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Carbon Nanotubes Supported Metal Nanoparticles for the Applications in Proton Exchange Membrane Fuel Cells (PEMFCs)

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs), as an important alternative energy source with great potentials for use in applications ranging from cellular phones, laptops, digital camera and other conventionally battery driven devices to long-term stationary monitoring electronics, have been extensively investigated (K. Matsumoto et al., 2009; P. Xing et al., 2004). In a PEMFC, the conversion of chemical energy to electrical energy occurs via a direct electrochemical reaction, and its efficiency is directly dependent upon the catalysts used (X. Wang et al., 2004). To be commercially viable, it is generally required that these catalysts have high durability, low cost and higher activities in oxygen reduction and/or fuel oxidation reaction (Kundu et al., 2009). Currently, the most widely used catalysts in the PEMFCs are metal nanoparticles (NPs), mainly Pt and/or Pt based alloys (W.Z. Li et al., 2002, 2003, 2004; Prabhuram et al., 2006; X. Wang et al., 2005). These metal NPs are usually characterized with high activities in oxygen reduction and/or fuel oxidation reaction due to their high surface to volume ratio and improved Fermi levels for redox reactions (W.Z. Li et al., 2006; S.Y. Wang et al., 2009; B.H. Wu et al., 2009; Y. Zhao et al., 2007). However, individual metal NPs are usually unstable and prone to loss of their catalytic activity due to their irreversible aggregation during the electrochemical processes. For practical uses, therefore, specific supports are mostly used to mobilize and prevent these metal NPs from aggregation.

Among various types of supports, carbon nanotubes (CNTs) are undoubtedly the most widely used. CNTs are allotropes of carbon with a cylindrical nanostructure, and are characterized as elongated fullerenes with diameters ranging from 1-100 nm (Wunderlich, 2007) and lengths of up to several microns. They can be single walled (called as single walled CNTs, SWCNTs) or multiple walled (called as multiple walled CNTs, MWCNTs) (Cassell et al., 1999; Iijima, 1991; Ijima & Ichihashi, 1993; Journet et al., 1997; Thess et al., 1996). These cylindrical carbon molecules have unique properties, such as high-surface area, good electronic conductivity, strong mechanical properties and high-chemical stability, which make them potentially useful in many applications in nanotechnology, electronics,

optics, and other fields of materials science, as well as potential uses in architectural fields (Baughman et al., 2002; Pham-Huu et al., 2002). Studies have shown that the deposition of metal NPs onto the surface of CNTs can not only protect these particles from aggregation, but also improve their catalytic activities, and even produce properties that are not accessible to CNTs and metal NPs alone, which are important for their use in PEMFCs (W.Z. Li et al., 2006; S.Y. Wang et al., 2009; B.H. Wu et al., 2009; Y. Zhao et al., 2007). However, due to the inertness of the CNT walls, the effective attachment of metal catalysts remains a challenge, especially for the solution-based methods for the preparation of metal deposited CNTs (metal/CNTs) (Balasubramanian & Burghard, 2005). Surface functionalization of CNTs is, therefore, generally required to enable a homogeneous and uniform deposition of metal NPs (J. Chen et al., 1998; Yu et al., 1998). It is, however, demonstrated that the surface functionalization methods have great influence on the structure and properties of CNTs. In some cases, harsh chemical or electrochemical oxidations applied with concentrated strong acid could lead to a structural destruction to CNTs, resulting in decrease in their electrical conductivity and correspondingly a possible reduction in the catalytic activity of the obtained metal/CNTs when used in PEMFCs (Koshio et al., 2001; J. Li et al., 1998; Qu et al., 2005, 2006). For rational design of metal/CNTs catalysts, it is therefore important to well understand the various methods used for the CNT functionalization.

Except for the methods used for the CNT functionalization, the catalytic activity of the metal/CNTs is also affected by the size and distribution of deposited metal NPs. Since the dispersion and particle size of metal NPs largely determine the utilization and catalytic activity of metal/CNTs, the synthesis of metal NPs supported by CNTs with a controlled manner is of fundamental and practical importance. Indeed, researches have demonstrated that the deposition, distribution, and crystalline size of metal NPs supported on CNTs are significantly dependent upon the method used to synthesize metal/CNTs, the types of functional groups on the surface of metal NPs, and the way that metal NPs are adsorbed. It is therefore necessary to well know about the various methods used to synthesize metal/CNTs for the preparation of catalysts of high efficiency.

In the chapter, we will first provide brief recapitulations of the concepts of various surface functionalization methods of CNTs, and some possible shortcomings associated with these methods. This is followed by descriptions of the various methods used for the preparation of metal/CNTs, and the way that the metal ions and metal NPs are adsorbed onto CNTs is also elucidated. For the activity validation of the synthesized catalysts, it is essential to directly use them in fuel cells. It is demonstrated that the performance of the catalysts in the fuel cell is also affected by the methods for synthesis of membrane electrode assembly (MEA), which is the core of a fuel cell. Thus, the activity validation of the synthesized catalysts and the methods used for the synthesis of MEAs are also described and discussed in this chapter.

2. Methods for functionalization of CNTs

Over the years, a great deal of research has been conducted on the surface modification of CNTs (Hirsch, 2002; Y. Lin et al., 2004; Tasis et al., 2006). The modification of these quasi one-dimensional structures can be carried out by the covalent attachment of chemical groups through reactions onto the π-conjugated skeleton of CNT or by the noncovalent adsorption or wrapping of various functional molecules (Saha & Kundu, 2010). Covalent surface modification of the CNTs leads to a permanent change to the CNT surface. In this

case, the CNTs are functionalized with reactive groups which can later form covalent bonds with another molecule (Hirsch, 2002; Tasis et al., 2006). Non-covalent surface modification does not involve the formal chemical bond formation between a molecule and the surface of CNT. The functionalization of CNTs is through adsorption of functional molecules via van der Waals forces, electrostatic forces, hydrogen bonding, or other attractive forces (Y. Lin et al., 2004). Studies have shown that the stability and catalytic activity of metal/CNT composites are strongly dependent upon the way that the CNTs are functionalized. In this section, various CNT functionalization methods based on covalent and noncovalent surface modifications will be discussed. Specifically, a novel CNT functionalization method based on a plasma treatment is also presented. The plasma surface modification is a newly reported method for the CNT functionalization, which is characterized to be a mild surface modification approach and effectively prevent CNTs from the structural destructions possibly caused by other surface functionalization methods (Jiang et al., 2009, 2011). The obtained metal/CNTs are reported to be with higher catalytic activity in a methanol oxidation. Therefore the plasma surface functionalization method has great potentials for the preparation of metal/CNTs of high efficiency as catalysts. Additionally, nitrogen dopped CNTs (N-CNTs) which show great promises as supports of metal NPs for the PEMFC applications, are also introduced. Due to the presence of N, the N-CNTs are reported to exhibit a strong binding to metals NPs. It can therefore avoid using functionalization processes that might be detrimental to the catalytic properties of the obtained metal/N-CNTs (Maiyalagan et al., 2005).

2.1 Covalent functionalization

2.1.1 Oxidative treatment of CNT surfaces

Among various surface functionalization methods, oxidative treatment of CNT surfaces is probably the most widely employed, which has been used to remove amorphous carbon for purification purposes, to open CNT ends for metal NP insertion and to create functional groups on their surface favoring the anchorage of metallic NPs. It can be performed by mixing CNTs with different oxidants such as HNO_3, H_2SO_4, $KMnO_4$, OsO_4, HNO_3/H_2SO_4, RuO_4, $K_2Cr_2O_7$, polyphosphoric acid, citric acid, ozone gas and H_2O_2 (Hernadi et al., 2001; Hirsch et al., 2002; Hwang et al., 1995; Kannan et al., 2008; Kyotani et al., 2001; Mawhinney et al., 2000a, 2000b; Y.C. Xing et al., 2004; Yu et al., 1998; J. Zhang et al., 2003; Zheng et al., 2006). The oxidized CNTs are usually functionalized with hydroxyl (–OH), carboxyl (–COOH), carbonyl (–C=O) and sulfate ($–OSO_3H$) groups, which can serve as metal-anchoring sites facilitating metal nuclei formation and subsequent particle growth (Georgakilas et al., 2002; Kongkanand et al., 2006a; Michelson et al., 2001).

Oxidation with nitric acid solutions is a simple, effective and commonly used approach to functionalize CNTs, which can lead to the formation of CNTs functionalized with carboxylic acid functions, as well as of lactones, phenols, carbonyls, anhydrides, ethers and quinones (Bambagioni et al., 2009). The oxidation of CNTs occurs primarily on the CH_n groups (MWCNT defects), giving rise to the formation of alcohols -OH, then C=O and finally carboxylic acid groups, and the density of the functional groups and subsequently deposited metal NPs are strongly dependent upon the concentration of HNO_3 used to treat the CNTs (Bambagioni et al., 2009; Reddy & Ramaprabhu, 2007). Since the oxidation with HNO_3 solutions can provide CNTs with a large amount of anchoring sites facilitating the deposition of metal NPs of smaller size with homogeneous dispersion, the subsequent fabricated metal/CNT composites usually exhibit a high efficiency in the PEMFC

application. As reported by Han et al. (K.I. Han et al., 2004), the electrocatalysts supported on CNTs functionalized by the HNO_3 treatment showed improved activity over a commercially available electrocatalyst, E-TEK.

For a better functionalization of CNTs, some oxidants mixtures are also employed to functionalize CNTs with suitable surface for the deposition of metal NPs. For example, Wei et al. (Wei et al., 2008) used a H_2SO_4/H_2O_2 solution to functionalize CNTs. The functionalized MWCNTs were characterized to be terminated with carboxyl groups. Halder et al. (Halder et al., 2009) tried a surface treatment of CNTs by its mixing with a combination of concentrated HNO_3 and H_2SO_4 which gave very good surface functionalization on the wall of CNTs. Liu et al. (Liu et al., 2002) reported a high density of oxygen containing species on the CNT surface by a $K_2Cr_2O_7/H_2SO_4$ oxidative treatment.

In general, the oxidative treatment technique can functionalize CNTs with oxygen-containing functional groups on their walls, which could increase the surface binding sites of CNTs, avoid the aggregation of the subsequent deposited metal NPs, improve the dispersion of metal NPs, and reduce the average size of metal NPs deposited. The surface functional groups (e.g., carboxyl, hydroxyl, carbonyl groups) on the oxidized CNTs are mostly concentrated at defects sites or at the end tips of CNTs, where the strain and/or the chemical reactivity are higher. However, such functionalization method is inevitably accompanied with a few problems, such as uneven distribution of the surface functional groups, structural damage, and thus partial loss in electrical conductivity of the CNTs. Additionally, due to the hydrophobic surface of CNTs which makes them tend to form aggregates in polar solvents, the surface oxidation of the CNTs is mostly incomplete. That is because during the functionalization process, the CNTs inside these aggregates may not be attacked by the oxidative agents but remain unmodified. However, to use CNTs as a heterogeneous catalyst support, the entire surface of CNTs needs to be oxidized for functionalization, so that highly dispersed catalysts could be achieved. Although prolonged acid oxidation at higher temperatures could lead to an improvement in the quality of CNT functionalization, this might result in more oxidative damage on the graphene structures, leading to potentially more severe loss in the electric conductivity of the carbon nanomaterials. Therefore, in an effort to prepare highly dispersed, high-loading Pt NPs on CNTs, an effective method of CNT functionalization should be sought.

2.1.2 Photochemical oxidation of CNT surfaces

Compared to the oxidation technique mentioned above, the functionalization of CNTs by a photochemical oxidation of surfaces is a more facile and eco-friendly surface functionalization method. The reaction can be conducted in a gas phase and dry process with zero-emission of liquid wastes, providing CNTs with a large amount of carbonyl and carboxyl groups in a very short period of time. Its high efficiency and adjustability in the CNT functionalization provides an additional advantage to control the chemical and physical properties of CNTs. As reported by Asano et al. (Asano et al., 2006), the functionalization of the CNTs by the photochemical oxidation with a short-wavelength ultraviolet irradiation could produce the CNT surface with a high density of oxygen-containing functional groups. An enhancement of the active surface area and the performance of methanol oxidation for the Pt NPs deposited on the photochemical oxidized CNTs, which was attributed to the high dispersion and dense deposition of Pt NPs on the oxygen groups-rich surface, was demonstrated by Jang et al (Jang et al., 2009).

2.1.3 Sonochemical treatment

Sonochemical treatment is reported to be a relatively mild surface modification technique, which can alleviate the damage of CNTs possibly caused by the higher temperature oxidation to a certain extent. During a sonochemical surface modification process, the ultrasonic waves can produce microscopic bubbles in the liquid. A collapsing of these microscopic bubbles results in shock waves, which produce dangling bonds on the surface of CNTs that undergo further chemical reactions and provide the oxidative power to incorporate acidic sites. It is found that the sonochemical treatment of CNTs under acidic aqueous solution (HNO_3 and/or H_2SO_4) conditions can provide CNTs functionalized with –C=O, -C-O-C-, -COO-, and –C-OH groups, which is important for the deposition of uniformly dispersed Pt NPs. The ability to produce CNTs with high densities of functional groups for high loading deposition of metal NPs on CNTs using the sonochemical technique makes it a promising way for the CNT functionalization. Reddy and Ramaprabhu (Reddy & Ramaprabhu, 2007) functionalized the purified SWCNTs by an ultrasonication of CNTs in concentrated nitric acid. The lower power was used to reduce the damage to CNTs during the ultrasonication. The treated CNTs with less structural damage were characterized to be functionalized with high concentrations of -OH and -COOH (Rajalakshmi et al., 2005). Xing et al. (Y.C. Xing et al., 2004, 2005) have shown that the Pt NPs deposited on sonochemically treated CNTs exhibited a much higher catalytic activity than those supported on the carbon black when used in the PEMFCs. This enhancement of electrochemical activity is attributed to the unique structures of CNTs and the strong interactions between the Pt NPs and the CNT support (Y.C. Xing, 2005).

2.1.4 Silane-assisted method

Several recent reports show that CNTs can be chemically functionalized by silane coupling agents (Kamavarama et al., 2009; Ma et al., 2006; X. Sun et al., 2003; Villers et al., 2006). In the silane assisted functionalization approach, CNTs are mixed with a solution containing a silane derivative and water in ethanol. Upon hydrolysis, the silane derivative form an acid silicate on the surface of CNTs, permitting the exchange of H^+ by the metal ions for the subsequent deposition of metal NPs by a reduction of the adsorbed metal ions. For example, Sun et al. (X. Sun et al., 2003) used a silane derivative to functionalize the CNT surface with -SO_3H group for the deposition of Pt NPs. The deposition of the Pt NPs was carried out by immersing the CNTs in a solution containing $PtCl_2$, a silane derivative and water in ethanol (X. Sun et al., 2003), which produced a Pt^{2+} adsorbed CNTs. The CNT supported Pt NPs were formed in a flow of H_2 and Ar. Fig. 1 shows the transmission electron microscopy (TEM) images of Pt NPs deposited on CNTs in the absence and the presence of the silane precursor. It shows that the functionalization with silane derivative could facilitate the uniform deposition of Pt on the CNT's surface, producing well dispersed Pt particles with a smaller size.

A major drawback of the silane-assisted functionalization method is that the electrocatalytic activity of the obtained metal/CNTs catalysts is improved not as largely as it is expected. In this method, an electrochemical insulating layer, organosilane, is inserted between metal and CNTs and thus decrease the interactions between them, which is unforvable for the improvement of the activity of the obtained catalysts. As reported by Ma et al. (Ma et al., 2006), Pt NPs deposited on a silane modified CNTs showed only slightly better electrocatalytic activity in the PEMFC than the commercial electrodes.

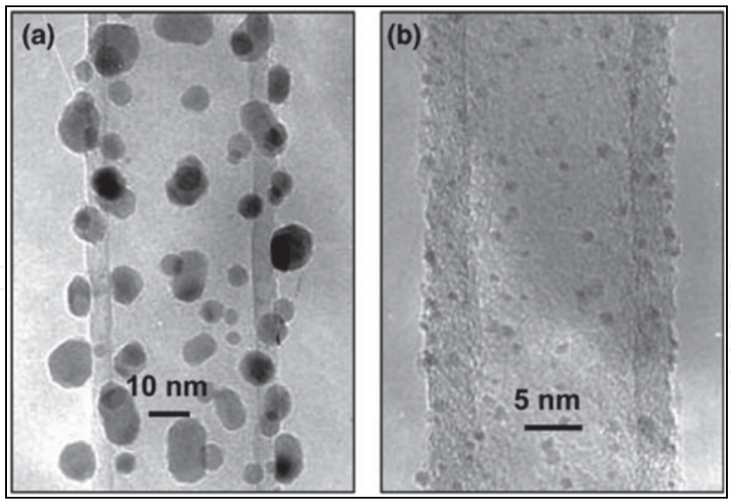


Fig. 1. TEM images of Pt NPs deposited on CNTs (a) in the absence and (b) in the presence of the silane precursor. Reprinted with permission from X. Sun et al., 2003. Copyright 2003 Elsevier Science Ltd.

2.1.5 Ionic liquids treatment

Ionic liquids (ILs) represent a group of solvents that consist only of ions existing in the liquid state at low temperatures. Due to their high thermal and chemical stability, high ionic conductivity, wide electrochemical windows, and negligible vapor pressure, ILs are expected to be superior solvents for many chemical processes (Parvulescu & Hardacre, 2007; Welton, 1999) and therefore attract considerable technological and scientific interests in recent years. Advanced progress in the development of catalysts for the PEMFCs applications indicates that an introduction of ILs into the reaction systems for preparing Pt/CNT composites provides a possible way to obtain composites with excellent catalytic and electrocatalytic performance (Park et al., 2009; B.H. Wu et al., 2009).

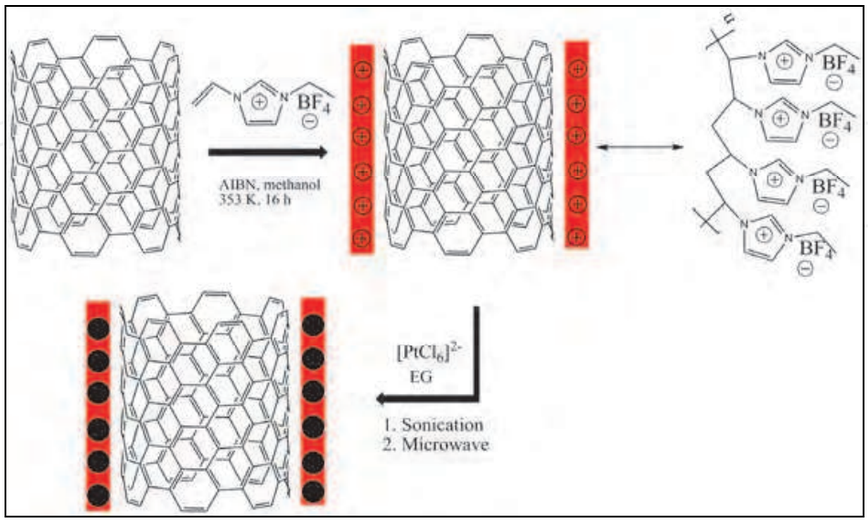


Fig. 2. Schematic of the modification of CNTs with PIL and the preparation of Pt/PIL-CNTs nanohybrids. EG: ethylene glycol, AIBN: 2,2′-azobisisobutyronitrile.

In an IL based method for the CNT surface functionalization, the CNTs are usually functionalized first to produce a suitable surface for the grafting of the IL molecules. As reported by Zhao et al. (Z.W. Zhao et al., 2006), MWCNTs used for the surface modification were pretreated in concentrated HNO_3 before functionalized with ILs, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. It was reported that the functionalization with the ILs made a big contribution to the formation of small, homogeneous Pt NPs and to the suppression of agglomeration of CNTs. The deposited Pt NPs exhibited an electrochemical surface area with 21% higher than the commercial Pt/C. For the better deposition of metal NPs, Wu et al. (B.H. Wu et al., 2009) reported a novel method based on the thermal-initiation free radical polymerization of the IL monomer, 3-ethyl-1-vinylimidazolium tetrafluoroborate ([VEIM]BF_4), to form an ionic-liquid polymer (PIL) on the CNT surface, which introduced a large number of surface functional groups on the CNTs with uniform distribution to anchor and grow metal NPs (Fig. 2). The process of modification by PIL would lead to less structural damage to CNTs than the typical acid-oxidation treatment because of the mild polymerization of the IL monomer. The subsequently deposited Pt and PtRu NPs therefore exhibited a smaller particle size, a better dispersion, a higher electrochemical active area and correspondingly better performance in the direct electrooxidation of methanol than those on the CNTs without the PIL modification.
The disadvantage of the IL based functionalized method is that this approach requires an initial step of the CNT functionalization for the subsequent IL or PIL functionalization. It does not only increase the complexity of process, but possibly causes a structural damage to CNTs although it is alleviated compared to oxidative treatment techniques.

2.1.6 Electrochemical modification

The surface modification of CNTs by an electrochemical method is an attractive approach for functionalization of CNTs. In comparison to other functionalization methods, the electrochemical modification of CNTs can produce CNTs with a C-C covalent bond, which is strong and suitable as a substrate for the deposition of NPs, provides a uniform functional surface, which can effectively prevent the undesired nucleation processes on the CNTs surface, and facilitate the formation of metal NPs with a narrower size distribution due to the specific electrostatic interaction between the substrate and the adsorbed metals. The surface functionalization of CNTs by an electrochemical coupling of aromatic diazonium salts and phenyl residues have been reported (Bahr et al., 2001; Balasubramanian et al., 2003). For example, Guo and co-workers (Guo & H.-L. Li, 2004) covalently functionalized CNTs by grafting an ordered 4-aminobenzene monolayer onto the CNT surface via electro-reduction of 4-nitrobenzenediazonium tetrafluoroborate through cyclic voltammetry (CV), as shown in Fig. 3.

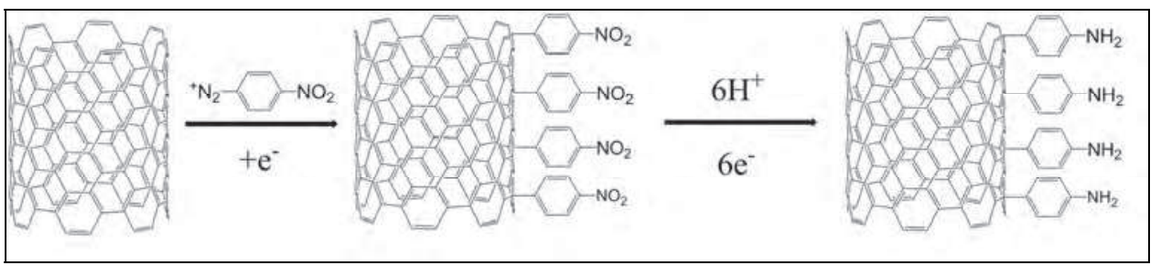


Fig. 3. Schematic for the electrochemical modification of CNTs.

The electrocatalytic properties of Pt/MWCNT composites for methanol oxidation have been investigated by the CV and the high electrocatalytic activity was observed. This might be attributed to the small particle size, high dispersion of platinum particles and the particular properties of the MWCNT supports.

2.2 Non-covalent functionalization

Surface modification of CNTs by non-covalent functionalization is particularly attractive due to its possibility to preserve the electronic network of CNTs (Dyke & Tour, 2004; Moghaddam et al., 2004). The non-covalent functionalization of CNTs is mainly through adsorption of functional molecules via their interactions with CNTs by van der Waals forces, electrostatic forces, hydrogen bonding, and other attractive forces (Y. Lin et al., 2004). Various species of polymers (Andrews et al., 2002; G. Wu et al., 2006), polyelectrolytes (S.W. Lee et al., 2009; S.Y. Wang et al., 2009; W. Yang et al., 2008), surfactants (J.F. Lin et al., 2010), proton-conducting polymers (Tian et al., 2007; Sarma et al., 2005; Scibioh et al., 2008) and other functional molecules (Du et al., 2008) can non-specifically bind with the external surface of CNTs without using non-covalent coupling.

The wrapping of CNTs by polymer molecules was developed by Connel and co-workers (Connel et al., 2001) to prepare individual, well dispersed CNTs in aqueous solution based on the non-covalent attachment of macromolecules on CNTs. The method relies on the thermodynamic favorability of the interactions of CNT–polymer with respect to that of CNT–water, which leads to the hiding of the hydrophobic surface of the CNTs by the attachment of the polymer molecules. When mixing with polyelectrolytes, the energy balance favors CNT wrapping, yielding a high density of charged surface sites which can then serve as a good starting point for the alternating monolayer adsorption of the oppositely charged components through a layer by layer (LBL) technique, driven by electrostatic and van der Waals interactions (Correa-Duarte et al., 2006; Ostrander et al., 2001). As schematically shown in Fig. 4, upon the wrapping of CNTs with a negatively charged polyelectrolyte, a positively charged monolayer can then be deposited, which serves as the real template for the NP adsorption via the electrostatic interactions.

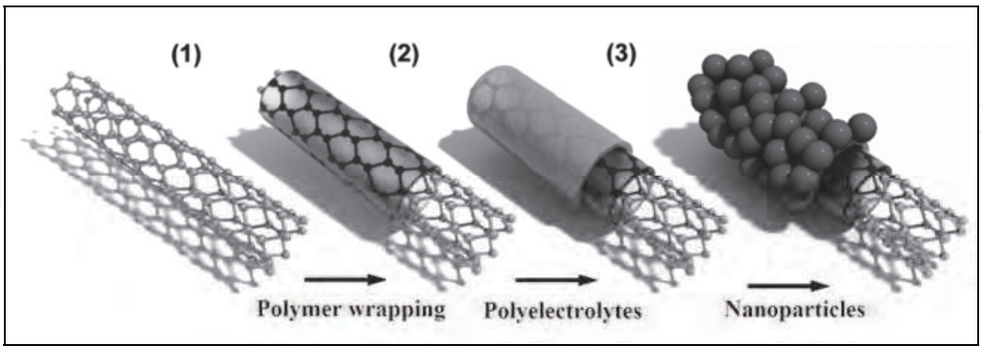


Fig. 4. Schematic illustration of a non-covalent functionalization of CNTs, involving (1) polymer wrapping, (2) self-assembly of polyelectrolytes and (3) NP deposition. Reprinted with permission from Correa-Duarte & Liz-Marzán, 2006. Copyright 2006 Royal Society of Chemistry.

Polybenzimidazole (PBI) (Chemical structure of PBI, Fig. 5a) and its derivatives are some of the most promising candidates for high temperature polymer electrolytes since the

proton transfer occurs not only by the vehicle mechanism but also by the hopping mechanism (Q. Li et al., 2004; J.T. Wang et al., 2004), which is an good feature for increasing the rate of the proton transfer and shows great promises in improving the performance of PEMFCs (Okamoto et al., 2008). From the point of view of materials science, PBI can act as a proton-conducting material for PEMFCs that can be operative even under dry conditions above 100°C (the PEMFC operations at higher temperatures afford many benefits such as decreased carbon monoxide poisoning of the catalyst metal NPs, increased catalytic reaction rate, easy removal of generated water, and so on (Q. Li et al., 2003), and therefore is a promising candidate as a substitution for Nafion, which is a widely used proton exchange membrane (PEM) in low-temperature PEMFC systems (Deluca et al., 2006; Heitner-Wirguin, 1996; Kerres, 2001). Especially, PBI is expected to act as i) a metal adsorbing material via the coordination of the metal ion with the aromatic nitrogen on PBI, ii) a MWCNT-solubilizing material, and iii) a proton conductor. Therefore, studies on the applications of PBI in PEMFCs are of great interests. Indeed, it has already reported that the aromatic compounds have a great potential to individually dissolve SWCNTs through a physical adsorption mechanism based on the π–π interactions (Okamoto et al., 2008). A MWCNT/PBI/Pt nanocomposite has been developed by Okamoto et al. (Okamoto et al., 2009). They reported that as a result of the PBI wrapping, the loading efficiency of the Pt NPs onto the MWCNTs was dramatically improved up to 58.8% compared to that of the pristine MWCNTs (41.0%). The process also allows homogeneous immobilization of Pt NPs onto the surface of MWCNTs. Far-Fourier transform infrared spectroscopy shows the existence of a peak from the Pt–N bonding, indicating that these improvements were derived from the coordination of the Pt ion with the PBI molecules. The CV measurements revealed that the Pt NPs deposited on the MWCNT/PBI showed higher utilization efficiency (74%) as electrocatalysts in the PEMFC application compared to those on the pristine MWCNT (39%).

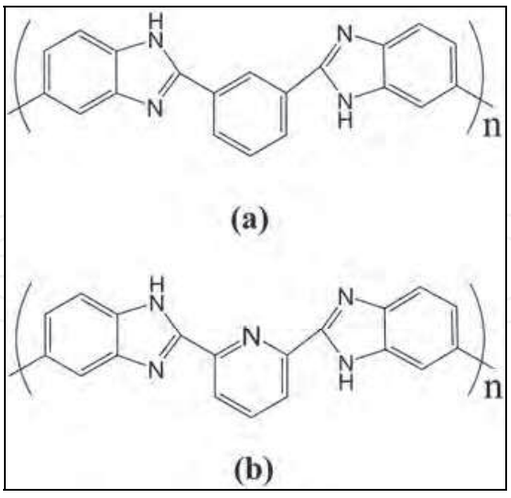


Fig. 5. Chemical structures of (a) PBI and (b) PyPBI.

A PBI derivative (pyridine-containing polybenzimidazole (PyPBI))-wrapped MWCNTs (PyPBI/MWCNTs) was fabricated by Fujigaya et al. (Fujigaya et al., 2009). Among various types of PBI derivatives reported to date, the pyridine-containing polybenzimidazoles (PyPBI, Fig. 5b) is known to possess significantly higher proton conductivity due to its

higher acid doping ability and better mechanical properties compared to the conventional PBIs, which endow them with higher capability of proton transfer and improved stability under the electrochemical process, and therefore is expected to exhibit improved properties in the applications of PEMFCs. The Pt ion can be efficiently adsorbed onto the obtained PyPBI-wrapped MWCNTs via the coordination reaction, and the successive reduction of the Pt ion forms rather uniform Pt NPs on the surfaces of the MWCNT/PyPBI. The CV measurements for the hybrids (MWCNT/PyPBI/Pt) showed a high electrochemical surface area (Fujigaya et al., 2009), which was due to the formation of the "ideal triple-phase boundary nanostructure" that was demonstrated by the high resolution TEM (HRTEM) observations as shown in Fig. 6. This result provides useful information for the design and fabrication of highly efficient CNT-based electrocatalysts for the PEFC systems.

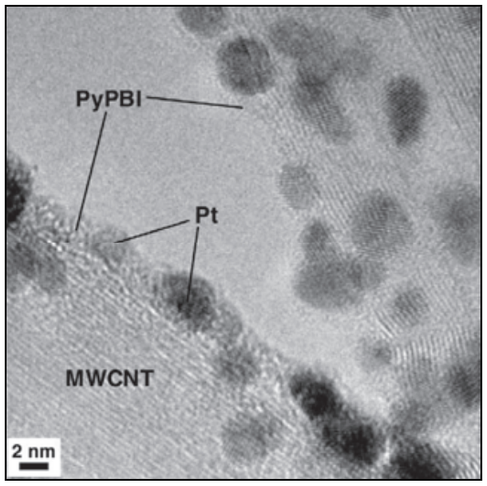


Fig. 6. Typical HRTEM image of the MWCNT/PyPBI/Pt. The Pt NPs are penetrated into the thin PyPBI-coating layer to contact closely with the MWCNT surfaces. Reprinted with permission from Fujigaya et al., 2009. Copyright 2009 Elsevier Science Ltd.

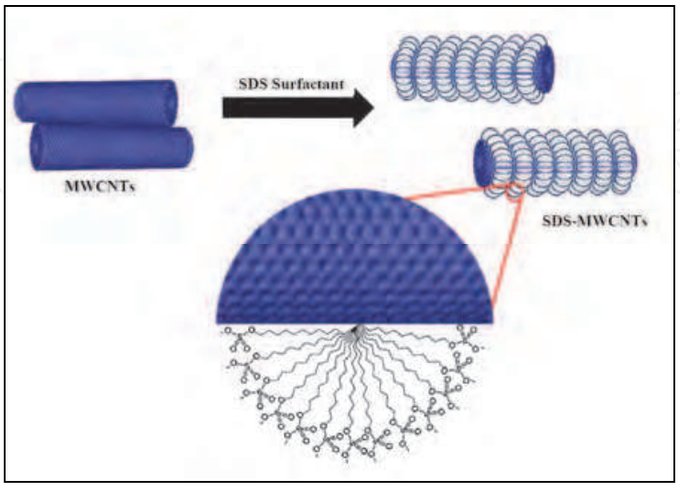


Fig. 7. Schematic representation of SDS-MWCNT micelles. Reprinted with permission from J.F. Lin et al., 2010. Copyright 2010 Elsevier Science Ltd.

Surfactants are a class of amphiphilic organic compounds, which contain both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, it is possible to functionalize CNTs with surfactant molecules by non-covalent adsorption of hydrophobic groups onto the surface of CNTs and extension of hydrophilic groups to the adsorption of metal ions and/or metal NPs. The adsorption of surfactants enables homogenous suspension of CNTs as individual tubes by decreasing the interfacial surface tension (Moore et al., 2003). As reported by Richard et al. (Richard et al., 2003) and Islam et al. (Islam et al., 2003), the SDS molecules could be chemically adsorbed on the surface of CNTs with the formation of hemimicelles along the graphite network of CNTs. As shown in Fig. 7 for the schematic structure of SDS-MWCNTs, the hydrophobic tails of the micelles enable attachment to the inert surface of MWCNTs and the hydrophilic heads with negative charge enable separation/dispersion of MWCNTs into individual tubes. Lin et al. (J.F. Lin et al., 2010a) used micelle-encapsulated MWCNTs with SDS as a catalyst support to deposit Pt NPs. The HRTEM images revealed the crystalline nature of Pt NPs with a diameter of ~4 nm on the surface of MWCNTs. A single PEMFC with total catalyst loading of 0.2 mg Pt cm^{-2} (anode 0.1 and cathode 0.1mg Pt cm^{-2}, respectively) has been evaluated at 80 ◦C with H_2 and O_2 gases using Nafion-212 electrolyte. The Pt/MWCNTs synthesized by using modified SDS-MWCNTs showed a peak power density of 950 mW cm^{-2}. Accelerated durability evaluation was carried out by conducting 1500 potential cycles between 0.1 and 1.2 V with 50 mV s^{-1} scan rate, H_2/N_2 at 80 ◦C. The PEMFC with Pt/SDS-MWCNTs as catalysts showed superior stability in performance compared to the commercial Pt/C composites.

Another promising and intriguing area of developing science is the surface modification of CNTs by the proton-conducting polymers owing to their novel applications in electronic and electro-optical devices. Innovative attempts have been developed to design and synthesize conducting polymer/CNT composite materials for various target applications such as electrochemical devices, light-emitting diodes, chromatography, electrostatic discharge protection, corrosion protecting paint and electrocatalysts. As reported by Selvaraj et al. (Selvaraj & Alagar, 2008), the combination of conducting polymers with CNTs would offer an attractive composite support for electrocatalysts in ethylene glycol (EG) oxidation to enhance the activity and stability based on the morphological modification or electronic interaction between the two components. In that work, polythiophene (PTh) was chosen as the conducting polymer matrix due to its relatively wide potential stability, reproducible synthesis and good electronic conducting properties. The prepared PTh/CNT composites were further decorated with Pt and PtRu NPs by the chemical reduction of the corresponding metal salts using HCHO as the reducing agent. The presence of CNTs in conjugation with a conducting polymer produced a good supports for the catalyst deposition, which allowed the formation of Pt and PtRu NPs with higher dispersion and thereby a better catalytic behavior towards EG oxidation. Results showed that the Pt/PTh–CNT and PtRu/PTh–CNT modified electrodes show enhanced electrocatalytic activity and stability towards the electro-oxidation of EG than the Pt/PTh electrodes.

Treatment of CNTs with surfactants, polymers and other capping agents, are generally tedious and in most cases, additional heat treatment steps are needed to get rid of the non-conducting polymer and surfactants attached to the Pt or Pt alloy NPs. In this respect, Wang et al. (D. Wang et al., 2010) reported a simple and novel method to functionalize the MWCNTs by using tetrahydrofuran (THF) solvent. To demonstrate the effectiveness of the method, they selected the syntheses of Pt and binary PtSn NPs on THF-functionalized

MWCNTs due to their importance for the electrooxidation reactions of methanol and ethanol in low temperature fuel cells. THF is an oxygen-containing heterocycle with five-membered rings. The presence of a σ–π attractive force between the π bonds of CNTs and the σ bonds of cyclopentanes of THF enabled the surface functionalization of CNTs due to a π–π stacking (D.Q. Yang et al., 2005a). Such interaction also makes the MWCNTs easily dispersible. The electronegativity difference between carbon and oxygen makes the C–O bond moderately polar with a sterically accessible oxygen atom. In a chloroplantic acid solution, THF adsorbed CNTs could be protonated, which makes the adsorption of $PtCl_6^{2-}$ and Sn^{4+} ions to the sterically accessible oxygen atoms by an electrostatic self-assembly. The formation of Pt and PtSn NPs on the MWCNTs could be realized by a H_2 treatment as shown in Fig. 8. The TEM image showed that the well-dispersed Pt and PtSn NPs can be directly deposited onto the THF-functionalized MWCNTs without any prior chemical oxidation treatments and the as-prepared Pt/MWCNT and PtSn/MWCNT catalysts show a high activity and stability for the ethanol oxidation in acid solutions. The advantages of the THF-functionalized CNT catalyst support are its simplicity and effectiveness in the deposition of highly dispersed Pt and Pt alloys on CNTs.

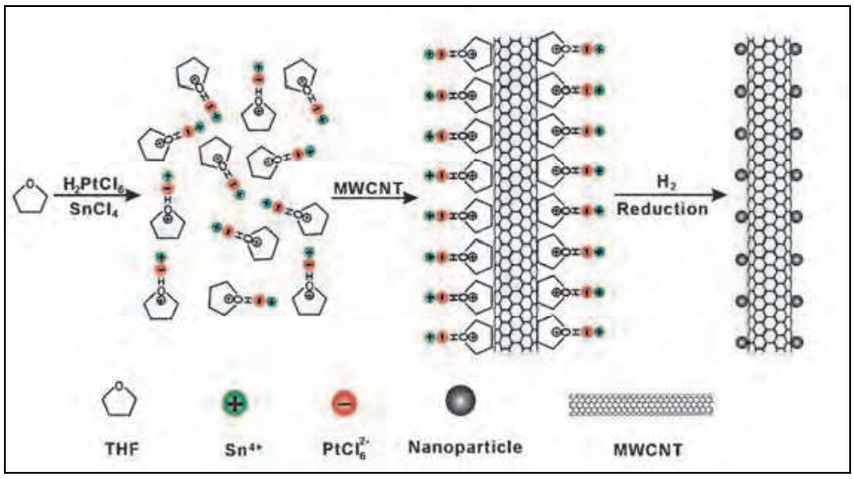


Fig. 8. Schematic of the synthesis of PtSn NP catalysts on the THF-functionalized MWCNTs. Reprinted with permission from D. Wang et al., 2010. Copyright 2010 Elsevier Science Ltd.

2.3 Plasma surface modification

The surface modification and functionalization methods described above, such as the addition of polyelectrolytes, supramolecular complexation with surfactants, functional organics, or polymers, could effectively increase the surface binding sites on the surface of CNTs for the subsequent deposition of metal NPs, avoid the aggregation of metal NPs, improve the dispersion of metal NPs, and simultaneously reduce the average size of metal NPs deposited (R.J. Chen et al., 2001, 2003; Holzinger et al., 2001; Star et al., 2001). In most cases, however, some severe problems accompanied with such surface modification and functionalization methods, such as uneven distribution of the surface functional groups, structural damage, blockage of the direct touch between metal NPs and MWCNTs, could lead to partial lose in the electrical conductivity of the carbon supports, reduce the interactions between metal and CNTs, and thereby the performance of the obtained

electrocatalysts (Anderson et al., 2002; Hsin et al., 2007). Additionally, these methods usually require the use of a large amount of chemicals, toxic solvents and/or extreme conditions, which is easier to cause environmental pollution. In order to minimize the above disadvantages during the preparation, it is highly desired to develop a mild surface functionalization technique to introduce homogeneous distributed functional groups with a high density onto the surface of CNTs, but cause less structural damage to the CNTs (and thus retain good electrical conductivity) and no pollution to the environment. Various dry processes, including both nonreactive and reactive plasmas (Brunetti et al., 2008; Q. Chen et al., 2000, 2001; Khare et al., 2004; Plank et al., 2003, 2004; Yan et al., 2005) and low-energy ion beam bombardment in a vacuum (D.Q. Yang et al., 2005), have been found as good candidates. Compared to wet approaches, dry plasma processing may be easier to control, with relatively less contamination. Plasma treatment is an efficient method in the field of surface modifications. The excited species, radicals, electrons, ions, and UV light within plasma strongly interact with the surfaces of CNTs breaking the C=C bonds and creating active sites for binding of functional groups, as a result, chemical and physical modifications occur on the surfaces. Compared to other chemical modification methods, the plasma treatment method has the advantages of shorter reaction time, nonpollution, and providing a wide range of different functional groups depending on plasma parameters such as power, used gases, treatment time, and pressure. Thus, this method offers the possibility of scaling up to produce large quantities necessary for commercial use. Plank et al. (Plank et al., 2003) reported the surface functionalization of CNTs by CF_4 plasma. The reaction was conducted at the room temperature in a short duration of time. Scanning electron microscopy (SEM) images indicates the dimension and morphology of CNTs have been preserved after a CF_4 plasma exposure. X-ray photoelectron spectroscopy (XPS) demonstrates the prevalence of covalent C–F bonds on the CNTs after CF_4 exposure. Recently, Yang et al. (D.Q. Yang & Sacher, 2006; G.X. Zhang et al., 2007) studied the effect of plasmas on highly oriented pyrolytic graphite (HOPG), where they found that Ar, O_2, N_2, and H_2O plasmas could break C-C bonds, producing -C· free radical defects that, on atmospheric exposure, reacted with components of air (H_2O and O_2) to produce oxidized carbon species (C-OH, C=O, and COOH). These oxidized carbon species could facilitate the deposition of metal NPs due to hydrogen bonding between the hydroxyl groups on the NP surface and these species on the HOPG that are introduced upon atmospheric exposure of the free radicals produced during the plasma treatment. Similar results were reported to a plasma modification of CNTs (D.Q. Yang & Sacher, 2008). It showed that the exposure of CNTs to Ar plasma or O_2 plasma produced surface defects on the surface of CNTs which could act as both nucleation and binding sites for the deposition of Pt NPs. The XPS and TEM analyses showed that the interactions between Pt NPs and CNTs were enhanced by the Ar or O_2 plasma treatment.

The possible mechanisms associated with the plasma treatment of CNTs include the generation of the C-O, C=O, and O-C=O bonds, as shown in Fig. 9 (C. Chen et al., 2009). Since the π bonds in C=C are active and are the most susceptible to the plasma attacks, it is believed that the radicals are first generated on the dissociated π bonds in C=C, which further react with active oxygen atoms (Fig. 9A). This explains the decrease in the C=C fraction after a plasma treatment. This process may produce C-O bonds, and then the C-OH bonds are formed through stabilization by hydrogen atom transfer from the same or a neighboring chain. The hydrogen atoms can also be introduced during the synthesis phase

of MWCNTs or via atmosphere exposure. Oxygen radicals are considered to be generated on the surfaces of MWCNTs, which could lead to the formation of the new C=O bonds through intramolecular reorganization on the C-C bonds, as shown in Fig. 9B. The formation of O-C=O bonds is believed to be due to the C=O bonds through the combination of the plasma-generated radicals on the C=O bonds with the active oxygen atoms. After stabilization with proton transfer, HO-C=O can be formed, as shown in Fig. 9C. Compared to pure O_2 plasma treatment, Ar/O_2 plasma treatment enhances the C-O and O-C=O fractions, and the C-O and O-C=O fractions increase with increasing plasma power and the treatment time. The efficiency of Ar/O_2 mixture gas plasma treatment is higher than that of pure O_2 plasma treatment, since the content of active oxygen in Ar/O_2 mixture gas plasma is higher than that in pure O_2 plasma. Ar atoms and/or ions present in the plasma can also interact with the surfaces of MWCNTs creating active sites for further oxygen functionalization. Indeed, in some case, N-containing groups can also be formed on the surface of CNTs (Ruelle et al., 2008 and C. Chen et al., 2010). A plasma discharge can create enough electron energy to fractionize NH_3, forming metastable ions of NH_2, NH, N, and H as well as radicals, which can be incorporated into the surface of CNTs during the plasma treament.

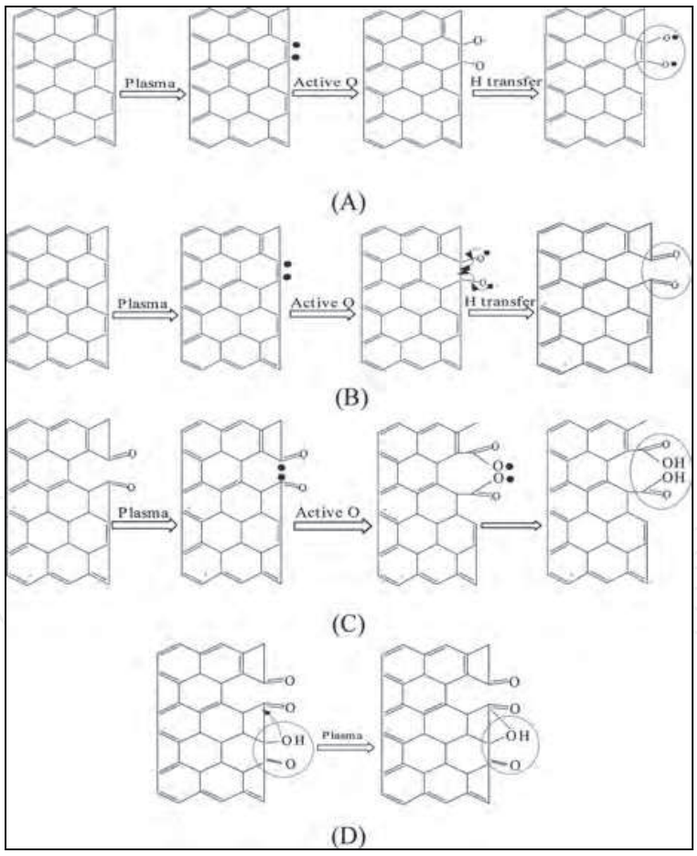


Fig. 9. Possible mechanism of MWCNT oxidation by Ar/O_2 mixture gas plasma treatment: (A) generation of C-O bonds; (B) generation of C=O bonds; (C) generation of O-C=O bonds; (D) transfer between carboxyl and lactone. Reprinted with permission from C. Chen et al., 2009. Copyright 2009 American Chemical Society.

The investigation of the electrocatalytic activity of Pt NPs on the plasma treated CNTs has been conducted by our group (Jiang et al., 2009, 2011). The results showed that the Pt NPs on the N_2 plasma treated CNTs exhibited a significantly higher electrochemical activity towards the methanol oxidation in an acid solution, in comparison to those on the CNTs functionalized by other modification methods. The structures of CNTs and the catalyst/CNTs interactions were found to play important roles in determining the performance of the catalysts. The Pt NPs deposited on the MWCNTs functionalized by a strong acid treatment which easily leads to the structural damage of MWCNTs showed a much lower performance of Pt/MWCNTs in methanol oxidation reaction, due to the decrease in the conductivity of MWCNTs caused by the structural damage. An insertion of impurities between Pt NPs and MWCNTs could also result in a decrease in electron migration from metal to MWCNTs and give rise to the decrease of electrochemical performance of Pt/MWCNTs in methanol oxidation reaction. It therefore suggests that to obtain Pt/MWCNTs with higher catalytic activities, it is necessary to adopt a mild surface modification approach and to make metal NPs directly deposit onto the CNT surface.

2.4 Nitrogen-doped CNTs

As mentioned above, a chemical modification of the surface of CNTs by covalent functionalization could reduce considerably the mechanical and electronic performance of CNTs due to the introduction of large numbers of defects, and in some cases, the electrocatalysts on the non-covalently functionalized CNTs shows low activity over fuel oxidation due to the poor conductivity of functional molecules and low conduction between the metal NPs and the CNTs and between the neighboring CNTs, which require us to seek for new approaches for the preparation of electrocatalysts. It is recently found that the use of nitrogen doped CNTs (N-CNTs) could be considered as one of promising options. The introduction of N can lead to the formation of CNTs with high surface areas (Feng et al., 2008), high densities of defects (Tao et al., 2007), chemically active impurity sites (Nxumalo et al., 2008; Tao et al., 2007) and narrow widths (the numbers of walls decrease with N inclusion) (Nxumalo et al., 2008). The N-doped nanotubes are found to be either metallic or narrow energy gap semiconductors (Huang et al., 2000; Miyamoto et al., 1997), thus offering the possibility of greater electrical conductivity as compared to the pure CNTs. Studies have shown that the N-doped CNTs and their composites can be used as support materials and have great potentiality in the PEMFC catalyst applications. Due to the presence of chemically active nitrogenated sites (substitutional and pyridinic nitrogen), the N-doped CNTs are reported to have enhanced activity and selectivity in many catalytic applications (Shao et al., 2008), and exhibit a strong binding to metals, leading to excellent metal dispersion in the metal/N-CNT materials (Droppa Jr. et al., 2002). It can therefore avoid using functionalization processes that might be detrimental to the catalytic properties of the obtained metal/N-CNT composites (Maiyalagan et al., 2005; C.L. Sun et al., 2005; C.-H. Wang et al., 2006, 2007; Zamudio et al., 2006). For example, Maiyalagan et al. (Maiyalagan et al., 2005) studied the electrocatalytic properties of Pt/N-CNTs synthesized by a reduction of Pt^{2+} adsorbed on the surface of unfunctionalized N-CNTs. The obtained N-CNT-supported Pt NPs were reported to be homogeneously dispersed on the nanotubes. An enhanced catalytic activity and stability toward methanol oxidation was observed with Pt/N-CNTs in comparison with commercial Pt/C catalyst supplied by E-TEK. The authors of that work attributed the enhanced catalytic activity and stability of Pt/N-CNTs to the factors, such as,

the higher dispersion of Pt NPs which increased the availability of electrochemically active surface area, the appearance of the specific active sites at the metal–support boundary and strong and specific metal–support interaction. The investigation of the microstructure and electrochemical activity of the PtRu supported by N-CNTs was reported by Wang et al. (C.-H. Wang et al., 2006). These N-CNTs were directly grown on the carbon cloth (N-CNTs–carbon cloth composite electrode) using a microwave plasma enhanced chemical vapour deposition, and then used as the template to support the subsequently sputtered PtRu nanoclusters. The ferricyanide/ferrocyanide redox reaction in CV measurements showed a faster electron transfer on the N-CNTs–carbon cloth composite electrode than the one with carbon cloth alone. In addition, it was found that the PtRu nanoclusters supported by the N-CNTs–carbon cloth composite electrode had considerably higher electrocatalytic activity in the methanol oxidation than the carbon cloth counterpart, which suggested a high performance of the N-CNTs/carbon cloth composite electrode, its suitability for direct methanol fuel cell applications.

3. Synthesis and characterization of metal NPs supported on CNTs

It is know that the electrocatalytic activities of catalysts on the CNTs are greatly dependent upon their size, morphology, composition and dispersion, which are determined by the way that they are produced and the way they are adsorbed onto the surface of CNTs. Since the dispersion and particle size of metal NPs largely determine the utilization and catalytic activity of metal/CNTs, the synthesis of metal NPs supported by CNTs with a controlled manner is of great importance for the design of catalysts of higher efficiency. Up to now, the most widely used catalysts for the application of PEMFCs are Pt and Pt-based alloys due to their large surface to volume ratio, improved catalytic activities relative to their bulk material. The synthesis of metal NPs/CNT composites can be performed either by nucleation and growth of metal NPs on the surface of CNTs or by attachment of preformed NPs in the bulk solution onto the surface of CNTs. In the following sections, the methods used to prepare NPs/CNTs will be reviewed and discussed.

3.1 Formation of metal NPs directly on CNTs

Nucleation and growth of metal NPs directly on the surface of CNTs is the mostly used method to prepare metal NPs/CNTs catalysts. The preparation of such NPs/CNT composites can be conducted either physically or chemically. Metal NPs are absorbed on the surface of MWCNTs mainly based on van der Waals interactions, electrostatic interactions and coordination interactions between metal particles and functional groups, which in some cases seem to be sufficiently strong to guarantee meaningful adhesion (K.C. Lee et al., 2006; X. Sun & Saha, 2008).

3.1.1 Physical methods

In a physical method, bulk metals are thermally vaporized followed by a sputtering of metal gases onto the surface of CNTs. The sputtering-deposition method is a recently developed approach to prepare the PEMFC cathode catalysts, aiming at metal loading reduction and metal utilization improvement. It has been demonstrated that the sputter-deposition technique is a good way to deposit small and uniform metal NPs on CNTs with sizes well controlled by the sputtering time and current. This method can also generate a thinner

catalyst layer that could give a higher fuel cell cathode performance and, at the same time, considerably reduce the metal loading. The physical deposition of Pt NPs on the surface of CNTs was reported by Tang et al. (Z. Tang et al., 2010), who produced Pt NPs with 4 nm in diameter and a narrow size distribution. A high maximum power density of 595 mW cm^{-2} was observed for a low Pt loading of 0.04 mg cm^{-2} at the cathode for the PEMFC application. The deposition of Pt NPs on nitrogen-dopped MWCNTs (N-MWCNTs) was done by Sun et al. (C.L. Sun et al., 2005). The well-separated Pt NPs with an average diameter of 2 nm were formed on the side-walls of N-MWCNTs. In that work, the nitrogen incorporation in the MWCNTs might play a critical role in the self-limited growth of the Pt NPs. The CV results showed that the Pt/N-MWCNT catalyst had improved electrochemical activity towards methanol oxidation and showed great promises for a future μDMFC device. However, because the preparation of Pt/CNT composites usually requires the use of extremely high temperatures, this technique may face some technical challenges with respect to the electrode mass production.

3.1.2 Chemical methods

Compared with the physical methods, the chemical methods have the significant advantage of being able to easily control the primary structures of NPs, such as size, shape, and composition, as well as to achieve mass production. A large variety of chemical methods such as impregnation method, colloidal method, ion-exchange method, electrochemical method, microwave heated polyol method, have been reported for the preparation of metal/CNTs composites as a catalyst for the DMFC applications. Different growth control mechanisms and strategies are used in each of the different chemical deposition methods.

3.1.2.1 Impregnation method

The impregnation method is the most widely used wet-chemical method, which is a simple and straightforward for depositing metal NPs on the CNTs for the preparation of the PEMFC catalysts and is thus an attractive choice for a large-scale synthesis. The method involves the impregnation of the support material with a salt solution containing the metal to be deposited, followed by a reduction step (Asano et al., 2006; Liao et al., 2006; Y. Lin et al., 2005; Lordi et al., 2001). During an impregnation process, metal ions are initially adsorbed to the surface of functionalized CNTs by homogeneously mixing CNTs with the metal precursors in a solution. The chemical reduction of the metal ions on the surface of the CNTs can either be carried out by a liquid phase reduction using borohydride, formic acid or hydrazine as a reductive agent, or by a gas phase reduction using a flowing hydrogen gas as a reductive agent under elevated temperature. For the impregnation method, the size and distribution of Pt NPs are affected by many factors, in which the chemical modifications of the surface of CNTs will play a major role since the pristine surface of CNTs is relatively inert unfavorable for the deposition of metal NPs. A desired way in this case is to functionalize the surface of CNTs first through a chemical reaction as discussed in Section 2. As one example, Li and coworkers (W.Z. Li et al., 2004) reported the synthesis of Pt/MWCNT nanocomposites by using the impregnation method, which was then used as electrocatalyst applied in a direct methanol fuel cell (DMFC). In that work, the Pt NPs were deposited on the pre-functionalized MWCNTs by reduction of Pt precursor with EG, which produced a Pt/MWCNT composite with a homogeneously dispersed spherical Pt NPs of a

narrow particle size distribution. The obtained Pt/MWCNTs were characterized to exhibit significantly higher performance than the Pt loaded on the commercial XC-72 carbon when used in the DMFC. This improvement in catalytic performance was attributed to the greater dispersion of the supported Pt particles.

3.1.2.2 Electrochemical method

The electrochemical method for the preparation of metal/CNTs is very similar to the process of the impregnation method, except for an electrochemical reduction of the adsorbed metal ions rather than the chemical reduction. In this process, functionalized CNTs are first mixed with the metal precursors in aqueous solution to produce a homogeneous solution. A pulse current, such as direct current or CV, is then added for the reduction of metal ions promoting the deposition of metal NPs on CNTs, which usually produces metal NPs/CNTs with high efficiency in PEMFCs as compared to those prepared by the conventional deposition techniques (Choi et al., 1998; Taylor et al., 1992; Thompson et al., 2001). An approach for the electrochemical deposition of Pt particles with a narrow size distribution on CNTs was reported by Tsai et al. (Tsai et al., 2006), who successfully electrodeposited Pt and PtRu NPs on the dense CNTs directly grown on carbon cloths in EG containing H_2SO_4 aqueous solutions. Prior to the electrodeposition of Pt or PtRu NPs, all the specimens with CNTs directly grown on carbon cloths (CNT/CC) underwent a hydrophilic treatment at 50 mV s^{-1} for 100 cycles with potential ranged from –0.25 to +1.25 V_{SCE} (V_{SCE} means that the potential was quoted against a saturated calomel electrode (SCE)) in an O_2 saturated 2 M H_2SO_4 aqueous solution at ambient condition. To achieve a larger driving force for dechlorination of the Pt and Ru precursors, more negative deposition potentials are usually favorable. EG acted as a stabilizing surfactant to prevent the particles from agglomeration during the electrodeposition processes and could also enhance the dechlorination of Pt and Ru precursor salts and led to the formation of NPs. In the meantime, nano-sized Pt and PtRu particles were also found in specimens treated at two pre-selected negative potentials. The particle sizes of Pt on CNTs ranging from ~4.5 to ~9.5 nm and PtRu on CNTs (PtRu/CNTs) ranging from ~4.8 to ~5.2 nm were obtained and was reported to exhibit improved electrocatalytic activity in methanol oxidation in comparison to the corresponding commercially available catalysts.

3.1.2.3 Colloidal method

Colloidal method involves the nucleation of metal clusters on the surface of CNTs, followed by growth of these clusters, or involves the formation of a metal oxide colloid, followed by simultaneous reduction and adsorption, or adsorption followed by chemical reduction. In this method, the size of the metal NPs is largely controlled or stabilized by the protecting agents, such as ligands, surfactants or polymers (Kuo et al., 2005). The colloidal metal NPs are stabilized by either steric hindrance or by electrostatic charges. In recent years, there have been considerable interests in the development of colloidal methods to prepare Pt catalysts supported on the CNTs with a narrow particle size distribution (Kongkanand et al., 2006b; C. Lee et al., 2005; W.Z. Li et al., 2003; X. Li et al., 2004, 2006; Yoshitake et al., 2002). For example, Li and co-worker (X. Li et al., 2004) used the surfactant 3-(N,N-dimethyldodecylammonio) propanesulfonate (SB12) as a stabilizer to prepare Pt NPs supported on the CNTs by reduction of H_2PtCl_6 with methanol (X. Li et al., 2004, 2006). The Pt NPs deposited on the functionalized CNTs were well-dispersed with an average size of 2.2 nm (X. Li et al., 2004).

Though the colloidal method can provide a narrow size distribution of metal NPs, the major drawback is the presence of a protecting agent, which may decrease the catalytic performance of the NPs. As a result, the organic protecting layers used for the protection of the electrocatalysts prepared by the colloid method must be removed prior to their use in the PEMFCs. The desired way is to prepare colloidal NPs without the use of protecting agents. Such fascinating way has been recently reported by Yoshitake et al. (Yoshitake et al., 2002), who synthesized a Pt/CNT catalyst for the use of PEMFCs by the colloid method. In the preparation, a colloidal Pt oxide was first prepared by adding $NaHSO_3$ and H_2O_2 into an aqueous solution of H_2PtCl_6 without using an organic stablizer. The adsorption of the Pt oxide colloids was done through its mixing with the single-wall carbon nanohorns (SWNH) powder. The reduction of Pt oxides was carried out by a H_2 gas. The produced Pt/SWNH catalyst showed very homogeneous dispersion of Pt NPs with an average size of 2 nm and exhibited higher electrocatalytic activity in a PEMFC.

3.1.2.4 Ion-exchange method

An ion-exchange method is an effective technique for depositing metal NPs on the CNTs without using protecting agents, reducing agents or precursor complexes. In this technique, a metal cation complex, such as $[Pt(NH_3)_4]^{2+}$, is ion-exchanged with hydrogen ions of the acid functional groups on the surface of the CNTs. After the ion-exchange process, the Pt cation complex is reduced to the Pt NPs in an H_2 atmosphere. The interaction between the acid functional groups and the Pt precursor determines the dispersion and size of the metal particles. The preparation of a Pt/CNT composite by the ion-exchange method has been reported by Yin and co-workers (Y. Shao et al., 2006; J. Wang et al., 2007). In their work, an electrochemically functionalized CNT electrode was immersed in a solution of the platinum cation-complex salt for 48 h, which resulted in the ion-exchange of the hydrogen ions of the functional group on the surface of the CNTs with the Pt cation complex. The immersed CNTs was then filtrated and washed thoroughly with distilled water. The reduction of the adsorbed platinum complex precursor to its metallic form was carried out by the treatment with hydrogen gas at 190 °C. It was reported the Pt NPs were highly dispersed on the CNTs with dispersion much better than those prepared by the borohydride method (J. Wang et al., 2007).

3.1.2.5 Microwave heated polyol method

In a microwave heated polyol method, a polyol (ethylene glycol) solution containing catalyst metal precursor salts is refluxed at high temperature by a microwave heating in order to homogeneously decompose EG and create an active reducing agent for metal ions (W. Chen et al., 2005; Z. Liu et al., 2005). A metal support could be optionally present to capture the depositing metal particles in this process. Unlike the conventional conductive heating strategy used to thermally activate the polyol, which has a heterogeneous temperature distribution, the fast heating by microwaves can accelerate the reduction of the metal precursor ions and the nucleation of the metal NPs. In addition, the homogeneous microwave heating could reduce the temperature and concentration gradients in the reacting sample solution, resulting in a more uniform environment for the nucleation and growth of metal particles (W. Chen et al., 2005; Z. Liu et al., 2005). The synthesis of Pt/CNT or PtRu/CNT catalysts using a microwave heated polylol process (W. Chen et al., 2005; Z. Liu et al., 2004, 2005) has been reported by several research groups. The obtained Pt/CNT or PtRu/CNT catalysts are usually characterized with greater catalytic activity towards oxygen

reduction than the catalysts fabricated by some other techniques although both catalysts had almost the same Pt particle sizes.

3.2 Connecting metal NPs and CNTs

In the methods presented above for the preparation of metal/CNT composites, the formation of metal NPs directly occurs on CNTs. However, in some cases, the deposition of metal NPs is realized by adsorption of preformed metal NPs in the solution through either the formation of covalent bonds between the functional groups on metal NPs and the functional groups present on the CNT surface or the intermolecular interactions such as hydrophobic, π–π stacking or electrostatic attractions between them (Georgakilas et al., 2007).

3.2.1 Covalent linkage

The metal NPs anchored on CNTs by a covalent linkage usually exhibit a long life and high catalytic performance when used in PEMFCs. Due to the high strength of the covalent interactions, the metal NPs are usually well separated on the CNTs and exhibit a higher stability during the electrochemical process. The higher degree of dispersity increases electrocatalytically active surface areas of metal NPs which therefore exhibit a high activity in methanol oxidation and oxygen reduction. For example, Yang et al. (D.Q. Yang et al., 2006b) reported the fabrication of Pt/CNTs by the covalent attaching of the Pt NPs onto the CNTs using benzyl mercaptan as an interlinker. In their work, the CNTs were first functionalized with benzyl mercaptan by a π-Stacking. The functionalized CNT surface interacted strongly with the Pt NPs through the formation of Pt-S bonds and resulted in a very high Pt NP loading both high dispersion and a narrow size distribution, as schematically illustrated in Fig. 10.

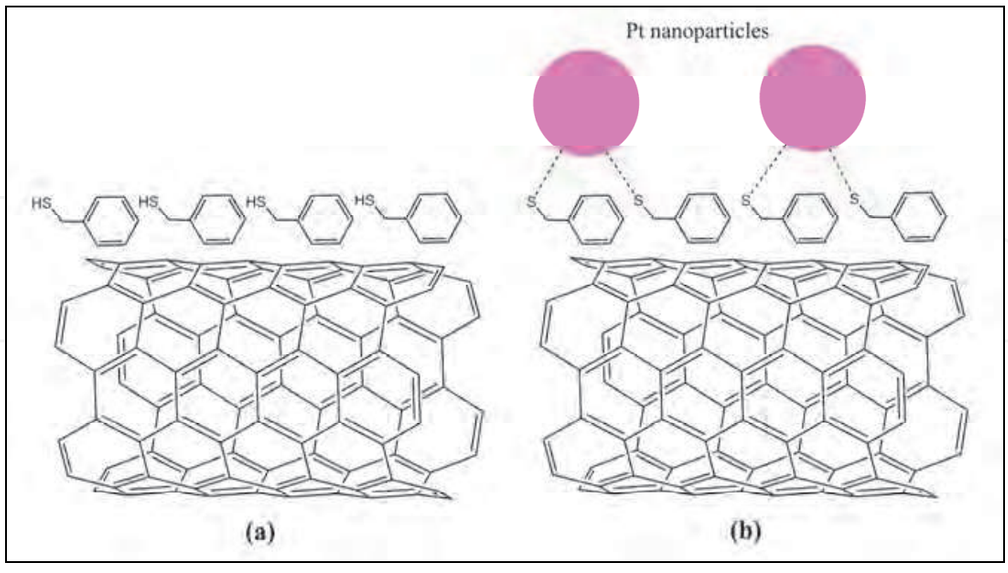


Fig. 10. Schematic of (a) a CNT functionalized with benzyl mercaptan via π-π bonding and (b) the bonding of Pt NPs to the functionalized CNT via covalent S-Pt bond formation. Reprinted with permission from D.Q. Yang et al., 2006b. Copyright 2006 American Chemical Society.

3.2.2 Hydrophobic interactions and hydrogen bonds

The interactions between hydrophobic ligands forming the monolayer passivating the metal surface with hydrophobic molecules adsorbed on CNTs and hydrogen bonds between the molecules on NPs and CNTs can be used to immobilize the metal NPs onto CNTs. A combination of hydrophobic and hydrogen bond interactions will make the attachment of metal NPs on CNTs more tightly, and therefore be employed as a promising way to the preparation of metal/CNT composites as catalysts for PEMFC applications (L. Han et al., 2004). As reported by Han et al. (L. Han et al., 2004), a Au/CNT composite has been synthesized by the hydrophobic interactions of the alkyl chains on decanethiol and mercaptoundecanoic acid adsorbed Au NPs with the CNT surface and hydrogen bonds between carboxylic groups of CNTs and those present on the NP surface. Due to the strong interactions provided by the hydrophobic interactions and the hydrogen bonds between ligated Au NPs and CNTs, the obtained Au/CNTs showed a very stable structure, cannot be disassembled by sonication in hydrophobic solvents. However, thermal treatment of the sample, for example, at 300 ℃ would induce aggregation of NPs that stick strongly to the nanotube surface due to the removal of the capping shells of the Au NPs, which decreased the interactions between Au NPs and CNTs (Georgakilas et al., 2007).

3.2.3 π-Stacking

The deposition of metal NPs through the π-Stacking involves a cover of metal NPs with phenyl-containing molecule and the adsorption onto the surface of CNTs by a π-Stacking interaction. As recently reported by Mu et al. (Mu et al., 2005), they have applied this method to prepare the Pt/CNTs by the surface modification of Pt NPs with triphenylphosphine (PPh_3) and the subsequent deposition of the modified Pt NPs onto the CNTs through the π-Stacking. The main disadvantage of the method is that a special annealing process is usually required to remove PPh_3 molecules, which might lead to some degree of aggregation of Pt NPs. Indeed, it is demonstrated that even though the thermal treatment would result in aggregation of Pt NPs, the mean size of the deposited Pt NPs remained small and showed higher electrocatalytic activity and better tolerance to poisoning species in the methanol oxidation than the commercial E-TEK catalyst.

3.2.4 Electrostatic interactions

Electrostatic interaction is a commonly used method to anchor metal colloids to CNTs. Because the functionalized CNTs with an ionic polyelectrolyte are charged, which can serve as an anchor for metal NPs oppositely charged. In typical examples, the oxidized CNTs are modified with a cationic polyelectrolyte and exposed to the negatively charged metal NPs. By choosing different kinds of polyelectrolytes the surface of the CNT can be also negatively charged in order to the deposit of positively charged NPs. The electrostatic approach has been used to build mixed Au/MWCNT layers using the LBL (layer-by-layer) methodology (Kim & Sigmund, 2004). In the work, the acid-functionalized MWCNTs were first covered with a layer of a positively charged polymer [PDDA, poly(diallyldimethylammonium chloride)] and then with a layer of a negatively charged polymer [PSS, poly(sodium 4-styrenesulfonate)]. Subsequently, the positively charged Au NPs were anchored through electrostatic interactions to the PSS layer. The positively charged Au NPs may also interact directly with the MWCNTs presenting carboxylate groups on their surface. However, the direct binding happened with a much lower density of Au deposition than that observed for the PDDA/PSS LBL method.

4. Activity validation of the synthesized catalysts in a fuel cell operation

The most direct and effective method for the activity validation of the synthesized catalysts is to directly use them in a single fuel cell. For fuel cells, the activity of a catalyst can be deduced from their performance. The most commonly used way to reflect the performance of the fuel cells is the polarization (or current-voltage) curve of the MEA which is the core of the PEM fuel cell, composed of an anode gas diffusion layer (GDL), an anode catalyst layer, a membrane (the PEM), a cathode catalyst layer, and a cathode gas diffusion layer, as shown in Fig. 11 which schematically shows a single typical PEMFC. Two data collection modes are frequently used in obtaining the polarization curve, conducted either by adjusting the cell voltage then recording the current density, or by adjusting the current density then recording the cell voltage, with the latter being the most popularly used in the fuel cell performance data collection. A typical polarization curve of a cell obtained by collecting the cell voltage as a function of current density is shown in Fig. 12, which can then used to yield the power density of the MEA (cell voltage × current density) plotted as a function of current density. From the power density curve, the maximum power density of the fuel cell MEA can be then known as well as the maximum volume power density and the mass power density of a fuel cell stack. In principal, beside the catalysts, the performance of a fuel cell (polarization curve) is also affected by the quality and property of MEA and the operating conditions, such as temperature, pressure, relative humidity (RH), gas flow rates, etc. Therefore, for the sake of systematical improvements in the efficiency of the fuel cell, a better understanding of the effects of the quality and property of the MEA on the performance of the fuel cell is essential.

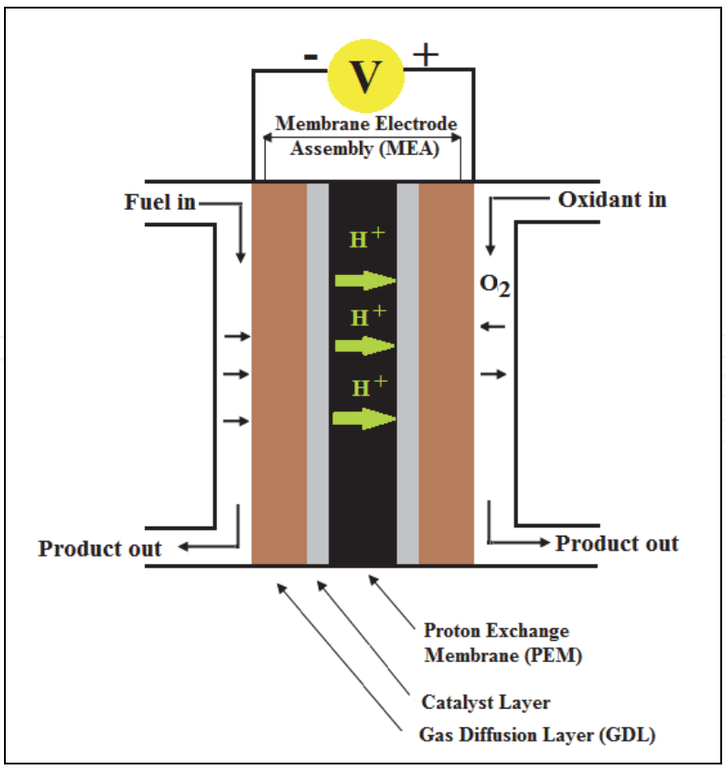


Fig. 11. Schematic of a single typical PEMFC.

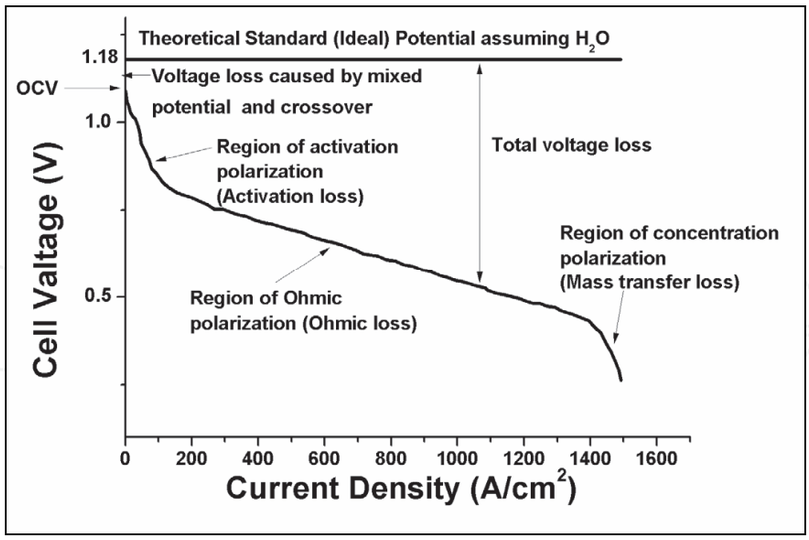


Fig. 12. Typical polarization curve of PEMFCs.

4.1 Synthesis of metal/CNT based MEA

As the core of the PEM fuel cell, the MEA conducts the conversion of the chemical energy of the fuel (i.e., hydrogen) into electricity through the electrochemical oxidation of fuel at the anode and the electrochemical reduction of oxygen at the cathode. Therefore, the MEA component materials, structure, and fabrication technologies largely determine the performance of a PEMFC. An optimization of MEA is of great importance for the improvement of the PEMFC performance (Shen, 2008). An ideal MEA allows all active sites of catalysts in the catalyst layer to be accessible to the reactant, protons and electrons, and can effectively remove produced water from the catalyst layer (CL) and gas diffusion layers (GDL). As mentioned above, a typical MEA for a single PEMFC (J.M. Tang et al., 2007), is composed of a PEM, anode and cathode electrodes, and anode and cathode GDL (schematically shown in Fig. 11). According to differences in preparation processes and structures, hydrophilic catalyst layers can be prepared either by a membrane-based or a GDL-based method, as shown in Fig. 13. For the membrane-based method, the MEA is fabricated by depositing the catalyst ink directly onto a dry and fixed membrane or by coating catalyst ink onto a blank substrate (e.g., PTFE film) and then transferring the coating catalyst ink onto the membrane (Wilson & Gottesfeld, 1992), which is then sandwiched between two GDLs and followed by a hot pressing step, while in the GDL based method, the catalyst ink is directly painted or sprayed onto the pre-treated GDL and then hot pressed onto the membrane. In these two methods, the catalyst ink used for coating the membrane and a blank substrate and the GDLs can be prepared by mixing the metal/CNT catalyst with ionomer firstly, which can improve the contact between the catalyst particles and the ionomer, and thus help to improve catalyst utilization. It has been reported that an ionomer-bonded hydrophilic catalyst layer could improve Pt utilization by up to 45.4% (Cheng et al., 1999). The notable advantages of such an ionomer-bonded hydrophilic electrode include (Girishkumar et al., 2005):

1. improved bonding between the membrane and the catalyst layer;
2. uniform continuity of the electronic and ionic paths for all catalyst sites due to the uniform dispersion of catalyst in the ionomer;

3. high metal NPs utilization resulting from good contact between the catalyst and the protonic conductor;
4. relatively low catalyst loading without performance losses.

However, there are still some inevitable drawbacks associated with this kind of catalyst layers. For example, due to the lack of hydrophobic passages, gas transportation from the GDL to the reaction sites becomes difficult, and the produced water tends to accumulate in the electrode and block the gas transport paths, leading to a decrease in fuel cell performance. In addition, due to the degradation of the ionomers, its ability to bind with the catalyst particles will decrease, causing lowered reliability as well as durability problems. Recent efforts, therefore, turn to the preparation of the catalyst layers with reduced thicknesses. A thin catalyst layer can minimize the shortcomings associated with an ionomer-bonded hydrophilic catalyst of thick layer and improve the efficiency of the mass transfer at the interface, such as the efficient movement of protons, electrons, and dissolved reactants in the reaction zone, which is beneficial to reduce catalyst loading and increase mass power density of a MEA. However, this requires the use of catalysts of higher efficiency.

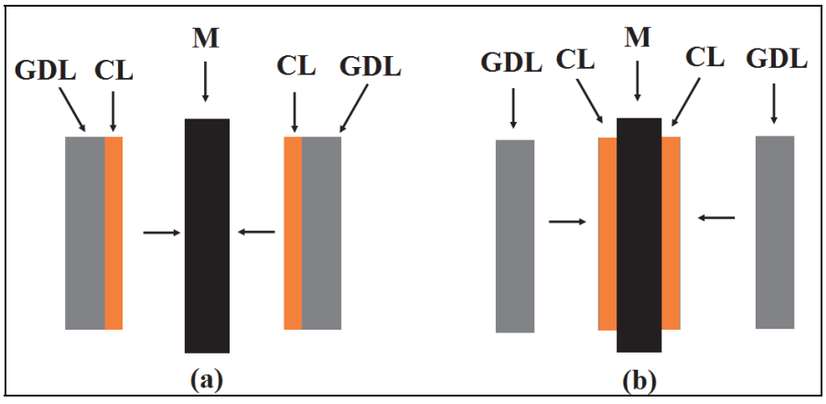


Fig. 13. Configuration of MEAs for (a) the CL on GDL mode and (b) the CL on membrane mode. GDL – gas diffusion layer; CL – catalyst layer; M – membrane.

4.2 Performance of metal/CNT based MEA

The performance of fuel cells with metal/CNT composites as catalysts in PEMFCs has been reported by many groups (Hernández-Fernández et al., 2010; W.Z. Li et al., 2005; J.F. Lin et al., 2010b; T. Matsumoto et al., 2004a, 2004b; Prabhuram et al., 2006; Saha et al., 2008; X. Wang et al., 2005), it is generally believed that the performance of a CNT-based MEA is better than that of conventional metal/supports MEA (T. Matsumoto et al., 2004a, 2004b; Prabhuram et al., 2006; Saha et al., 2008; X. Wang et al., 2005). Although the detailed mechanism how the CNTs affect the catalytic activity of the metal/CNTs are still not well understood, it is generally believed that the enhancement of the electro-catalytic activity of the metal/CNT composites may arise from the following reasons:

1. Good dispersion of metal NPs. The well-dispersed NPs on the surface of CNTs make them more accessible to the fuel oxidation reaction.
2. Unique structure of CNTs. Because of the novel morphology and electrical properties of CNTs, a fast transfer of charges through the composites is possible, which results in their high electrocatalytic activity.

3. Small sizes of deposited metal NPs. The surface-to-volume ratio becomes larger when the size of NPs decreases, which increases the percentage of atoms at the surface accessible to the fuel oxidation reaction. In addition, with decreasing the size of metal NPs, their Fermi level improves, which make the electron transfer easier, favoring the subsequent redox reaction.
4. High purification of CNTs. The metal NPs are reported to be sensitive to some elements, such as sulfur. Trace amount of sulfur adsorption would lead to a decrease in the catalytic activity of metal NPs. The CNT supports contain fewer organic impurities, unlike other carbon materials such as the XC-72 carbon (contain ca. 0.2 at. % sulfur), which is important to maintain the high catalytic activity of metal/CNTs.
5. Porous structures of CNTs. Porous structures influence the reactant-product mass transport and therefore have a big effect on the activities of catalysts.

5. Conclusions and outlooks

In the PEMFCs, the conversion of chemical energy of the fuel (i.e., hydrogen) into electricity is carried out by the catalysts, which is of great importance in determining the performance of the PEMFCs. Many years of studies give strong evidences that metal/CNTs are more active in the fuel catalytic oxidation and provide better performance than other catalyst systems when used in the PEMFCs and thus attract tremendous attentions in recent years. However, for the preparation of metal/CNTs, surface functionalization of the CNTs is mostly required to produce the CNTs with suitable surface properties for metal deposition. The surface functionalization might lead to the structural destruction of the CNTs, which is detrimental to prepare the metal/CNTs of high efficiency in catalysis. It is generally believed that a mild surface modification method is desired for the functionalization of CNTs, which can effectively prevent the CNTs from the structural destruction and has great promises to synthesize the high efficient metal/CNT catalysts. Additionally, besides the functionalization methods, the catalytic activity of the metal/CNTs is also affected by the size and dispersion of the deposited metal NPs. For rational design of catalysts of high efficiency, it is therefore essentially important to know exactly the factors that affect the activity of the catalysts.

Currently, although the development of PEMFCs is moving toward commercialization due to the impressive research effort in recent years, significant challenges including detailed mechanism how the CNTs affect the catalytic activity of the metal/CNTs and high materials cost remain to be solved. It is clear that this research in these areas would be one of important on-going topics in the development of more highly efficient catalysts with low cost to meet the requirements of fuel cell commercialization.

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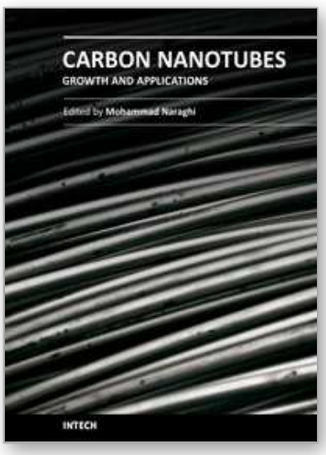
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