



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Kanninen, Petri; Nguyen Dang, Luong; Sinh, Le Hoang; Flórez-Montaño, Jonathan; Jiang, Hua; Pastor, Elena; Seppälä, Jukka; Kallio, Tanja

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

Published in: Electrochimica Acta

DOI: 10.1016/j.electacta.2017.05.019

Published: 10/07/2017

Document Version Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

Published under the following license: CC BY-NC-ND

Please cite the original version:

Kanninen, P., Nguyen Dang, L., Sinh, L. H., Flórez-Montaño, J., Jiang, H., Pastor, E., Seppälä, J., & Kallio, T. (2017). Highly active platinum nanoparticles supported by nitrogen/sulfur functionalized graphene composite for ethanol electro-oxidation. *Electrochimica Acta*, *242*, 315-326. https://doi.org/10.1016/j.electacta.2017.05.019

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

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

Petri Kanninen^a, Nguyen Dang Luong^b, Le Hoang Sinh^{b,c}, Jonathan Flórez-Montaño^d, Hua Jiang^e, Elena Pastor^d, Jukka Seppälä^b, Tanja Kallio^a*

^aResearch Group of Electrochemical Energy Conversion and Storage, Department of Chemistry, School of Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.

^bLaboratory of Polymer Technology, Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland.

^cInstitute of Research and Development, Duy Tan University, R.809, K7/25 Quang Trung, Da Nang, Vietnam.

^dDepartamento de Química, Instituto de Materiales y Nanotecnología, Universidad de La Laguna, Avda. Astrofísico Francisco Sánchez s/n, 38206, La Laguna, Santa Cruz de Tenerife, Spain.

^eNanomicroscopy Center, Department of Applied Physics, Aalto University, P.O. Box 15100, FI-00076 Aalto, Finland.

^{*}Corresponding author. Tel: +358505637567, email: tanja.kallio@aalto.fi

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 electrooxidation 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 NSfunctionalization and enhanced mass transfer from the DWCNT filler.

Keywords

Graphene; carbon nanotube; nitrogen sulfur functionalization; platinum nanoparticles; ethanol electrooxidation

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 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 is compared with untreated composite, graphene and commercial Pt catalysts at several temperatures in conditions closely approximating those of a DEFC anode. Fig. 1 shows the suggested mechanism for improved EOR activity through the prevention of graphene restacking and anchoring of nanoparticles to heteroatoms. Further understanding of the reaction is achieved by studying CO poisoning applying differential electrochemical mass spectrometry (DEMS), as this adsorbate is formed during the EOR. Finally, electrocatalytic properties toward EOR and stability of the functionalized composite catalyst are established.

2. Experimental

2.1. Materials

Graphite flake (particle size $\leq 200 \,\mu$ m), sulfuric acid (95-97%), potassium permanganate (99+%), sodium nitrate (99.5%), hydrochloric acid (32%), perchloric acid (60%), hydrogen peroxide (30%), 1-propanol (\geq 99.5%), N,N-dimethylformamide (DMF), 2,2'-azobis(2-methyl propionitrile) (AIBN), cysteamine hydrochloride, ethylene glycol (99%) (EG), hydrazine hydrate (50-60%), sodium hydroxide (\geq 97%) and Nafion solution (5 wt%) were purchased from Sigma-Aldrich Co. Chloroplatinic acid hydrate (H₂PtCl₆·xH₂O) (38-40% Pt) was obtained from Acros Organics. Double-walled carbon nanotubes (DWCNT) were obtained from Nanocyl. Platinum (40 wt%) on high surface area advanced carbon support (HiSpec 4100TM) was purchased from Alfa Aesar. Ethanol (Etax Aa, 99.5%) was obtained from Altia Corporation. De-ionized (DI) water was used in the experiments.

2.2. Synthesis of NS-functionalized graphene oxide by thiol-ene click reaction

Graphite was oxidized to obtained graphite oxide using a modified Hummer's method, which is described in our previous study [63]. Graphite oxide was then exfoliated to obtain graphene oxide (GO). NS-GO was synthesized by a thiol-ene click reaction as reported before [62]. In brief, 100 mg of GO powder was dispersed in DMF solvent using ultrasonication for 30 min. This dispersion was charged in a threenecked round bottom flask equipped with a condenser, nitrogen inlet and a magnetic stirrer. A solution of AIBN and cysteamine hydrochloride was added to the reaction mixture. The reaction was carried at 70 °C for 12 h, after which it was cooled to room temperature. An excess amount of 1 M solution of NaOH was used to neutralize the HCl. The mixture was vacuum filtrated and washed first with ethanol and then with water to remove impurities. The NS-GO product was obtained after vacuum drying.

2.3. Synthesis of Pt/NS-rGO/DWCNT nanocomposite

A mixture of NS-GO (70 mg) and DWCNT (30 mg) was dispersed in EG with a solid content of 1.5 mg mL⁻¹. The dispersion was added to the flask reactor. Then, a solution of H₂PtCl₆ in EG was injected to the reaction mixture. The reaction mixture was heated to 140 °C and kept for 4 h to reduce Pt ions to metallic Pt nanoparticles. The mixture was then cooled down to room temperature and then 100 μ L of hydrazine hydrate solution (60%) was added. The temperature was raised to 95 °C for 1 h for further reduction. After cooling down to room temperature, the reaction mixture was precipitated in 200 mL of DI water. The precipitate was collected by centrifugation and washed with DI water (x 5 times). The Pt/NS-rGO/DWCNT composite was obtained after freeze-drying and subsequently vacuum drying at 60 °C.

Pt/rGO and Pt/rGO/DWCNT composites were prepared and used as references. Preparation of these two samples were similar to that of the Pt/NS-rGO/DWCNT composite. GO was used instead of

NS-GO in preparation of Pt/rGO/DWCNT composite and GO was used without DWCNT in the synthesis of Pt/rGO composite.

2.4. Physical characterization

Sample morphology and Pt nanoparticle distribution on the graphene were studied using a transmission electron microscope (TEM, JEOL JEM-2200FS). High resolution X-ray photoelectron spectroscopy (XPS, AXIS 165, Kratos Analytical) equipped with monochromated Al Kα irradiation at 100 W was used to confirm the composition of nitrogen and sulfur on the graphene. Platinum content of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.5. CO electro-oxidation with DEMS

Differential electrochemical mass spectrometry (DEMS) measurements were obtained with an electrochemical cell connected to a Pfeiffer-Vacuum mass spectrometer (Prisma QMS 200 detector) through a PTFE membrane (Scimat Ltd. 200/40/60). This membrane forms the interface between the electrochemical cell and the ionization chamber of the mass spectrometer. DEMS technique was used to follow the CO_{ad} electro-oxidation reaction. The experimental setup allows the simultaneous detection of mass spectrometric cyclic voltammograms (MSCVs) for a selected mass-to-charge ratio (m/z = 22, 44) corresponding to CO_2 production and cyclic voltammograms (CVs). Details of the method have been given elsewhere [64].

Shortly, the working electrode was prepared by deposition of a catalytic ink on a glassy carbon disc according to the method referenced except only water was used as the solvent because isopropanol dissolves the PTFE membrane which is used in the DEMS configuration. For each catalyst, ink is made

from 5 mg catalyst powder mixed with 200 μ L of water and 10 μ L Nafion® dispersion (5 wt%, Aldrich). A carbon counter electrode and a reversible hydrogen reference electrode (RHE) were used in the electrochemical cell. All potentials in this work are given against the RHE. The electrolyte solution was 0.1 M HClO₄. Electrochemical measurements were performed with an Autolab potentiostat-galvanostat (Metrohm). Before each measurement several voltammetric cycles were performed from 0.05 to 1.2 V at 0.1 V s⁻¹ for the activation of the catalyst. CO adsorption was performed by keeping the potential at 0.20 V first during 10 min with CO bubbling for adsorption and then 20 min with Ar bubbling for removal of free CO. Finally, CO stripping was achieved by a CV from 0.05 to 1.2 V at 0.005 V s⁻¹. Subsequently, a second CV was recorded to serve as a baseline for the clean Pt surface.

2.6. Ethanol electro-oxidation

Electrodes for the EOR characterization were made from a catalytic ink. 5 mg of the studied catalyst material was mixed with 1-propanol and deionized water with a magnetic stirrer for 5 min and then 10 μ l of 5 wt% Nafion solution was added. The ink was further mixed with a magnetic stirrer for several hours and sonicated for 15 min in between. A 4 μ L aliquot was placed on a polished glassy-carbon disc electrode (\emptyset 5 mm) and it was let to dry overnight in ambient conditions.

A three-electrode electrochemical cell was soaked with sodium permanganate solution overnight and washed with 5 wt% hydrogen peroxide solution and boiling water before measurements. The working electrode was the prepared glassy-carbon electrode attached to a rotating device, the counter electrode a coiled Pt wire and the reference electrode RHE. All the potentials reported in this study are given against the RHE. The electrolyte was a freshly prepared 0.1 M HClO₄ solution (Merck, 60 wt%) instead of H₂SO₄ in order to prevent sulfate adsorption to Pt [65]. The temperature of the cell was controlled at 20°C by a water sheath and a thermostat. The cell voltage and current were controlled with Autolab PGSTAT100 (Metrohm).

The catalyst was first cleaned with CO adsorption/stripping method by bubbling CO gas (Aga, 99.99%) through the electrolyte while cycling the potential between 0.05 and 0.25 V until the current stabilized. The electrolyte was then purged with N₂ gas (Aga, 99.999%) and potential swept to 1.2 V to oxidize the adsorbed CO. This process was repeated 4-8 times until the hydrogen adsorption/desorption region between 0.05 and 0.40 V was stable between consecutive CO cycles. A clean cyclic voltammogram was recorded for calculating the active area of the electrode from the hydrogen underpotential deposition (UPD) region by assuming 0.20 mC cm⁻² for the adsorption/desorption charge in HClO₄ [66]. All the measured EOR currents were normalized with this area. Subsequently, ethanol was added to 1 M concentration and its electro-oxidation was measured either at different temperatures or for 500 potential cycles.

In the temperature series, the catalyst was first aged for 30 potential cycles between 0.05 and 0.80 V. The upper limiting potential is low to resemble the conditions on a DEFC anode, where potentials are low for practical power generation. Subsequently, 3 cyclic voltammograms and a 600 s chronoamperometric curve at 0.5 V were recorded at 1800 rpm. The rotation was used also to mimic the flowing fuel solution in a DEFC. The measurements were repeated at 40, 50, 60 and 70°C. The third CV is reported in this work.

The durability of the electrode at 20°C was determined by cycling the potential between 0.05 and 0.80 V for 500 times at 50 mV s⁻¹ while evaluating the EOR current at 0.8 V. After 500 cycles, the electrolyte was replaced with pure 0.1 M HClO₄ and one CO cycle was repeated to clean the electrode and the changes in the electrochemically active area from H-UDP region were assessed.

Between the measurements, the potential of the working electrode was kept at 0.1 V and nitrogen was kept flowing through the cell.

3. Results and discussion

3.1. Material characterization

Thiol-ene click reaction is successfully carried for GO modification, which is confirmed by XPS. The obtained NS-GO contains approximately 1.5 at% of S and 1.5 at% of N [62]. In this study, we used the NS-GO as a substrate for Pt deposition and DWCNT as electrically conductive filler. Moreover, DWCNT is also used to prevent the restacking of NS-GO sheets during chemical reduction by ethylene glycol and hydrazine reducing agents.

TEM images of three composites in Fig. 2 show that Pt is successfully deposited on the surface of the functionalized graphene sheets. The average diameter of Pt nanoparticles for three samples are calculated from TEM images and are 5.0 ± 0.6 nm for Pt/rGO, 5.7 ± 0.7 nm for Pt/rGO/DWCNT and 4.6 ± 1.2 nm for Pt/NS-rGO/DWCNT. The size distributions are presented in Fig. S1 and the total Pt content in Table 2. Although the average sizes of the particles are overlapping within the error margins, the main difference between Pt/NS-rGO/DWCNT and the other catalysts is that it contains a significant amount of particles less than 4 nm in diameter. This could indicate that while Pt nanoparticles are formed on many different sites on the graphene, the particles formed on or near N or S sites are smaller. This is in agreement with previous studies with doped carbon supports [67-69].

The incorporation of DWCNT in the hybrid with graphene sheets can be seen in the TEM image in Fig. 3, which was taken at a region containing many graphene sheets. DWCNTs serve as spacers between the graphene layers, preventing them from restacking during reduction process. It was observed that with the addition of DWCNT in the reaction mixture for the preparation of the Pt/NS-rGO/DWCNT composite the final suspension remained stable, which was not the case without DWCNT. It can also be seen clearly that Pt nanoparticles deposit only on the graphene surface, while the DWCNT surfaces remains Pt-free (Fig. 3).

3.2. Electrochemical characterization

3.2.1. Cyclic voltammograms in acid solution

The CVs of each catalyst in 0.1 M HClO₄ are given in Fig. 4. The composite catalysts Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT show higher double layer charging currents between 0.45-0.70 V in the positive scan than the other catalyst indicating that mixing DWCNTs into the catalyst opens the electrode structure for larger contact area between the carbon and the electrolyte. The charging currents are especially high with Pt/NS-rGO/DWCNT probably due to increased porosity from the NS containing groups [60] or to the formation of defect sites on the rGO during grafting [70]. This should facilitate mass transfer in a fuel cell catalyst layer which is important for optimum performance [21].

3.2.2. CO tolerance studied by DEMS

Fig. 5 shows CO stripping experiments for the Pt/rGO catalyst recorded at two different temperatures (25 and 60 °C) in 0.1 M HClO₄ at 0.005 V s⁻¹. CO stripping voltammograms were obtained after bubbling CO through the cell for 10 min keeping the electrode in the bulk of the solution at 0.20 V, followed by Ar purging for 20 min to remove the excess of CO from the solution. The first cycle is characterized by the CO_{ad} oxidation peak, which is absent in the second cycle (Fig. 5A). The appearance of the hydrogen

adsorption/desorption peak at potentials lower than 0.3 V in the reverse scan and second cycle further confirm the complete oxidation of CO_{ad} in the first positive-going scan. Also, it is observed that the onset and peak potentials for CO oxidation reaction shift toward more negative values (around 0.2 V) with the increment of the temperature as expected for Pt [71]. This was true for all the tested catalysts as shown in Table 1.

The recorded mass spectrometric cyclic voltammograms (MSCVs) related to CO₂ formation are given in Fig. 5B. The signals for m/z = 22 (CO₂⁺⁺) and m/z = 44 (CO₂⁺), which are detected at the mass spectrometer, are both associated to the formation of carbon dioxide during the CO_{ad} electro-oxidation reaction and are almost completely superimposed. Fig. 5A and 5B clearly show a close correlation between faradaic and ionic currents confirming that the CO_{ad} oxidation reaction occurs between 0.2 - 1.2 V. Even more, due to the absence of interference associated to the double layer charging, oxide formation or other reactions, the MSCV allows for a better determination of the onset potential for the CO_{ad} electro-oxidation reaction. The shift of CO_{ad} oxidation reaction onset toward negative potentials with increasing temperature can thus be confirmed as the onset of ionic current signal shifts approximately 0.15 V lower. The same trend was observed for all the tested catalysts as shown from the onset and peak potential values summarized in Table 1.

Fig. 6 compares the stripping voltammetry observed for a CO saturated electrode for the three synthesized catalysts (Pt/rGO, Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT) at 60 °C. Fig. 6A shows the faradaic CO_{ad} stripping and the subsequent voltammogram obtained with the three electrocatalysts, while Fig. 6B shows the corresponding mass signal during the positive scan from m/z = 44 (assigned to CO₂ production). The CO_{ad} onset and oxidation peak potentials from the ionic signal at both 25 and 60 °C are given in Table 1.

CO peak	Onset		Pre-peak		Main peak	
Temperature	25 °C	60 °C	25 °C	60 °C	25 °C	60 °C
Pt/rGO	0.31	0.40		0.39	0.68	0.57
Pt/rGO/DWCNT	0.48	0.08		0.20	0.66	0.56
Pt/NS-rGO/DWCNT	0.25	0.10		0.26	0.75	0.60

Table 1. Onset and peak potentials of CO_{ad} electro-oxidation from DEMS CO_2^+ (m/z = 44) signal.

The Pt/rGO catalyst presents two different oxidation peaks at 0.55 and 0.61 V (Fig. 6A) during the CO-stripping voltammogram. On the other hand, Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT catalysts present a main CO oxidation peak at 0.55 and 0.59 V, respectively and an anodic pre-peak around 0.20 and 0.26 V respectively. The pre-peak cannot be discerned at 25 °C for any of the catalysts. The differing CO_{ad} stripping curves with multiple peaks for the different catalysts are related to the differing Pt nanoparticles they contain (Fig. 2) as CO_{ad} stripping has been shown to be very sensitive toward the Pt crystal structure [72].

From DEMS data (Fig. 6B), it can be observed that the pre-peak in the CV coincides with the rise of the m/z = 44 signal, which proves that the current density produced during the CO oxidation pre-peak is caused by the CO_{ad} oxidation to CO₂. Consequently, it is concluded that the current (ionic and faradaic) generated during the appearance of CO oxidation peak comes from the electro-oxidation of CO_{ad} to CO₂.

From these results (Fig. 6 and Table 1) differences in the CO tolerance of the catalysts can be established. Generally, it can be said the composite catalysts offer a significant reduction of the CO oxidation onset potential, especially at high temperature (0.3 V). At low temperature, no clear improvement results from the composite structure, although, NS-functionalization of rGO seems to lower

the onset potential compared to the untreated catalysts. This is likely due to changes in Pt – graphene interaction that can lower the activation energy of the catalyst and make its catalytic activity less sensitive to changes in temperature. The main CO oxidation peak also shifts to lower potentials as the temperature increases but NS-functionalization has a negative effect on its value: Pt/NS-rGO/DWCNT shows the highest oxidation peak potential and Pt/rGO/DWCNT the lowest. Finally, it has to be kept in mind that the lowering of the onset potential for CO_{ad} stripping is a very important feature for the oxidation of carbon containing substances (*e.g.* methanol, ethanol) as CO is one of the poisoning intermediates generated during their oxidation. For fuel cell applications, it is even more important as the oxidation of the fuel occurs at the anode where the potential should be low for high output voltage. Therefore, our composite catalysts are very promising for applications in energy conversion due to the low CO electrooxidation onset potential they exhibit.

3.2.3. Ethanol electro-oxidation

The applicability of the synthesized catalysts for a fuel cell reaction was tested with EOR. The CVs of each catalyst between 0.05 and 0.8 V at 20-70 °C and 1800 rpm in 1 M ethanol and 0.1 M HClO₄ solution are presented in Fig. 7. The current densities at 0.5 and 0.8 V as a function of temperature are presented in Fig. 8a-b and Table 2. The conditions were selected so that situation represents fuel cell anode conditions, in other words flow was maintained and the potentials kept low. It is observed that Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT perform better than Pt/rGO and Pt/C at all temperatures and potentials indicating the beneficial effect that the opening of the graphene structure by DWCNTs has. The performance of Pt/rGO is especially low at high current densities, which indicates mass transfer resistance in the electrode due to stacked rGO layers [15]. In the low potential region (<0.5 V) relevant to fuel cell applications, Pt/NS-rGO/DWCNT has the best performance emphasizing the combined beneficial effects of the DWCNT and NS-functionalization.

It is also noteworthy that Pt/rGO/DWCNT performs better than or equally well as Pt/NSrGO/DWCNT at low temperature (20-40°C) at high potential (>0.5 V). This is likely due to the fact that rGO stacking is enhanced through the local charges created by functionalization [73] which leads to hindered mass transfer for Pt/NS-rGO/DWCNT. However, as mass transfer is enhanced by increasing temperature, Pt/NS-rGO/DWCNT shows the highest EOR currents at 50-70 °C at all potentials. Another reason for the activity enhancement may be due to the small Pt particles (<4 nm) present in Pt/NSrGO/DWCNT that have different catalytic properties than larger particles in regards to adsorption of oxygenated species [74,75] and have been found to be most active for EOR at 25°C [76,77] and 90°C [78]. Similar enhancement effect against temperature was also described for PtRu on an N-doped CNTgraphene composite compared to an undoped catalyst in DMFC, where the maximum power density ratio between the catalysts (undoped/doped) decreased from 0.80 to 0.65 as the cell temperature was raised from 30 to 90 °C [49]. Another reason for the improved performance of Pt/NS-rGO/DWCNT at high temperatures can be noted by examining the onset potential region of the catalysts (insets in Fig. 7). At 20 °C, the onset potentials are roughly equal for all the catalysts but at 70 °C there is a clear improvement for Pt/NS-rGO/DWCNT compared to the other catalysts (~50 mV lower onset) indicating an activating effect between the NS-functionalized graphene support and Pt nanoparticle.

Table 2. Electrochemical properties of the catalysts.

Catalyst	Pt content	$EA_{\mathrm{H},0}{}^{a}$	$\mathrm{EA}_{\mathrm{H},500}^{\mathrm{b}}$	i _{0.5 V} 20°C	i _{0.5 V} 70°C	$E_{a,app,0.5V}{}^c$
	wt%	$m^2 g^{-1}$	$m^2 g^{-1}$	mA cm ⁻²	mA cm ⁻²	kJ mol ⁻¹
Pt/NS-rGO/DWCNT	42.3	27.3	25.3	0.038	0.088	36.3
Pt/rGO/DWCNT	40.9	26.7	24.0	0.037	0.066	29.3
Pt/rGO	46.3	28.6	24.8	0.029	0.043	29.8
Pt/C	39.4 ^d	38.0	25.5	0.020	0.036	28.4

^a Electrochemically active surface area of a fresh catalyst

 $^{\rm b}$ Electrochemically active surface area of a catalyst aged for 500 potential cycles between 0.05 and 0.8 V in 1 M ethanol and 0.1 M HClO₄

^c The apparent activation energy of ethanol electro-oxidation at 0.5 V.

^d From the manufacturer (Alfa Aesar)

Further analysis of the temperature dependency of the catalytic activity was done by studying the apparent activation energy ($E_{a,app}$) of EOR for each catalyst. $E_{a,app}$ was determined for the catalysts at different potentials from the cyclic voltammograms and are presented in Fig. 8c. Current values from the cathodic sweeps in Fig. 7 were used for the calculations to reduce the effect of poisoning intermediates on the Pt surface [79]. Pt/NS-rGO/DWCNT shows the highest activation energy values (46 to 28 kJ mol⁻¹ in the potential range from 0.45 to 0.8 V). The catalysts without NS-functionalization show similar activation energies from 32 to 23 kJ mol⁻¹ in this potential range. Generally, values between 20 and 50 kJ mol⁻¹ have been reported for $E_{a,app}$ of EOR on Pt supported on unfunctionalized carbon in acidic media [80-90], which are in good agreement with our results. $E_{a,app}$ for EOR at Pt supported on N-functionalized carbon or rGO-CNT composites has not been reported previously to best of our knowledge.

The large variance of the reported values is due to the sensitivity of the apparent activation energy to poisoning intermediates formed in EOR: measuring methods (positive and negative scans or steady-

state currents), potential ranges, electrolyte and catalyst nanostructure affect the values [79]. However, the fact that activation energy is higher with Pt/NS-rGO/DWCNT than with the untreated catalysts indicates that the NS-functionalization of the graphene support has a significant effect on the catalytic properties of the Pt nanoparticles because of increased interaction between the support and the nanoparticles [91]. Although NS-functionalization increases $E_{a,app}$, the catalytic activity of Pt/NS-rGO/DWCNT is excellent highlighting the importance of the improvement in the catalyst particle distribution (Fig. 2 and S2).

The change of $E_{a,app}$ with potential suggest to a potential dependent reaction mechanism. It has been shown that at low potentials ethanol dissociates to CO and CH_x on Pt and at high potential ethanol oxidizes to acetaldehyde and further to acetic acid [92]. Similar potential dependence was reported by Comignani [81] but also other potential dependencies have been observed, *e.g.* almost constant values (0.15-0.35 V vs SCE) [83] or increasing values with increasing potential (0.4-0.6 V vs Ag/AgCl) [88]. As with the absolute $E_{a,app}$ values, these differences are likely due to the differences in measuring methods, electrolyte and catalyst nanostructure.

The durability of the catalysts was studied by making 500 consecutive cyclic voltammograms between 0.05 and 0.8 V vs RHE and the oxidative current at 0.8 V relative to the first cycle as a function of the cycle number is presented in Fig. 8d. This high potential was chosen to make the differences between the catalysts clearer. However, the relative order of the catalysts is also the same at 0.5 V (not shown). All the synthesized catalysts show significantly better stability than the commercial alternative. After 500 cycles, only 50% of the current remains for Pt/C while 73%, 70% and 67% remains for Pt/NS-rGO/DWCNT, Pt/rGO/DWCNT and Pt/rGO, respectively. These results were confirmed by measuring the electrochemically active surface area (EA) of the catalysts after the cycling by replacing the electrolyte with 0.1 M HClO4. Before cycling, Pt/C had clearly the largest EA determined from H-UPD

region (Table 2), while the synthesized catalyst show similar EAs. However, after cycling the EA of Pt/C had dramatically decreased to a similar value with the synthesized catalysts. The order of the decrease was: Pt/C (-12.3 m² g⁻¹) > Pt/rGO (-3.8 m² g⁻¹) > Pt/rGO/DWCNT (-2.7 m² g⁻¹) > Pt/NS-rGO/DWCNT (-2.0 m² g⁻¹) indicating that both the mixing of DWCNTs and the NS-functionalization improve the stability of the Pt nanoparticles on graphene during EOR. In the former case, it is likely that DWCNT separate the particles further away from each other so that they do not coalesce as much as without [93] and in the latter, the anchoring effect of NS-groups stabilizes the nanoparticles [91].

Chronoamperometry at 0.5 V was measured to determine the tendency of catalyst poisoning (Fig. 9). Again, Pt/rGO/DWCNT and Pt/NS-rGO/DWCNT show highest currents as is expected from the cyclic voltammetry. At low temperatures, there is no decrease in the current due to the low currents and slow reaction rate, so that the generation of poisoning species is low. When the temperature is raised, steady decrease in current is recorded for all the catalysts. It is likely that a slow decrease would have been seen also at lower temperatures if the chronoamperometry was continued longer for larger amounts of poisoning species to be generated. Nevertheless, at high temperatures (50 and 70 °C) it can be seen that the current decrease is slower for Pt/NS-rGO/DWCNT indicating that NS-functionalization decreases the adsorption of poisoning products on Pt. This is in contrast with the CO_{ad} electro-oxidation results (Fig. 6 and Table 1) where Pt/rGO/DWCNT showed lowest CO oxidation potential at 60 °C, however, the difference was small (20 mV) and other poisoning intermediates are also created in EOR, *e.g.* CH_x fragments, which can display different temperature dependence [94].

4. Conclusions

NS-functionalized graphene prepared by thiol-ene click chemistry was prepared as a potential catalyst support for Pt nanoparticles combined with the use of DWCNT as a spacer and conductive filler material.

This functionalization does not require high temperature pyrolysis step and is a simple alternative to doping for introducing locally charged nucleation sites in graphene. DEMS studies with CO electro-oxidation demonstrated a significant decrease in its onset potential demonstrating its high resistance to poisoning. Further tests with ethanol electro-oxidation showed high activity especially at low potentials (<0.5 V vs RHE), which are relevant for fuel cell applications. The catalyst was also very stable during potential cycling and exhibited little tendency for poisoning from reaction products. Our results showed that both ethanol electro-oxidation activity and stability of graphene supported Pt catalysts can be improved by NS-functionalization and furthermore that using DWCNT as filler material enhances the mass transfer in stacked graphene layers. This makes the catalyst a highly promising candidate as anode catalyst for direct ethanol fuel cells.

Acknowledgements

Aalto Multidisciplinary Institute of Digitalisation and Energy (MIDE), Jane and Aatos Erkko Foundation, Academy of Finland as well as Project BIOGRAF from Fundación Cajacanarias (Spain) are acknowledged for funding of this research. Mr. Hannu Revitzer is thanked for help in platinum content analysis. This work made use of the facilities of Nanomicroscopy Center at Aalto University (Aalto-NMC) and RaMI RawMaterial infrastructure.

References

[1] E. Antolini, Carbon supports for low-temperature fuel cell catalysts, Appl. Catal., B 88 (2009) 1.

[2] S. Sharma, B.G. Pollet, Support materials for PEMFC and DMFC electrocatalysts—A review, J. Power Sources 208 (2012) 96.

[3] A. Brouzgou, A. Podias, P. Tsiakaras, PEMFCs and AEMFCs directly fed with ethanol: a current status comparative review, J. Appl. Electrochem. 43 (2013) 119.

[4] E. Antolini, Graphene as a new carbon support for low-temperature fuel cell catalysts, Appl. Catal. , B 123–124 (2012) 52.

[5] L. Dong, R.R.S. Gari, Z. Li, M.M. Craig, S. Hou, Graphene-supported platinum and platinum– ruthenium nanoparticles with high electrocatalytic activity for methanol and ethanol oxidation, Carbon 48 (2010) 781.

[6] C. Kung, P. Lin, Y. Xue, R. Akolkar, L. Dai, X. Yu, C. Liu, Three dimensional graphene foam supported platinum–ruthenium bimetallic nanocatalysts for direct methanol and direct ethanol fuel cell applications, J. Power Sources 256 (2014) 329.

[7] F. Li, Y. Guo, T. Wu, Y. Liu, W. Wang, J. Gao, Platinum nano-catalysts deposited on reduced graphene oxides for alcohol oxidation, Electrochim. Acta 111 (2013) 614.

[8] Y. Xin, J. Liu, X. Jie, W. Liu, F. Liu, Y. Yin, J. Gu, Z. Zou, Preparation and electrochemical characterization of nitrogen doped graphene by microwave as supporting materials for fuel cell catalysts, Electrochim. Acta 60 (2012) 354.

[9] K. Kakaei, M. Zhiani, A new method for manufacturing graphene and electrochemical characteristic of graphene-supported Pt nanoparticles in methanol oxidation, J. Power Sources 225 (2013) 356.

[10] H. Chang, Y. Tsai, C. Cheng, C. Lin, P. Wu, Preparation of graphene-supported platinum nanoparticles in aqueous solution by femtosecond laser pulses for methanol oxidation, J. Power Sources 239 (2013) 164.

[11] D. Chen, Y. Zhao, Y. Fan, X. Peng, X. Wang, J. Tian, Synthesis of Ni@PbPt supported on graphene by galvanic displacement reaction for improving ethanol electro-oxidation, J. Mater. Chem. A 1 (2013) 13227.

[12] L. Rao, Y. Jiang, B. Zhang, Y. Cai, S. Sun, High activity of cubic PtRh alloys supported on graphene towards ethanol electrooxidation, Phys. Chem. Chem. Phys. 16 (2014) 13662.

[13] F. Ren, H. Wang, C. Zhai, M. Zhu, R. Yue, Y. Du, P. Yang, J. Xu, W. Lu, Clean Method for the Synthesis of Reduced Graphene Oxide-Supported PtPd Alloys with High Electrocatalytic Activity for Ethanol Oxidation in Alkaline Medium, ACS Appl. Mater. Interfaces 6 (2014) 3607.

[14] J. Lv, S. Li, J. Zheng, A. Wang, J. Chen, J. Feng, Facile synthesis of reduced graphene oxide supported PtAg nanoflowers and their enhanced electrocatalytic activity, Int. J. Hydrogen Energy 39 (2014) 3211.

[15] R. Zacharia, H. Ulbricht, T. Hertel, Interlayer cohesive energy of graphite from thermal desorption of polyaromatic hydrocarbons, Phys. Rev. B 69 (2004) 155406.

[16] Y. Wang, S. Yang, S. Li, H. Tien, S. Hsiao, W. Liao, C. Liu, K. Chang, C.M. Ma, C. Hu, Threedimensionally porous graphene–carbon nanotube composite-supported PtRu catalysts with an ultrahigh electrocatalytic activity for methanol oxidation, Electrochim. Acta 87 (2013) 261.

[17] C. Wang, H. Gao, H. Li, Y. Zhang, B. Huang, J. Zhao, Y. Zhu, W.Z. Yuan, Y. Zhang, Graphene nanoribbons hybridized carbon nanofibers: remarkably enhanced graphitization and conductivity, and excellent performance as support material for fuel cell catalysts, Nanoscale 6 (2014) 1377.

[18] J. Tang, T. Wang, X. Sun, Y. Hu, Q. Xie, Y. Guo, H. Xue, J. He, Novel synthesis of reduced graphene oxide-ordered mesoporous carbon composites and their application in electrocatalysis, Electrochim. Acta 90 (2013) 53.

[19] S. Park, Y. Shao, H. Wan, P.C. Rieke, V.V. Viswanathan, S.A. Towne, L.V. Saraf, J. Liu, Y. Lin, Y. Wang, Design of graphene sheets-supported Pt catalyst layer in PEM fuel cells, Electrochem. Comm. 13 (2011) 258.

[20] F. Jiang, Z. Yao, R. Yue, Y. Du, J. Xu, P. Yang, C. Wang, Electrochemical fabrication of long-term stable Pt-loaded PEDOT/graphene composites for ethanol electrooxidation, Int. J. Hydrogen Energy 37 (2012) 14085.

[21] P. Kanninen, M. Borghei, O. Sorsa, E. Pohjalainen, E.I. Kauppinen, V. Ruiz, T. Kallio, Highly efficient cathode catalyst layer based on nitrogen-doped carbon nanotubes for the alkaline direct methanol fuel cell, Appl. Catal., B 156–157 (2014) 341.

[22] J. Jhan, Y. Huang, C. Hsu, H. Teng, D. Kuo, P. Kuo, Three-dimensional network of graphene grown with carbon nanotubes as carbon support for fuel cells, Energy 53 (2013) 282.

[23] N. Jha, R.I. Jafri, N. Rajalakshmi, S. Ramaprabhu, Graphene-multi walled carbon nanotube hybrid electrocatalyst support material for direct methanol fuel cell, Int. J. Hydrogen Energy 36 (2011) 7284.

[24] B.F. Machado, A. Marchionni, R.R. Bacsa, M. Bellini, J. Beausoleil, W. Oberhauser, F. Vizza, P. Serp, Synergistic effect between few layer graphene and carbon nanotube supports for palladium catalyzing electrochemical oxidation of alcohols, J. Energy Chem. 22 (2013) 296.

[25] E.H. Yu, U. Krewer, K. Scott, Principles and materials aspects of direct alkaline alcohol fuel cells, Energies (Basel, Switz.) 3 (2010) 1499.

[26] C. Wang, H. Wang, C. Zhai, F. Ren, M. Zhu, P. Yang, Y. Du, Three-dimensional Au0.5/reduced graphene oxide/Au0.5/reduced graphene oxide/carbon fiber electrode and its high catalytic performance toward ethanol electrooxidation in alkaline media, J. Mater. Chem. A 3 (2015) 4389.

[27] Y. Zhou, K. Neyerlin, T.S. Olson, S. Pylypenko, J. Bult, H.N. Dinh, T. Gennett, Z. Shao, R. O'Hayre, Enhancement of Pt and Pt-alloy fuel cell catalyst activity and durability via nitrogen-modified carbon supports, Energy Environ. Sci. 3 (2010) 1437.

[28] H. Wang, T. Maiyalagan, X. Wang, Review on Recent Progress in Nitrogen-Doped Graphene: Synthesis, Characterization, and Its Potential Applications, ACS Catal. 2 (2012) 781.

[29] D. Higgins, M.A. Hoque, M.H. Seo, R. Wang, F. Hassan, J. Choi, M. Pritzker, A. Yu, J. Zhang, Z. Chen, Development and Simulation of Sulfur-doped Graphene Supported Platinum with Exemplary Stability and Activity Towards Oxygen Reduction, Adv. Func. Mat. 24 (2014) 4325.

[30] J. Park, S. Kim, Nitrogen Modified-Reduced Graphene Oxide Supports for Catalysts for Fuel Cells and Their Electrocatalytic Activity, J. Electrochem. Soc. 161 (2014) F518.

[31] M.H. Seo, S.M. Choi, E.J. Lim, I.H. Kwon, J.K. Seo, S.H. Noh, W.B. Kim, B. Han, Toward New Fuel Cell Support Materials: A Theoretical and Experimental Study of Nitrogen-Doped Graphene, ChemSusChem 7 (2014) 2609.

[32] Y. Zhao, Y. Zhou, R. O'Hayre, Z. Shao, Electrocatalytic oxidation of methanol on Pt catalyst supported on nitrogen-doped graphene induced by hydrazine reduction, J. Phys. Chem. Solids 74 (2013) 1608.

[33] J. Nakamura, T. Kondo, Support Effects of Carbon on Pt Catalysts, Top. Catal. 56 (2013) 1560.

[34] Y. Feng, D. Bin, K. Zhang, F. Ren, J. Wang, Y. Du, One-step synthesis of nitrogen-doped graphene supported PdSn bimetallic catalysts for ethanol oxidation in alkaline media, RSC Adv. 6 (2016) 19314.

[35] D. Hiltrop, J. Masa, A. Maljusch, W. Xia, W. Schuhmann, M. Muhler, Pd deposited on functionalized carbon nanotubes for the electrooxidation of ethanol in alkaline media, Electrochem. Commun. 63 (2016) 30.

[36] H. Jin, T. Xiong, Y. Li, X. Xu, M. Li, Y. Wang, Improved electrocatalytic activity for ethanol oxidation by Pd@N-doped carbon from biomass, Chem. Commun. 50 (2014) 12637.

[37] Y. Li, L. Yao, L. Zhang, A. Liu, Y. Zhang, S. Liu, Palladium nanoparticles supported on nitrogendoped carbon spheres as enhanced catalyst for ethanol electro-oxidation, J. Electroanal. Chem. 730 (2014) 65.

[38] Q. Liu, J. Fan, Y. Min, T. Wu, Y. Lin, Q. Xu, B, N-codoped graphene nanoribbons supported Pd nanoparticles for ethanol electrooxidation enhancement, J. Mater. Chem. A 4 (2016) 4929.

[39] Y. Qin, Z. Xiong, J. Ma, L. Yang, Z. Wu, W. Feng, T. Wang, W. Wang, C. Wang, Enhanced electrocatalytic activity and stability of Pd nanoparticles supported on TiO2-modified nitrogen-doped carbon for ethanol oxidation in alkaline media, Int. J. Hydrogen Energy (2016) http://dx.doi.org/10.1016/j.ijhydene.2016.09.060.

[40] P. Wu, Y. Huang, L. Zhou, Y. Wang, Y. Bu, J. Yao, Nitrogen-doped graphene supported highly dispersed palladium-lead nanoparticles for synergetic enhancement of ethanol electrooxidation in alkaline medium, Electrochim. Acta 152 (2015) 68.

[41] M. Zhang, Y. Li, D. Pan, Z. Yan, S. Meng, J. Xie, Nickel core-palladium shell nanoparticles grown on nitrogen-doped graphene with enhanced electrocatalytic performance for ethanol oxidation, RSC Adv. 6 (2016) 33231.

[42] Z. Zhu, J. Wang, A. Munir, H.S. Zhou, Electrocatalytic activity of Pt nanoparticles on bamboo shaped carbon nanotubes for ethanol oxidation, Electrochim. Acta 55 (2010) 8517.

[43] A. Navaee, A. Salimi, S. Soltanian, P. Servati, Facile one-pot synthesis of platinum nanoparticles decorated nitrogen-graphene with high electrocatalytic performance for oxygen reduction and anodic fuels oxidation, J. Power Sources 277 (2015) 268.

[44] X. Wang, H. Xue, L. Yang, H. Wang, P. Zang, X. Qin, Y. Wang, Y. Ma, Q. Wu, Z. Hu, Convenient immobilization of Pt–Sn bimetallic catalysts on nitrogen-doped carbon nanotubes for direct alcohol electrocatalytic oxidation, Nanotech. 22 (2011) 395401.

[45] H. Wang, Y. Ma, W. Lv, S. Ji, J. Key, R. Wang, Platinum-Tin Nanowires Anchored on a Nitrogen-Doped Nanotube Composite Embedded with Iron/Iron Carbide Particles as an Ethanol Oxidation Electrocatalyst, J. Electrochem. Soc. 162 (2015) H79.

[46] H. Wang, Q. Zhao, Q. Ma, PtSn nanoparticles supported on iron nanoparticles wrapped inside nitrogen-doped carbon for ethanol oxidation, Ionics 21 (2015) 1703.

[47] P. Kanninen, M. Borghei, J. Hakanpää, E.I. Kauppinen, V. Ruiz, T. Kallio, Temperature dependent performance and catalyst layer properties of PtRu supported on modified few-walled carbon nanotubes for the alkaline direct ethanol fuel cell, J. Electroanal. Chem. (2016) http://dx.doi.org/10.1016/j.jelechem.2016.10.019.

[48] Y. Chang, F. Hong, J. Liu, M. Xie, Q. Zhang, C. He, H. Niu, J. Liu, Nitrogen/sulfur dual-doped mesoporous carbon with controllable morphology as a catalyst support for the methanol oxidation reaction, Carbon 87 (2015) 424.

[49] R. Lv, T. Cui, M. Jun, Q. Zhang, A. Cao, D.S. Su, Z. Zhang, S. Yoon, J. Miyawaki, I. Mochida, F. Kang, Open-Ended, N-Doped Carbon Nanotube?Graphene Hybrid Nanostructures as High-Performance Catalyst Support, Adv. Func. Mat. 21 (2011) 999.

[50] H. Song, L. Yang, Y. Tang, D. Yan, C. Liu, S. Luo, Three-Dimensional Nitrogen-Doped Reduced Graphene Oxide–Carbon Nanotubes Architecture Supporting Ultrafine Palladium Nanoparticles for Highly Efficient Methanol Electrooxidation, Chem. Eur. J. 21 (2015) 16631.

[51] P. Wang, T. Kottakkat, M. Bron, Pt supported on Nanostructured NCNTs/RGO Composite Electrodes for Methanol Electrooxidation, ChemElectroChem 2 (2015) 1396.

[52] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril, K.S. Kim, Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications, Chem. Rev. 112 (2012) 6156.

[53] J. Shi, G. Yang, J. Zhu, Sonoelectrochemical fabrication of PDDA-RGO-PdPt nanocomposites as electrocatalyst for DAFCs, J. Mater. Chem. 21 (2011) 7343.

[54] Y. Fan, Y. Zhao, D. Chen, X. Wang, X. Peng, J. Tian, Synthesis of Pd nanoparticles supported on PDDA functionalized graphene for ethanol electro-oxidation, Int. J. Hydrogen. Energy 40 (2015) 322.

[55] Y. Li, L. Han, B. An, Y. Wang, L. Wang, X. Yin, J. Lu, Preparation of platinum catalysts supported on functionalized graphene and the electrocatalytic properties for ethanol oxidation in direct ethanol fuel cell, J. Mater. Sci. : Mater. Electron. 27 (2016) 6208.

[56] M. Zhang, J. Xie, Q. Sun, Z. Yan, M. Chen, J. Jing, A.M.S. Hossain, In situ synthesis of palladium nanoparticle on functionalized graphene sheets at improved performance for ethanol oxidation in alkaline media, Electrochim. Acta 111 (2013) 855.

[57] R. Yue, H. Wang, D. Bin, J. Xu, Y. Du, W. Lu, J. Guo, Facile one-pot synthesis of Pd-PEDOT/graphene nanocomposites with hierarchical structure and high electrocatalytic performance for ethanol oxidation, J. Mater. Chem. A 3 (2015) 1077.

[58] S. Li, H. Yang, Z. Dong, S. Guo, J. Zhao, G. Gou, R. Ren, J. Huang, J. Jin, J. Ma, The role of reducing agent in perylene tetracarboxylic acid coating on graphene sheets enhances Pd nanoparticleselectrocalytic ethanol oxidation, Catal. Sci. Technol. 3 (2013) 2303.

[59] A. Navaee, A. Salimi, Anodic platinum dissolution, entrapping by amine functionalized-reduced graphene oxide: a simple approach to derive the uniform distribution of platinum nanoparticles with efficient electrocatalytic activity for durable hydrogen evolution and ethanol oxidation, Electrochim. Acta 211 (2016) 322.

[60] F. Ren, K. Zhang, D. Bin, B. Yang, H. Wang, P. Yang, Z. Fei, Y. Du, Ultrafine Pd Nanoparticles Anchored on Porous 1,6-Hexanediamine-Functionalized Graphene as a Promising Catalyst towards Ethanol Oxidation in Alkaline Media, ChemCatChem 7 (2015) 3299.

[61] C. Sun, J. Tang, N. Brazeau, J. Wu, S. Ntais, C. Yin, H. Chou, E.A. Baranova, Particle size effects of sulfonated graphene supported Pt nanoparticles on ethanol electrooxidation, Electrochim. Acta 162 (2015) 282.

[62] N.D. Luong, L.H. Sinh, L. Johansson, J. Campell, J. Seppälä, Functional Graphene by Thiol-ene Click Chemistry, Chem. Eur. J. 21 (2015) 3183.

[63] M.U.M. Patel, N.D. Luong, J. Seppälä, E. Tchernychova, R. Dominko, Low surface area graphene/cellulose composite as a host matrix for lithium sulphur batteries, J. Power Sources 254 (2014) 55.

[64] O. Guillén-Villafuerte, G. García, M.C. Arévalo, J.L. Rodríguez, E. Pastor, New insights on the electrochemical oxidation of ethanol on carbon-supported Pt electrode by a novel electrochemical mass spectrometry configuration, Electrochem. Commun. 63 (2016) 48.

[65] C. Buso-Rogero, V. Grozovski, F. Vidal-Iglesias, J. Solla-Gullon, E. Herrero, J.M. Feliu, Surface structure and anion effects in the oxidation of ethanol on platinum nanoparticles, J. Mater. Chem. A 1 (2013) 7068.

[66] Q. Chen, J. Solla-Gullón, S. Sun, J.M. Feliu, The potential of zero total charge of Pt nanoparticles and polycrystalline electrodes with different surface structure: The role of anion adsorption in fundamental electrocatalysis, Electrochim. Acta 55 (2010) 7982.

[67] G. Wu, D. Li, C. Dai, D. Wang, N. Li, Well-Dispersed High-Loading Pt Nanoparticles Supported by Shell–Core Nanostructured Carbon for Methanol Electrooxidation, Langmuir 24 (2008) 3566.

[68] Y. Chen, J. Wang, H. Liu, R. Li, X. Sun, S. Ye, S. Knights, Enhanced stability of Pt electrocatalysts by nitrogen doping in CNTs for PEM fuel cells, Electrochem. Commun. 11 (2009) 2071.

[69] Q. Sun, S. Kim, Synthesis of nitrogen-doped graphene supported Pt nanoparticles catalysts and their catalytic activity for fuel cells, Electrochim. Acta 153 (2015) 566.

[70] M. Lillethorup, M. Kongsfelt, M. Ceccato, B.B.E. Jensen, B. Jørgensen, S.U. Pedersen, K. Daasbjerg, High- versus Low-Quality Graphene: A Mechanistic Investigation of Electrografted Diazonium-Based Films for Growth of Polymer Brushes, Small 10 (2014) 922.

[71] E. Herrero, B. Álvarez, J.M. Feliu, S. Blais, Z. Radovic-Hrapovic, G. Jerkiewicz, Temperature dependence of the COads oxidation process on Pt(1 1 1), Pt(1 0 0), and Pt(1 1 0) electrodes, J. Electroanal. Chem. 567 (2004) 139.

[72] P. Urchaga, S. Baranton, C. Coutanceau, G. Jerkiewicz, Electro-oxidation of COchem on Pt Nanosurfaces: Solution of the Peak Multiplicity Puzzle, Langmuir 28 (2012) 3658.

[73] G. Wu, R. Swaidan, D. Li, N. Li, Enhanced methanol electro-oxidation activity of PtRu catalysts supported on heteroatom-doped carbon, Electrochim. Acta 53 (2008) 7622.

[74] A. Gamez, D. Richard, P. Gallezot, F. Gloaguen, R. Faure, R. Durand, Oxygen reduction on well-defined platinum nanoparticles inside recast ionomer, Electrochim. Acta 41 (1996) 307.

[75] Y. Takasu, N. Ohashi, X.-. Zhang, Y. Murakami, H. Minagawa, S. Sato, K. Yahikozawa, Size effects of platinum particles on the electroreduction of oxygen, Electrochim. Acta 41 (1996) 2595.

[76] R. Juang, C. Hsieh, J. Hsiao, H. Hsiao, D. Tzou, M.M. Huq, Size-controlled platinum nanoparticles prepared by modified-version atomic layer deposition for ethanol oxidation, J. Power Sources 275 (2015) 845.

[77] X. Li, X. Qiu, H. Yuan, L. Chen, W. Zhu, Size-effect on the activity of anodic catalysts in alcohol and CO electrooxidation, J. Power Sources 184 (2008) 353.

[78] J. Perez, V.A. Paganin, E. Antolini, Particle size effect for ethanol electro-oxidation on Pt/C catalysts in half-cell and in a single direct ethanol fuel cell, J. Electroanal. Chem. 654 (2011) 108.

[79] J.L. Cohen, D.J. Volpe, H.D. Abruna, Electrochemical determination of activation energies for methanol oxidation on polycrystalline platinum in acidic and alkaline electrolytes, Phys. Chem. Chem. Phys. 9 (2007) 49.

[80] F. Colmati, E. Antolini, E.R. Gonzalez, Effect of temperature on the mechanism of ethanol oxidation on carbon supported Pt, PtRu and Pt3Sn electrocatalysts, J. Power Sources 157 (2006) 98.

[81] V. Comignani, J.M. Sieben, M.E. Brigante, M.M.E. Duarte, Carbon supported Pt-NiO nanoparticles for ethanol electro-oxidation in acid media, J. Power Sources 278 (2015) 119.

[82] B. Jin, H. Sun, M. Huang, L. Zhao, Ethanol Electro-oxidation on Novel Electrocatalyst PtVSnO2/C in Acidic Media, Electrochim. Acta 142 (2014) 223.

[83] E. Habibi, H. Razmi, Kinetics of direct ethanol fuel cell based on Pt-PoPD nano particle anode catalyst, Int. J. Hydrogen Energy 38 (2013) 5442.

[84] L. Zheng, L. Xiong, Q. Liu, K. Han, W. Liu, Y. Li, K. Tao, L. Niu, S. Yang, J. Xia, Enhanced electrocatalytic activity for the oxidation of liquid fuels on PtSn nanoparticles, Electrochim. Acta 56 (2011) 9860.

[85] J. Datta, S. Sen Gupta, S. Singh, S. Mukherjee, M. Mukherjee, Significant Role of Ru-Oxide Present in the Pt-Ru Alloy Catalyst for Ethanol Electro-Oxidation in Acid Medium, Mater. Manuf. Processes 26 (2011) 261.

[86] S. Sun, M.C. Halseid, M. Heinen, Z. Jusys, R.J. Behm, Ethanol electrooxidation on a carbonsupported Pt catalyst at elevated temperature and pressure: A high-temperature/high-pressure DEMS study, J. Power Sources 190 (2009) 2.

[87] L. Jiang, A. Hsu, D. Chu, R. Chen, Ethanol electro-oxidation on Pt/C and PtSn/C catalysts in alkaline and acid solutions, Int. J. Hydrogen Energy 35 (2010) 365.

[88] Z. Teng, Y. Wang, B. Wu, Y. Tang, T. Lu, Y. Gao, Relationship among the physicochemical properties, electrocatalytic performance and kinetics of carbon supported Pt catalyst for ethanol oxidation, Appl. Catal., B 84 (2008) 400.

[89] S. Sen Gupta, J. Datta, A comparative study on ethanol oxidation behavior at Pt and PtRh electrodeposits, J. Electroanal. Chem. 594 (2006) 65.

[90] H. Wang, Z. Jusys, R.J. Behm, Ethanol Electrooxidation on a Carbon-Supported Pt Catalyst: Reaction Kinetics and Product Yields, J. Phys. Chem. B 108 (2004) 19413.

[91] S. Pylypenko, A. Borisevich, K.L. More, A.R. Corpuz, T. Holme, A.A. Dameron, T.S. Olson, H.N. Dinh, T. Gennett, R. O'Hayre, Nitrogen: unraveling the secret to stable carbon-supported Pt-alloy electrocatalysts, Energy Environ. Sci. 6 (2013) 2957.

[92] S.C.S. Lai, M.T.M. Koper, Electro-oxidation of ethanol and acetaldehyde on platinum singlecrystal electrodes, Faraday Discuss. 140 (2009) 399.

[93] D. He, K. Cheng, T. Peng, M. Pan, S. Mu, Graphene/carbon nanospheres sandwich supported PEM fuel cell metal nanocatalysts with remarkably high activity and stability, J. Mater. Chem. A 1 (2013) 2126.

[94] J. Flórez-Montaño, G. García, O. Guillén-Villafuerte, J.L. Rodríguez, G.A. Planes, E. Pastor, Mechanism of ethanol electrooxidation on mesoporous Pt electrode in acidic medium studied by a novel electrochemical mass spectrometry set-up, Electrochim. Acta 209 (2016) 121.



Figure 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.



Figure 2. TEM images of the synthesized composites in our study taken at one-layer-thick graphene flakes: Pt/rGO (a-b), Pt/rGO/DWCNT (c-d), and Pt/NS-rGO/DWCNT (e-f). Scale bars are 100 nm (a-c) and 10 nm (d-f).



Figure 3. A TEM image of Pt/NS-rGO/DWCNT composite taken at multi-layer-thick graphene showing the presence of DWCNT.



Figure 4. Cyclic voltammograms of the different catalysts in 0.1 M HClO₄ after CO cleaning (v = 0.05 V s⁻¹). • Pt/NS-rGO/DWCNT, • Pt/rGO/DWCNT, • Pt/rGO, • Pt/C.



Figure 5. CO stripping on the Pt/rGO catalyst. **A)** CVs and **B)** MSCVs. Solid line: $m/z = 44 [CO_2^+]$ and dash line: $m/z = 22 [CO_2^{++}]$. 0.1 M HClO₄, v = 0.005 V s⁻¹. Temperature: 25 °C (black line) and 60 °C (red line).



Figure 6. CO stripping for Pt/rGO (black line), Pt/rGO/DWCNT (red line) and Pt/NS-rGO/DWCNT (blue line) catalysts in 0.1 M HClO₄ at 60 °C. Scan rate 0.005 V s⁻¹. A) Faradaic current and B) current calculated from CO_2^+ signal (m/z = 44).



Figure 7. Cyclic voltammograms of the catalysts between 0.05 and 0.8 V vs RHE at a) 20 °C, b) 40 °C, c) 50 °C, d) 60 °C and e) 70 °C in 1 M ethanol and 0.1 M HClO₄ (0.02 V s⁻¹). ■ Pt/NS-rGO/DWCNT,
Pt/rGO/DWCNT, ▲ Pt/rGO, ◆ Pt/C. The onset potential regions of the anodic scans are shown as insets. The electrodes were rotated at 1800 rpm.



Figure 8. Ethanol electro-oxidation performance and stability of the tested catalysts in 1 M ethanol and 0.1 M HClO₄ (1800 rpm). a) Currents as a function of the temperature at 0.5 V and b) at 0.8 V vs RHE. The currents are taken from the positive sweep of the cyclic voltammograms. c) Apparent activation energies ($E_{a,app}$) as a function of potential. d) The remaining relative current at 0.8 V vs RHE as function of potential cycle number between 0.05 and 0.8 V.



Figure 9. Chronoamperometric measurements at 0.5 V vs RHE at a) 20 °C, b) 40 °C, c) 50 °C, d) 60 °C and e) 70 °C in 1 M ethanol and 0.1 M HClO₄. ■ Pt/NS-rGO/DWCNT, ● Pt/rGO/DWCNT, ▲ Pt/rGO, ◆ Pt/C. The electrodes were rotated at 1800 rpm.