tolerance of Pt when supported on SWCNTs and MWCNTs over E-TEK Pt/C catalyst, a commercial sample often used by fuel cell companies. The peak potential for CO striping are observed at 0.75 V, 0.78 V and 0.82 V respectively for Pt/SWCNT, Pt/MWCNT and E-TEK Pt/C catalysts suggesting an easy removal of the adsorbed CO at a much lower onset potential.[49] This could help in achieving better performance even with increased CO level in the hydrogen stream.

4. Application of CNTs in composite electrolytes of PEMFCs

Solid polymer electrolyte membrane is one of the key materials that restrict the performance as well as the cost of the PEMFCs as electrolyte is an important component of the integral MEAs. A good PEM should have high protonic conductivity, yet electrically insulating in order to avoid short circuiting, and should have very low permeability values towards fuels such as Hydrogen, methanol and ethanol, in addition to having very high chemical stability to withstand high acidic conditions of fuel cell operating environment and sufficiently mechanical stability to withstand the stresses of stack fabrication. PEMs that are either used or being developed could be classified in to two categories; PEM operating at temperatures less than 100°C often with perfluorosulphonic acid (PFSI) electrolyte and that operating above 100°C with a variety of new thermally stable polymeric electrolytes. In the latter type, however, life time data more than ∼5000 hours has rarely been reported despite the availability of many types of polymeric, blended and organo-inorganic hybrid membrane electrolytes. Consequently, these are far from commercialization although many prototype stacks are undergoing field trials in various parts of the world. Considering Nafion as a typical ionmer, we now discuss some promising aspects of CNT-based polymeric composite electrolytes for PEMFC applications especially for temperature less than 100°C.[62]

Nafion based membranes are well known to show proton conductivities in the range of 0.1 Scm^{-1}. However, their conductivity relies mainly on the water content which restricts their operating temperatures to less than 100°C. Further, the swelling and contraction of these membranes (dimensional change) with change in water content is of severe concern as it affects the integrity and durability of MEAs. Typical thickness values of membranes range 50–120 microns as indicated in the names (Nafion 112, and 115 etc). A possible method to reduce the cost of PEM is reducing the thickness, which might also help in decreasing the membrane resistance thereby improving the performance of PEMFC. However, reduction in thickness could lead to increased hydrogen and methanol permeability coupled with reduced mechanical stability.

Efforts directed on improving the proton conductivity of these membranes include various approaches to mainly increase the water content by incorporating hygroscopic inorganic and organic additives such as SiO_2, ZrO_2, TiO_2, zirconium phosphate, and zeolites which can keep the membrane humid at higher temperatures during the operation.[63–67] However, most of these composite membranes show higher conductivity than Nafion only at higher temperatures, their base value being less than that of Nafion. More significantly, long term operation of these membranes in MEAs face severe limitations due to the agglomeration of these particles during operation resulting in extensive degradation in performance with time. Also as these membranes do not have any cross-linking, these dispersed particles often reduce the mechanical stability of the composite membranes.[65] Solution cast membranes made up of commercial Nafion solutions and porous PTFE matrix helps in some extent, to increase the mechanical strength and structural integrity, finally enabling the use of reduced thickness of the membrane without any change in performance. However, the proton conductivity of the resulting membranes is very poor to limit their power density.[67]

Even though CNTs have been used earlier to fabricate polymer composites with increased mechanical stability, applications meant for their use as an additive for composite membrane electrolyte have not been tried mainly due to the fear of electrical short circuiting.[68] The addition of CNTs can be expected to give increased mechanical robustness and integrity as it is well known for its highest young's modulus. Liu et al., studied the impact of CNTs on the electrolytic behaviour of Nafion membranes upon reinforcement to observe several improved features.[68–70] Fabrication of composite membranes of CNTs and Nafion at 1:99 wt% after ball-milling and solution casting show similar performance to pure nafion membrane in terms of proton conductivity, but with significantly less dimensional change for the case of CNT reinforced composite membranes. Similarly, Thomassin *et al* have used melt extrusion to incorporate the CNTs on to Nafion membrane to observe reduced methanol permeability to about 60% along with an unusual increase in the Young's modulus up to 140–160% in comparison to that of commercial Nafion membranes.[70]

In all the above applications, one has to naturally consider the effect of electronic conductivity of CNTs. Certain type of functionalization indeed enhances the electronic conductivity and it is always important to consider the risk of electrical short-circuiting despite the use of very low amounts of CNTs ($<0.1\%$). Proper dispersion is essential for ensuring uniform behaviour and the normally reported value of percolation threshold for CNTs in Nafion is around 5–11% depending upon the CNTs used and their mode of preparation. Lie et al., in yet another report have prepared a three phase composite membrane where a Pt-CNT-Nafion composite membrane was sandwiched between two pure Nafion membrane phases.[68] This has improved the performance of Nafion membranes significantly in both mechanical stability and water management perspectives. The addition of CNTs results in both improved mechanical stability and chemical inertness while the Pt particles supported on it helps to produce water by reacting with H_2 and O_2 that penetrates the membrane and thereby keeping the membrane wet under dry conditions. However critical life time data about Pt dissolution and carbon corrosion are necessary to comment on the benefits of these composite materials with respect to robustness and durability.

4.1. *Role of funtionalization of CNTs*

All the above reports are primarily intended to use CNTs as mechanical stability boosters or reinforcing phases albeit in small amounts, for Nafion in order to withstand the high processing conditions of stack fabrication and to prolong membrane life. As a result, the CNT-Nafion composite membranes have shown conductivity values similar or less than that of pure Nafion membranes, especially if pristine single or multi walled CNTs are used for composite fabrication. However, CNTs can be functionalized on the sidewalls with desired groups through careful chemical process, which can be used in a constructive manner to increase the conductivity of Nafion membranes. The main advantages of using functionalized CNTs for composite polymer electrolytes are

1. Reduction in electronic conductivity: since all type of CNTs are known to have electronic conductivity and functionalization can effectively reduce the electronic conductivity.
2. Tuning the interfacial structure: it is always desirable to attach molecules structurally analogous to that of the polymer backbone to ensure uniform properties in the composite
3. Better dispersion and adhesion: agglomeration and phase segregation of CNTs at isolated regions could be avoided using appropriate functionalization
4. Easy processability: Since CNTs can be made soluble either in aqueous or organic solvents using different types of chemical functionalization approaches, these composites can be easily processed in the form of films of uniform thickness and properties. However, the choice of functionalization is critical since some functional methods could on the other hand enhance carrier density to finally yield better electronic conductivity.

Table 2: Variation of proton conductivity, domain size and yield strength with s-MWCNT composition and water content.

Membrane composite	Proton conductivity (S cm^{-1})	Hydrophilic domain size (nm)	Water content (%)	Yield strength (MPa)
Nafion 115	0.028	48	29.2	2.68
Recast Nafion	0.020	51	42.3	2.4
Naf-sMWCNT 0.01%	0.029	54	39.7	2.5
Naf-sMWCNT 0.05%	0.036	72	33.4	2.62
Naf-sMWCNT 0.1%	0.032	70	30.4	2.67
Naf-sMWCNT 0.5%	0.031	67	28.1	3.1
Naf-sMWCNT 1%	0.030	35	27.2	4.3

The choice of functionalization of CNTs for a composite electrolyte with Nafion is obvious. Since sulfonic acid groups on the side chains are responsible for the conductivity of PFSI membranes like Nafion, CNTS are to be functionalized with sulphonic acid groups as any increase in their concentration is expected to improve the proton transport. We have utilized this concept and functionalized both single walled and multiwalled CNTs with sulfonic acid moieties through microwave treatment in HNO_3–H_2SO_4 mixture.[71–72] Interestingly, this sulfonic acid functionalized CNTs (s-CNTs) are soluble in water and dimethyl acetamide, offering additional advantages of flexibility in terms of membrane processability.

We have prepared several composite membranes based on Nafion-s-CNTs, with a systematic variation in CNT weight percentage from 0.01 to 1%, beyond which there is a saturation in proton conductivity. The results show that for both types of s-CNT-Nafion composite membranes, there is an increase in proton conductivity coupled with increased mechanical stability of the membrane. The cause for this enhancement is revealed by the small angel X-ray scattering experiments (SAXS) where the hydrophilic ionic domain size change shows a strong correlation with the increase of CNT content and proton conductivity. The domain size measured from SAXS measurements reveal approximately 50 Å clusters for commercial Nafion 115 membranes while composites exhibit a saturation limit of about 70 Å both for 0.05 and 0.1% of s-CNT content (Table 2) in the composite.

These results are well supported by the fuel cell polarization experiments where 0.05% and 0.1% composites have shown increased current and power densities than that of commercial and recast Nafion membranes of similar nature (figure 4). This result sheds some light on the possibility of s-CNTs to play a vital role in enhancing the conductivity of composite electrolyte and also on the improved robustness of the membrane, presumably due to the amount of functionalized CNTs. Our further attempts to vary the $-SO_3H$ content by changing the microwave treatment time and related parameters are compared in Table 2 with available data from other reports. For Example, Peng et al., have prepared sulfonated CNTs by heat treatment with H_2SO_4 at 250°C under N_2 atmosphere to attain a sulfonic acid content of 15 wt% which is much higher than the 2.5 wt% sulfonated CNTs that we used for composite membrane fabrication. However, there is no fuel cell polarization data and the presence of too much of sulphonic acid groups might create adverse effects in terms of corrosion and membrane degredation.[75,76]

5. Use of Graphene as electrode materials for PEMFC

Very recently Graphene, a two dimensional means of graphite took the centre stage of research in many critical areas due to its similarity in properties with graphite coupled with the ability to tune its band gap by controlling their size. Functionalized graphene sheets have been used as the cathode support material for Pt electrocatalysts and found to show higher electrochemical surface area and oxygen reduction activity with improved stability as compared with the commercial catalyst. Similarly Pt decorated graphene has been shown to have better methanol oxidation activity than its commercial counterpart. However, it would be premature to draw a conclusion on the utility of graphene at this stage as very few reports are available on it and its bulk preparation itself is yet to be optimized.[77–81]

6. Limitations of CNTs in PEMFC

Even though the use of CNTs have shown promising results both as an electrode support and as novel composite polymer electrolytes, it still has few limitations to overcome before being considered for widespread use. For example, the preparation of SWCNTs yields a mixture of metallic and semi conducting SWCNTs which may have significant variation in properties. Further, both SWCNTs and

Table 3: Variation of Sulfonation in the CNTs by varying the microwave treatment time and preparation method.

S. No	Preparation method	Sulfonation level (wt%)	Reference
1	Microwave method	2.26	73
2	Microwave method	10.1	74
3	235°C $(NH_4)_2SO_4$ treatment	—	75
4	250°C H_2SO_4 treatment	15.3	76

MWCNTs contain minimal amount of impurities which may have deteriorating effect on PEMFC performance. It has been demonstrated that even trace level of Fe impurities can degrade Nafion due to the presence of sulphonic acid moieties in the back bone.[80] The use of highly purified CNTs is more expensive which will ultimately increase the cost of MEAs and PEMFC stacks which is not desirable since cost is the single overriding concern preventing widespread application of PEMFCs.

Another important limitation of using CNTs is lack of enough data related to durability. Although the use of CNTs as electrode support has shown better corrosion resistance over Vulcan XC-72 in short time scale, its sustained utility for extended period of operation (such as 1000 hours or more) is yet to be evaluated. Moreover, CNTs are normally surface oxidised for increased binding with Pt nanoparticles. The stability of these surface groups under severe potential cycling has not been investigated. The effect of potential induced morphology changes is another major concern which may have severe impact on the use of CNT as a supporting material. Similarly different processing conditions of catalyst preparation and MEA fabrication are expected to create defects on the CNT surface. For example, the use of ultrasonic homogenizer for prolonged time is known to chop carbon nanotubes into smaller dimensions to help dispersion although for certain applications this is harmful.[82–83] Further, the non-toxicity of CNTs is yet to be completely established which necessitates cautions handling of them in bulk.[84] Despite the favourable improvements in performance by the use of CNTs both as electrode support and as a composite electrolyte, these limitations require further extensive research to fulfil the enormous application potential of CNTs and related carbonaceous materials in PEMFC.

7. Conclusions

Carbon nanotubes are wonderful materials with highly desired properties that suit many of the requirements of a supporting material for PEMFC. The use of CNTs as support in PEMFC cathodes is shown to have increased electrocatalytic activity towards ORR due to the intrinsic properties of CNTs. Further due to their higher electrical conductivity and lesser defects or pores in them the catalytic nanoparticles supported on them are assured to have better electrical contact with the external circuit which increases the Pt utilization to 58% from 34% for normally used materials like Vulcan XC-72. Besides this powerful advantage, properly oriented CNTs will also enable better mass transport of gasses and liquids, which helps to have better diffusion of reactant gases and product water across the electrode. Thus the overall utilization of CNTs as catalyst supports in PEMFCs can help in decreasing the three different types of overpotentials associated with activation, ohmic and mass transport. While the higher conductivity of CNTs helps in electrode fabrication, careful use of them below their percolation threshold would help in increasing the mechanical stability of the electrolyte membranes. Furthermore, suitably functionalized CNTs can in fact increase the conductivity of the state-of-the-art Nafion membranes beyond its base value along with improved mechanical and structural stability. The ability to vary the degree of functionalization of CNTs would help to fine tune the proton conductivity of the membrane with out any significant electronic conductivity. Although these findings prove the importance of CNTs in improving the PEMFC performance, there are several limitations as well. For example, the durability of none of these MEAs has been reported so far while the purity of CNTs used is also questionable mainly due to the fact that most of the CNT synthesis involves metal precursors as catalysts which are very difficult to remove completely.

The use of nanocomposite polymer electrolytes with the help of selectively functionalized carbon nanotubes open prospects to combine the nanostructure-tuning capabilities of carbon nanotubes with the unique ionic transport properties of polymeric membrane electrolytes to enable key benefits. Although the illustrated examples of Nafion-sulphonated CNT are in areas of hydrogen-oxygen fuel cells exploiting the nanostructured electrolyte membrane's ionic transport and improved mechanical properties, the basic principles are expected to be applicable to many other applications like electrolyzers, chemical sensors and rechargeable lithium batteries that are structurally defined for harnessing the enhanced ionic transport. In all of these aspects, a further detailed investigations of the CNT-ionmer composite design and functionalization control should have a profound impact on the exploration of CNT based composite electrolytes for a wide range of technological applications.

Received 18 November 2009; revised 19 December 2009.

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