Characteristics and performance of urea modified Pt-MWCNTs for electro-oxidation of methanol

Amideeddin Nouralishahi\textsuperscript{a,b,}\textsuperscript{*}, Yadollah Mortazavi\textsuperscript{c}, Abbas Ali Khodadadi\textsuperscript{c}, Mohammad Mehdi Choolaei\textsuperscript{d}, Levi T. Thompson\textsuperscript{b}, Bahman Amini Horri\textsuperscript{d}

\textsuperscript{a} Energy, Environment and Nanostructure Materials Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, P.O. Box 43841-119, Tehran, Iran

\textsuperscript{b} Department of Chemical Engineering and Hydrogen Energy Technology Laboratory, University of Michigan, Ann Arbor, MI 48109, USA

\textsuperscript{c} Analysis and Nanostructure Materials Research Laboratory, School of Chemical Engineering, University of Tehran, P.O. Box 11155/4863, Tehran, Iran

\textsuperscript{d} Department of Chemical and Process Engineering, University of Surrey, P.O. Box GU2 7XH, Guildford, United Kingdom

\textbf{ARTICLE INFO}

\textbf{Keywords:}

- Methanol oxidation reaction
- Platinum
- Carbon nanotubes
- Urea
- Amine functional group

\textbf{ABSTRACT}

Multiwalled carbon nanotubes are modified by urea (MWCNTs-U), as an amine group, through a simple amination method to be used as support for Pt nanoparticles in methanol electro-oxidation reaction (MOR). The amination method involves a covalent grafting of urea molecules onto the surface of acid treated multivall carbon nanotubes (MWCNTs-A) using O-(7-azabenzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HATU) as the coupling agent. Platinum nanoparticles are impregnated on the surface of MWCNTs-U using NaBH\textsubscript{4}. Pt/MWCNTs-U shows an enhanced electrocatalytic activity and durability with exposing larger accessible surface area and 27% higher active surface area compared to Pt/MWCNTs-A. In addition, urea incorporation can improve the electrocatalyst tolerance against CO-poisoning, due to the enhanced formation kinetics of the chemisorbed hydroxyl groups. The onset potential of CO\textsubscript{ad} oxidation indicates a decrease from 553 mV to 530 mV for Pt/MWCNTs-A and Pt/MWCNTs-U, respectively. It is observed that in the presence of amide group the forward peak current density and exchange current density, in CV and LSV experiments, respectively increase from 378 to 515 mA/mg\textsubscript{Pt} and 1.59 × 10\textsuperscript{-8} A/cm\textsuperscript{2} to 2.12 × 10\textsuperscript{-8} A/cm\textsuperscript{2}. These results are also in a good agreement with the theoretical activation energies obtained from Arrhenius plots, indicating a decrease from 41.7 to 38.8 kJ/mol methanol in the case of Pt/MWCNTs-A and Pt/MWCNTs-U, respectively.

1. Introduction

Since the recognition of direct alcohol fuel cells, e.g. direct methanol fuel cells, the high activity of Pt particles in the oxidation reaction of short chain alcohols has attracted a great deal of interest for researches working in this field. However, due to the high cost and low stability of Pt in MOR, various approaches, such as applying bi- or triple-metallic Pt-based carbon-supported electrocatalysts [1,2], improved synthesis strategies and procedures [3,4], and new supports with different morphologies [5,6], have been suggested. Also, some attention has been given to the effect of surface chemical properties of carbon support on the electrocatalysts activity [7-11]. Due to the inert properties of carbon materials, the introduction of hydrophilic functional groups (e.g. oxygen containing groups) on the surface of carbon supports can improve their proton conductivity through the enhancement of interactions within electrode/electrolyte interface. The role of oxygen containing groups on the morphology and electrocatalytic properties of Pt/C and PtRu/C electrocatalysts has been investigated by many researchers [12-18]. It has been shown that in comparison with pristine carbon, oxidized carbon support can be impregnated with smaller size Pt nanoparticles with higher dispersion, resulting in an enhanced electrocatalytic performance in MOR [17,19]. Chen et al. reported that the introduction of oxygen containing groups on carbon support through oxidizing treatments (in corrosive media) could strengthen the interactions between the metallic clusters and support [14]. Glezou et al. believed the relation between the enhanced electrocatalytic activity and the amount of "surface oxides" can be possibly due to the availability of hydroxyl groups formed on the carbon support and their role in oxidative removal of absorbed intermediates formed during MOR [9]. Sharma et al. suggested that high

*Corresponding author at: Energy, Environment and Nanostructure Materials Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, P.O. Box 43841-119, Tehran, Iran.

E-mail address: nouralishahi@ut.ac.ir (A. Nouralishahi).

https://doi.org/10.1016/j.apsusc.2018.10.126

Received 30 April 2018; Received in revised form 1 August 2018; Accepted 15 October 2018

Available online 16 October 2018

0169-4332/ © 2018 Published by Elsevier B.V.
concentration of covalently bounded oxygen containing functional groups can enhance the removal of carbonaceous poisoning species on the platinum active sites via a synergetic effect [20]. It has been observed that the dissociative adsorption of H\textsubscript{2}O molecules on a highly hydrophille surface of an oxidized carbon support leads to the formation of surface hydroxyl groups. This matter plays a very important role in oxidative removal of adsorbed CO containing intermediates on the platinum active sites via the bi-functional mechanism. However, the presence of highly concentrated oxygen atoms on the defected sites of carbon supports may decrease their electrical conductivity, hindering electron transportation through catalytic layers. In this regard, Seger and Komat reported that partial reduction of highly oxidized carbon support can improve the overall electrocatalytic performance of Pt nanoparticles [21]. Adding nitrogen containing functional groups on the surface of supports has been frequently reported to increase hydrophilicity of electrocatalyst layers without decaying the electron transport properties [22,23]. Although this method could distort the carbon structure, but it may enhance the overall electron conductivity via electron donation from nitrogen atoms into the carbon structure [24]. Chetty et al. reported that nitrogen plasma treatment can create pyridinic nitrogen on the surface of carbon nanotubes, improving the performance of PtRu/N-CNTs in methanol electrooxidation reaction by acting as strong anchoring sites for Pt and Ru clusters [25]. Yi Cheng et al. [26] investigated the influence of nitrogen-containing functional groups on the activity of PtRu nanoparticles supported on carbon nanotubes for methanol electrooxidation reaction. The results demonstrated the critical role of nitrogen-containing groups in the enhanced electrocatalytic activity of PtRu nanoparticles supported on CNTs. The considerable activity of PtRu supported on nitrogen containing CNTs is believed to be most likely due to the strong interaction of the electron rich nitrogen-containing functional groups and the PtRu nanoparticles.

Although many studies have reported the use of nitrogen doped carbon nanostructures, little research has been reported on the application of amide functionalized carbon supports. The purpose of the present study is therefore to analyze the effect of applying urea modified multiwall carbon nanotubes as support for Pt nanoparticles. This study will further compare the effect of two types of surface modifications, oxidation and amination, on Pt/MWCNTs with respect to the electrocatalytic behaviors and physicochemical characteristics. The synthesized electrocatalysts are characterized with TEM, XRD, FTIR, XPS and different electrochemical measurements to understand the effect of amide functional groups on the MWCNTs support in improving the performance of platinum nanoparticles in MOR.

2. Materials and methods

2.1. Reagents

Multiwall carbon nanotubes, MWNs (10–30 nm in diameter), provided from Neutrino Co., were rinsed with ultra-pure water and acetone several times and dried in an oven at 60°C for 72 h. All other chemicals were used as received without any further purification. O-(7-azabenzo-triazol-1-yl)-N,N,N’-tetramethyluronium hexafluorophosphate (HATU) were purchased from Sigma-Aldrich. Other materials such as Urea, Dimethylformamide (DMF), potassium hydroxide, ethanol, methanol, nitric acid and sulfuric acid, all came from Merck.

2.2. Amination of MWCNTs

To prepare urea-functionalized MWCNTs, 1 g MWCNTs was mixed with 30 cc sulfuric acid and 10 cc nitric acid. The resulted suspension went through a 3 h sonication (60°C), several washing steps with deionized water, and dried at 60°C for 12 h in a vacuum oven. The acid washed MWCNTs (MWCNTs-A) were mixed with a solution of 50 cc dimethylformamide (DMF), 3 g urea and 0.1 g HATU (O-(7-azabenzo-triazol-1-yl)-N,N,N’-tetramethyluronium hexafluorophosphate). The mixture was then placed in a 100 cc flask and heated up to 65 ± 2°C. The amination reaction was performed for 48 h under reflux condition and extreme stirring. In the next step, urea functionalized MWCNTs (MWCNTs-U) were filtered and properly washed with ethanol. At the end, the resulted MWCNTs-U were dried in a vacuum oven at 60°C. Fig. 1a schematically represents the general procedure applied for the amination of MWCNTs. Here, HATU was applied as the coupling reagent [27,28]. Fig. 1b represents the proposed mechanism of the amination reaction of carboxylic groups using HATU. According to this figure, at first —COO- (from carboxyl groups) is replaced by O-7-azabenzo-triazol (OAT) groups in HATU molecule through a nucleophile attack. Then, the OAT- ions attack the carbon atom of acyl group and replaces the hydroxyl group, providing an active ester to be replaced by amine/amide group (urea). Finally, the amide group completely substitutes the OAT group by providing a hydrogen atom for its reformation to 1-hydroxy-7-azabenzo-triazole (HOAT).

2.3. Synthesis of electrocatalysts

The precipitation method was used for impregnation of platinum nanoparticles on MWCNT-A and MWCNT-U through the following steps: 75.4 mM H\textsubscript{2}PtCl\textsubscript{6} \textsubscript{6}H\textsubscript{2}O solution was added drop-wise to a well dispersed mixture of MWCNT-A (or MWCNT-U) in 20 cc deionized water. In order to allow Pt containing complexes to reach the nucleation sites, the solution was then placed in an ultrasonic bath for 30 min. Then, a 1 M sodium hydroxide solution was set to the pH at 9, followed by adding 20 cc fresh Na\textsubscript{2}H\textsubscript{2}O\textsubscript{2} solution while the mixture was magnetically stirred until forming a homogeneous suspension. The homogeneous mixture was then placed in a bath (30 ± 2°C) under argon atmosphere for 24 h to be reduced. The synthesized electrocatalysts were rinsed with deionized water several times and dried in a vacuum oven at 70°C for 8 h (Fig. 1c).

2.4. Characterization methods

In this work, transmission electron microscopy (TEM, ZEISS EM 900) was used to study the surface morphologies of the synthesized electrocatalysts. The chemical compositions of the electrocatalysts were measured by energy-dispersive X-ray spectroscopy (EDS, Philips XL-30) and induced coupled plasma (ICP) analysis (TERMO ICAP6000). FTIR measurement (Bruker, Vertex 70) was used to detect the functional groups on the surface of MWCNTs. The X-ray powder diffraction (XRD) analysis of the synthesized electrocatalysts was studied using a PW 1840 Philips diffractometer in the 20 range of 15–90° at a scanning rate of 0.02° (2θ) s\textsuperscript{-1}. Finally, X-ray photoelectron spectroscopy (XPS, Bestec instruments, ultra-spectrometer Mg Ka and monochromatic Al Ka source operating) was also applied to evaluate the electronic structure of nitrogen atoms on the surface of MWCNTs.

2.5. Electrochemical measurements

An Ivium Stat electrochemical analyzer (Ivium Technologies, Ivium Stat type 10 V/5 A) was used to collect the electrochemical data. The electrochemical testing was performed in a conventional one-compartment-three-electrode cell. Glassy carbon (0.0314 cm\textsuperscript{2}), Pt plate (5.5 cm\textsuperscript{2}), and Ag/AgCl electrodes were respectively served as the working, counter, and reference electrodes. All experiments were conducted in well deaerated argon bubbled electrolyte and all potentials are given versus Ag/AgCl reference electrode at 25°C. Cyclic voltammograms (CVs) was used to describe the electrocatalytic activity toward methanol oxidation reaction. In this regard, a standard half-cell three electrode setup was used, consisting of a Ag/AgCl reference electrode and a 0.5 M sulfuric acid and 1 M methanol mixture as the electrolyte. The potential sweeps were made from −200 mV to 1200 mV at scan rate of 50 mV s\textsuperscript{-1}. In order to determine the CO tolerance of the electrocatalysis, CO-stripping experiment was performed with the following
procedure: First, existing oxygen molecules in the electrolyte were swept out by bubbling argon into the cell for 30 min. Small bubbles of CO were injected through the cell for the next 30 min until the electrolyte was saturated. Afterwards, the potential applied to the working electrode was adjusted at -200 mV for 5 min to ensure that all Pt active sites were effectively blocked by CO ads molecules. After removing the dissolved CO using gaseous Ar bubbling, the first cycle of cyclic voltammetry profile in potential range of -200 mV to 1200 mV at scan rate of 50 mV s⁻¹ was recorded. The electrochemical active surface area (ECSA) of the electrocatalysts were determined by cyclic voltammetry experiment in deaerated 1 M H₂SO₄ solution at room temperature. The chronopotentiometry curves were recorded in 0.5 M sulfuric acid and 1 M methanol at 600 mV and 25 °C. The electrochemical impedance spectroscopy (EIS) data were reported in form of Nyquist diagrams in a frequency range of 100 kHz–100 mHz, in a constant potential mode at an amplitude of 5 mV.

2.6. Preparation of working electrode

For electrochemical analysis, working electrodes were prepared by adding 5 mg of prepared electrocatalysts powder to a mixture of 50 µL nafion solution and 2 mL ethanol (stirred for 30 min). Then, a small amount (6.3 µL) of the prepared ink was dripped on a glassy carbon electrode with 2 mm diameter. An ordinary 100 W lamp was used to slowly dry the electrode, and then the modified electrode was placed in an oven at 80 °C for 30 min.

3. Result and discussion

The results of Fourier transform infrared spectroscopy (FTIR) are shown in Fig. 2a. As for MWCNTs-A, the observed peaks at 842 cm⁻¹ and 3441 cm⁻¹ respectively indicate the presence of C-H and O-H bonds on the surface of MWCNTs [29,30]. Moreover, while 1189 cm⁻¹ and 1698 cm⁻¹ peaks correspondingly illustrate the stretch mode of C=O and C=O bonds, the slight peak observed at 1559 cm⁻¹ is linked with the bending of O-H bonds in the available functional groups [31–34]. On the other hand, the presence of C-H, C=C, and C=O in the MWCNTs-U are confirmed by the observed peaks at 860 cm⁻¹, 1505 cm⁻¹, and 1623 cm⁻¹, respectively. In both samples, the twin peaks located between 2000 and 2500 cm⁻¹ are ascribed to CO₂ molecules, probably either exists in the surrounding air or physiosorbed on the surface [35–38]. Similar to MWCNTs-A, the relatively weak peaks in the range of 2850 cm⁻¹ to 2960 cm⁻¹ are related to the symmetric and asymmetric stretch of C-H bond [33]. In addition to the similarities observed between the FTIR patterns, MWCNTs-U indicated specific peaks related to the presence of nitrogen containing groups. In this regard, the peak at 1130 cm⁻¹ indicates the stretch in N= C bonds [39]. In addition, the peak related to oscillation of NH₂ can be observed at 1461 cm⁻¹ [40]. The two adjacent peaks at 1675 cm⁻¹ and 1717 cm⁻¹ can respectively be related to the symmetric and asymmetric bending vibrations of H—N—H bonds [40]. The broad twin peaks observed at 3366 cm⁻¹ and 3447 cm⁻¹ frequencies attribute to the symmetric and asymmetric stretching vibrations of urea’s NH₂ group, respectively [39,40].
Fig. 2. (a) FTIR results for MWCNTs-A and MWCNTs-U. (b) and (c) XPS data of MWCNTs-A and MWCNTs-U: (b) Wide scan view, (c) The MWCNTs-U XPS spectra in the N 1s region. (— raw data; — fit data; — deconvoluted data).

Fig. 2b and c represent the XPS results, analyzing the surface chemistry of urea-functionalized MWCNTs (MWCNTs-U). The wide scan view of the XPS results in Fig. 2b clearly indicates the peaks corresponding to O 1s and N 1s on the MWCNTs-U surface. Fig. 2c shows the XPS data of MWCNTs-U in the N 1s region, consisting of two peaks centered at 399.3 eV and 401.2 eV. The peak at lower binding energy (399.3 eV) can be tailored to the amide bonds or free amine groups [41,42]. The peak located at 401.2 eV suggests the presence of protonated ammonium ions (NH₃⁺) on the surface of MWCNTs-U [43], which may act as effective anchoring sites by involving electrostatic interactions with Pt containing complexes [44]. The data presented in Fig. 2 suggests successful graft of amine groups on MWCNTs through the formation of amide bonds.

Fig. 3 shows the X-ray diffraction spectra of the synthesized electrocatalysts (Pt/MWCNTs-A and Pt/MWCNTs-U). The XRD patterns clearly show the five main characteristic peaks of the face-centred cubic (fcc) crystalline Pt at 39°, 46°, 68°, 81° and 87° assigned to planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), respectively [45,46]. By selecting the strongest peak at 39° as the main characteristic peak and considering Debye–Scherrer's equation [47], the average size of Pt nanoparticles was estimated to be 4.7 nm and 5.4 nm, respectively for Pt/MWCNTs-U and Pt/MWCNTs-A.

Fig. 4 shows the transmission electron microscopy (TEM) images and particle size distribution histograms, within at least 130 randomly selected particles, of the nanoparticles of platinum supported on MWCNT-A and MWCNT-U. It can be observed that the size distribution of Pt nanoparticles is dependent on the chemical functional groups present on MWCNTs. In this regard, Pt/MWCNTs-U showed a slightly smaller platinum particle size with a better size distribution in
Fig. 4. TEM photographs and Pt particle size distribution diagrams of Pt/MWCNTs-U and Pt/MWCNTs-A.

comparison with Pt/MWCNTs-A. Such behavior has also been observed in the case of nitrogen doped carbon supports [48]. This matter could be attributed to the stronger interaction between the platinum nanoparticles and electrocatalyst support, hindering the growth of Pt nanoparticles [49]. Yu and Ye believe basic sites available on carbon surface act as anchoring sites for $[\text{PtCl}_4]^{2-}$ anions and are responsible for the strong adsorption of Pt on the carbon support [44]. Wu et al. reported that the presence of nitrogen atoms improve the hydrophilic property of carbon nanotubes, facilitating the access of precursor to the active sites and anchoring these particles on the MWCNTs surface [50].

Fig. 5a represents the CO-stripping results of the Pt/MWCNTs-A and Pt/MWCNTs-U electrocatalysts in 0.5 M H$_2$SO$_4$ solution at a sweep rate of 50 mV/s. It can be understood that the presence of urea on the surface of MWCNTs decreases in the onset potential, from 553 mV for Pt/MWCNTs-A to 530 mV for Pt/MWCNTs-U. This can confirm the positive effect of adding urea in improving the bifunctional mechanism by facilitating the adsorption of OH groups [51]. In addition, the presence of nitrogen containing groups has decreased the tendency of Pt active sites in adsorbing poisonous species [51,52]. Since nitrogen atoms in MWCNTs-U have lower electronegativity than oxygen atoms in MWCNTs-A, the addition of urea can increase the electron density in Pt nanoparticles [49]. This matter can also weaken the CO$_{ads}$ groups bonds with the surface of platinum nanoparticles, resulting in an increase in the mobility and desorption of CO$_{ads}$ groups.

The results of cyclic voltammetry in a 0.5 M sulfuric acid electrolyte have been presented in Fig. 5b. Both curves demonstrate several features at different potential ranges: first, hydrogen adsorption and desorption peaks taking place between $-200$ mV and $100$ mV (Eq. (1)), second, the formation of surface Pt oxide species at the forward scan taking place between 600 mV and 900 mV (Eq. (2)), and third, the reduction of platinum oxides to Pt$^0$ observed at the cathodic peak centered at 500–600 mV (Eqs. (3–5)). Furthermore, the broad peak between 200 and 600 mV can be attributed to the formation of hydroxyl groups on the surface of support [53]. This peak intensifies by incorporation of urea into the support, indicating that the formation of OH$_{ads}$ groups is facilitated on MWCNTs-U. In fact, Girishkumar et al.
[54] reported that the formation of \( \text{OH}_{\text{ads}} \) groups, from dehydration of \( \text{H}_2\text{O} \), is favorable on surfaces with low work functions. Considering the reported reduction of work function on MWCNTs in the presence of nitrogen atoms [55], it can be concluded that the split of O-H bond in a water molecule is facilitated by the support of Pt/MWCNTs-U.

\[
\begin{align*}
\text{Pt} + \text{H}^+ + e^- & \Rightarrow \text{Pt-H}_{\text{ads}} \\
\text{Pt} + \text{H}_2\text{O} & \rightarrow \text{Pt(OH)} + \text{H}^+ + e^- \\
\text{Pt(OH)} + \text{H}_2\text{O} & \rightarrow \text{Pt(OH)}_2 + \text{H}^+ + e^- \\
\text{Pt(OH)}_2 & \rightarrow \text{PtO} + \text{H}_2\text{O} \\
\text{PtO} + 2\text{H}^+ + 2e^- & \rightarrow \text{Pt} + \text{H}_2\text{O}
\end{align*}
\]

By calculating the integrated area below the hydrogen desorption peaks in the range of \(-200 \text{ mV} \) to \(200 \text{ mV}\), it is possible to estimate the amounts of active surface area of Pt nanoparticles. Doing so, an increase in the ECSA of the electrocatalysts from \(27.8 \text{ m}^2/\text{mgPt}\) to \(36.0 \text{ m}^2/\text{mgPt}\) was observed upon the incorporation of urea to the support.

Table 1 presents the ECSA and geometrical surface area \(S_{\text{geo}}\) of Pt nanoparticles. The estimated \(S_{\text{geo}}\) was calculated using Eq. (6), assuming a spherical shape for platinum nanoparticles [56]:

\[
S_{\text{geo}} = \frac{6000}{(\rho \cdot d)}
\]

where \(S_{\text{geo}}\) is the geometrical surface area of Pt nanoparticles \((\text{m}^2/\text{gPt})\), \(\rho\) is the particle density \((21.4 \text{ g/cm}^3\) for platinum), and \(d\) is the average diameter of the nanoparticles, estimated from TEM micrographs. Table 1 indicates that the incorporation of urea has increased the roughness factor, \(R_A\), (i.e. ECSA/\(S_{\text{geo}}\)) of the synthesized electrocatalysts from 0.49 to 0.57 for Pt/MWCNTs-A and Pt/MWCNTs-U, respectively. In fact, the presence of nitrogen atoms in MWCNTs structure could increase the electron density on the surface of support, which

<table>
<thead>
<tr>
<th>Electro catalysts</th>
<th>Average Pt particle size ((\text{nm}))</th>
<th>(S_{\text{geo}}^{**}) ((\text{m}^2/\text{gPt}))</th>
<th>ECSA ((\text{cm}^2/\text{mgPt}))</th>
<th>(R_A) ((\text{ECSA}/S_{\text{geo}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MWCNTs-A</td>
<td>4.9</td>
<td>57.2</td>
<td>27.8</td>
<td>0.49</td>
</tr>
<tr>
<td>Pt/MWCNTs-U</td>
<td>4.4</td>
<td>63.7</td>
<td>36.0</td>
<td>0.57</td>
</tr>
</tbody>
</table>

* Estimated from TEM results.
** Calculated from Eq. (6).
facilities the metal reduction reaction (i.e. Pt) during the synthesis procedure, improving the total amount of ECSA [50].

Fig. 5c shows the cyclic voltammetry of the synthesized supports, i.e. MWCNTs-A and MWCNTs-U, in a 0.5 M solution of H$_2$SO$_4$. It is observed that the ionic conductivity of the electrocatalytic layers has increased dramatically as a result of incorporation of urea, as a nitrogen containing group. By considering the potential window of $-100$ mV to 1100 mV, the charge transfer for MWCNTs-A and MWCNTs-U was calculated to be 0.38 mC and 0.52 mC, respectively. This enhancement can be tailored to the superior hydrophilic properties of urea functionalized MWCNTs [50], which is completely along with the contact angle data (inset of Fig. 5c). According to the results presented here, the contact angle is increased from 144° to 156° upon participation of nitrogen containing molecules on the MWCNTs side walls, confirming higher hydrophilic properties of MWCNTs-U, in comparison to that of MWCNTs-A. The improved hydrophilicity of carbon supports in the presence of urea molecules can increase accessible surface area for water molecules. This matter may greatly improve the performance of Pt nanoparticles located in very small pores.

The results of cyclic voltammetry of the synthesized electrocatalysts in 1 M methanol and 0.5 M H$_2$SO$_4$ at 25 °C are presented in Fig. 5d. Each voltammogram shows two remarkable anodic peaks, one in the forward scan related to methanol electrooxidation reaction and the other in the backward scan representing the oxidation removal of the adsorbed CO-containing species from partial methanol oxidation reaction. Studying the peaks in the forward scan shows an increase in the current density of Pt/MWCNTs-U when compared to Pt/MWCNTs-A (515.3 mA/mg Pt and 378.6 mA/mg Pt, respectively). This matter indicates the positive effect of MWCNTs-U on the electrochemical performance of Pt nanoparticles in methanol electrooxidation, which is in good agreement with the ECSA data in Fig. 5b. Besides peak current density, the onset potential of methanol electrooxidation is another critical Index, indicating the electrocatalytic activity of electrode materials. Fig. 5d illustrates the decrease in the onset potential of methanol oxidation reaction from 492 mV for Pt/MWCNTs-A to 422 mV for Pt/ MWCNTs-U. Such a shift in the onset potential can indicate an enhancement in the kinetic of methanol electrooxidation at low potentials in the presence of urea [33]. The presence of nitrogen in the support facilitates the adsorption of water molecules on the support through bifunctional mechanism, in addition to decreasing the tendency of Pt nanoparticles in interacting with CO$_{ads}$ groups (Ligand Effect) [57,58], facilitating the oxidative removal of CO$_{ads}$-containing poisoning groups from active sites. Some works also suggest that the strong interaction between Pt nanoparticles and nitrogen containing supports can be accounted for the enhancement in the Pt activity observed in the forward scan [48,59]. As for the backward scan, the anodic peak observed in this scan of cyclic voltammograms can be attributed to the oxidation of intermediates, which have not been completely oxidized during the forward scan [60,61]. As an index for the ability of electrocatalysts in complete oxidation of methanol, the ratio of the peak current density in the forward to backward scan ($J_p/J_b$) has been tabulated in Table 2. The data presented in Table 2 shows that the presence of urea in the support can increase the ability of the electrocatalysts in the oxidative removal of poisoning species, which is in a good agreement with the CO-stripping results in Fig. 5a.

![Fig. 6. The Chronoamperometry results of the synthesized electrocatalysts in an electrolyte consisting of 0.5 M sulfuric acid and 1 M methanol at 600 mV and 25 °C.](https://reader.elsevier.com/reader/sd/pii/S0169433218328800?token=6E772019E8BFA81DCBD056469A8D0382A3B4EA9E0434C77676D4B75C81F4B5A)

Table 2: The effect of amide groups on the performance of CV graph in the presence of methanol.

<table>
<thead>
<tr>
<th>Electrocatalsys</th>
<th>$J_p$ (mA/mg Pt)</th>
<th>$J_b$ (mA/mg Pt)</th>
<th>$J_p/J_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/MWCNTs-A</td>
<td>378.6</td>
<td>474.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Pt/MWCNTs-U</td>
<td>515.3</td>
<td>569.3</td>
<td>0.97</td>
</tr>
</tbody>
</table>

$^1$ $J_p$: Forward peak current density.
$^2$ $J_b$: Backward peak current density.

Fig. 6 presents the effect of urea on the stability of the synthesized electrocatalysts in the form of chronoamperometry diagrams. In general, the gradual decrease observed in the performance of both synthesized electrocatalysts can be attributed to the gradual poisoning of platinum active sites due to the accumulation of CO containing group from partial oxidation of methanol molecules [62]. As calculated from Fig. 6, the decay ratio, the ratio of the current density at 5400 s to its values after 600 s ($J_{5400}/J_{600}$), in Pt/MWCNT-U reaches 0.26, which shows higher values when compared with the corresponding value for Pt/MWCNT-A ($J_{5400}/J_{600}$ = 0.16). The improvement of the decay ratio for Pt/MWCNT-U illustrates the positive role of nitrogen atoms in increasing the resistance of Pt nanoparticles to the poisoning intermediates resulted from methanol electrooxidation, which is in complete agreement with the CO-stripping results.

To further investigate the effect of nitrogen containing groups on the performance of MWCNTs, Linear Sweep Voltammetry (LSV) assay was performed in a solution containing 1 M methanol and 0.5 M H$_2$SO$_4$. Fig. 7a illustrates the LSV diagrams of Pt/MWCNTs-A and Pt/MWCNTs- U at 25 °C. A limiting current density in the LSV curves, achieved at overpotentials between 750 mV and 850 mV, could be explained by the oxidation of Pt atoms to PtO$_{4n}$ taking place at the same potential range (see also Fig. 5b). The peak current density in the LSV graphs increased from 78.9 mA/mg Pt to 115.8 mA/mg Pt by adding amide groups to the support structure. In addition, a decrease was also observed in the onset potential of LSV curves (Fig. 7a) in the presence of amide molecules on the MWCNTs surface, due possibly to higher activity of Pt nanoparticles on MWCNTs-U. In order to determine the exchange current density and Tafel slopes, the LSV plots have also been presented in the form of Tafel curves in Fig. 7b. Table 3 represents a summary of the theoretically estimated values of the kinetic parameters, such as Tafel slope and charge transfer coefficient. Each Tafel plot can be divided into two different linear regions with different slopes. Region I indicates the linear fit for Tafel graphs at low overpotentials (124 mV/dce to 129 mV/dce), while Region II represents its linear fit at high overpotentials (360 mV/dce to 377 mV/dce). It can be observed from Fig. 7b that the slopes of the linear fits to the Tafel plots in Region II are almost three times higher than Region I, indicating a clear change in the rate determining step of methanol electrooxidation reaction at different potential range.

It is suggested, from the calculated slopes, that dehydrogenation of methanol by cleavage of the first C-H bond is the rate determining step for Region I, while it changes to the oxidation of CO$_{ads}$ groups on the catalytic active sites in the second region [63,64]. The exchange current density related to electrode reactions on Pt/MWCNTs-A and Pt/
Fig. 7. (a) The results of LSV and (b) Tafel plot of Pt/MWCNTs-A and Pt/MWCNTs-U in an electrolyte containing 1 M methanol and 0.5 M H₂SO₄ at a scan rate of 1.25 mV/s at 25 °C.

Table 3
The kinetic parameters of MOR on the synthesized electrocatalysts.

<table>
<thead>
<tr>
<th>Electro catalysts</th>
<th>Low potentials region</th>
<th>High potentials region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tafel slope (mV/dec)</td>
<td>α</td>
</tr>
<tr>
<td>Pt/MWCNTs-U</td>
<td>124</td>
<td>0.46</td>
</tr>
<tr>
<td>Pt/MWCNTs-A</td>
<td>129</td>
<td>0.46</td>
</tr>
</tbody>
</table>

α: Charge transfer coefficient.
Iα: Exchange current density.

MWCNTs-U was calculated from Tafel equation, as follows:

\[
\eta = \frac{2.3RT}{2nF} \log(I) - \frac{2.3RT}{2nF} \log(I_0)
\]

where \( \eta \), \( I \), \( I_0 \), \( \alpha \), and \( T \) are defined as the electrode overpotential, current density, exchange current density, charge transfer coefficient, and absolute temperature, respectively. \( R \) is the global gas constant, \( F \) is the Faraday constant, and \( n \) is the number of electrons exchanges during the rate determining step. According to values in Table 3, the addition of urea into the MWCNTs structure results in remarkable increase in exchange current density changing from 1.59 × 10⁻⁸ A cm²⁻² to 2.12 × 10⁻⁸ A cm⁻², in the low potential region. The same trend was observed in the high potential region, indicating a higher exchange current density for supports containing nitrogen functional groups (3.24 × 10⁻⁸ A cm⁻²) in comparison with MWCNTs-A (4.62 × 10⁻⁸ A cm⁻²). These data confirm the improved electrochemical activity of the Pt nanoparticles both in methanol dehydrogenation reaction and CO₃⁻ oxide reaction in the presence of amide functionalized MWCNTs.

In order to estimate the activation energy of methanol electrooxidation reaction, the effect of temperature (K) on the exchange current density, \( I_0 \), was investigated in the form of Arrhenius curves in Fig. 8. Here, the exchange current densities were obtained by LSV data at five different temperatures from 15 °C to 55 °C. The linear trend observed in Arrhenius plots was along with what is expected from Arrhenius equation (Eq. (8)).

\[
E_a = -R \frac{d \ln(I_0)}{d(1/T)}
\]

The results indicated a decrease in the activation energy of methanol electrooxidation reaction upon addition of urea to the support. The decrease in the activation energy from 41.7 kJ/mol methanol to 38.8 kJ/mol methanol (for Pt/MWCNTs-A and Pt/MWCNTs-U, respectively) show the positive effect of the presence of nitrogen atoms into the support structure on the activity of the synthesized electrocatalysts towards methanol electrooxidation. These observations are in good agreement with the results of cyclic voltammetry and LSV and can be explained by higher CO tolerance of Pt/MWCNTs-U compared to Pt/MWCNTs-A, mainly as a result of enhanced bi-functional mechanism and ligand effect upon incorporation of amide functional groups into the support structure. Other parameters such as large ECSA, improved proton conductivity and high accessible surface area of Pt/MWCNTs-U should be also considered as other possibilities for superior electrocatalytic activity and stability of Pt/MWCNTs-U compared to Pt/MWCNTs-A.
4. Conclusion

In this paper, ura covalently grafted carbon nanotubes were employed as the support of Pt nanoparticles in methanol electrooxidation reaction. The TEM micrographs indicated slightly smaller platinum particle with a more uniform size distribution for Pt/MWCNTs-U in comparison with Pt/MWCNTs-A, due possibly to high hydrophilic properties of amide groups on MWCNTs-U. The electrochemical active surface area of Pt nanoparticles and the accessible surface area of the electrocatalytic layer both were improved remarkably upon the addition of ura into the support structure. Moreover, the formation kinetics of the chemisorbed hydroxyl groups produced from the split of water molecules, improved in the presence of ura in the support structure, resulting in an enhanced tolerance against CO-poisoning via bi-functional mechanism. In addition, the presence of amide functional groups on MWCNTs, in Pt/MWCNTs-U, led to a higher electrocatalytic activity and stability of Pt active sites in methanol electrooxidation reaction. In fact, the results of cyclic voltammetry assay suggest a 36% increase in electrocatalytic activity in MOR as ura incorporated into the support. These results were in a good agreement with ISV data, where the exchange current density and activation energy of methanol were correspondingly improved by $1.59 \times 10^{-4}$ A cm$^{-2}$ and 41.7 kJ mol$^{-1}$, in Pt/MWCNTs-A, to $2.12 \times 10^{-4}$ A cm$^{-2}$ and 38.8 kJ mol$^{-1}$ in Pt/ MWCNTs-U. Moreover, as ura was covalently bonded on MWCNTs, the Tafel slopes decreased at both low and high applied overpotential regions, where methanol first C bond cleavage and CO$_2$, adsorption to CO$_2$ are respectively supposed as the rate limiting steps.

References


