



Citation for published version:

Hotchen, CE, Attard, GA, Bull, SD & Marken, F 2014, 'One-step electroless growth of nano-fibrous platinum catalyst from "paint-on" PtCl₆ 2- solution in poly-(ethylene-glycol)', *Electrochimica Acta*, vol. 137, pp. 484-488.
<https://doi.org/10.1016/j.electacta.2014.06.001>

DOI:

[10.1016/j.electacta.2014.06.001](https://doi.org/10.1016/j.electacta.2014.06.001)

Publication date:

2014

Document Version

Peer reviewed version

[Link to publication](#)

Publisher Rights

CC BY-NC-ND

The published version is available via: <http://dx.doi.org/10.1016/j.electacta.2014.06.001>

University of Bath

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

REVISION

28th April 2014

**One-step electroless growth of nano-fibrous platinum catalyst
from “paint-on” PtCl_6^{2-} solution in poly-(ethylene-glycol)**

Christopher E. Hotchen ^a, Gary A. Attard ^b, Steven D. Bull ^a, and Frank Marken ^a

^a Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

^b School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

To be submitted to Electrochimica Acta

Proofs to F. Marken

F.Marken@bath.ac.uk

Tel. 01225 383694

Fax 01225 386231

Highlights

- A convenient one-step synthesis of nano-platinum is suggested based on PEG solution thermolysis
- Stable nano-fibrous platinum on ITO is formed and characterised in 0.5 M H₂SO₄
- Effective methanol oxidation electrocatalysis is demonstrated with catalyst activity comparable to other nano-platinum materials

Abstract

The electrochemically reducing nature of the poly-(ethylene-glycol) solvent (PEG200) is exploited in a one-step electroless deposition of nano-fibrous platinum electrocatalyst. K₂PtCl₆ is dissolved in poly-(ethylene-glycol) and applied to a substrate (here tin-doped indium oxide, ITO). The deposition process is conducted by rapid heating in a furnace in air. Upon ramping the temperature up (with 10 °C per minute to 500 °C) a complex sequence of nucleation and growth reactions leads via (i) formation of nano-fibrous platinum and (ii) complete removal of all organic components directly to an electrochemically highly active platinum deposit. When characterised in aqueous 0.5 M H₂SO₄, typical poly-crystal Pt surface oxidation and hydrogen adsorption features were observed. Electrocatalysis is demonstrated for methanol oxidation, for which the rate of catalysis per electrochemically active area is increased compared to that for a conventional polycrystalline platinum macro-disc.

Keywords: fuel cell, nano-fibrous platinum, nanoparticles, electrocatalysis, voltammetry, energy.

1. Introduction

Platinum is a widely used catalyst in particular in applications in electrochemical fuel cells [1], solar cells [2], and in water electrolysis systems [3]. The formation of nano-platinum catalysts is well-documented [4] and the tuning of platinum nano-crystal shape [5] and reactivity [6,7] are possible with control over nucleation and growth conditions. For example, in electro-deposition procedures the presence of sulphuric acid has been reported to lead to nano-flower-like deposits with good electrocatalytic activity for methanol oxidation [8]. In a recent study the formation of platinum nano-wire arrays on graphene was reported for a high performance electrocatalysis application [9]. Most commercial nano-platinum electrocatalyst applications are based on carbon substrates.

The role of the substrate in platinum catalysed electrochemical reactions has been thoroughly reviewed [10]. Tin-doped indium oxide (ITO) with platinum electrocatalyst has been employed previously, especially for solar fuel cells [11] or for transparent catalytic electrodes [12]. Liang et al. [13] reported ion-implantation methods for making Pt nano-grains of 8 nm average radius on ITO. The pulsed electrodeposition of platinum nanoparticles on ITO has been reported by Liu et al. [14]. This study demonstrated the importance of the electrochemically active catalyst area as compared to the apparent size of the nano-platinum deposits. Generally, platinum on ITO has been reported to exhibit a similar activity towards methanol oxidation when compared to bulk platinum [15]. Tin alloyed into platinum has been shown to promote methanol oxidation catalysis [16].

In order to avoid complex procedures for the formation of nano-platinum catalysts, one-step deposition processes are desirable, in particular processes which avoid the need for inert atmosphere and complex separation and cleaning steps. Based on the well-known properties of poly-ethylene-glycol (PEG) as a universal (benign, non-volatile) solvent system [17] with reducing chemical nature [18], we investigated novel approaches for the formation of nano-platinum catalysts *directly* by thermolysis of precursors in PEG.

PEG and PEG-derivatives are commonly employed as additives, templates, and/or reducing agents, for example in hydrothermal “poly-ol” syntheses [19]. The shape-controlled formation of platinum nanocrystals [20] has been identified as an important field of electrocatalyst optimisation and PEG additives affect platinum nano-particle formation, for example in microemulsion environments [21].

In this report we explore the direct thermolysis of a solution of PtCl_6^{2-} in a low molecular weight poly-ethylene-glycol (PEG200) in a one-step electroless deposition process to form nano-fibrous platinum.

2. Experimental

2.1 Reagents

Poly-(ethylene-glycol) (Sigma-Aldrich, average molecular weight = 200 g mol⁻¹) was used as the solvent for nanoparticle preparation. Potassium hexachloroplatinate(IV) (Sigma-Aldrich, 99.99 % metal basis) was used as the precursor for Pt deposits with an indium-tin-oxide (ITO)

glass substrate (Image Optics, Basildon, 15 Ohm per square). Sulphuric acid (H₂SO₄) (BDH, 98 %) and methanol (MeOH) (Fisher Scientific, HPLC Grade), were used as analytes to investigate the structure and catalytic activity of the Pt deposits, respectively.

2.2 Instrumentation

Heating was performed using a TSH12 furnace (Elite Thermal Systems Ltd.). Field emission scanning electron microscopy (FESEM) images were taken using a JEOL FESEM6301F microscope. All electrochemical measurements were performed using an Autolab PGSTAT12 potentiostat (Autolab, Utrecht, NL) and in a three-electrode conical glass cell with platinum wire counter electrode and KCl-saturated calomel electrode (SCE) at room temperature (20 +/- 2 °C). The GPES software package (version 4.9005, Autolab, Utrecht, NL) was employed for data acquisition with a potential step parameter not higher than 1 mV.

2.3 Preparation of nanofibrous platinum deposits

A solution of either 5 mM, 10 mM, or 20 mM potassium hexachloroplatinate(IV) (K₂PtCl₆) were prepared by stirring in PEG200. A volume of 20 μL of the resulting solution was placed on the ITO glass substrate and distributed over an area of ca. 1 cm². The sample temperature was ramped up (10 °C per minute) to 500 °C and then maintained for 30 minutes. The samples were then gradually cooled to room temperature and rinsed with deionised water (resistivity 18.2 MΩ cm) to remove any remaining soluble inorganics. The structure of the platinum deposits was observed using FESEM imaging and energy-dispersive X-ray (EDX) analysis was used for elemental analysis. The crystallinity and the electrochemically active surface area (ESA) of the Pt deposits were determined using cyclic voltammetry in aqueous 0.5 M H₂SO₄ solution.

3. Results and discussion

3.1. Electroless formation of nano-fibrous platinum from PEG solution

The thermolysis of K_2PtCl_6 solutions in PEG200 yielded platinum deposits on ITO-coated glass substrates. Figure 1A and 1B show FESEM images for the nanofibrous platinum (appearing as micron-sized aggregates of smaller nano-scale fibres) formed from 10 mM PtCl_6^{2-} solution. EDX analysis (not shown) of the deposit confirmed that the fibrous deposit was composed of Pt metal without any significant traces of K or Cl residues from the precursor.

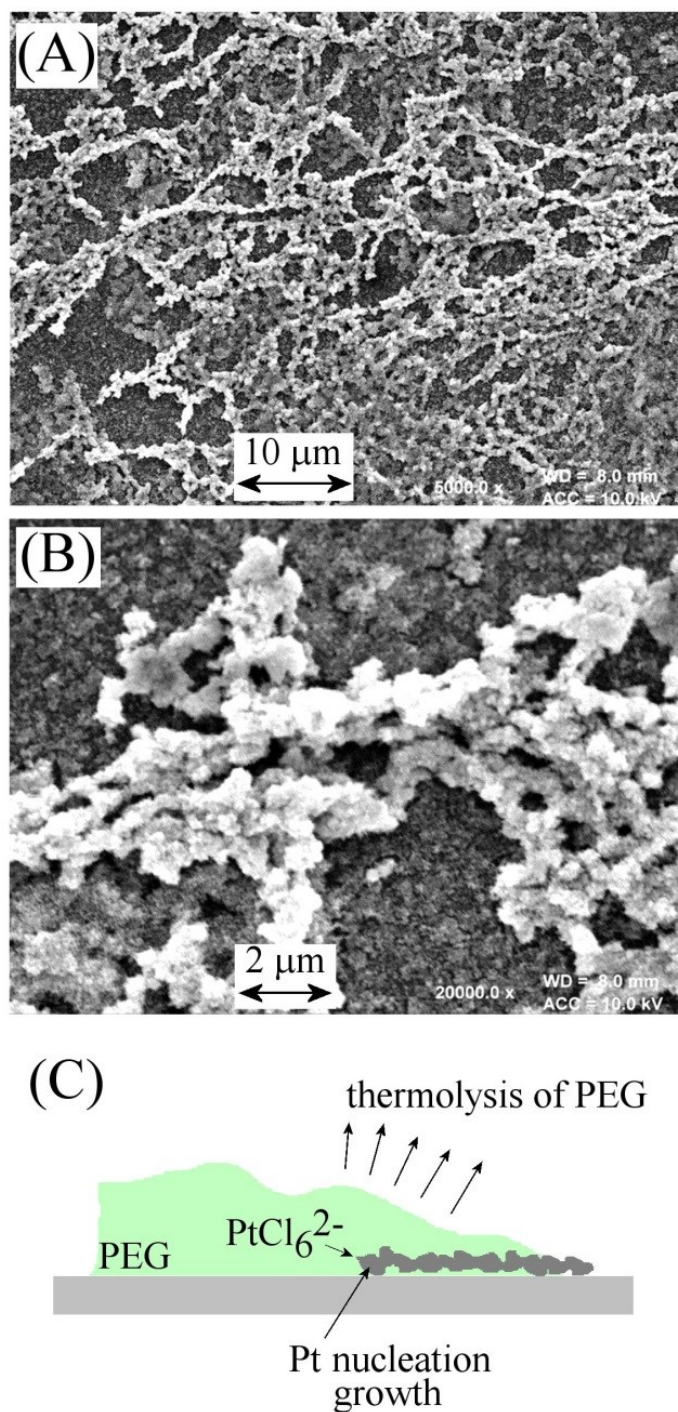


Figure 1. FE-SEM images of Pt deposits from thermolysis of 10 mM K₂PtCl₆/PEG200 solution at (A) 5,000 × and (B) 20,000 × magnification. (C) Schematic drawing of the thermolysis process.

The surface coverage appeared to increase with PtCl₆²⁻ concentration with the characteristic nanofibrous appearance remaining. PEG is a mild reducing agent, which reduces the Pt(IV) in

a multi-step process to Pt metal with an increasing rate as the temperature is elevated. The high temperatures also cause the polymer solvent to evaporate (boiling point ca. 250 °C [22]) and hence prevent further reactions from occurring. A schematic drawing summarising this complex multi-step mechanism is shown in Figure 1C.

3.2. Voltammetric characterisation of nano-fibrous platinum in H₂SO₄

The nano-Pt deposits on ITO were investigated by cyclic voltammetry in aqueous 0.5 M H₂SO₄ in order to determine the electrochemically active area of the electrodes (see Figure 2A). The two peaks at -0.09 V and -0.17 V *vs.* SCE correspond to weak and strong H adsorption (H_{ads}) on the Pt surface consistent with poly-crystalline bulk platinum (see Figure 2B). Repeated cycling at anodic potentials (up to +1.3 V *vs.* SCE) allowed to clean and activate the Pt surface. Consequently, the H_{ads} peaks became more clearly resolved. The hydrogen evolution reaction (HER) occurs at potentials more negative than -0.21 V *vs.* SCE.

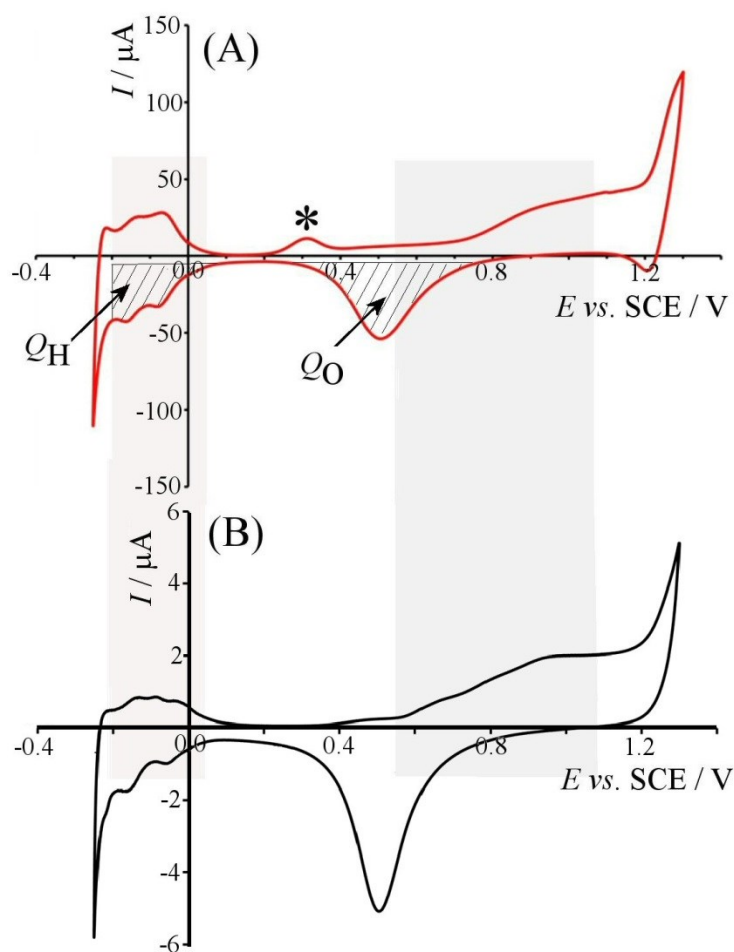


Figure 2. (A) Cyclic voltammograms (scan 5, scan rate 5 mV s^{-1}) for the platinum deposit (formed from 5 mM PtCl_6^{2-}) immersed in $0.5 \text{ M H}_2\text{SO}_4$. (B) As above but for a conventional 2 mm diameter Pt disc electrode.

The oxidation of the platinum surface and back reduction to platinum metal occur centred around 0.7 V vs. SCE with a further anodic process at 1.2 V vs. SCE indicative of the electrolyte oxidation. A peak response at 0.3 V vs. SCE (indicated by *) is observed in addition to the conventional platinum processes and this must be attributed to an interaction with the underlying ITO substrate. The same peak response has been reported by Liu et al. [14]. Perhaps interestingly, this peak response is observed only after the potential has been swept into hydrogen evolution potential range and therefore could be linked to the ITO substrate being reduced.

The electrochemically active surface area (ESA) of the Pt deposits can be calculated using either the H adsorption [23,24] or carbon monoxide oxidation [25], or (with less precision) the PtO_x/PtOH desorption [26] region of the cyclic voltammogram assuming full coverage of adsorbate on the surface and 1:1 linkages between adsorbate and adsorbent. Here both the PtO_x/PtOH desorption peak (Q_O) and the H_{ads} region (Q_H) were employed but only the more reliable Q_H value was used to calculate the ESA (see deviations in Q_O/Q_H in Table 1). The charge density used was 210 $\mu\text{C cm}^{-2}$ [20] and data are summarised in Table 1.

Table 1. Summary of the electrochemical data (obtained in 0.5 M H₂SO₄ or in 0.5 M H₂SO₄ /0.5 M MeOH) and surface area (ESA, from H_{ads} region assuming 210 $\mu\text{C cm}^{-2}$ [20]) and methanol oxidation catalysis data (see text) for nanofibrous Pt deposits on ITO with different catalyst loadings compared to a conventional 2 mm diameter Pt disc electrode.

	Q_H : Charge under H _{adsorption} region / mC	Q_O : Charge under (PtO _x /PtOH) _{desorption} peak / mC	Q_O/Q_H	Electrochemically active surface area (ESA) / cm ²	Current density i_p for MeOH oxidation / $\mu\text{A cm}^{-2}$
2 mm diameter Pt disc	0.05	0.15	2.93	0.24	50.9
Sample 1 (5 mM PtCl₆²⁻)	1.02	1.79	1.75	4.87	96.5
Sample 2 (10 mM PtCl₆²⁻)	1.23	2.31	1.88	5.86	79.7
Sample 3 (20 mM PtCl₆²⁻)	2.14	3.64	1.70	10.2	106

The area estimate suggests a roughness factor of ca. 8 for the 2 mm diameter platinum disc electrode and a substantially higher roughness for the nano-fibrous samples. The general trend in ESA increase with PtCl₆²⁻ concentration suggests that the amount of platinum on the ITO

surface increases with precursor concentration (given a similar feature size for nano-fibrous deposits). Perhaps interestingly, the Q_O/Q_H ratio seems to be lower for the nano-fibrous material, which could be linked to curvature or disorder effects [27], or perhaps more likely to substrate effects such as slower growth of the oxide film on ITO (see Figure 2B compared to Figure 2A). For further interpretation of these data a more extended/systematic data set would be required.

3.3. Voltammetric characterisation of nano-fibrous platinum in the catalytic oxidation of methanol

The catalytic electro-oxidation of MeOH on a Pt electrode has been studied extensively on poly-crystalline and on single crystal platinum [28] and is highly relevant for advances in direct methanol fuel cells (DMFCs) [29]. In this study, MeOH was used as the analyte to determine and compare the catalytic activity of the Pt nano-structures. Voltammetric investigation of the oxidation of a 0.5 M MeOH solution in 0.5 M H₂SO₄ electrolyte showed a characteristic peak current on the positive-going scan at 0.6 V vs. SCE (see Figure 3A), which was independent of the scan rate (with appropriate background subtraction). This is a tell-tale sign for this process to be kinetically controlled (catalytic) rather than diffusion limited. The negative-going scan also showed a MeOH oxidation peak with onset at the PtO_x/PtOH desorption region potential. The removal of oxide from the Pt surface leaves behind a clean and highly catalytic Pt region, which rapidly converts MeOH into products. Both anodic oxidation peaks for methanol oxidation increase with methanol concentration (see Figure 3B) with plateauing at concentrations higher than 1 M.

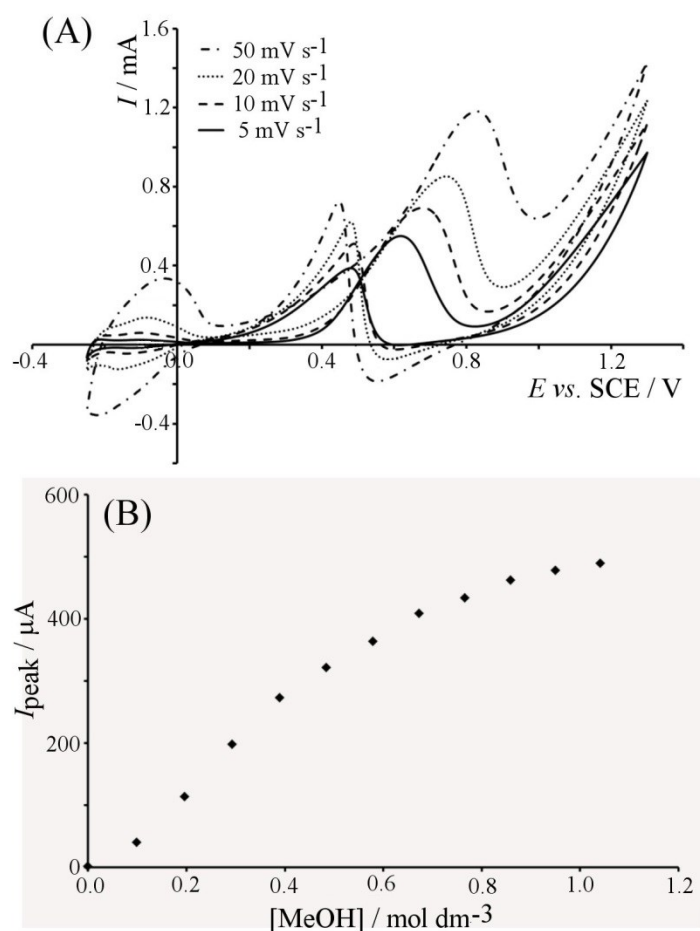


Figure 3. (A) Cyclic voltammograms (scan rate 5, 10, 20, 50 mV s^{-1}) for the oxidation of 0.5 M MeOH in 0.5 M H_2SO_4 at various scan rates using sample **3** as the working electrode. (B) Plot of the methanol oxidation peak current versus methanol concentration.

The peak current density (i_p) for the MeOH oxidation process (for the positive-going potential scan) at a given scan rate can be used as a measure of the catalytic activity of the Pt nanostructures and is calculated here using equation 1.

$$i_p = \frac{I_p}{ESA} \quad (1)$$

Voltammetric data for different types of platinum electrodes in the presence and in the absence of 0.5 M methanol are shown in Figure 4. A polished 2 mm diameter Pt disc electrode was used

for comparison with the nano-fibrous platinum samples. It was observed that for all platinum samples a positive potential window up to 1.3 V vs. SCE is required to maintain good electrocatalytic responses.

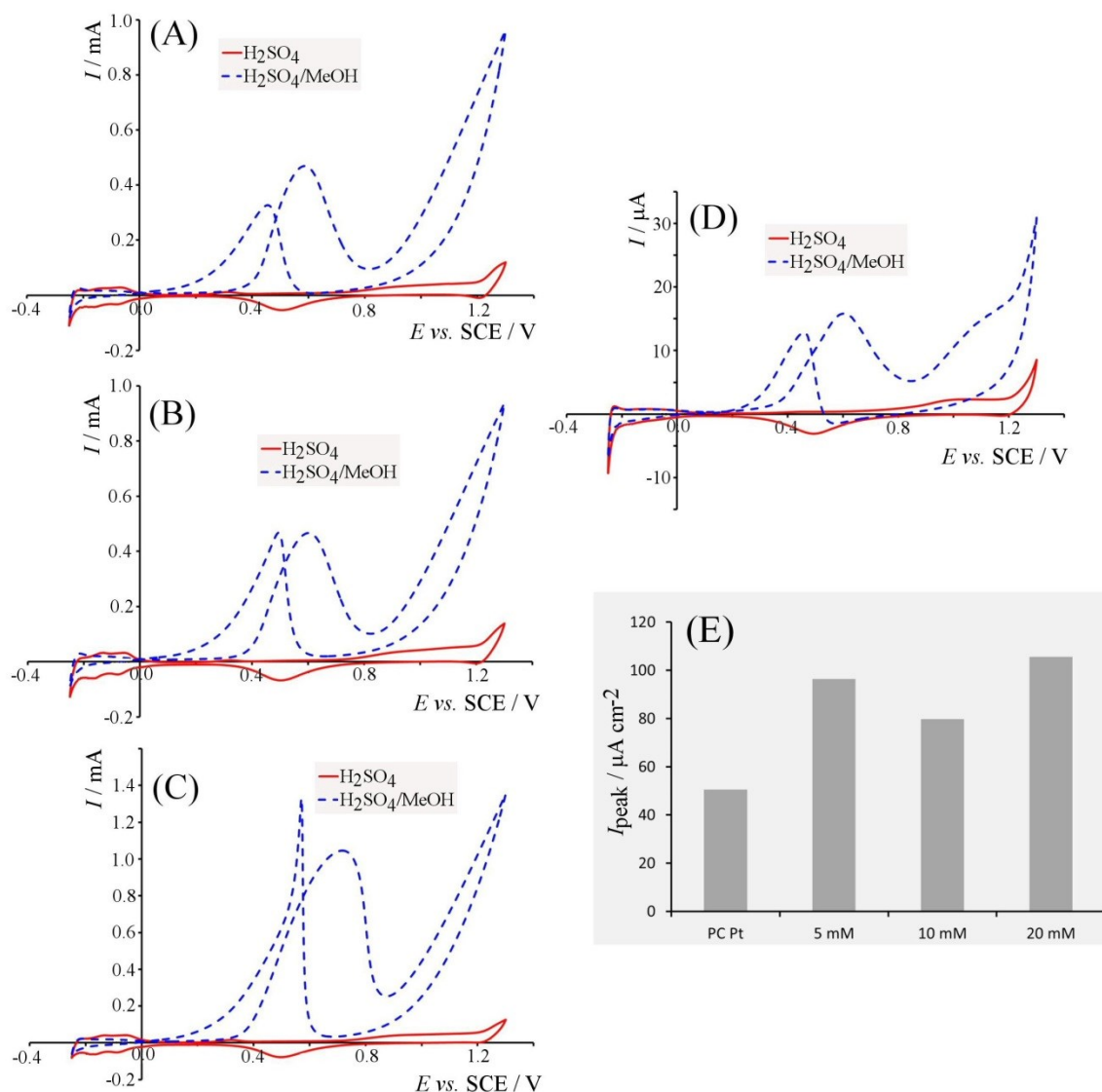


Figure 4. Cyclic voltammograms (scan rate 5 mV s^{-1}) for platinum electrodes immersed in $0.5 \text{ M H}_2\text{SO}_4$ without (red) and with (blue) 0.5 M MeOH for (A) the deposit formed from 5 mM PtCl_6^{2-} , (B) the deposit formed from $10 \text{ mM PtCl}_6^{2-}$, (C) the deposit formed from $20 \text{ mM PtCl}_6^{2-}$, and (D) a conventional 2 mm diameter platinum disc electrode. (E) Bar graph showing the current density for the electro-oxidation of MeOH (peak observed during forward scan) for the four types of electrodes (estimated error ca. $\pm 30 \%$).

The catalytic methanol oxidation response appears most pronounced in Figure 4C for the nano-fibrous platinum from 20 mM precursor solution. The sharp peak-like current observed during the negative-going potential sweep is probably caused by a combination of substrate resistance delaying the onset of the methanol oxidation and formation of highly active platinum surface (compare [30,31]). The bar-graph in Figure 4E shows a comparison of all four types of electrodes (errors estimated +/- 30 %) where there is only a minor increase in catalytic activity or current relative to ESA for nano-fibrous platinum. This is consistent with literature reports for nano-platinum on ITO [14,15]. The long term stability of the nano-fibrous platinum on ITO is limited and, for example, after performing 100 potential cycles in 0.5 M H₂SO₄ / 0.5 M methanol a clear decrease of catalytic current and some “flaking” of the catalyst from the electrode surface into the solution was observed. The type of substrate (chemical nature, roughness, adhesion layer, composition, etc.) appears to be important and will be addressed in future work to improve the long term stability.

4. Conclusion

A one-step method is reported for the synthesis of nano-fibrous platinum from a PEG200 precursor solution by thermolysis under atmospheric conditions. Upon heating the PEG solvent evaporates, whilst simultaneously promoting the reductive deposition of metallic platinum onto ITO. The nano-fibrous deposits form a network of platinum on the surface with a high surface area. The electrocatalytic reactivity towards methanol oxidation normalised to active platinum surface area was only slightly increased when compared to bulk polycrystalline platinum. This suggests that also for other applications e.g. ethanol oxidation [32] similar performance to literature catalysts is likely. The catalyst deposition procedure could be further optimised for different types of substrates by altering the ramp rate, maximum heating temperature, length

of heating, or precursor solution composition. The applicability of this catalyst is most likely on carbon surfaces, e.g. in fuel cell or sensor systems. When deposited onto glass substrates, nano-fibrous platinum could be employed directly without the thin conducting oxide layer [33]. This method could also be of interest for the formation of mixed-metal catalysts.

Acknowledgements

C.E.H. thanks the University of Bath for a PhD scholarship.

References

-
- [1] O.T. Holton, J.W. Stevenson, The Role of Platinum in Proton Exchange Membrane Fuel Cells Evaluation of platinum's unique properties for use in both the anode and cathode of a proton exchange membrane fuel cell, *Platinum Met. Rev.* 57 (2013) 259.
 - [2] Y.T. Tang, X. Pan, S.Y. Dai, C.N. Zhang, H.J. Tian, New Sight Towards Dye-Sensitized Solar Cells: Material and Theoretical, *Key Engineer. Mater.* 451 (2011) 63.
 - [3] S. Marini, P. Salvi, P. Nelli, R. Pesenti, M. Villa, M. Berrettoni, G. Zangari, Y. Kiros, Advanced Alkaline Water Electrolysis, *Electrochim. Acta* 82 (2012) 384.
 - [4] H.J. You, S.C. Yang, B.J. Ding, H. Yang, Synthesis of Colloidal Metal and Metal Alloy Nanoparticles for Electrochemical Energy Applications, *Chem. Soc. Rev.* 42 (2013) 2880.
 - [5] G.J. Leong, M.C. Schulze, M.B. Strand, D. Maloney, S.L. Frisco, H.N. Dinh, B. Pivovar, R.M. Richards, Shape-Directed Platinum Nanoparticle Synthesis: Nanoscale Design of Novel Catalysts, *Appl. Organomet. Chem.* 28 (2014) 1.

-
- [6] L.L. Lu, G.P. Yin, Shape-Controlled Synthesis and Applications of Platinum Nanocrystals, *Progress Chem.* 22 (2010) 338.
- [7] J.B. Wu, H. Yang, Platinum-Based Oxygen Reduction Electrocatalysts, *Acc. Chem. Res.* 46 (2013) 1848.
- [8] H.M. Zhang, W.Q. Zhou, Y.K. Du, P. Yang, C.Y. Wang, One-Step Electrodeposition of Platinum Nanoflowers and their High Efficient Catalytic Activity for Methanol Electro-oxidation, *Electrochem. Commun.* 12 (2010) 882.
- [9] R.Y. Wang, D.C. Higgins, M.A. Hoque, D.U. Lee, F. Hassan, Z.W. Chen, Controlled Growth of Platinum Nanowire Arrays on Sulfur Doped Graphene as High Performance Electrocatalyst, *Sci. Reports* 3 (2013) 2431.
- [10] S. Sharma, B.G. Pollet, Support Materials for PEMFC and DMFC Electrocatalysts- A review, *J. Power Sources* 208 (2012) 96.
- [11] D. Gust, T.A. Moore, A.L. Moore, Solar Fuels via Artificial Photosynthesis, *Acc. Chem. Res.* 42 (2009) 1890.
- [12] V.D. Dao, C.Q. Tran, S.H. Ko, H.S. Choi, Dry Plasma Reduction to Synthesize Supported Platinum Nanoparticles for Flexible Dye-sensitized Solar Cells, *J. Mater. Chem. A* 1 (2013) 4436.
- [13] F.F. Liang, H.F. Tian, M.Z. Jia, J.B. Hu, Pt Nanoparticles Ion-implanted onto Indium Tin Oxide Electrodes and their Electrocatalytic Activity Towards Methanol, *J. Power Sources* 225 (2013) 9.
- [14] J. Liu, C. Zhong, X.T. Du, Y.T. Wu, P.Z. Xu, J.B. Liu, W.B. Hu, Pulsed Electrodeposition of Pt Particles on Indium Tin Oxide Substrates and their Electrocatalytic Properties for Methanol Oxidation, *Electrochim Acta* 100 (2013) 164.

-
- [15] G. Chang, M. Oyama, K. Hirao, In situ Chemical Reductive Growth of Platinum Nanoparticles on Indium Tin Oxide Surfaces and their Electrochemical Applications, *J. Phys. Chem. B* 110 (2006) 1860.
- [16] A. Velazquez-Palenzuela, F. Centellas, E. Brillas, J.A. Garrido, C. Arias, R.M. Rodriguez, P.L. Cabot, Sn-modified Carbon-supported Pt Nanoparticles Synthesized using Spontaneous Deposition as Electrocatalysts for Direct Alcohol Fuel Cells, *Inter. J. Hydr. Energy* 38 (2013) 16418.
- [17] M. Gohain, J. Jacobs, C. Marais, B.C.B. Bezuidenhout, Al(OTf)₃ Catalysed Friedel-Crafts Michael Type Addition of Indoles to α,β -Unsaturated Ketones with PEG-200 as Recyclable Solvent, *Austral. J. Chem.* 66 (2013) 1594.
- [18] C.L. Yu, K. Yang, Y. Xie, Q.Z. Fan, J.C. Yu, Q. Shu, C.Y. Wang, Novel Hollow Pt-ZnO Nanocomposite Microspheres with Hierarchical Structure and Enhanced Photocatalytic Activity and Stability, *Nanoscale* 5 (2013) 2142.
- [19] T. Herricks, J. Chen, Y. Xia, Polyol Synthesis of Platinum Nanoparticles: Control of Morphology with Sodium Nitrate, *Nano Lett.*, 4 (2004) 2367.
- [20] J. Chen, B. Lim, E.P. Lee, Y. Xia, Shape-controlled Synthesis of Platinum Nanocrystals for Catalytic and Electrocatalytic Applications, *Nano Today* 4 (2009) 81.
- [21] O.P. Yadav, A. Palmqvist, N. Cruise, K. Holmberg, Synthesis of Platinum Nanoparticles in Microemulsions and their Catalytic Activity for the Oxidation of Carbon Monoxide, *Coll. Surf. A: Physicochem. Engineer. Aspects* 221 (2003) 131.
- [22] J.F. Li, Z.L. Xu, H. Yang, C.P. Feng, J.H. Shi, Hydrophilic Microporous PES Membranes Prepared by PES/PEG/DMAc Casting Solutions, *J. Appl. Polym. Sci.* 107 (2008) 4100.

-
- [23] T. Biegler, D.A.J. Rand, R. Woods, Limiting Oxygen Coverage on Platinized Platinum - Relevance to Determination of Real Platinum Area by Hydrogen Adsorption, *J. Electroanal. Chem.* 29 (1971) 269.
- [24] Y. Ohkubo, S. Seino, S. Kageyama, J. Kugai, T. Nakagawa, K. Ueno, T.A. Yamamoto, Effect of Decrease in the Size of Pt Nanoparticles Using Sodium Phosphinate on Electrochemically Active Surface Area, *J. Nanoparticle Res.* 16 (2014) 2237.
- [25] E.M. Crabb, R. Marshall, D. Thompsett, Carbon Monoxide Electro-oxidation Properties of Carbon-supported PtSn Catalysts Prepared Using Surface Organometallic Chemistry, *J. Electrochem. Soc.* 147 (2000) 4440.
- [26] B.E. Conway, Electrochemical Oxide Film Formation at Noble-Metals as a Surface-Chemical Process, *Progress Surf. Sci.* 49 (1995) 331.
- [27] S. Guerin, B.E. Hayden, C.E. Lee, C. Mormiche, J.R. Owen, A.E. Russell, B. Theobald, D. Thompsett, Combinatorial Electrochemical Screening of Fuel Cell Electrocatalysts, *J. Combinat. Chem.* 6 (2004) 149.
- [28] T.H.M. Housmans, M.T.M. Koper, Methanol Oxidation on Stepped Pt[n(111) x (110)] Electrodes: A Chronoamperometric Study, *J. Phys. Chem. B* 107 (2003) 8557.
- [29] X.L. Li, A. Faghri, Review and Advances of Direct Methanol Fuel Cells (DMFCs) Part I: Design, Fabrication, and Testing with High Concentration Methanol Solutions, *J. Power Sources* 226 (2013) 223.
- [30] N.C. Cheng, R.A. Webster, M. Pan, S.C. Mu, L. Rassaei, S.C. Tsang, F. Marken, One-step Growth of 3-5 nm Diameter Palladium Electrocatalyst in a Carbon Nanoparticle-chitosan Host and Characterization for Formic Acid Oxidation. *Electrochim. Acta* 55 (2010) 6601.

-
- [31] Y.E. Seidel, A. Schneider, Z. Jusys, B. Wickman, B. Kasemo, R.J. Behm, Transport Effects in the Electrooxidation of Methanol Studied on Nanostructured Pt/Glassy Carbon Electrodes, *Langmuir* 26 (2010) 3569.
- [32] A. Ramanavicius, A. Kausaite, A. Ramanaviciene, Enzymatic Biofuel Cell Based on Anode and Cathode Powered by Ethanol, *Biosens. Bioelectronics* 24 (2008) 761.
- [33] J.W. Kim, J.H. Kang, U. Jeong, H. Kim, H. Lee, Catalytic, Conductive, and Transparent Platinum Nanofiber Webs for FTO-Free Dye-Sensitized Solar Cells, *ACS Appl. Mater. Interfaces* 5 (2013) 3176.