The effect of amine functionalized carbon nanotubes as promising support for platinum nanoparticles on oxygen reduction reaction

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Abstract
In this study, multiwall carbon nanotubes (MWCNTs) were chemically oxidized (OMWCNTs) and functionalized with ethylenediamine (EDAMWCNTs) and diethylenetriamine (DETAMWCNTs) as amine precursors. The electrocatalysts were prepared through deposition of Pt nanoparticles on the functionalized MWCNTs by polyol method. The average size of Pt nanoparticles was found to lie between 4 and 5 nm. Cyclic Voltammetry (CV), Rotating Disk Electrode (RDE), Electrochemical Impedance Spectroscopy (EIS), and Chronoamperometry (CA) were employed to evaluate the electrochemical properties of the electrocatalysts. The Electrochemical active surface area (EASA), number of electron transferred (n), and onset potential for EDAMWCNTs and DETAMWCNTs were found to be about 32.2 and 45.8 (m²/g Pt), 4.03 and 4.10 (electron per oxygen molecule), and 0.986 and 0.997 (V vs RHE), respectively. However, in the case of Pt-OMWCNTs the above mentioned electrochemical characteristics were calculated to be 24.2 (m²/g Pt), 3.34 (electron per oxygen molecule), and 0.824 (V vs RHE), respectively. Moreover, EIS and CA indicate that introducing amine functional groups lead to less electron transfer resistance and better electrocatalytic activity and stability during oxygen reduction. The results show that the higher number of nitrogen atoms within the amine functional groups the more enhanced electrocatalytic performance of Pt nanoparticles in ORR.

Key words: amine functional groups, electrocatalysts, carbon nanotubes, oxygen reduction reaction, Pt nanoparticles.

1. Introduction
The augmentation of energy demand has led researchers to develop a novel, high performance, and economical energy resources instead of using fossil fuels [1-3]. The rate of current consumption of energy, and environmental restrictions which is chiefly emerged from the emission of greenhouse gases rings the alarming-bell [2, 4]. In the last five decades, renewable energy has attracted enormous attention due to its appropriate performance and environmental
friendly energy storage and conversion [3]. Amongst all renewable energy sources and systems, solar cells [5], supercapacitors [6-8], and fuel cells [1] have recently been extremely examined. However, the limitation of platinum based catalysts [9] and, the sluggish rate of the oxygen reduction reaction (ORR) [10] have restricted the development of fuel cells in an industrial scale. Therefore, decreasing the platinum loading on support, enhancing the nanoparticles distribution, and optimizing the nanoparticles size are the most prominent factors to overcome the aforementioned restrictions [11]. Up to now, carbon black has been utilized as platinum support as a commercial electro catalyst; however, it was not satisfactory at all chiefly due to its feeble interaction with platinum nanoparticles [12, 13]. Hence, numerous studies have been performing on declining the platinum loading by utilizing carbon nanostructures as a promising support for fuel cells catalysis in order to subdue both the cost and slow kinetics of ORR [14]. Owing to outstanding characteristics of carbon nanostructures such as convenient stability in alkaline and acidic media [15], proper electron conductivity [16], and high specific surface area [17] they have demonstrated a pivotal role for utilizing as electrocatalyst support for ORR in fuel cells. Carbon nanotubes are one-dimension carbon nanostructures which have been widely utilized as an encouraging catalytic support for ORR [18]. In spite of the fact that carbon nanotubes are suitable electrocatalyst support, having an inactive surface has made the pristine carbon nanotubes contestable to reach the best Pt nanoparticles distribution [19-21]. Thus, altering the surface properties or modification of carbon nanotubes should be considered to increase its electrocatalytic activity [22]. Due to enhancing the electron donation by juxtaposing heteroatoms such as nitrogen on the neighboring of carbon atoms, functionalization and doping carbon nanotubes with heteroatoms has been vastly inspected as metal free catalyst and promising supports for ORR [23-28]. Even though the synthesis of doped carbon nanotubes has enhanced the catalytic performance, sophisticated techniques, high temperature conditions, and the product purification to remove residual metals, and ambiguity of improved ORR activity, have partially overshadowed the utilization of heteroatom doped carbon nanotubes [22]. In addition, functionalization of carbon nanotubes with amine and amide group is widely proposed for enhancing the platinum nanoparticles distribution and ORR kinetics [10, 15, 29-32]. In the present study, we utilized ethylenediamine (EDA) and diethylenetriamine (DETA) as amine precursors to chemically functionalize the surface of multiwall carbon nanotubes. For better demonstration of the critical impact of amine functional groups, the same strategy was applied to
synthesize oxygen containing functional carbon nanotubes which is denoted as OMWCNTs. It is worth noting that, nitrogen containing functional groups can supply as the active sites for more effective nucleation and growth of platinum nanoparticles on the surface of MWCNTs. Additionally, it is proposed that the adsorption of oxygen molecules active sites can be promoted due to superior accessibility of platinum nanoparticles.

2. Experimental

2.1 Materials
All the chemicals were used as it was received without any further treatment. Ethylenediamine, diethylenetriamine, sulfuric acid (98%), nitric acid (70%), hydrochloric acid (37%), N,N-dimethylformamide (99.8%), thionyl chloride (99%), tetrahydrofuran, and ethanol were purchased from Merck. Nafion (5.0 wt% solution) and hexachloroplatinic acid (H₂PtCl₆·6H₂O 37.0%) were purchased from Sigma Aldrich.

2.1.1 Synthesis and purification of multiwall carbon nanotubes
The multiwall carbon nanotubes were synthesized by chemical vapor deposition of 20% methane in hydrogen in the presence of Co-Mo/MgO as catalyst at 800-1000°C [33]. Purification of multiwall carbon nanotubes was carried out to remove the metallic particles. Briefly, as synthesized MWCNTs were refluxed in 2 M HCl solution at 70°C for 6 h. Subsequently, it was thoroughly washed with deionized water to reach the neutral pH, and then was heated up to 250°C for 1 h.

2.2 Oxidation of MWCNTs
The graphitic surface of MWCNTs was oxidized by putting multiwall carbon nanotubes into three-neck flask containing concentrated H₂SO₄ and HNO₃ (3:1 V/V) at 70°C for 5 h. The main purpose of the oxidation of MWCNTs was based on the comparison of oxygen containing functional groups such as hydroxyl and carboxyl which can be obtained in this stage, and amine functional group which is described in the following section.

2.3 Amine-functionalization MWCNTs
Amine-functionalization of OMWCNTs was carried out by two different amine precursors to investigate the effect of adding the nitrogen atoms concentration by replacing diethylenetriamine instead of ethylenediamine. Briefly, 1.0 g of OMWCNTs was ultrasonically dispersed in a solution of thionyl chloride (SOCl₂) and dimethylformamide (DMF) (25:1). The black suspension was vigorously stirred at 70°C for 24 h under nitrogen atmosphere. The resulted
sample were filtered and washed with an ample amount of tetrahydrofuran (THF) and then placed in a vacuum oven at 50°C for 8 h. Afterwards, in order to attach amine functional groups on the surface of carbon nanotubes, 500 mg of the OMWCNTs were mixed with 2.5 g of ethylenediamine or diethylenetriamine and sonicated in an ultrasonic bath for 2 h. The amination reaction was taken place then in a deaerated medium under reflux condition for 48 h. The sample was washed with copious amount of pure ethanol and filtered. Finally, the amine-functionalized OMWCNTs which are denoted as EDAMWCNTs and DETAMWCNTs were dried at 65°C under vacuum condition overnight. From mow on OMWCNTs, EDAMWCNTs and DETAMWCNTs are denoted as FMWCNTs. The schematic synthesis procedure has been illustrated in Figure 12.

2.4 Preparation of Pt-FMWCNTs

Pt nanoparticles were precipitated on the functionalized MWCNTs, i.e. FMWCNTs, through a polyol process using ethanol as the reducing agent. At the beginning, 0.2 g of treated carbon nanotubes was ultrasonically dispersed in 1 L of ethanol for 1h. Then, 100 cc of hexachloroplatinic acid (H₂PtCl₆·6H₂O) solution in ethanol was added drop wise into the above suspension under vigorous stirring. The suspension was agitated in an ultrasonic bath for another 1 h. The mixture was then deaerated by argon and the reduction reaction was conducted under reflux condition at 85°C for 18 h. The resulted electro catalyst was washed with an ample amount of deionized water to remove chlorine ions and dried in a vacuum oven at 70°C for 12 h.

2.5 Preparation of electrocatalysts and electrochemical measurements

An ink type electrocatalyst was prepared from the synthesized Pt-FMWCNTs electrocatalysts. 5 mg of each electrocatalyst was ultrasonically dispersed for 30 minutes in a mixture of solvent containing 950 µl of ethanol and deionized water (1:1 V/V) and 50 µl of 1.0 wt% nafion solution. A rotating glassy carbon electrode (GCE) with the diameter of 3 mm was used to load the as prepared ink. Before loading the electrocatalysts onto glassy carbon electrode, it was carefully polished on a micro cloth with a 0.05 and 0.3 µm alumina slurry and washed with deionized water and ethanol, respectively to remove any pollutant. Then, the GCE was further cleaned ultrasonically by immersing into double distilled water to remove any remaining alumina particles. Subsequently, 5 µl of each electrocatalyst ink was loaded on the surface of GCE under irradiation of infrared lamp. Afterwards, the loaded GCE was held in an oven at 60°C for 10 minutes to cure the nafion polymer. Electrochemical measurements were conducted with a
conventional three-electrodes cell in a 0.5 M H₂SO₄ solution as electrolyte and at room temperature. As it was mentioned earlier a rotating GCE was used as the working electrode, Ag/AgCl and Pt wire were used as the reference and counter electrodes, respectively. All the electrochemical data were recorded by using an Autolab potentiostat/galvanostat (PGSTAT30 Eco Chemie, B.V, The Netherlands) instrument along with rotating disk electrode (RDE) system. Prior to the electrochemical experiments, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry, and electrochemical impedance spectroscopy (EIS), 25 ml of 0.5 M H₂SO₄ were properly purged with pure oxygen for 30 minutes to remove other soluble gases, if any. All the measured potentials in this study are based on the reversible hydrogen electrode (RHE).

2.6 Physical characterization instruments

The X-ray powder diffraction was performed on PW 1840 Philips diffractometer by using Cu Kα1 (λ= 1.54056 Å) to examine crystalline structure of the electrocatalysts. The diffraction patterns were recorded in the 2θ extent from 15 to 90° with a scan rate of 1.2° (2θ)/min. X-ray photoelectron spectroscopy (XPS, Bestec instruments, ultra-spectrometer Mg Kα and monochromatic Al Kα source operating) was also done to evaluate the electronic structure of carbon, nitrogen, and oxygen atoms on the surface of electrocatalysts. The operating pressure and base pressure was set about 2×10⁻¹⁰ and 1×10⁻¹⁰ torr, respectively. A wide scan survey at high resolution spectra was also conducted to evaluate the accuracy of FMWCNTs. Moreover, Fourier transition infrared (Perkin Elmer FTIR Analyzer) was used to further investigate the attachment of functional groups on MWCNTs. The distribution of platinum nanoparticles and the morphology of the electrocatalysts was characterized by transmission electron microscopy (TEM, ZEISS 900).

3. Results and discussion

3.1 Physicochemical characterization

Figure 13 depicts the XRD patterns of the electrocatalysts. The diffraction peaks in the vicinity of 25, 43, 55, and 76° (2θ) can be attributed to the graphitic structure and hexagonal crystallinity of carbon atoms at (002), (100), (004), and (110) planes of OMWCNTs, respectively [34, 35]. The diffraction peaks at 39, 45, 67, 80, and 85 (2θ) degrees in the spectrum (b), (c), and (d) in Figure 13 may be ascribed to the crystallinity of Pt nanoparticles at (111), (200), (220), (311), and (222) planes, respectively [36]. As a result, the XRD patterns confirm the deposition of Pt
nanoparticles as a face-centered-cubic structure on the functionalized carbon nanotubes. The average size of Pt nanoparticles was estimated by Scherrer equation, regarding the (200) or (111) plane of Pt crystals which shows the largest intensity among other Pt planes [37, 38].

\[
d = \frac{0.9 \lambda}{B \cos 2\theta}
\]  

(1)

In this equation, \(d\) stands for the average size of Pt nanoparticles (nm), \(\lambda\) is related to the X-ray wavelength which is 1.5406 Å for the Cu Kα radiation, \(B_{2\theta}\) is regarded as the width of the diffraction peak at half maximum height, and \(\theta\) is defined as the angle corresponding to the maximum peak (degree). Considering the Scherrer equation, the average size of platinum nanoparticles on functionalized multiwall carbon nanotubes was calculated to be about 4.8, 4.0, and 3.2 nm for OMWCNTs, EDAMWCNTs, and DETAMWCNTs, respectively. These sizes are reasonably confirmed by TEM images which are presented later on. The size of Pt calculated from the XRD patterns indicate that platinum dispersed on surface of the amine-functionalized CNTs have smaller sizes. Due to the fact that amine functional groups provide basic sites on the surface of carbon nanotubes, the presence of EDA and DETA functional groups not only improve the nucleation and growth of Pt nanoparticles on the surface of modified carbon nanotubes, but also accelerate the precipitation process [34, 39, 40].

TEM images of the pristine multiwall carbon nanotubes and electrocatalysts are shown in Figure 14. The image of the as synthesized multiwall carbon nanotubes (Figure 14a) clearly indicates the presence of carbonaceous and residual metal particles impurity. As the Figure 14b shows, these impurities were obviously removed by refluxing the multiwall carbon nanotubes in 2 M HCL solution. After the oxidation process, there are more individual nanotubes along with more open or broken tubes which could be attributed to the functionalization of carbon nanotubes. The images of the Pt-OMWCNTs, Pt-EDAMWCNTs, and Pt-DETAMWCNTs samples reveal that platinum nanoparticles have been successfully deposited on surface of the functionalized carbon nanotubes without any noticeable agglomeration; however, the size distribution of Pt nanoparticles ranges from 1 to about 8 nm in each case. According to these images, the deposition and distribution of Pt nanoparticles can be changed when the amine functionalized carbon nanotubes have been utilized as the support instead of OMWCNTs. In the case of Pt-EDAMWCNTs, the presence of two amine groups can play an important role to enhance the nucleation sites on the support due to creation of more basic sites for anchoring Pt nanoparticles.
in comparison with Pt-OMWCNTs electro catalyst. Moreover, regarding the Figure 14d, the
dispersion of Pt nanoparticles has been even more improved owing to the presence of one more
nitrogen atom in the case of DETAMWCNTs which could act as a favorable site for better
distribution of Pt nanoparticles on the surface of carbon nanotubes.

The functionalization of carbon nanotubes with oxygen or amine containing groups was
confirmed by FTIR spectra, presented in Fig. 4. The weak peak near 680 cm\(^{-1}\) for all the samples
can be related to C-H aromatic bending vibrations due to the formation of C-H bonds on the
defect structure of carbon nanotubes and acidic hydrogen in the oxidized sample. Also, two weak
peaks at 1374 and 1443 cm\(^{-1}\) could be ascribed to the backbone structures of multiwall carbon
nanotubes which is present in all the spectra. The FTIR spectrum of OMWCNTs is shown in
Figure 15a. The distinctive peaks at 1212, 1536, 1698, 2947 and 3479 cm\(^{-1}\) are attributed to C-O,
C=C, C=O, C-H and O-H bonds, respectively [41-43]. As it can be observed in Figure 15b and c,
the appearance of distinctive peaks in the vicinity of 1096 and 1088 cm\(^{-1}\) are regarded as the C-N
stretching band in the spectra of EDAMWCNTs and DETAMWCNTs, respectively [44, 45].
Accordingly, the wave numbers of the C-O, C=C, C=O, and O-H peaks of the EDAMWCNTs
and DETAMWCNTs, have been shifted as compared with those of OMWCNTs, due to
formation of amine functional groups on the carbon nanotubes. Also, two peaks at 1680 and
1688 cm\(^{-1}\) are attributed to the N-H bending for EDAMWCNTs and DETAMWCNTs,
respectively [45]. The peaks at 3155 and 3271 cm\(^{-1}\) are assigned to the C-H bond stretching of
the EDA and DETA precursors [45]. Additionally, the presence of two twin peaks at 3426 and
3479 cm\(^{-1}\) for EDAMWCNTs and 3410 and 3450 cm\(^{-1}\) for DETAMWCNTs is related to N-H\(_2\)
bond stretching as symmetric or asymmetric mode [46]. Hence, formation of amine functional
groups on the surface of OMWCNTs could be verified according to the FTIR spectra.

In addition to FTIR spectra, X-ray photoelectron spectroscopy was further conducted for
investigation of the formation of functional groups on the surface of MWCNTs. The XPS survey
spectra of the pristine multiwall carbon nanotubes, i.e. OMWCNTs, EDAMWCNTs, and
DETAMWCNTs are shown in Figure 16a. The strong peaks in the vicinity of 284 eV can be
clearly observed in the wide spectra for all the samples which is related to sp\(^{2}\) hybridized carbon
nanotubes [47]. As it is observed in this figure, there is no other obvious peak in the spectrum of
the pristine carbon nanotubes; while in the spectrum of OMWCNTs the appearance of O1s peak
at around 532 eV is noticeable [48]. Moreover, the presence of distinctive peaks at 400 eV in the
XPS spectra of EDAMWCNTs and DETAMWCNTs can be assigned to N1s peaks whereas there are no peaks in this region in the spectrum of OMWCNTs and the pristine carbon nanotubes indicating the formation of amine functional groups [13, 49]. High resolution XPS spectra of C1s for OMWCNTs is shown in Figure 16b. The C1s spectra of OMWCNTs is divided into three major components at 284.3, 285.9, and 288.8 eV which are attributed to C-C, C-O, and C=O bonds, respectively [46, 50]. The high resolution XPS spectra of C1s and N1s for EDAMWCNTs are depicted in Figure 16c and d, respectively. The C1s peaks is composed of two main components at 284.8 and 287.8 eV relating to C-C and C-N bonds, respectively [50]. Higher energy bonding at 287.8 eV which is related to C-N bond in comparison with C1s main peaks of OMWCNTs indicates the formation of amine functional groups [51]. Furthermore, the elimination of a peak at around 288.8 eV indicates the reduction of carboxylic functional groups to an amine functional groups [52]. Due to the fact that N1s energy bindings for amine functional groups are reported to be between 399.5 and 400.5 eV [53, 54], the N1s peaks of EDAMWCNTs peaks at 399.8 and 401.2 eV are related to C-N and N-H bonds, respectively [52]. The high resolution XPS spectra of C1s and N1s for DETAMWCNTs are illustrated in Figure 16e and f, respectively. The two distinctive C1s peaks at 284.4 and 287.6 eV are attributed to C-C and C-N bonds, respectively [49]. Compared with EDAMWCNTs the C1s peak at 287.6 eV shows a stronger peak that might be associated with the formation of more amine functional groups in the case of functionalization with diethyleneetriamine or more reduction of carboxylic acid to amine functional groups. The N1s peaks of DETAMWCNTs shows two main energy bindings at 399.8 and 401.5 eV which are assigned to C-N and N-H bonds, respectively [49]. As predicted, the absence of N1s peaks in the pristine and OMWCNTs XPS spectra confirms the formation of amine functional groups through functionalization of oxidized multiwall carbon nanotubes with ethylendiamine and diethylenetriamine. Hence, the XPS results are quite consistent with the FTIR spectra; both techniques indicate the functionalization of carbon nanotubes with oxygen and nitrogen containing functional groups. The atomic concentrations of carbon, nitrogen, and oxygen were estimated on the basis of XPS results and summarized in Table 4. The higher oxygen concentration of the OMWCNTs is due to the formation of carboxylic and hydroxyl functional groups; whereas for EDAMWCNTs and DETAMWCNTs lower oxygen content is indicative of amine functionalization of carbon nanotubes. Moreover, nitrogen atomic concentration of EDAMWCNTs and DETAMWCNTs
were found to be about 5.3 and 8.7 %, respectively. Increasing the concentration of nitrogen atoms in DETAMCNTs may be ascribed to the amount of amine groups in DETA which is more than that of EDA. Therefore, according to the XPS results, the formation of the larger amount of amine functional groups, which is favorable for oxygen reduction reaction, is more likely by using DETA as compared to EDA.

3.2 Electrochemical characterization of the electrocatalysts

3.2.1 Cyclic Voltammetry

Figure 17 shows the cyclic voltammetry of the synthesized electrocatalysts in oxygen saturated H$_2$SO$_4$ at 25°C. At the beginning of each CV test the surface of electrodes were cleaned by sweeping two or three cycles to remove any residual impurities. The electrochemical active surface area (EASA) of the electrocatalysts was calculated according to adsorption and desorption charge associated with hydrogen on Pt crystals which is known as Hupd (under-potential deposition on Pt) [55]. The EASA was estimated assuming 0.21 mC/cm$^2$ Pt and summarized in Table 5. According to Figure 17 and Table 5, the amount of EASA for Pt-DETAMWCNTs is higher than those of Pt-EDAMWCNTs and Pt-OMWCNTs, indicating better dispersion of Pt nanoparticles due to the presence of amine functional groups. The role of amine functional groups is accentuated by increasing the number of nitrogen atoms at DETAMWCNTs as compared to EDAMWCNTs. Therefore, the higher EASA and the more positive onset potential is ascribed to the role of amine functional groups as a prominent factor for improving the catalytic activity of Pt nanoparticles via better nucleation and growth, resulting in higher platinum dispersion [56].

3.2.2 Rotating disk electrode measurement (RDE)

Linear sweep voltammetry was conducted using rotating disk electrode at various rotational speeds in an oxygen saturated 0.5 M H$_2$SO$_4$ at 25°C. The polarization curves of the electrocatalysts are shown in Figure 18 at the rotational speed of 1500 rpm. The onset potential of Pt-DETAMWCNTs (0.997 V vs RHE) and Pt-EDAMWCNTs (0.984 V) is clearly higher than that of Pt-OMWCNTs (0.824 V), due to the presence of amine functional groups. Amine functional groups on the surface of carbon nanotubes lead to a uniform distribution of Pt nanoparticles [56, 57]. Moreover, ORR activity is significantly influenced by the dispersion and
coordination of platinum nanoparticles [58-60]. Hence, the positive shift of onset potential for Pt-DETAMWCNTs and Pt-EDAMWCNTs may be ascribed to better accessibility of Pt nanoparticles for oxygen molecules due to the role of amine functional groups for improving the nucleation, growth, and dispersion of Pt nanoparticles. Also, according to the most of the proposed ORR mechanisms, the formation of oxygenated radicals and other oxygenated species intermediates, specifically OH$_{ads}$ during the ORR reaction leads to decreasing or inhibiting the normal reduction of oxygen molecules [61]. The augmentation of intermediate species conducts ORR reaction toward the 2 electron pathway instead of the 4 electron pathway [62]. According to Figure 18, the polarization curves show that any probable formation of oxygenated species is decreased by introducing the amine functional groups. As is observed, this behavior is further supported by increasing the amount of cathodic current density due to the better electrocatalytic activity of Pt nanoparticles in the presence of amine functionalized carbon nanotubes. The higher electrocatalytic activity of Pt-DETAMWCNTs in comparison with Pt-EDAMWCNTs and Pt-OMWCNTs can be also attributed to weaker chemical adsorption energy of the produced intermediate, i.e. hydroxyl species during reduction of oxygen [58, 63]. It should be mentioned that enhancing the electrocatalytic activity of Pt nanoparticles through decreasing the chemical adsorption energy of hydroxyl species firmly depends on the geometry and homogeneous dispersion of nanoparticles on the surface of supports [64]. Thus, the better dispersion and coordination of Pt nanoparticles, the higher electrocatalytic activity of Pt nanoparticles towards ORR. As can be seen in the polarization curves, the onset potential of the adsorbed hydroxyl species for Pt-DETAMWCNTs is much higher than those of Pt-EDAMWCNTs and Pt-OMWCNTs, indicating the more attenuation of the chemical adsorption energy by increasing the concentration of nitrogen atoms. This observation is supported by TEM images and XPS results which revealed better dispersion of Pt nanoparticles and higher content of nitrogen atoms for Pt-DETAMWCNTs sample. The kinetics behavior of the electrocatalysts was also investigated by increasing the rotational speed of the RDE electrode from 250 to 4500 rpm. Figure 19 presents the polarization curves and the corresponding Koutecky-Levich plots for all of the electrodes at various rotational speeds and potentials, respectively. The number of electron transferred was calculated by plotting the Koutecky-Levich equation which includes a plot of inverse current density ($1/J$) versus the inverse of the square root of the
rotational speed ($\omega^{-1/2}$). The slope of this plot leads to calculating the number of electron transferred in oxygen reduction reaction through the following equations.

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{0.5}}$$  \hspace{2cm} (2)

where, $J$ (mA/cm$^2$) is the measured current at linear sweep voltammetry, $J_k$ (mA/cm$^2$) is the kinetic current, $\omega$ is the rotational speed (rpm), and $B$ is defined as the following equation.

$$B = 0.2nFAD_{O_2}^{2/3}v^{-1/6}C_{O_2}\omega^{1/2}$$  \hspace{2cm} (3)

Here, $n$ is the number of transferred electron, $F$ is the Faraday constant (96500 C/mol), $A$ is the surface area of the electrode, $D_{O_2}$ the diffusion coefficient of oxygen in electrolyte (1.61×10$^{-5}$ cm$^2$/s), $v$ is the kinematic viscosity of the electrolyte (1.00×10$^{-2}$ cm$^2$/s), $C_{O_2}$ the concentration of the dissolved oxygen in the electrolyte (1.15×10$^{-6}$ mol/cm$^3$) [65]. The number of electron transferred was found to be 3.34, 4.03, and 4.10 for Pt-OMWNCTs, Pt-EDAMWCNTs, and Pt-DETAMWCNTs, respectively. Due to the fact that the desirable pathway in ORR is the 4e$^-$ reduction pathway [66], the number of electron transferred indicates that functionalization of carbon nanotubes with amine functional groups improves the catalytic efficiency of the Pt nanoparticles throughout the reduction of oxygen molecules by increasing the number of transferred electrons.

3.2.3 Electrochemical Impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy was also performed to further investigate the electrochemical behavior of the electrocatalysts. Figure 20 shows the equivalent circuit for fitting experimental EIS data in which $R_s$, $R_{ct}$, CPE, and $W$ stand for the solution ohmic resistance, charge transfer resistance, constant phase element which is used as double layer capacitance owing to inhomogeneous electrocatalysis surface, and Warburg impedance, respectively [67-69]. The equivalent circuit proposes that polarization is assigned to a combination of kinetics and diffusion process [67]. Figure 21 shows that all of the experimental EIS results were conveniently fitted on the model EIS plots for Pt-OMWNCTs, Pt-EDAMWCNTs, and Pt-DETAMWCNTs at open circuit potentials (0.65 V vs Ag/AgCl). According to the Nyquist plots, the formation of arc curves indicates that the charge transfer resistance is the dominated resistance over electrolyte resistance owing to initiation of the Nyquist curves from the origin [70]. Thus, it can be observed that the amount of charge transfer resistance or mass transport
limitation is increased by increasing the diameter of the Nyquist arc curves. As can be seen, the resistance of the electrocatalysts is decreased by attaching the amine functional groups on the surface of carbon nanotubes. The amount of $R_s$ and $R_{ct}$ are summarized in Table 6. On the other hand, the low amounts of $R_{ct}$ verifies that the electrochemical reduction of oxygen is extremely fast; hence, the amount of $R_{ct}$ is negligible versus Warburg impedance. As the Nyquist curves represent, the mass transfer limitation and Warburg impedance for Pt-DETAMWCNTs and Pt-EDAMWCNTs are less than that of Pt-OMWCNTs due to the high electron conductivity of the nitrogen atoms in amine functional groups. Furthermore, the mass transfer limitation has been decreased by increasing the number of nitrogen atoms in the case of Pt-DETAMWCNTs. Therefore, the smaller slope of Nyquist curves implies that the number of transferred electron increased by amine functionalization of carbon nanotubes which facilitates the oxygen reduction through enhancing the accessibility of Pt nanoparticles for oxygen molecules.

3.2.4 Chronoamperometry (CA)

In addition to the above mentioned electrochemical techniques, chronoamperometry was applied to further evaluate the stability and catalytic activity of the electrocatalysts. Figure 22 shows chronoamperometry plots of Pt-OMWNCTs, Pt-EDAMWCNTs, and Pt-DETAMWCNTs at three different applied potentials. According to Figure 22, at all of the applied potentials, Pt-DETAMWCNTs exhibits the most stable electro catalytic behavior due to the highest steady current density among the three electrocatalysts. Moreover, this behavior is confirmed by chronoamperometry curves of Pt-EDAMWCNTs as compared with Pt-OMWCNTs which has the minimum current density and stability at all the applied potentials. The chronoamperometry results are consistent with all of the previous electrochemical observations. As a result, the role of amine functional groups is again indicative of improvement of the catalytic performance of Pt nanoparticles.

4. Conclusion

The effect of amine functional groups on the reduction of oxygen at the cathode electrode of proton exchange membrane fuel cell was investigated by functionalization of multiwall carbon nanotubes. Also, platinum nanoparticles were dispersed on the amine functionalized and oxidized carbon nanotubes for further evaluation of the role of amine functionalization. Electrochemical and physicochemical characterization of the Pt-OMWCNTs, Pt-EDAMWCNTs, and Pt-DETAMWCNTs reveal that the existence of amine functional groups on the surface of
carbon nanotubes not only improves the nucleation, growth, and the dispersion of Pt nanoparticles, but also enhances the reduction of oxygen molecules. It was found that, the quantity of nitrogen atoms plays an important role in electrochemical reduction of oxygen. XPS and TEM results revealed that DETAMWCNTs better improve the catalytic activity of Pt nanoparticles due to the number of attached amine groups and higher dispersion of platinum nanoparticles as compared to EDAMWCNTs. Cyclic and linear sweep voltammetry showed that EASA, onset potential, and number of electron transfer were increased by amine functionalization of carbon nanotubes. Furthermore, EIS and CA confirmed the role of amine functional groups by decreasing the mass transfer limitation and higher stability. All in all, nitrogen atoms in the form of amine functional groups facilitate the accessibility of Pt nanoparticles for ORR which leads to decreasing Pt loading while keeping 4 electron pathway reduction of oxygen.

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**References**


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Ali Morad Rashidi received his MSc and PhD in Chemical Engineering from University of Tehran. He is currently a Professor at Research Institute of Petroleum Industry (RIPI). His main research interests include various applications of nanomaterials mainly carbon nanostructures such as CNT, CNF, and graphene. He also works on preparation, characterization, and evaluation of nanomaterials in chemical engineering.

**Figures**

**Figure 1.** Schematic illustration of OMWCNTs functionalization with EDA or DETA

**Figure 2.** XRD patterns of electrocatalysts (a) MWCNTs, (b) Pt-OMWCNTs, (c) Pt-EDAMWCNTs, and (d) Pt-DETAMWCNTs.

**Figure 3.** TEM images of electrocatalysts including: (a) unpurified MWCNTs, (b) purified MWCNTs with 2M HCl, (c) oxidized MWCNTs with H_2SO_4 and HNO_3 (3:1 V: V), (d) Pt-OMWCNTs, (e) Pt-EDAMWCNTs, (f) Pt-DETAMWCNTs, Particle size distribution of (g) Pt-OMWCNTs, (h) Pt-EDAMWCNTs, and (i) DETAMWCNTs.

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Figure 14. TEM images of electrocatalysts including: (a) unpurified MWCNTs, (b) purified MWCNTs with 2M HCl, (c) oxidized MWCNTs with H$_2$SO$_4$ and HNO$_3$ (3:1 V: V), (d) Pt-OMWCNTs, (e) Pt-EDAMWCNTs, (f) Pt-DETAMWCNTs, Particle size distribution of (g) Pt-OMWCNTs, (h) Pt-EDAMWCNTs, and (i) DETAMWCNTs.
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Figure 20. Equivalent circuit used for fitting EIS experimental data.
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### Table 4. Calculated atomic concentration of functionalized carbon nanotubes from XPS

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<thead>
<tr>
<th>Sample</th>
<th>Concentration of nitrogen (atomic %)</th>
<th>Concentration of oxygen (atomic %)</th>
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<tbody>
<tr>
<td>OMWCNTs</td>
<td>NA</td>
<td>15.4</td>
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<tr>
<td>EDAMWCNTs</td>
<td>5.3</td>
<td>2.6</td>
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<tr>
<td>DETAMWCNTs</td>
<td>8.7</td>
<td>&lt;0.8</td>
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### Table 5. The amount of EASA, onset potential, and number of transferred electron for electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Pt loading wt%</th>
<th>EASA m² g⁻¹ Pt</th>
<th>Onset Potential (V vs RHE)</th>
<th>Number of Transferred Electron (n)</th>
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</thead>
<tbody>
<tr>
<td>Pt-OMWCNTs</td>
<td>10</td>
<td>24.2</td>
<td>0.824</td>
<td>3.34</td>
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<tr>
<td>Pt-EDTAMWCNTs</td>
<td>10</td>
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<tr>
<td>Pt-DETAMWCNTs</td>
<td>10</td>
<td>45.8</td>
<td>0.997</td>
<td>4.10</td>
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### Table 6. Equivalent circuit parameters of the electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Rs (Ω.cm²)</th>
<th>Rct (Ω.cm²)</th>
<th>CPE (µF)</th>
<th>W (µMho)</th>
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<tbody>
<tr>
<td>Pt-OMWCNTs</td>
<td>0.09</td>
<td>2.19</td>
<td>546</td>
<td>195</td>
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<tr>
<td>Pt-EDAMWCNTs</td>
<td>0.05</td>
<td>1.78</td>
<td>881</td>
<td>122</td>
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<tr>
<td>Pt-DETAMWCNTs</td>
<td>0.03</td>
<td>0.52</td>
<td>990</td>
<td>118</td>
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