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Islam M. Al-Akraa Dr.

The British University in Egypt, islam.ahmed@bue.edu.eg

Yaser M. Asal Mr

The British University in Egypt, yasser.mohamed@bue.edu.eg

Aya A. Khalifa Ms.

The British University in Egypt, aya157868@bue.edu.eg

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A promising Modification of Pt Surfaces with CNTs for Decreasing Poisoning Impact in Direct Methanol Fuel Cells

Islam M. Al-Akraa*, Yaser M. Asal, Aya A. Khalifa

Department of Chemical Engineering, Faculty of Engineering, The British University in Egypt, Cairo 11837, Egypt

*E-mail: islam.ahmed@bue.edu.eg, islam0886@yahoo.com

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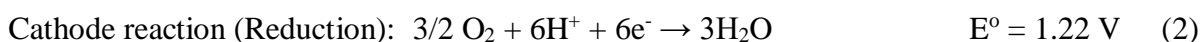
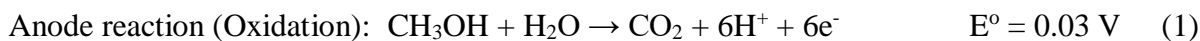
Direct methanol fuel cells (DMFCs) are clean energy sources that have many applications due to the high energy density of methanol as a fuel. However, this type of fuel cells (FCs) has limitations that are preventing it from being commercialized. One such limitation is the adsorption of intermediates such as CO into the surface of the Platinum (Pt) catalyst during methanol oxidation (MO) which deactivates its active sites, where the reaction is taking place, and leads to poisoning of the electrode over the long term. In this study, multi-walled carbon nanotubes (MWCNTs) have been introduced to the Pt-modified glassy carbon (Pt/GC) electrode aiming to improve MO efficiency. The results showed that MWCNTs could help in enhancing the electrocatalytic activity of the modified electrode which reflected from increasing the direct oxidation current, I_p^d , by a factor of 1.6. This increases the electrode' activity and durability during continuous electrolysis.

Keywords: Methanol oxidation; Fuel cells; Carbon nanotubes; Poisoning; Platinum.

1. INTRODUCTION

The need for clean and renewable energy sources continues to increase day by day as the planet suffers from the consequences of global warming. There is no doubt that global warming is happening and one of the main causes are the greenhouse gases emitted by the combustion of fossil fuels in order to provide electricity for powering vehicles and other machines [1, 2]. Greenhouse gases such as CO₂ and N₂O trap the heat coming from the sun and the more these gases are released into the atmosphere, the more heat they trap. Furthermore, we are running out of fossil fuels, the current oil and natural gas reserves are expected to last for about 50 years only [3]. Therefore, it has become necessary to look for more environment friendly energy sources. One of the reliable and green alternatives is the FCs [4-6].

Of which, direct methanol fuel cells (DMFCs) [7, 8]. DMFCs involve supplying an aqueous solution of methanol into the anode where methanol is oxidized into CO₂ releasing six protons that pass through the electrolyte membrane over to the other side and six electrons that pass through an external circuit to the cathode. At the cathode, air is supplied where the oxygen together with the six electrons and six protons is reduced into water vapor [9]. This is governed by two half reactions represented in the following equations:



Compared with the hydrogen fuel cells (HFCs), DMFCs are considered a more reliable alternative as methanol has a higher energy density compared to hydrogen and is easier to be transported and stored [10]. However, one of the main limitations of commercializing DMFCs is the poisoning of the Pt catalyst where CO is adsorbed which blocks the active sites of Pt [11, 12]. This reduces the surface area available for MO which in turn reduces the efficiency of the catalyst and diminishes the performance of the FC. In the long term, the electrode becomes less effective and eventually deactivated.

Electrocatalysis has been introduced to study and track such problems besides that of catalysis [13] and sensing [14]. Overcoming the CO poisoning in DMFCs occurred in different ways by modifying Pt with either a transition metal or metal oxide that could facilitate the oxidation of CO_{ads} at low overpotential or distorting the required Pt geometry for CO adsorption [15, 16]. According to the multiplet theory of catalysis by Balandin [17], a three contiguous Pt active sites are necessary for CO adsorption [13, 18, 19]. If this geometry is not available, the Pt-CO bonding would not form. The modifications of Pt surfaces with foreign atoms may change its electronic structure in the way weakening the CO adsorption, enhancing the oxidative removal of CO_{ads} or improving MO.

In this study, we tried to modify the GC electrode, as a support, with platinum nanoparticles (PtNPs) and further with MWCNTs, that have a high chemical stability, high electrical conductivity and most importantly a high surface area [20], (this electrode will be abbreviated as Pt@CNTs/GC) in order to decrease the poisoning impact and in turns increase the activity and stability towards MO. The electrode morphology will be monitored by a scanning electron microscope (SEM).

2. EXPERIMENTAL

2.1. Electrodes' preparation

A spiral Pt wire and a saturated calomel electrode (SCE) electrodes served as the counter and reference electrodes, respectively. The working electrode used was a GC electrode with a 5.0 mm diameter. The electrode was subjected to mechanical cleaning with a smooth (no. 2000) emery paper, then polished with fine alumina powder using a microfiber cloth and then rinsed with double distilled water.

Next, two modified electrodes will be prepared. One is the Pt/GC electrode where 10 mC of PtNPs were deposited from 0.1 M Na₂SO₄ solution containing 1 mM H₂PtCl₆ at 0.1 V. The other is the Pt@CNTs/GC electrode where the GC surface is firstly modified with MWCNTs, as reported in literature [21, 22], and then with PtNPs as in the first electrode.

2.2. Electrochemical and Material characterization

The electrochemical measurements were carried out at room temperature (around 25 °C) in a three-electrode glass cell using a Bio-Logic SAS potentiostat (model SP-150) operated with EC-Lab software. The catalytic performance of the modified electrodes toward MO was investigated in 0.3 M methanol solution.

A Field-emission scanning electron microscope (FE-SEM) (FEI, QUANTA FEG250, ThermoFisher) was used to evaluate the morphology of the prepared modified electrodes.

3. RESULTS AND DISCUSSION

3.1. Electrochemical and material characterization

Figure 1 shows cyclic voltammograms (CVs) obtained at (a) Pt/GC and (b) Pt@CNTs-GC modified electrodes measured in 0.5 M H₂SO₄ at a potential scan rate of 100 mV s⁻¹.

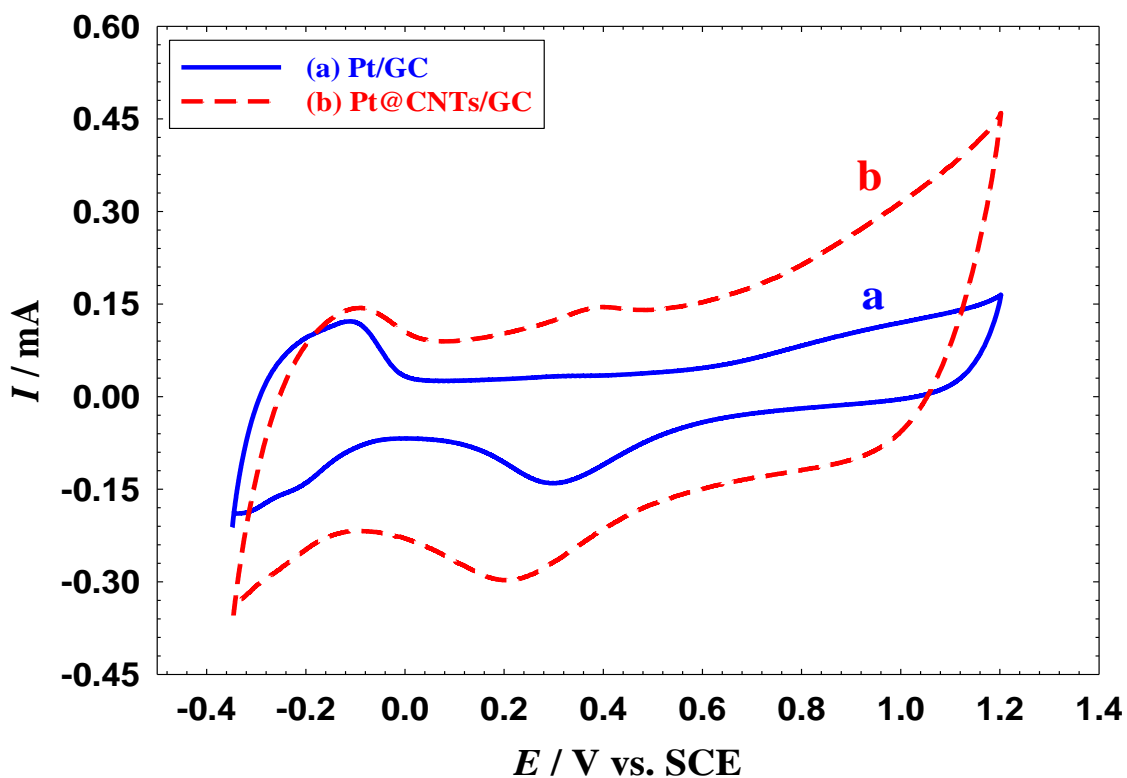


Figure 1. CVs obtained at (a) Pt/GC and (b) Pt@CNTs/GC modified electrodes in 0.5 M H₂SO₄ at a potential scan rate of 100 mV s⁻¹.

In both electrodes, the characteristic behavior of Pt has been observed [23, 24], where its oxidation is clearly occurring between 0.7 V and 1.2 V, whereas the reduction peak is obvious at 0.3 V in the backward scan. The hydrogen adsorption/desorption peaks also evidently located between 0 and -0.3 V.

When comparing the two curves, it is worth noting that there are four new observations upon the modification with MWCNTs (Fig. 1b). The first is increasing the double layer charging current. The second one is shifting the potential of the reduction peak of Pt by a value of 0.05 V. The third is the quinone/hydroquinone transformation peaks at ca. 0.4 V [25]. The last and the most important one is increasing the surface area of Pt, as which could be reflected from the Pt reduction peak at ca. 0.25 V, although we have deposited the same amount of Pt in both cases (5 μg). This could be explained by the presence of MWCNTs as a base network where the Pt atoms are embedded within, this greatly increases the surface area of Pt where the oxidation of methanol can take place.

Morphologically, Fig. 2 displays the FE-SEM images of Pt/GC (image a) and Pt@CNTs/GC (image b) electrodes respectively. In both images, spherical PtNPs could be observed with an average particle size of 95 nm. The difference is that in Fig. 2b, the PtNPs has been deposited in a non-aggregated form as a result of being deposited on the network of MWCNTs in the modified electrode.

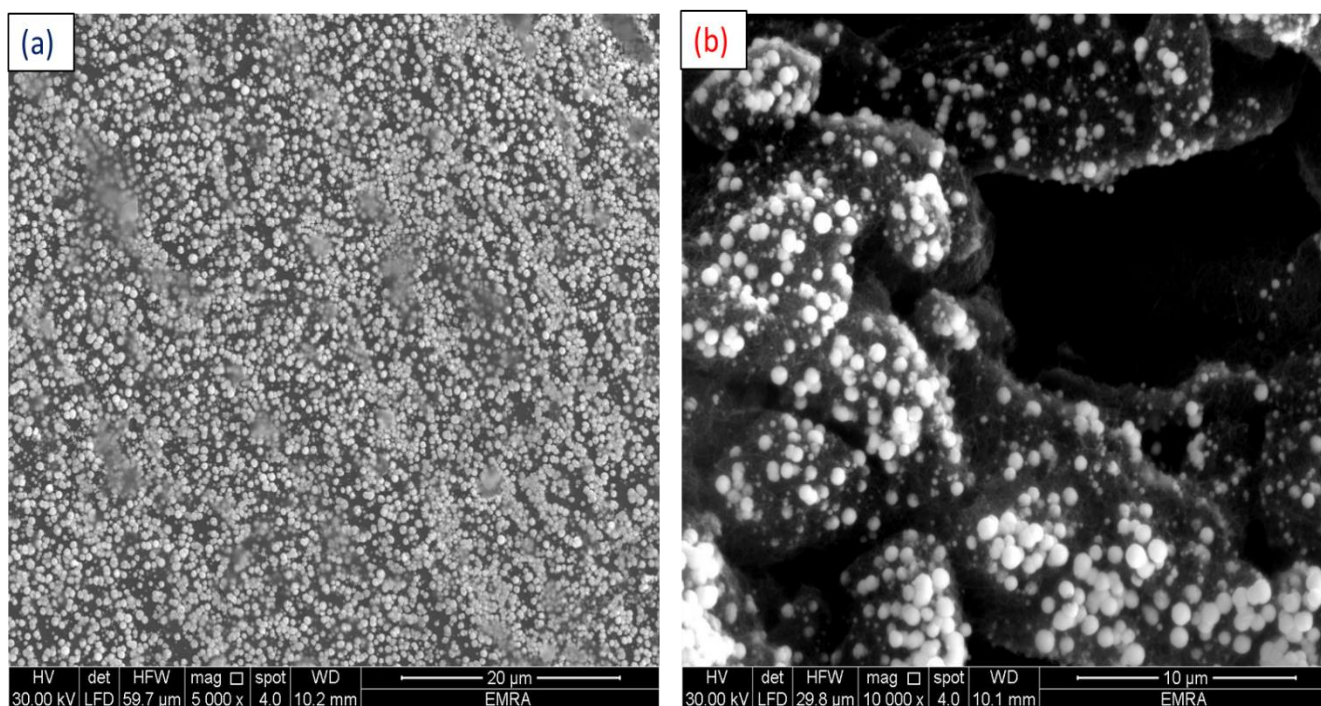
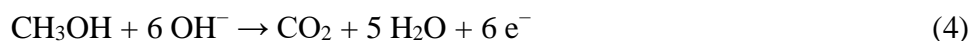


Figure 2. FE-SEM images of (a) Pt/GC and (b) Pt@CNTs/GC electrodes.

3.2. Electrocatalytic activity and stability towards Methanol Oxidation

CVs of MO at Pt/GC and Pt@CNTs/GC electrodes in 0.1 M NaOH containing 0.3 M CH_3OH solution are demonstrated in Figs. 3a and 3b respectively. Two oxidation peaks can be observed in each figure (one in the forward scan between 0.05 and 0.1 V and the other in the backward scan at -0.3 V)

as reported previously [26]. To clarify what is going on, the MO mechanism should be stated. The direct oxidation of Methanol, occurred at 0.1 V, in an alkaline medium is governed by the following reaction [27, 28]:



The current corresponds to this direct way indicated by I_p^d . Unfortunately, this process might be interrupted by the formation of intermediates such as CO (see Eq. 5) which deactivate the electrode [28]. The current corresponds to this poisoning way indicated by I_b .

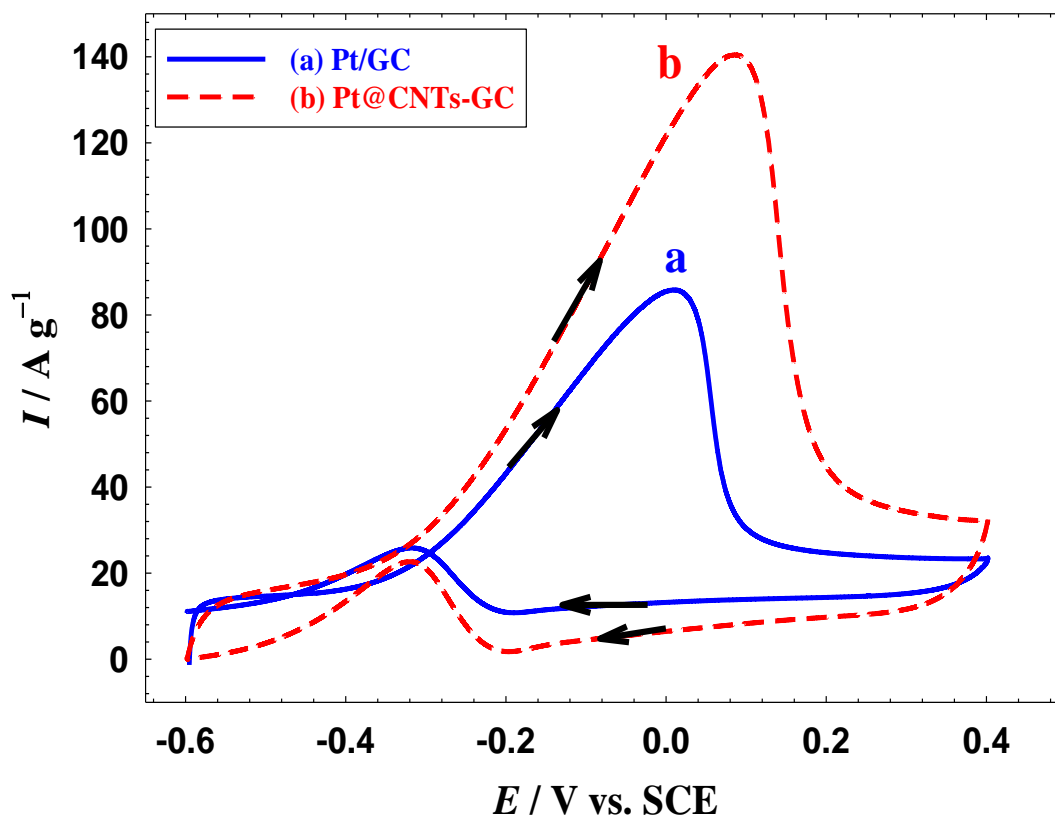
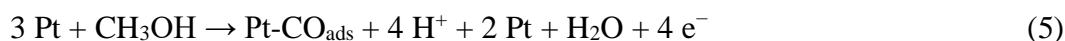


Figure 3. CVs obtained at (a) Pt/GC electrode and (b) Pt@CNTs/GC electrode in 0.1 M NaOH solution containing 0.3 M Methanol at a potential scan rate of 100 mVs^{-1} .

The ratio (I_p^d / I_b) is an indication of the ability of the electrode to resist CO poisoning and is important to track the electrode durability and electrocatalytic activity. The higher the ratio, the higher the resistance of the electrode [29, 30]. For the Pt/GC electrode, the I_p^d / I_b ratio was 3.3, while for the Pt@CNTs/GC modified electrode, the ratio increased to 6.1. This infers that the modified electrode is

1.85 times more effective in resisting the carbon monoxide poisoning. Also the I_p^d obtained at the Pt@CNTs/GC electrode is 1.6 higher than that obtained at the Pt/GC electrode, which indicates the increased rate of direct oxidation of methanol after the modification with CNTs. The I_p^d/I_b ratio obtained at the Pt@CNTs/GC electrode in this investigation is interestingly higher than that appeared in other previous publications [31, 32].

Moreover, Fig. 4 shows a stability test, in terms of measuring I_p^d with continuous cycling, during MO for each of the conventional and the modified electrodes. Stability was measured over 50 cycles and as can be seen, the current is slowly decays in the case of the Pt@CNTs/GC electrode (Fig. 4b) compared with its fast decay observed in the case of the conventional Pt/GC electrode (Fig. 4a).

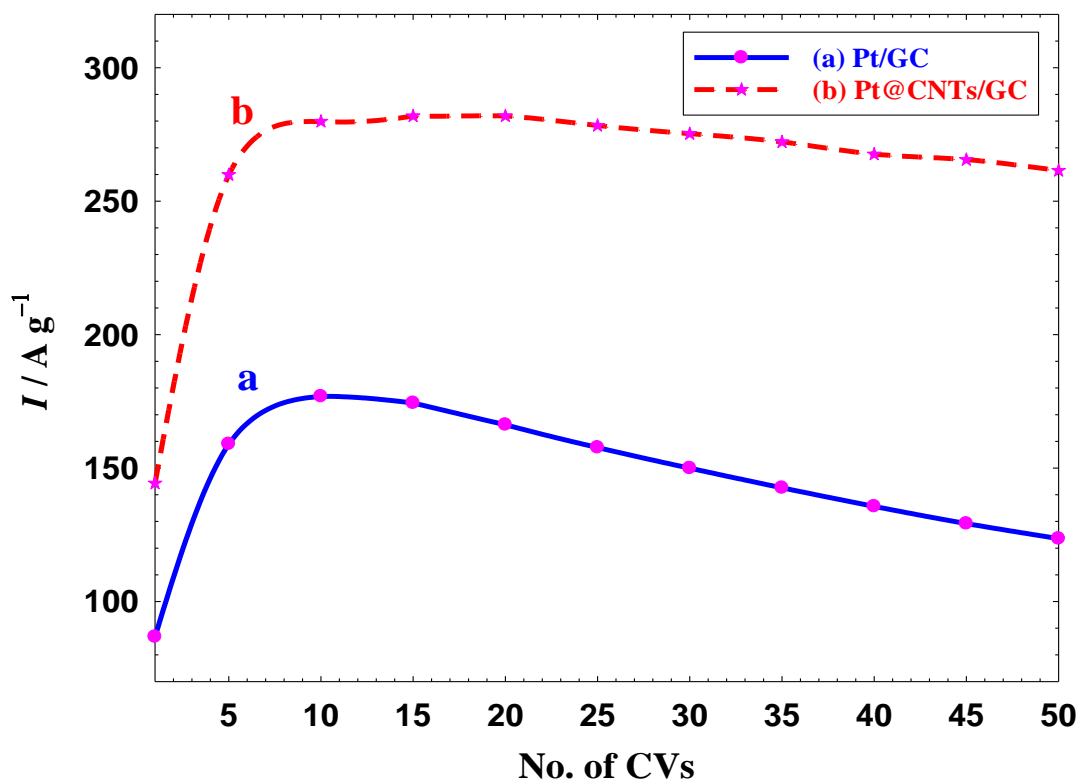


Figure 4. Stability measurement for MO at (a) Pt/GC electrode and (b) Pt@CNTs/GC modified electrode for 50 cycles.

The enhancement observed in Figs. 3 and 4 after the modification with CNTs could be described as follows [20]; the CNTs are introduced to the GC surface in the form of a network where the PtNPs can be deposited in. This additional step could increase the surface area of PtNPs which provides more active sites for the MO and so the I_p^d could be seen to increase. At the same time, this network allows the PtNPs to be deposited in a well-distributed and non-aggregated form which in turns may decrease the possibility of CO adsorption at the Pt surface and so the ratio I_p^d/I_b could be seen to increase [31]. This is beside the high electronic conductivity, good structural, mechanical and chemical stability and the high corrosion resistance in the fuel cell operating conditions of CNTs [33].

4. CONCLUSION

Overall, it may be concluded that the modified Pt@CNTs/GC electrode outperformed the conventional Pt/GC electrode in all areas of comparison. The I_p^d/I_b ratio obtained at the modified Pt@CNTs/GC was 1.85 times more tolerant to CO poisoning than its ordinary counterpart. It also showed that CNTs were able to improve the efficiency of the electrode, in terms of 1.6 increase in I_p^d , and its stability, in terms of lower current decay with continuous cycling. Therefore, it can be concluded that the modification with CNTs is an effective way to enhance the electrocatalytic efficiency towards MO and they're considered to be a good step in the commercialization of DMFCs.

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