



Highly active platinum nanoparticles supported by nitrogen/sulfur functionalized graphene composite for ethanol electro-oxidation



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ABSTRACT

In this study, Pt nanoparticles are deposited on the surface of nitrogen-sulfur functionalized reduced graphene oxide and mixed with double wall carbon nanotubes (Pt/NS-rGO/DWCNT). The obtained nanocomposite is used as an electrocatalyst for the ethanol electro-oxidation reaction (EOR). CO oxidation studies with differential electrochemical mass spectroscopy (DEMS) show a lower onset potential indicating higher poisoning tolerance of these materials. The electrocatalytic activity of the Pt/NS-rGO/DWCNT nanocomposite is studied at different temperatures (40, 50, 60, and 70 °C) and compared with that of Pt/rGO, Pt/rGO/DWCNT composites and commercial carbon-supported Pt catalyst. Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT display significantly higher ethanol electro-oxidation currents especially at low potentials relevant to fuel cell applications. At high temperatures (>50 °C), Pt/NS-rGO/DWCNT is the most active catalyst in concordance with its higher apparent activation energy. Pt/NS-rGO/DWCNT is also the most durable of the catalysts after a 500 potential cycle test and suffers the least from poisoning effects during chronopotentiometric testing. These results allow to conclude that combining NS-functionalized graphene catalyst support with DWCNT to form a composite provides excellent performances due to enhanced Pt electrocatalytic activity from NS-functionalization and enhanced mass transfer from the DWCNT filler.

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1. Introduction

Liquid-fed fuel cells, like the direct methanol fuel cell (DMFC), are very promising candidates as power sources of low-power electronic devices. However, methanol is toxic and it would be beneficial to replace it with less harmful ethanol (direct ethanol fuel cell, DEFC), which also has larger energy density. However, full electro-oxidation of ethanol is not a straight-forward reaction as it involves the scission of the carbon-carbon bond and therefore, new catalysts are sought to improve the kinetics of the reaction. Fuel cell catalysts are commonly composed of an active metal and its

carbonaceous support and their performance depends on the optimization of both the components. Thus, there are several alternatives for both components that have been studied lately [1–3].

Particularly, graphene has recently been proposed as a new catalyst support in fuel cells due to its high theoretical surface area and excellent electrical conductivity [4]. Graphene supported Pt and its alloys have been tested as alcohol electro-oxidation catalysts (methanol [5–10], ethanol [5–7,11–13], ethylene glycol [14]) resulting in better performances than with state-of-the-art carbon black supported catalysts. However, graphene itself has a strong tendency to stack [15], thus reducing the porosity of the catalyst layer and blocking the active catalyst particles. This problem can be mitigated by mixing the graphene with other carbon nanomaterials, like carbon nanotubes (CNT) [16], carbon

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nanofibers [17], mesoporous carbon [18], carbon black [19] or conducting polymers [20]. These materials can be located between graphene layers separating them and increasing the porosity of the catalyst. Thus, a highly porous and conductive 3D structure is formed with even distribution of metal particles on graphene surfaces. This is especially important when a fuel cell electrode is made, since its performance is highly dependent on the porosity of the catalyst layer allowing good access of the reactants to the active sites [21]. For example, Jhan et al. [22] grew carbon nanotubes directly between graphene sheets and formed Pt nanoparticles on this composite. With this catalyst at the anode of a DMFC, 30%, 63% and 70% higher power density than with commercial, blended graphene-CNT and graphene supports, respectively, were obtained. Similarly, Jha et al. [23] used a mixture of graphene and MWCNT to prepare both supported Pt and PtRu catalysts. However, no comparison was made to a commercially available catalyst. For ethanol electro-oxidation reaction (EOR) specifically, only one study has been made with graphene-CNT composite catalysts. Machado et al. [24] used Pd as the active metal with few-layered graphene and multi-walled carbon nanotube (MWCNT) support in alkaline medium and showed higher mass specific activity, electrochemically active surface area and DEFC performance with the composite compared to similar graphene supported catalyst. However, at the moment alkaline membranes for DMFCs and DEFCs are a limiting factor as their conductivity and durability is not as high as with acidic membranes [25]. No graphene-CNT composite support study has been made in acidic medium for EOR but several methanol electro-oxidation reaction (MOR) studies have shown high performances [22,23,26].

Another problem with graphene and other graphitic materials is their non-reactive surface, which makes attachment of catalyst particles difficult and lowers the stability of the catalyst [27]. One way to increase the binding energy of Pt to graphene is to dope it with heteroatoms, such as nitrogen [28] or sulfur [29]. This also results in a narrower particle size distribution for the Pt nanoparticles due to the anchoring effect of the heteroatoms [30–32] and it affects the activity of the metal directly by changing its electronic structure [33]. It has been demonstrated that nitrogen-doping can increase the EOR activity of metal catalyst supported on carbon materials. Previous studies have mostly focused on Pd and Pd alloys on N-doped carbon supports in alkaline environment [34–41] but few reports on improved Pt and Pt alloys performances

have also been reported, namely Pt on bamboo-shaped CNTs [42] and graphene [43], PtSn on CNTs [44,45] and carbon [46], and PtRu on few-walled carbon nanotubes [47]. Also, dual-doping mesoporous carbon with nitrogen and sulfur and using the material as Pt support yielded high MOR activity compared to Vulcan supported Pt [48].

As combinations of the previously described approaches for the enhancement of catalytic activity, few studies have been published recently considering MOR. Lv et al. [49] used PtRu supported by N-doped carbon nanotubes mixed with *in-situ* grown graphene in acidic conditions. They showed very promising results indicating lowered onset potential and several times higher current densities compared to a commercial and CNT-supported PtRu catalyst. Song et al. [50] doped graphene-CNT with nitrogen using ammonia precursor after Pd deposition and observed a reduction in Pd nanoparticle size. The resulting catalyst was 7.5 times more active than a commercial Pd/C and 1.7 times more active than undoped Pd composite towards MOR in alkaline conditions. Wang et al. [51] grew nitrogen-doped CNTs on graphene coated carbon cloth and deposited Pt on them. The doped catalyst version had 1.3 times higher peak current density for MOR than the undoped material but presented higher onset potential in acidic conditions.

Modification of graphene to improve its properties as carbon support material can also be done with covalent or non-covalent attachment of molecules and groups that act as spacers between graphene layers and as anchor sites for metal nanoparticles [52]. Highly efficient EOR catalysis has been achieved with graphene supported Pd and Pt catalysts for example with noncovalent attachment of poly(diallyldimethylammonium chloride) (PDDA) [53–55], dimethyldiallylammonium chloride (DMDAAC) [56], poly(3,4-ethylenedioxythiophene) (PEDOT) [57] and perylene tetracarboxylic acid [58] to graphene. Similar results with covalent attachment of amine [59], hexanediamine [60] and sulfonate groups [61] have also been shown.

In this work, we fabricate a novel graphene based composite catalyst for EOR based on the different methods described above. Reduced graphene oxide is functionalized with nitrogen and sulfur by thiol-ene click chemistry approach [62] and mixed with double-walled carbon nanotubes (DWCNT). This approach does not include pyrolysis step requiring specialized oven and temperatures over 700 °C in contrast to for example nitrogen and sulfur doping. Pt nanoparticles are deposited on this material and its performance

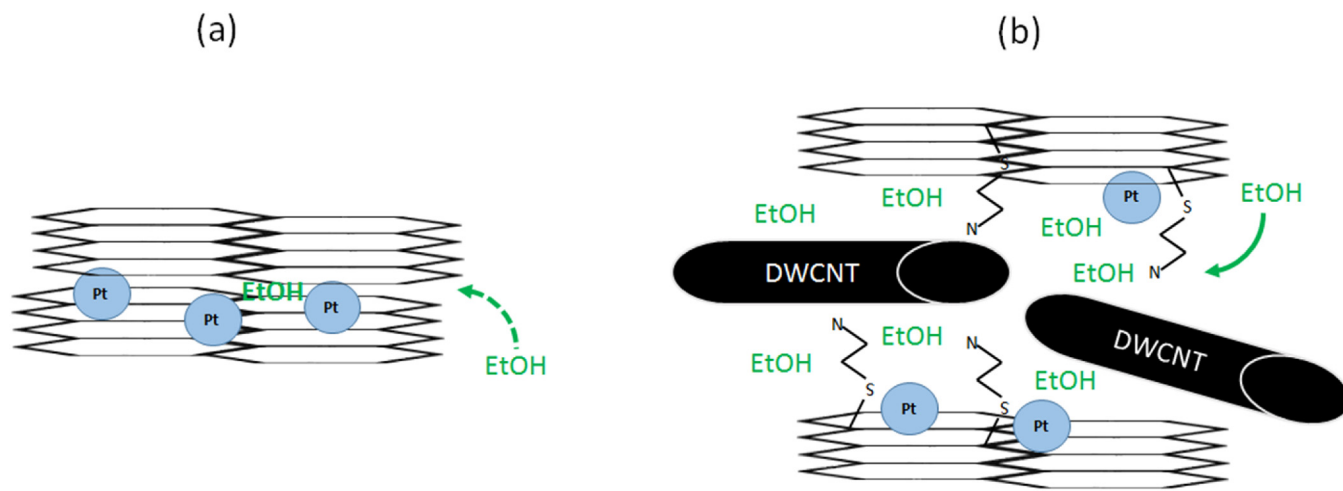


Fig. 1. The proposed mechanism on how grafting cysteamine on graphene and mixing it with DWCNT can improve the activity, stability and mass-transfer with ethanol electro-oxidation on Pt nanoparticles. The figure is not in scale. (a) Restacked graphene sheets hinder ethanol from reaching the active Pt nanoparticles. (b) DWCNT help to separate graphene sheets from each other allowing ethanol to easily reach Pt nanoparticles, while grafted cysteamine molecules function as anchoring sites for Pt nanoparticles.

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