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Chapter

Platinum-Based Carbon Nanodots Nanocatalysts for Direct Alcohol Fuel Cells

Sandile Surprise Gwebu, Philiswa N. Nomngongo and Nobanathi W. Maxakato

Abstract

Platinum and its alloys are regarded as best nanocatalysts for the electro-oxidation of alcohol fuels especially in acidic conditions. The performance of nanocatalysts for alcohol fuel cells depends greatly on the support material. A good support material should have high surface area to obtain high metal dispersion. It should also bond and interact with the nanocatalysts to improve the activity of the overall electrode. Most importantly, the support material should offer great resistance to corrosion under the harsh fuel cell conditions. In this chapter, the use of carbon nanodots as support materials for Pt-Sn and Pt-TiO_2 nanoparticles is discussed. The electrochemical activity of Pt/CNDs, Pt-Sn/CNDs and Pt/CNDs-TiO_2 nanocatalysts was studied using cyclic voltammetry (CV) in acidic and alkaline conditions. Chronoamperometry (CA) was used to investigate the long-term stability of the nanocatalysts under the fuel cell environment. Electrochemical results demonstrated that binary Pt nanocatalysts are more active compared to monocatalysts. It was also observed that carbon nanodots are better support materials than carbon black. Blending carbon nanodots with titanium dioxide (a ceramic material) improves the corrosion resistance of the nanocatalyst. Cyclic voltammetry results also proved that alcohol electro-oxidation is enhanced in alkaline conditions.

Keywords: nanocatalyst, platinum, carbon nanodots, alcohol fuel cell, electrooxidation

1. Introduction

A fuel cell is an electrochemical device that transforms the chemical energy from a fuel into electrical energy through an electrochemical reaction without combusting the fuel [1, 2]. Fuel cell technology is one of the innovative future energy technologies all over the world. Fuel cells are environmentally friendly and more efficient than combustion engines. They operate at low temperatures quietly without vibration or noise; hence, can be used for both stationary and mobile applications. There are numerous types of fuel cells, classified according to the type of the electrolyte they use which governs the operating temperature and the catalyst suitable for those conditions.

Among the numerous types of fuel cells, direct alcohol fuel cells (DAFCs) are the most attractive using liquid and renewable alcohols (ethanol and methanol) as a

fuel [3]. DAFCs are a very promising type when fuel consumption and feed strategies are taken into consideration. Unlike hydrogen fuel cells, which have safety, storage, and distribution challenges, DAFCs employ a liquid fuel that can easily be kept and transported [4, 5]. The electro-oxidation of alcohol fuels occurs on the surface of the positive electrode (anode) whereas the reduction of oxygen takes place on the negative electrode (cathode). DAFCs electrodes are made of conductive support material with a high surface onto which platinum nanoparticles are deposited. Platinum is the best electrocatalyst for alcohol oxidation reactions (AORs) in acidic conditions, nonetheless, it is expensive and it can effortlessly be poisoned by the intermediates that are formed during the AORs [6]. For these reasons, novel catalyst materials and catalyst preparation methods are still key topics studied in alcohol fuel cells. The efficiency of the electrocatalyst nanoparticles depends on the support material and its morphology [7]. Carbon nanomaterials have been considered for use as support materials because of their large surface area, great electrical conductivity, tensile strength, good thermal stability, corrosion resistance, ease of recovery and recyclability [8, 9]. In this chapter, the electrochemical performance of Pt/CNDs, Pt-Sn/CNDs and Pt/CNDs-TiO_2 nanocatalysts is discussed. All the metal nanoparticles used in the studies reviewed were deposited on to the support materials by the alcohol reduction method.

2. Direct alcohol fuel cells (DAFCs)

DAFCs belong to either polymer electrolyte membrane (PEM) or alkaline fuel cells (AFCs) depending on the pH of the electrolyte. Low molecular weight alcohol fuels are more attractive compared to pure hydrogen because they can be handled and transported easily. The design of DAFCs is greatly simplified; no reformer or humidifier is required. **Figure 1** shows a simple illustration of DAFC components.

Electrochemical reactions take place in the catalyst layers, which are attached to the sides of the membrane. The catalyst layers are designed in a way that can facilitate the movement of protons, electrons and reactants. The membrane serves

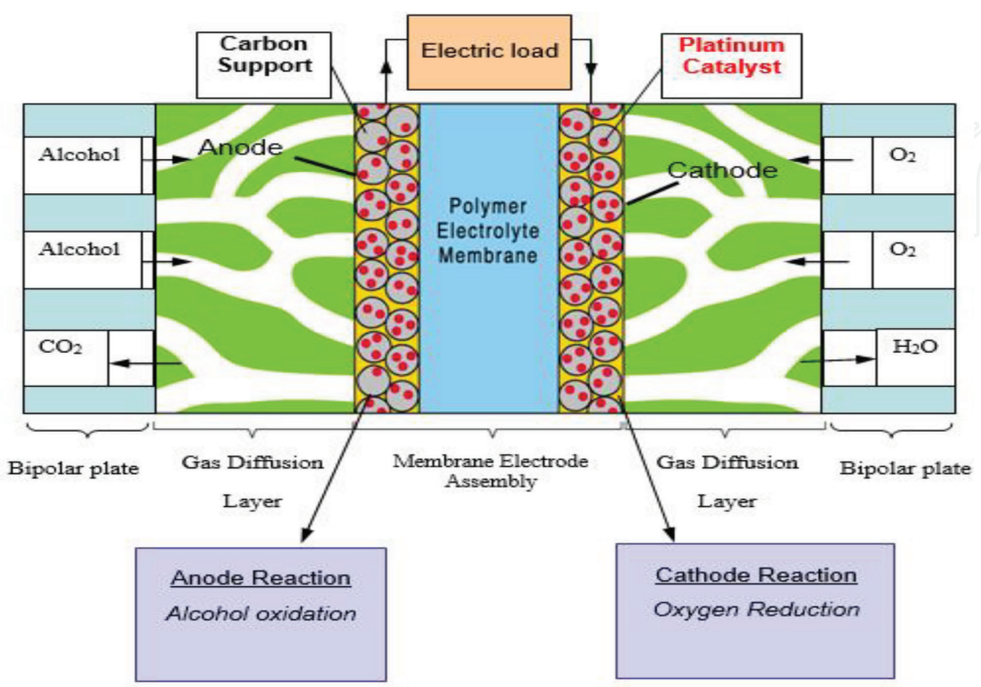


Figure 1.
Illustration of direct alcohol fuel cell components.

as an insulator for electrons and promotes the movement of protons from the anode to the cathode. The alcohol fuel is fed into the anode compartment where it gets oxidised, at the cathode side oxygen is reduced, both reactions produce electrons that migrate along the circuit and serves an electric load. The protons and other ions combine to form by-products, water and carbon dioxide.

The commercialisation of the DAFC technology has been hindered by (i) the inflated cost of the system, (ii) slow electro-oxidation reaction kinetics and fuel crossover. Platinum is the best electrocatalyst particularly in acid media, but it is very expensive. It is required in both electrodes of the fuel cell. Methanol is oxidised to produce CO, which poisons the platinum electrocatalyst. The poisoning of the platinum catalyst surface by carbon monoxide results in sluggish electro-kinetics of methanol electro-oxidation and this increases the rate of methanol crossover through the membrane. Carbon monoxide is the most stable intermediate formed during methanol electro-oxidation. It strongly adsorbs on the surface of the electrocatalyst, therefore preventing further methanol electro-oxidation. The removal of CO is the slowest reaction, hence, becomes the rate-limiting step. Ethanol is incompletely oxidised in acidic media producing intermediates such as CH_3CHO and CH_3COOH liberating only 2 and 4 electrons, respectively, in alkaline conditions it is selectively oxidised to acetate, this greatly reduces the overall fuel cell performance. Fuel crossover is a challenge, especially in acidic conditions. The simultaneous electro-oxidation of fuel and the reduction of oxygen at the cathode results in mixed potential and reduces the cell voltage. The fuel crossover also results in fuel wastage. In addition to this, the platinum surface gets poisoned by intermediates produced from alcohol electro-oxidation. All these factors diminish the overall fuel cell output.

2.1 Direct alcohol fuel cell working principle

At the anode side, alcohol fuel (methanol, ethanol) is oxidised with the aid of the electrocatalyst, generating electrons (e^-) and protons (H^+) according to the following equations:

In acidic conditions

$$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \quad (1)$$

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad (2)$$

In alkaline conditions

$$CH_3OH + 8OH^- \rightarrow CO_3^{2-} + 6e^- + 6H_2O \quad (3)$$

$$C_2H_5OH + 12OH^- \rightarrow 2CO_2 + 12e^- + 9H_2O \quad (4)$$

Electrons migrate to the cathode side through the external circuit, resulting in an electrical current. The protons diffuse to the cathode through the electrolyte and oxygen is reduced by these electrons to form anions, which react with the protons (H^+) to form water according to the following equations:

In acidic conditions

$$3O_2 + 12H^+ + 12e^- \rightarrow 6H_2O \quad (5)$$

In alkaline conditions

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \quad (6)$$

2.2 Support materials for fuel cell nanocatalysts

Support materials play a vital role in fuel cells as they strongly impact on the performance, stability and effectiveness of the electrocatalyst. Support materials can be classified as either primary or secondary. Primary supports are novel nanostructured carbon based such carbon nanotubes and carbon nanodots whereas secondary supports are metal oxides, which have been used mainly to modify, promote the primary supports and improve corrosion resistance. Corrosion of carbon support material is one of the major problems hindering the commercialization of direct alcohol fuel cells. A good support material must exhibit the following properties:

- High surface area to obtain maximum and uniform metal dispersion.
- Satisfactory electrical conductivity so that it can serve as a path for the movement of electrons.
- Suitable porosity to boost electrolyte flow.
- Electrochemical stability in the fuel cell environment.
- Availability and low cost.
- Suitable functional groups to enable bonding and interaction with the nanocatalysts to increase the activity and durability of the metal nanoparticles.

2.2.1 Carbon supports

Carbon is unique among all elements in the periodic table. It exists in radically different forms with variable micro-textures. This makes carbon an attractive material suitable for wide ranges of electrochemical applications [9]. Carbon is usually used for supporting nano-sized electrocatalyst particles for fuel cells owing to its excellent electrical conductivity, huge surface area, pore diameter and pore volume [10]. Carbon exists in many allotropic forms owing to its valency of 4 electrons. The most common types of carbon are carbon black, fullerenes, diamond, graphene and carbon nanotubes. Carbon black, graphene and carbon nanotubes have been extensively used as supports for fuel cell nanocatalysts. Carbon black is amorphous, usually contains spherical shaped graphite particles, characteristically with sizes below 50 nm. These particles combine to form aggregates and agglomerates with diameters around 250 nm [8]. Carbon black is mainly manufactured by the "furnace black" process, this process involves fractional oxidation of petrochemical or coal tar oils [11]. There are many varieties of carbon blacks, the most common types are vulcan XC-72, ketjen black and acetylene black. These carbon blacks exhibit good physicochemical properties such as surface functional groups, electrical conductivity, porosity and a reasonable amount of surface area. Carbon black is commonly used as electrocatalyst support material in fuel cells but still suffers from stability issues that reduce the electro-activity of the electrode [12, 13]. Carbon black is very unstable in highly acidic/alkaline media of a fuel cell, it gets corroded resulting in agglomeration and detachment of platinum catalyst, this decreases the overall fuel cell performance [14, 15].

Carbon nanotubes (CNTs) are cylindrical and hollow graphite layers with closed ends. They exist as either single wall or multi-walled nanotubes, with thicknesses of a few nanometres and lengths of about 1 mm [8]. A fascinating property of carbon nanotubes is their capability to capture other elements/nanocatalysts inside their wall structure. CNTs (single or multi-walled) are also used as catalysts supports in low-temperature fuel cells [16–19]. SWCNTs have huge surface areas whereas MWCNTs are better electrical conductors than SWCNTs [20]. CNTs have chemically unreactive surfaces making it difficult to deposit metal nanoparticles on their surfaces, hence, metal nanoparticles on CNTs generally have poor dispersion and large particle sizes, this decreases the electro-activity of the nanocatalyst [21]. Researchers have developed functionalisation methods in order to incorporate oxygen-containing groups on CNTs so as to improve their reactivity and interaction with nanocatalysts [15, 40]. These functionalisation methods include impregnation [22], acid treatment (such as a mixture of HNO_3 and H_2SO_4) [23, 24], polyol processing [25], ion-exchange [26] and electrochemical deposition [27].

Carbon nanofibers (CNFs) are industrially produced by the decomposition and graphitization of rich organic carbon-containing polymers. CNFs are also used as catalysts supports in fuel cells [28–30]. They have a thin cavity and some CNFs have no hollow cavity. CNFs are much thicker than CNTs. They can be classified into six types according to their structures which are; ribbon-like, platelet, herringbone, tubular, faceted tubular and faceted tubular multiwall [31]. Herringbone CNFs exhibit intermediate features of parallel and platelet types, thus providing higher catalytic activity and better durability than the other types [32].

The major difference between CNFs and CNTs is the exposure of reactive edge planes. Anchoring sites for the nanocatalysts resulting from the edge planes are exposed in CNFs while the basal planes are exposed in CNTs. Recent studies reveal that platinum electrocatalyst supported on CNFs show lower poisoning rates than platinum electrocatalyst supported on carbon black [31].

2.2.2 Carbon nanodots

Carbon nanodots (CNDs) are a newest type in the carbon nano family with particle diameters less than 10 nm. They were first obtained during the purification of SWCNTs through preparative electrophoresis in 2004 [33]. CNDs have gradually attracted too much attention because of their availability and inexpensive nature. Carbon nanodots core is sp^2 conjugated and it contains multiple oxygen moieties such as the carboxyl (—COOH), hydroxyl (—OH), and aldehyde (—COH) groups [34]. Synthesis of carbon nanodots can be categorised into two groups namely; top down (chemical) and bottom up (physical) methods [35, 36]. Top-down method employs treating starting materials such as graphitic powder or MWCNTs in harsh chemical conditions [36]. Bottom-up approaches include ultra-sonication [37], microwave pyrolysis [38] and hydrothermal treatment of small molecules such as starch [39], citric acid [40] glucose [37] and leeks [41]. Carbon nanodots used in the studies described in this chapter were prepared by the pyrolysis of oats grains [42]. Pyrolysis is a bottom up (physical) method.

In the same study we used the freshly prepared CNDs to deposit Pt nanoparticles. The prepared Pt/CNDs electrocatalyst outperformed the platinum nanoparticles supported on carbon black. Wei et al. prepared naked palladium nanoparticles supported on carbon nanodots for methanol electro oxidation. It was observed that freshly prepared CNDs act as reductants resulting in attachment of metal nanoparticles on their surfaces [37].

What makes carbon nanodots superior?

- They are easy to synthesise from various starting materials such as carbohydrates and waste carbonaceous sources such paper and avocado seed.

- No need to functionalise-they contain oxygen content of about 10% wt.
- Unlike carbon nanotubes, carbon nanodots are non-toxic and non-carcinogenic.
- They are biocompatible.
- Due to their small particle sizes (below 10 nm) they provide high surface area which enhances metal nanoparticle dispersion.
- Carbon nanodots also bond with the metal nanoparticles; thus, improving the interaction between the catalyst and the support material.

2.2.3 Inorganic support materials

Inorganic metal oxides such as TiO_2 [15, 43–47], WO_3 [48–50], CeO_2 [29, 30, 51], Al_2O_3 [52] SnO_2 [53] and MoO_3 [54] are very stable under the harsh fuel cell environment. These ceramic materials are not good conductors of electricity; hence, they can be only utilized as secondary support materials; they cannot be used on their own as nanocatalyst supports.

2.2.3.1 Titanium dioxide (TiO_2)

Titanium dioxide commonly referred to as "titania" is a naturally occurring oxide of titanium. Titanium oxides have been employed in numerous applications that depend on its photo-electrochemical, catalytic and outstanding corrosion resistance in both alkaline and acidic media. Titania generally exists in three major forms which are; anatase, rutile, and brookite crystallography. Each of these structures exhibits unique physical properties which make them suitable for different applications. It has been reported that the anatase crystallography is more effective as an electrocatalyst than rutile titania. The chemical and physical properties displayed by these crystallographic forms depend on the synthesis route [55]. Titanium dioxide nanoparticles can be produced by approaches such as the sol-gel technique [55, 56], microwave assisted hydrolysis [57], hydrothermal method [58], co-precipitation route [59], flame combustion method [60, 61] and chemical vapour deposition (CVD) [62].

3. Nanocatalysts for direct alcohol fuel cells

3.1 Platinum (Pt) electrocatalyst

Platinum monometallic catalyst has been widely used in fuel cells and has shown good results for both DMFC and DEFC in acidic media [63–69]. This is because platinum shows better activity, selectivity, stability and resistance to poison than other metals. Platinum catalyst allows chemical bonds to cleave but weakly enough to yield the product when the reaction has taken place, this is a required property for a good heterogeneous catalyst [70]. However, the crystalline orientation of platinum is a very important factor that governs the activity and poisoning rates of the electrode.

Platinum crystallises in face-centred cubic structure (FCC) and the shape of the resulting facet is predicted using Wulff's rule [71]. The surface energy increases as follows; Pt (111) < Pt (110) < Pt (100). The (111) orientation is the energetically

favourable growth plane of platinum crystals. Polycrystalline platinum is prone to oxidation due to the symmetric polycrystalline structure. Reactant molecules adsorb strongly on the Pt (111) orientation, hence, it has a lower electrocatalytic activity compared to the Pt (110) and Pt (100) orientations. On the other hand, Pt (111) orientation has a lower poisoning rate than the Pt (110) and Pt (100) orientations [72, 73]. The desired crystal orientations can be obtained by adding a shape-directing agent to modify the crystallisation process. Many researchers have reported that platinum is the best electrocatalyst in acidic media. However, contrary results have been observed when using carbon nanodots as supports. It was observed that the Pt/CNDs electrocatalyst in alkaline media yields more current compared to acidic conditions as can be seen from **Figure 2**.

Gwebu et al. [42] went on to study the electro-oxidation of ethanol on the Pt/CNDs electrode in both acidic and alkaline solutions. A similar trend was observed; high current densities were recorded in alkaline conditions. The results are shown in **Figure 3**.

3.2 Platinum-tin (Pt-Sn) electrocatalyst

Researchers have demonstrated that tin (Sn) enhances the electrocatalytic performance of platinum towards ethanol oxidation and works even better than ruthenium. Among the platinum-based binary catalysts, the Pt-Sn/C electrocatalyst is the most promising for EOR; due its low cost, and high current densities at low potentials. Neto et al. [3] synthesised Pt-Sn/C and Pt-Ru/C by the alcohol reduction process using water and ethylene glycol as the solvent and reducing agent respectively. The activity for methanol and ethanol electro-oxidation was studied at room temperature. The Pt-Sn/C electrocatalyst yielded current values higher than those of Pt-Ru/C for both ethanol and methanol oxidation. The superior activity of the Pt-Sn/C nanocatalyst is brought by the "bifunctional" mechanism where Sn provides oxygen-containing species to react with the CO poisoning intermediates on the platinum sites [74–78].

Spinacé et al. [79] studied the effect of the synthesis method and atomic composition of Pt and Sn. They synthesised Pt-Sn/C nanocatalysts with Pt:Sn ratios of 50:50 and 90:10 by the alcohol reduction method, using ethylene glycol as a reducing agent, and by borohydride reduction. The Pt-Sn/C nanocatalysts prepared by the

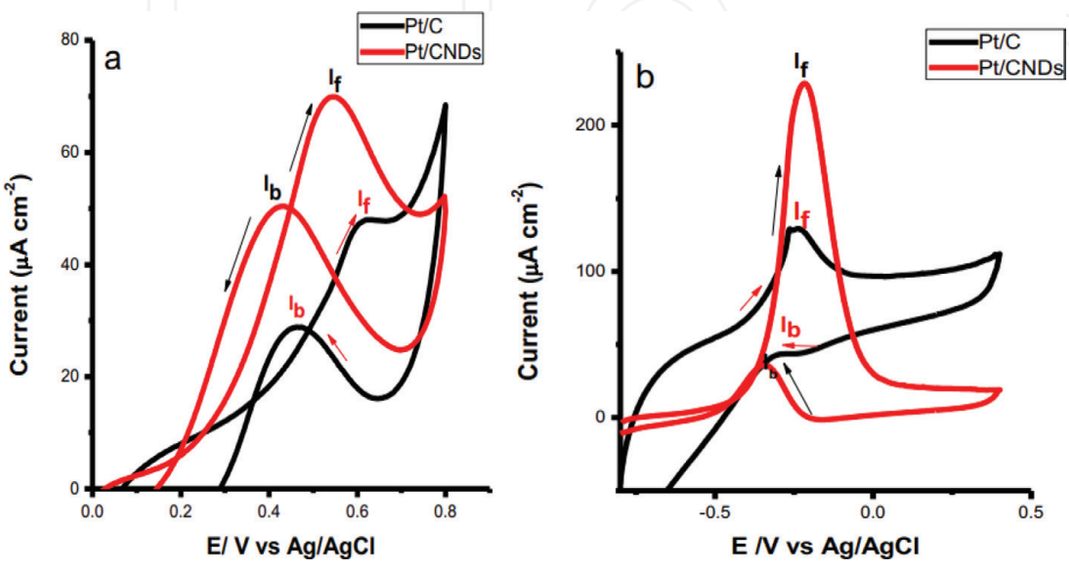


Figure 2.
Comparable CV for Pt/C and Pt/CNDs in (a) 0.5 CH_3OH in 0.5 M H_2SO_4 and (b) 0.5 M CH_3OH in NaOH. Reproduced with permission from Gwebu et al. [42]. Copyright 2017, ESG.

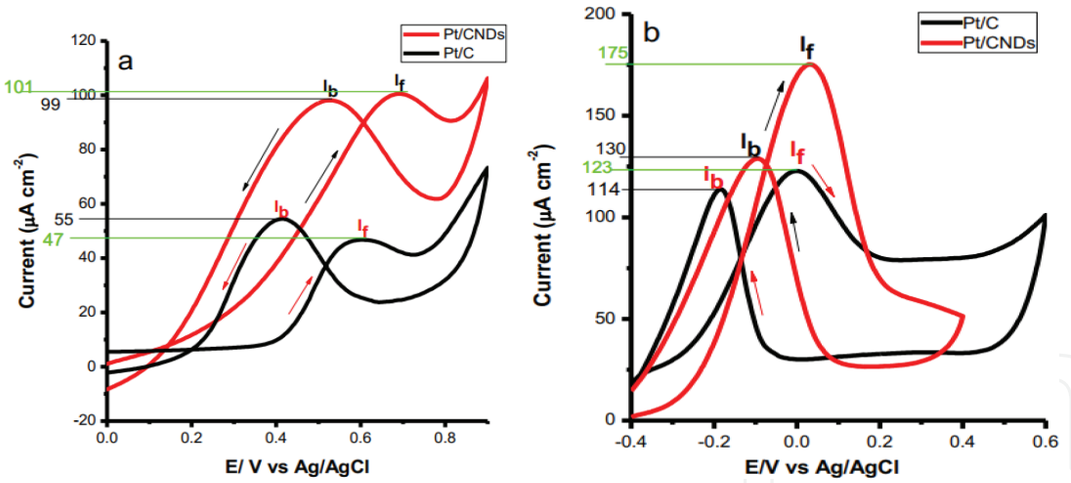


Figure 3.
CV graphs for Pt/C and Pt/CNDs in (a) 3 M CH_3CH_2OH in 0.1 M H_2SO_4 and (b) 2 M CH_3CH_2OH in 0.1 M NaOH. Reproduced with permission from Gwebu et al. [42]. Copyright 2017, ESG.

alcohol reduction method had smaller sizes compared to the Pt-Sn nanocatalysts prepared by borohydride method. The difference in particle sizes was attributed to the stabilising influence of ethylene glycol that minimises nanoparticle growth. The best activity for the electro-oxidation of ethanol was observed for the electrocatalyst containing 50:50 Pt:Sn prepared by the alcohol reduction method. For the borohydride method, higher current densities were observed for the electrocatalyst containing Pt:Sn in the ratio 90:10. Lamy and co-workers [80] demonstrated that Pt-Sn/C nanocatalysts perform better than Pt-Ru/C nanocatalysts for ethanol oxidation. For nanocatalysts synthesized by co-impregnation hydrogen reduction and Bönneman methods, they found that the optimal tin composition was between 10 and 20%.

Zhou and co-workers [81, 82] prepared Pt-Ru/C and Pt-Sn/C nanocatalysts by a polyol method and tested for ethanol oxidation. They observed that the activities of the Pt-Ru/C nanocatalysts were inferior to those of Pt-Sn/C nanocatalysts. They also observed that Pt-Sn/C nanocatalysts with Pt:Sn atomic ratios of 60:40 and 50:50 are more electroactive than nanocatalysts with 75:25 and 80:20 atomic ratios. Some scientists have reported that methanol electro-oxidation is low or insignificant on the Pt-Sn/C electrocatalysts. In actual fact, such observations were later found to be due to other intervening factors than the effect of Sn on methanol oxidation, normally involving "ensemble" effects [83]. Colmati et al. [74] reported that the adsorption-dehydrogenation of methanol turns out to be more difficult due to alloying of Sn with Pt and methanol electro-oxidation occurs only at reasonable alloying ratios.

The performance of Pt-Sn/C nanocatalysts greatly depends on their preparation procedure and composition. Carbon nanodots have been used as support materials for Pt-Sn nanoparticles. It has been found that carbon nanodots supported nanocatalysts show greater electroactivity and slow poisoning rates compared to carbon black supported nanocatalysts as shown in **Figure 4** [84]. The electrochemical activity is usually assessed by cyclic voltammetry and the poisoning rates are normally studied by chronoamperometry.

3.3 Pt-TiO_2 composites

Chemical blending a carbon support material such as a CNTs, CNDs, etc., with TiO_2 helps to improve the anti-poisoning and anti-corrosion properties of the electrode. The synergistic interaction between the carbon support, TiO_2 and the Pt catalyst enhances the electroactivity of the catalyst as it changes the Pt-d electronic and geometric properties [65]. This synergistic effect causes the contraction of Pt-Pt

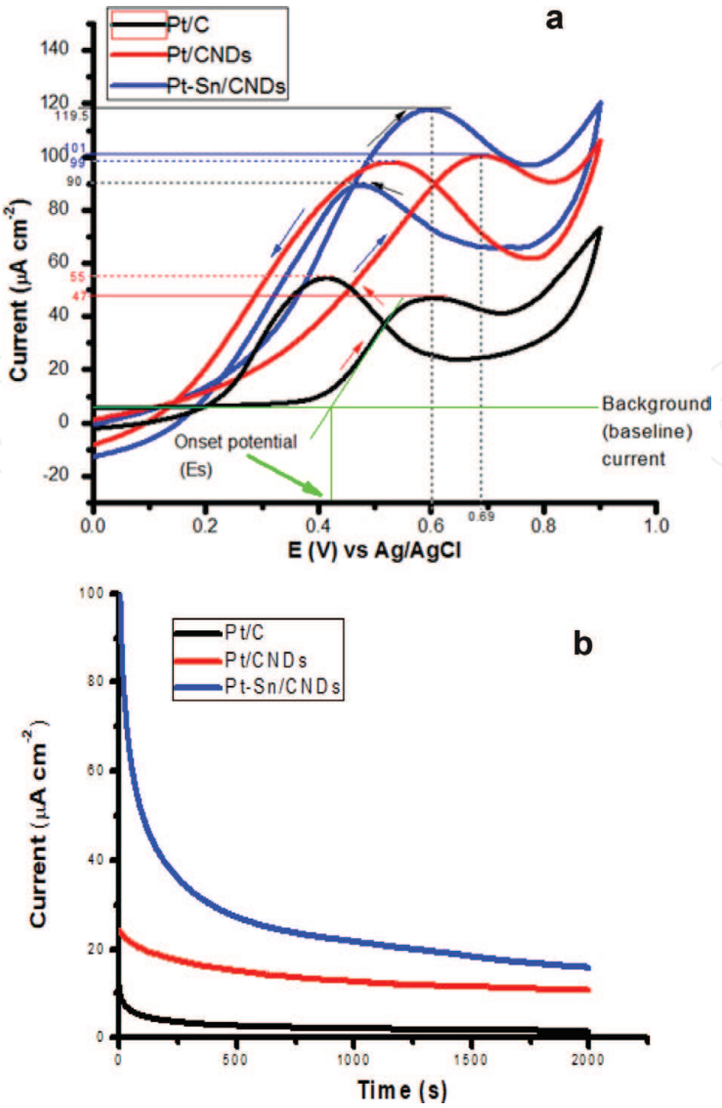


Figure 4.
Cyclic voltammograms showing low onset potentials and high current densities yielded by the Pt-Sn/CNDs nanocatalyst (a), and chronoamperometry curves showing improved poisoning of the Pt-Sn/CNDs nanocatalyst (b). Reproduced with permission from Gwebu et al. [84]. Copyright 2018, Wiley.

bond length leading to a condition favourable for the alcohol electro-oxidation reactions [44]. Titanium dioxide is a semiconductor, hence the quantity of TiO_2 and the crystallography (anatase/rutile) governs the degree of the interaction between the electrocatalyst components [85]. Previous X-ray photoelectron spectroscopic studies reveal that when Pt nanoparticles are supported on CNDs-TiO_2 the electronic structure of Pt is altered by titanium from the composite support. The binding energy for pure Pt_0 is around 71.12 eV, however, upon addition of TiO_2 the binding energy of $4f_{7/2}$ Pt_0 shifts to 71.53 eV. The positive shift indicates a strong metal-support interaction (SMSI) between the support material and the platinum catalyst [86] (**Figure 5**).

The enhanced electrochemical performance provided by metal oxides is brought by their hydrophilic nature due to the availability of H_2O molecules within the oxide network. The water molecules act as a continuous reversible membrane resulting in enhanced hydroxide transfer [43]. Bedolla-Valdez et al. [45] prepared a Pt/CNT/TiO_2 composite for methanol electro-oxidation using the sonochemical method. They concluded that the TiO_2 surface area can offer sites to adsorb water to form hydroxyl groups, which then react with CO adsorbed on the Pt surface to form CO_2. They recommended that the functionalisation of CNT should be optimized. Gwebu et al. [86] prepared a novel Pt/CNDs-TiO_2 nanocatalyst for methanol and ethanol electro-oxidation

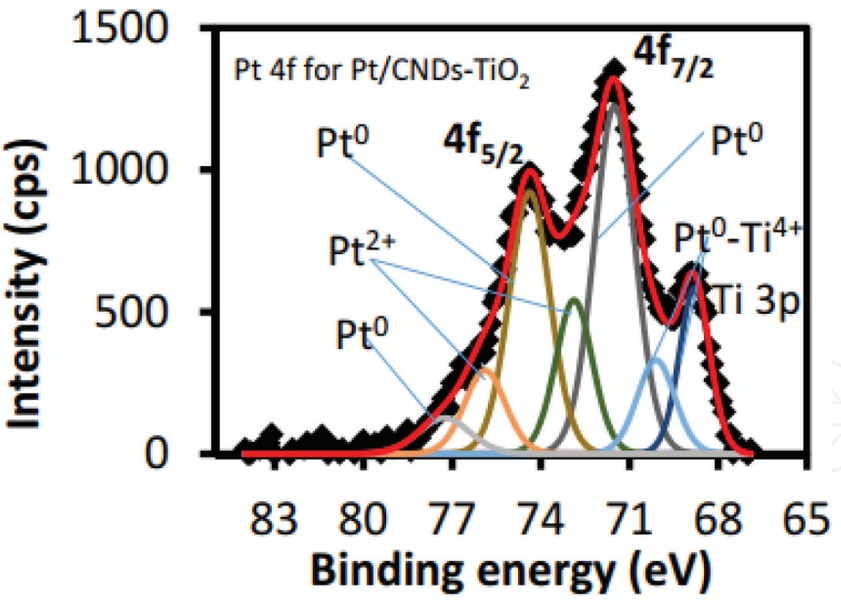


Figure 5.
Pt 4f XPS spectra for Pt/CNDs-TiO_2. Reproduced with permission from Gwebu et al. [86]. Copyright 2018, Elsevier.

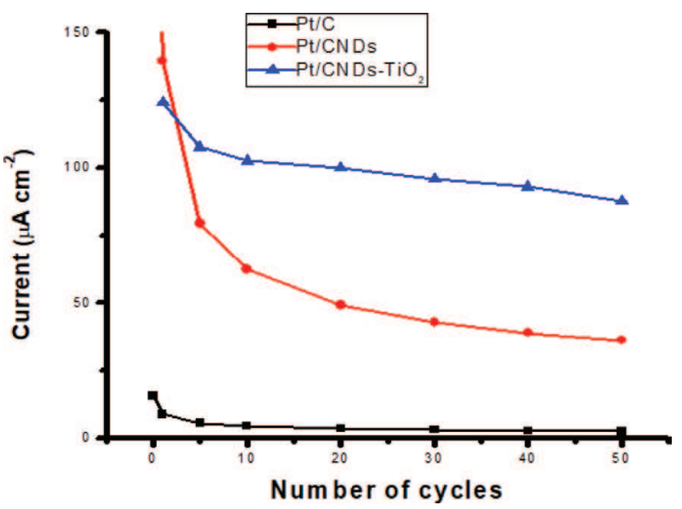


Figure 6.
Stability curves for the Pt/CNDs-TiO_2 nanocatalyst. Reproduced with permission from Gwebu et al. [86]. Copyright 2018, Elsevier.

in acidic media. Observed results proved that blending carbon nanodots with TiO_2 not only improves the electroactivity of the nanocatalyst but also enhances the tolerance to poisoning and resistance to corrosion. **Figure 6** shows the durability curves for the Pt/CNDs-TiO_2 nanocatalyst against Pt/CNDs and Pt/C nanocatalysts.

After exposure to 50 cycles, the Pt/CNDs-TiO_2 nanocatalyst retained the highest current indicating great tolerance to poisoning and resistance to acidic conditions of the fuel cell. The improved resistance to poisoning and corrosion was credited to the presence of ceramic TiO_2 nanoparticles which promote the oxidation of poisoning species at the same time minimising the detachment of Pt nanoparticles from the CNDs-TiO_2 composite support.

4. Conclusion

In this chapter, the use of carbon nanodots as primary support materials for direct fuel cell nanocatalysts is discussed. Other carbon nanomaterials such as

CNTs and CNFs were also reviewed. After their discovery in 2004, carbon nanodots have not been extensively used in fuel cells. This chapter demonstrated that carbon nanodots are potential support materials for direct alcohol fuel cells operating in both acidic and alkaline conditions. It is demonstrated that platinum nanoparticles supported on carbon nanodots are better anode nanocatalysts compared to platinum nanoparticles supported on carbon black. Alloying platinum with a cheaper metal such a tin modifies the face centred cubic structure of platinum resulting in a geometry which favours alcohol electrooxidation. The binary Pt-Sn catalyst yielded higher current density at low potentials compared to the mono Pt/CNDs nanocatalyst. It is revealed that incorporating TiO_2 into the Pt/CNDs nanocatalyst improves the nanocatalyst's electroactivity and resistance to corrosion by acidic electrolytes. Chronoamperometry results proved that Pt, Pt-Sn and Pt-TiO_2 nanoparticles supported on carbon nanodots are more resistant to poisoning compared to Pt nanoparticles supported on carbon black.

From the recent studies conducted, it was observed that carbon nanodots are easily synthesized by the bottom-up (physical) methods. However, in most cases CNDs prepared by these methods are amorphous, this compromises their resistance to corrosion under the harsh fuel cell conditions. Further work should be done to develop top-down methods for synthesizing carbon nanodots. Owing to great catalytic activity exhibited by Pt binary catalysts, ternary and quaternary catalysts should be developed to improve performance and reduce platinum loading.

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Conflict of interest

No conflicts of interest are declared by the authors.

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References

[1] Rong H, Zhang S, Muhammad S, Zhang J. Noble metal-based nanocomposites for fuel cells. In: Kyzas G, editor. Novel Nanomaterials. London, UK: IntechOpen; 2018. pp. 291-310. DOI: 10.5772/intechopen.71949

[2] Kreuer KD. Fuel cells, introduction. In: Kreuer KD, editor. Fuel Cells. New York, NY: Springer; 2013. pp. 1-7. DOI: 10.1007/978-1-4614-5785-5_1

[3] Neto AO, Spinacé EV, Dias RR, Brandalise M, Linardi M. Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process. Journal of Power Sources. 2007;**116**:87-91. DOI: 10.1016/j.jpowsour.2006.12.088

[4] Lamy C, Belgsir EM, Leger JM. Electrocatalytic oxidation of aliphatic alcohols: Application to the direct alcohol fuel cell (DAFC). Journal of Applied Electrochemistry. 2001;**31**(7):799-809. DOI: 10.1023/A:1017587310150

[5] Soloveichik GL. Liquid fuel cells. Beilstein Journal of Nanotechnology. 2014;**5**:1399-1418. DOI: 10.3762/bjnano.5.153

[6] Zhang L, Wang H, Li X, Xia F, Liu Y, Xu X, et al. One-step synthesis of palladium-gold-silver ternary nanoparticles supported on reduced graphene oxide for the electrooxidation of methanol and ethanol. Electrochimica Acta. 2015;**172**:42-51. DOI: 10.1016/j.electacta.2014.11.152

[7] Park YC, Tokiwa H, Kakinuma K, Watanabe M, Uchida M. Effects of carbon supports on Pt distribution, ionomer coverage and cathode performance for polymer electrolyte fuel cells. Journal of Power Sources. 2016;**315**:179-191. DOI: 10.1016/j.jpowsour.2016.02.091

[8] Dicks AL. The role of carbon in fuel cells. Journal of Power Sources. 2006;**156**(2):128-141. DOI: 10.1016/j.jpowsour.2006.02.054

[9] Trogadas P, Fuller TF, Strasser P. Carbon as catalyst and support for electrochemical energy conversion. Carbon. 2014;**75**:5-42. DOI: 10.1016/j.carbon.2014.04.005

[10] Antolini E, Gonzalez ER. Polymer supports for low-temperature fuel cell catalysts. Applied Catalysis A: General. 2009;**365**(1):1-19. DOI: 10.1016/j.apcata.2009.05.045

[11] Harris PJF. New perspectives on the structure of graphitic carbons. Critical Reviews in Solid State and Materials Sciences. 2005;**30**:235-253. DOI: 10.1080/10408430500406265

[12] Yaldagard M. Carbonaceous nanostructured support materials for low temperature fuel cell electrocatalysts: A review. World Journal of Nano Science and Engineering. 2013;**3**:121-153. DOI: 10.4236/wjnse.2013.34017

[13] Goel J, Basu S. Effect of support materials on the performance of direct ethanol fuel cell anode catalyst. International Journal of Hydrogen Energy. 2014;**39**(28):15956-15966. DOI: 10.1016/j.ijhydene.2014.01.203

[14] Liu J, Liu CT, Zhao L, Zhang JJ, Zhang LM, Wang ZB. Effect of different structures of carbon supports for cathode catalyst on performance of direct methanol fuel cell. International Journal of Hydrogen Energy. 2015;**41**(3):1859-1870. DOI: 10.1016/j.ijhydene.2015.11.103

[15] Jiang ZZ, Wang ZB, Chu YY, Gu DM, Yin GP. Carbon riveted microcapsule Pt/MWCNTs-TiO_2 catalyst prepared by in situ carbonized glucose

with ultrahigh stability for proton exchange membrane fuel cell. Energy & Environmental Science. 2011;**4**(7): 2558-2566. DOI: 10.1039/C1EE01091C

[16] Wang Y, Sheng ZM, Yang H, Jiang SP, Li CM. Electrocatalysis of carbon black- or activated carbon nanotubes-supported Pd-Ag towards methanol oxidation in alkaline media. International Journal of Hydrogen Energy. 2010;**35**(19):10087-10093. DOI: 10.1016/j.ijhydene.2010.07.172

[17] Yang G, Zhou Y, Pan H, Bin ZC, Fu S, Wai CM, et al. Ultrasonic-assisted synthesis of Pd-Pt/carbon nanotubes nanocomposites for enhanced electro-oxidation of ethanol and methanol in alkaline medium. Ultrasonics Sonochemistry. 2016;**28**:192-198. DOI: 10.1016/j.ultsonch.2015.07.021

[18] Wang H, Kakade BA, Tamaki T, Yamaguchi T. Synthesis of 3D graphite oxide-exfoliated carbon nanotube carbon composite and its application as catalyst support for fuel cells. Journal of Power Sources. 2014;**260**:338-348. DOI: 10.1016/j.jpowsour.2014.03.014

[19] Wen Y, Ye JS, Zhang WD, Sheu FS, Xu GQ. Electrocatalytic oxidation of methanol on a platinum modified carbon nanotube electrode. Microchimica Acta. 2008;**162**:235-243. DOI: 10.1007/s00604-007-0882-0

[20] Acosta DR, Martınez L. Growth of carbon nanotubes and nanofibres in porous anodic alumina film. Carbon. 2002;**40**:1011-1016. DOI: 10.1016/S0008-6223(01)00230-5

[21] Prasanna D, Selvaraj V. Development of non-covalent ternary polymer–CNT composites as a novel supporting material for electrooxidation of glycerol. RSC Advances. 2015;**5**(120):98822-98833. DOI: 10.1039/C5RA17172E

[22] Soin N, Roy SS, Sharma S, Thundat T, Mclaughlin JA. Electrochemical and oxygen reduction properties of pristine and nitrogen-doped few layered graphene nanoflakes (FLGs). Journal of Solid State Electrochemistry. 2013;**17**(8):2139-2149. DOI: 10.1007/s10008-013-2073-8

[23] Brouzgou A, Podias A, Tsiakaras P. PEMFCs and AEMFCs directly fed with ethanol: A current status comparative review. Journal of Applied Electrochemistry. 2013;**43**(2):119-136. DOI: 10.1007/s10800-012-0513-2

[24] Murphy H, Papakonstantinou P, Okpalugo TIT. Raman study of multiwalled carbon nanotubes functionalized with oxygen groups. Journal of Vacuum Science & Technology B. 2006;**24**(2):715-720. DOI: 10.1116/1.2180257

[25] Knupp SL, Li W, Paschos O, Murray TM, Snyder J, Haldar P. The effect of experimental parameters on the synthesis of carbon nanotube/nanofiber supported platinum by polyol processing techniques. Carbon. 2008;**6**:1276-1284. DOI: 10.1016/j.carbon.2008.05.007

[26] Guha A, Lu W, Zawodzinski TA, Schiraldi DA. Surface-modified carbons as platinum catalyst support for PEM fuel cells. Carbon. 2007;**45**(7):1506-1517. DOI: 10.1016/j.carbon.2007.03.023

[27] Day TM, Unwin PR, Wilson NR, Macpherson JV. Electrochemical templating of metal nanoparticles and nanowires on single-walled carbon nanotube networks. American Chemical Society. 2005;**127**(20):10639-10647. DOI: 10.1021/ja051320r

[28] Kunitomo H, Ishitobi H, Nakagawa N. Optimized CeO_2 content of the carbon nanofiber support of PtRu catalyst for direct methanol fuel cells. Journal of Power Sources. 2015;**297**:400-407. DOI: 10.1016/j.jpowsour.2015.07.002

[29] Ghouri ZK, Barakat NAM, Obaid M, Lee JH, Kim HY. Co/CeO_2-decorated carbon nanofibers as effective non-precious electro-catalyst for fuel cells application in alkaline medium. Ceramics International. 2015;**41**(2):2271-2278. DOI: 10.1016/j.ceramint.2014.10.031

[30] Ghouri ZK, Barakat NAM, Kim HY, Park M, Khalil KA, El-Newehy MH, et al. Nano-engineered ZnO/CeO_2 dots@CNFs for fuel cell application. Arabian Journal of Chemistry. 2016;**9**(2):219-228. DOI: 10.1016/j.arabjc.2015.05.024

[31] Sharma S, Pollet BG. Support materials for PEMFC and DMFC electrocatalysts: A review. Journal of Power Sources. 2012;**208**:96-119. DOI: 10.1016/j.jpowsour.2012.02.011

[32] Zheng J, Zhang X, Li P, Zhu J, Zhou X, Yuan W. Effect of carbon nanofiber microstructure on oxygen reduction activity of supported palladium electrocatalyst. Electrochemistry Communications. 2007;**9**:895-900. DOI: 10.1016/j.elecom.2006.12.006

[33] Baker S. Luminescent carbon nanodots: Emergent nanolights luminescent carbon nanodots: Emergent nanolights angewandte. Angewandte Chemie, International Edition. 2010;**49**:6726-6744. DOI: 10.1002/anie.200906623

[34] Li H, Kang Z, Liu Y, Lee S-T. Carbon nanodots: Synthesis, properties and applications. Journal of Materials Chemistry. 2012;**22**(46):24230. DOI: 10.1039/C2JM34690G

[35] Roy P, Chen PC, Periasamy AP, Chen YN, Chang HT. Photoluminescent carbon nanodots: Synthesis, physicochemical properties and analytical applications. Materials Today. 2015;**18**(8):447-458. DOI: 10.1016/j.mattod.2015.04.005

[36] Zhu S, Song Y, Zhao X, Shao J, Zhang J, Yang B. The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): Current state and future perspective. Nano Research. 2015;**8**(2):355-381. DOI: 10.1007/s12274-014-0644-3

[37] Wei W, Chen W. "Naked" Pd nanoparticles supported on carbon nanodots as efficient anode catalysts for methanol oxidation in alkaline fuel cells. Journal of Power Sources. 2012;**204**:85-88. DOI: 10.1016/j.jpowsour.2012.01.032

[38] Qin X, Lu W, Asiri AM, Al-Youbi AO, Sun X. Microwave-assisted rapid green synthesis of photoluminescent carbon nanodots from flour and their applications for sensitive and selective detection of mercury(II) ions. Sensors and Actuators B: Chemical. 2013;**184**:156-162. DOI: 10.1016/j.snb.2013.04.079

[39] Sonthanasamy RSA, Ahmad WYW, Fazry S, Hassan NI, Lazim AM. Transformation of crystalline starch nanoparticles into highly luminescent carbon nanodots: Toxicity studies and their applications. Carbohydrate Polymers. 2016;**137**:488-496. DOI: 10.1016/j.carbpol.2015.11.021

[40] Yan F, Kong D, Fu Y, Ye Q, Wang Y, Chen L. Construction of carbon nanodots/tungsten trioxide and their visible-light sensitive photocatalytic activity. Journal of Colloid and Interface Science. 2016;**466**:268-274. DOI: 10.1016/j.jcis.2015.12.043

[41] Shi L, Li Y, Li X, Zhao B, Wen X, Zhang G, et al. Controllable synthesis of green and blue fluorescent carbon nanodots for pH and Cu^{2+} sensing in living cells. Biosensors & Bioelectronics. 2016;**77**:598-602. DOI: 10.1016/j.bios.2015.10.031

[42] Gwebu SS, Nomngongo PN, Mashazi PN, Nyokong T, Maxakato

NW. Platinum nanoparticles supported on carbon nanodots as anode catalysts for direct alcohol fuel cells. International Journal of Electrochemical Science. 2017;**12**:6365-6378. DOI: 10.20964/2017.07.09

[43] Meenakshi S, Nishanth KG, Sridhar P, Pitchumani S. Spillover effect induced Pt-TiO_2/C as ethanol tolerant oxygen reduction reaction catalyst for direct ethanol fuel cells. Electrochimica Acta. 2014;**135**:52-59. DOI: 10.1016/j.electacta.2014.04.142

[44] Ruiz-Camacho B, Martínez-Álvarez O, Rodríguez-Santoyo HH, Granados-Alejo V. Pt/C and Pt/TiO_2-C electrocatalysts prepared by chemical vapor deposition with high tolerance to alcohols in oxygen reduction reaction. Journal of Electroanalytical Chemistry. 2014;**725**:19-24. DOI: 10.1016/j.jelechem.2014.04.019

[45] Bedolla-Valdez ZI, Verde-Gomez Y, Valenzuela-Muniz AM, Gochi-Ponce Y, Oropeza-Guzman MT, Berhault G, et al. Sonochemical synthesis and characterization of Pt/CNT, Pt/TiO_2, and Pt/CNT/TiO_2 electrocatalysts for methanol electro-oxidation. Electrochimica Acta. 2015;**186**:76-84. DOI: 10.1016/j.electacta.2015.10.084

[46] Odetola C, Trevani L, Easton EB. Enhanced activity and stability of Pt/TiO_2/carbon fuel cell electrocatalyst prepared using a glucose modifier. Journal of Power Sources. 2015;**294**:254-263. DOI: 10.1016/j.jpowsour.2015.06.066

[47] Yang F, Ma L, Gan M, Zhang J, Yan J, Huang H, et al. Polyaniline-functionalized TiO_2–C supported Pt catalyst for methanol electro-oxidation. Synthetic Metals. 2015;**205**:23-31. DOI: 10.1016/j.synthmet.2015.03.017

[48] Zhang J, Tu JP, Du GH, Dong ZM, Su QM, Xie D, et al. Pt supported self-assembled nest-like-porous WO_3 hierarchical microspheres as electrocatalyst for methanol oxidation. Electrochimica Acta. 2013;**88**:107-111. DOI: 10.1016/j.electacta.2012.10.060

[49] Georgieva J, Sotiropoulos S, Valova E, Armyanov S, Karanasios N. Methanol oxidation and photo-oxidation at Pt/WO_3 electrocatalysts on graphite substrates. Journal of Electroanalytical Chemistry. 2014;**727**:135-140. DOI: 10.1016/j.jelechem.2014.06.011

[50] Hernández-Pichardo ML, González-Huerta RG, Del Angel P, Tufiño-Velazquez M, Lartundo L. The role of the WO_3 nanostructures in the oxygen reduction reaction and PEM fuel cell performance on WO_3-Pt/C electrocatalysts. International Journal of Hydrogen Energy. 2015;**40**(48):17371-17379. DOI: 10.1016/j.ijhydene.2015.06.165

[51] Wu M, Han M, Li M, Li Y, Zeng J, Liao S. Preparation and characterizations of platinum electrocatalysts supported on thermally treated CeO_2-C composite support for polymer electrolyte membrane fuel cells. Electrochimica Acta. 2014;**139**:308-314. DOI: 10.1016/j.electacta.2014.07.029

[52] Naeem R, Ahmed R, Ansari MS. TiO_2 and Al_2O_3 promoted Pt/C nanocomposites as low temperature fuel cell catalysts for electro oxidation of methanol in acidic media. IOP Conference Series: Materials Science and Engineering. 2014;**60**:012031. DOI: 10.1088/1757-899X/60/1/012031

[53] Gharibi H, Sadeghi S, Golmohammadi F. Electrooxidation of Ethanol on highly active and stable carbon supported $PtSnO_2$ and its application in passive direct ethanol fuel cell: Effect of tin oxide synthesis method. Electrochimica Acta. 2016;**190**:1100-1112. DOI: 10.1016/j.electacta.2015.12.208

[54] De A, Datta J, Haldar I, Biswas M. Catalytic intervention of MoO_3 toward ethanol oxidation on PtPd nanoparticles decorated MO_3—Polypyrrole composite support. ACS Applied Materials & Interfaces. 2016;**8**(42):28574-28584. DOI: 10.1021/acsami.6b07455

[55] Devi RS, Venckatesh DR, Sivaraj DR. Synthesis of titanium dioxide nanoparticles by sol-gel technique. International Journal of Innovative Research in Science, Engineering and Technology. 2014;**3**(8):15206-15211. DOI: 10.15680/IJIRSET.2014.0308020

[56] Falaras P, Xagas P. Roughness and fractality of nanostructured TiO_2 films prepared via sol-gel technique. Materials Science. 2002;**37**:3855-3860. DOI: 10.1023/A:1019686902277

[57] Shen PS, Tseng CM, Kuo TC, Shih CK, Li MH, Chen P. Microwave-assisted synthesis of titanium dioxide nanocrystalline for efficient dye-sensitized and perovskite solar cells. Solar Energy. 2015;**120**:345-356. DOI: 10.1016/j.solener.2015.07.036

[58] Li W, Zhao Y, Yuan S, Shi L, Wang Z, Fang J, et al. Synthesis and characterization of highly dispersed TiO_2 nanocrystal colloids by microwave-assisted hydrothermal method. Journal of Materials Science. 2012;**47**:7999-8006. DOI: 10.1007/s10853-012-6689-3

[59] Padmamalini N, Ambujam K. Structural and dielectric properties of ZrO_2–TiO_2–V_2O_5 nanocomposite prepared by CO-precipitation calcination method. Materials Science in Semiconductor Processing. 2016;**41**:246-251. DOI: 10.1016/j.mssp.2015.09.009

[60] Zhang X, Sun Y, Cui X, Jiang Z. Carbon-incorporated TiO_2 microspheres: Facile flame assisted hydrolysis of tetrabutyl orthotitanate and photocatalytic hydrogen production. International Journal of Hydrogen Energy. 2012;**37**(2):1356-1365. DOI: 10.1016/j.ijhydene.2011.09.133

[61] Liu J, Hu Y, Gu F, Li C. Large-scale synthesis of hollow titania spheres via flame combustion. Particuology. 2011;**9**(6):632-636. DOI: 10.1016/j.partic.2010.12.004

[62] Piccirillo C, Denis CJ, Pullar RC, Binions R, Parkin IP, Darr JA, et al. Aerosol assisted chemical vapour deposition of hydroxyapatite-embedded titanium dioxide composite thin films. Journal of Photochemistry and Photobiology A Chemistry. 2017;**332**:45-53. DOI: 10.1016/j.jphotochem.2016.08.010

[63] Nguyen TGH, Pham TVA, Phuong TX, Lam TXB, Tran VM, Nguyen TPT. Nano-Pt/C electrocatalysts: Synthesis and activity for alcohol oxidation. Advances in Natural Sciences: Nanoscience and Nanotechnology. 2013;**4**(3):035008/1-035008/8. DOI: 10.1088/2043-6262/4/3/035008

[64] Kuppan B, Selvam P. Platinum-supported mesoporous carbon (Pt/CMK-3) as anodic catalyst for direct methanol fuel cell applications: The effect of preparation and deposition methods. Progress in Natural Science: Materials International. 2012;**22**(6):616-623. DOI: 10.1016/j.pnsc.2012.11.005

[65] Jukk K, Kongi N, Tarre A, Rosental A, Treshchalov AB, Kozlova J, et al. Electrochemical oxygen reduction behaviour of platinum nanoparticles supported on multi-walled carbon nanotube/titanium dioxide composites. Journal of Electroanalytical Chemistry. 2014;**735**:68-76. DOI: 10.1016/j.jelechem.2014.10.008

[66] Chung DY, Lee KJ, Sung YE. Methanol electro-oxidation on the Pt surface: Revisiting the cyclic voltammetry interpretation. Journal of Physical Chemistry C.

2016;**120**(17):9028-9035. DOI: 10.1021/acs.jpcc.5b12303

[67] Wang X, Hu C, Xiong Y, Liu H, Du G, He X. Carbon-nanosphere-supported Pt nanoparticles for methanol and ethanol electro-oxidation in alkaline media. Journal of Power Sources. 2011;**196**(4):1904-1908. DOI: 10.1016/j.jpowsour.2010.09.072

[68] Figueiredo MC, Solla-Gullón J, Vidal-Iglesias FJ, Nisula M, Feliu JM, Kallio T. Carbon-supported shape-controlled Pt nanoparticle electrocatalysts for direct alcohol fuel cells. Electrochemistry Communications. 2015;**55**:47-50. DOI: 10.1016/j.elecom.2015.03.019

[69] Perez J, Paganin VA, Antolini E. Particle size effect for ethanol electro-oxidation on Pt/C catalysts in half-cell and in a single direct ethanol fuel cell. Journal of Electroanalytical Chemistry. 2011;**654**(1-2):108-115. DOI: 10.1016/j.jelechem.2011.01.013

[70] Holton OT, Stevenson JW. The role of platinum in proton exchange membrane fuel cells. Platinum Metals Review. 2013;**57**(4):259-271. DOI: 10.1595/147106713x671222

[71] Barmparis GD, Lodziana Z, Lopez N, Remediakis IN. Nanoparticle shapes by using Wulff constructions and first-principles calculations. Beilstein Journal of Nanotechnology. 2015;**6**(1):361-368. DOI: 10.3762/bjnano.6.35

[72] Antoniassi RM, Otubo L, Vaz JM, Oliveira Neto A, Spinacé EV. Synthesis of Pt nanoparticles with preferential (100) orientation directly on the carbon support for direct ethanol fuel cell. Journal of Catalysis. 2016;**342**:67-74. DOI: 10.1016/j.jcat.2016.07.022

[73] Khudhayer WJ, Shaikh AU, Karabacak T. Platinum nanorod arrays with preferred morphological and crystal properties for oxygen reduction reaction. Advanced Science Letters. 2011;**4**(3):3551-3559. DOI: 10.1166/asl.2011.1867

[74] Colmati F, Antolini E, Gonzalez ER. Pt-Sn/C electrocatalysts for methanol oxidation synthesized by reduction with formic acid. Electrochimica Acta. 2005;**50**(28):5496-5503. DOI: 10.1016/j.electacta.2005.03.030

[75] López-Suárez FE, Bueno-López A, Eguiluz KIB, Salazar-Banda GR. Pt-Sn/C catalysts prepared by sodium borohydride reduction for alcohol oxidation in fuel cells: Effect of the precursor addition order. Journal of Power Sources. 2014;**268**:225-232. DOI: 10.1016/j.jpowsour.2014.06.042

[76] Lim DH, Choi DH, Lee WD, Park DR, Lee HI. The effect of Sn addition on a Pt/C electrocatalyst synthesized by borohydride reduction and hydrothermal treatment for a low-temperature fuel cell. Electrochemical and Solid-State Letters. 2007;**10**(5):B87-B90. DOI: 10.1149/1.2710182

[77] De Souza EA, Giz MJ, Camara GA, Antolini E, Passos RR. Ethanol electro-oxidation on partially alloyed Pt-Sn-Rh/C catalysts. Electrochimica Acta. 2014;**147**:483-489. DOI: 10.1016/j.electacta.2014.09.141

[78] Lopez-Suarez FE, Carvalho-Filho CT, Bueno-Lopez A, Arboleda J, Echavarrea A, Eguiluz KIB, et al. Platinum-tin/carbon catalysts for ethanol oxidation: Influence of Sn content on the electroactivity and structural characteristics. International Journal of Hydrogen Energy. 2015;**40**(37):12674-12686. DOI: 10.1016/j.ijhydene.2015.07.135

[79] Spinacé EV, Vale LAI, Dias RR, Neto AO. PtSn/C electrocatalysts prepared by different methods for direct ethanol fuel cell. Studies in surface science and catalysis. 2006;**162**:617-624. DOI: 10.1016/S0167-2991(06)80960-2

[80] Lamy C, Rousseau S, Belgsir EM, Coutanceau C, Léger JM. Recent progress in the direct ethanol fuel cell: Development of new platinum-tin electrocatalysts. Electrochim Acta. 2004;**49**(22-23 SPEC. ISS):3901-3908. DOI: 10.1016/j.electacta.2004.01.078

[81] Zhou W, Zhou Z, Song S, Li W, Sun G, Tsiakaras P, et al. Pt based anode catalysts for direct ethanol fuel cells. Applied Catalysis B: Environmental. 2003;**46**(2):273-285. DOI: 10.1016/S0926-3373(03)00218-2

[82] Zhou WJ, Song SQ, Li WZ, Sun GQ, Xin Q, Kontou S, et al. Pt-based anode catalysts for direct ethanol fuel cells. Solid State Ionics. 2004;**175**(1-4):797-803. DOI: 10.1016/j.ssi.2004.09.055

[83] Song C, Zhang J. Electrocatalytic oxygen reduction reaction. In: Zhang J, editor. PEM Fuel Cell Electrocatalysts and Catalyst Layers. Springer: London; 2008. pp. 89-134. DOI: 10.1007/978-1-84800-936-3_2

[84] Gwebu SS, Nomngongo PN, Maxakato NW. Pt-Sn nanoparticles supported on carbon nanodots as anode catalysts for alcohol electro-oxidation in acidic conditions. Electroanalysis. 2018;**30**:1125-1132. DOI: 10.1002/elan.201800098

[85] Silva JCM, Buzzo GS, De Souza RFB. Enhanced electrooxidation of ethanol using Pd/C + TiO_2 electrocatalysts in alkaline media. Electrocatalysis. 2015;**6**:86-91. DOI: 10.1007/s12678-014-0224-z

[86] Gwebu SS, Nomngongo PN, Maxakato NW. Pt/CNDs-TiO_2 electrocatalyst for direct alcohol fuel cells. Materials Today Proceedings. 2018;**5**(4):10460-10469. DOI: 10.1016/j.matpr.2017.12.377