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Towards the Scalable Synthesis of NiPt Nanowires for PEMFC Applications

Pete Mardle (PJM556@bham.ac.uk) and

Dr Shangfeng Du

CDT Fuel Cells and their Fuels

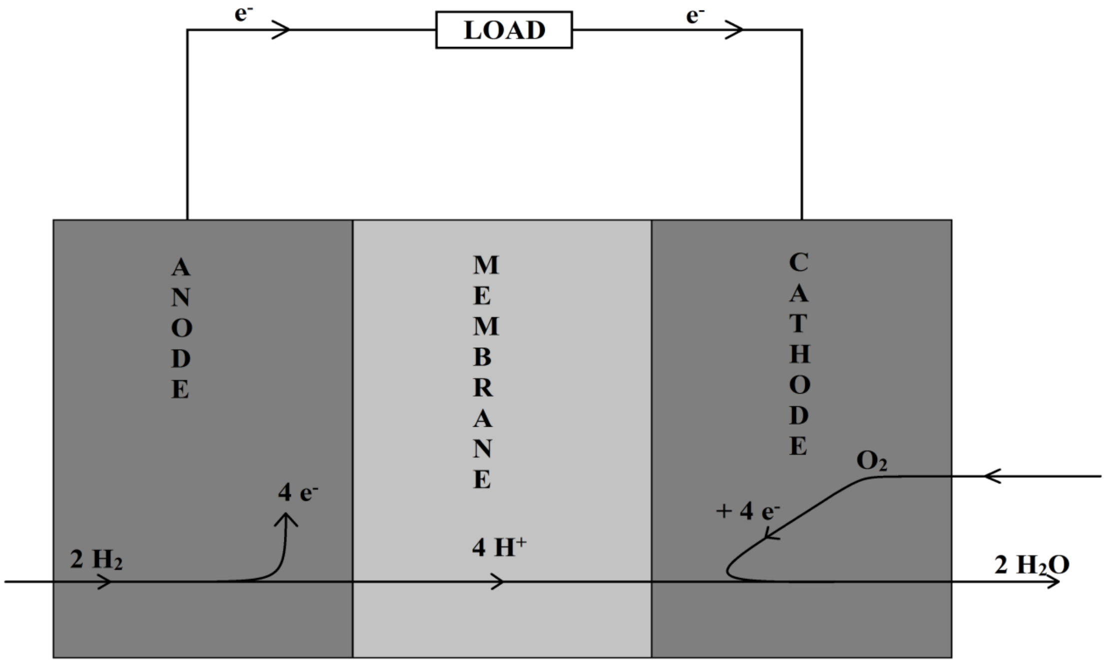
University of Birmingham

EPSRC

Engineering and Physical Sciences Research Council

The PEMFC Cathode Problem

$$2\,H_2 + O_2 \rightarrow 2\,H_2O \qquad E^{o}_{Cell} = 1.23\,V\ vs.RHE$$



$$2\,H_2 \rightarrow 4\,H^+ + 4\,e^-$$

FAST

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$

SLOW

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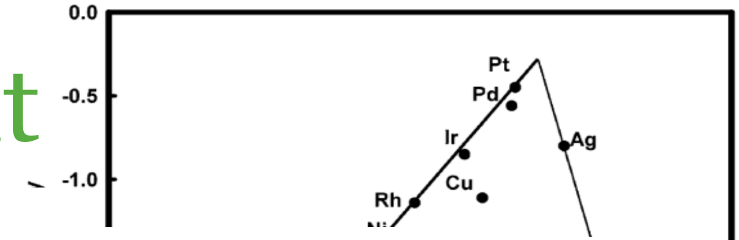
Catalyst Development



SCIENCE ADVANCES | RESEARCH ARTICLE

PHYSICAL SCIENCE

Efficient oxygen reduction catalysis by subnanometer Pt alloy nanowires

Kezhu Jiang,[1] Dandan Zhao,[1] S... Gang Lu,[5] Xiaoqing Huang[1]*

Communication

VIP Platinum Nan...

A Highly D... Membrane...

Shuhui Sun, Ga... Xueliang Sun*

Three-d... for oxyg...

Yaxiang Lu, Shangfeng Du*, Robert S...

ELSEVIER journal homep...

Cite this: *Chem. Commun.*, 2011, 47, 1...

www.rsc.org/chemcomm

Au/Pt and Au/Pt_3Ni nanow... high activity and durability ...

Yueming Tan,[a] Jingmin Fan,[a] Guangxu Chen,[a] Nanfeng Zheng*[a] and Qingji Xie[b]

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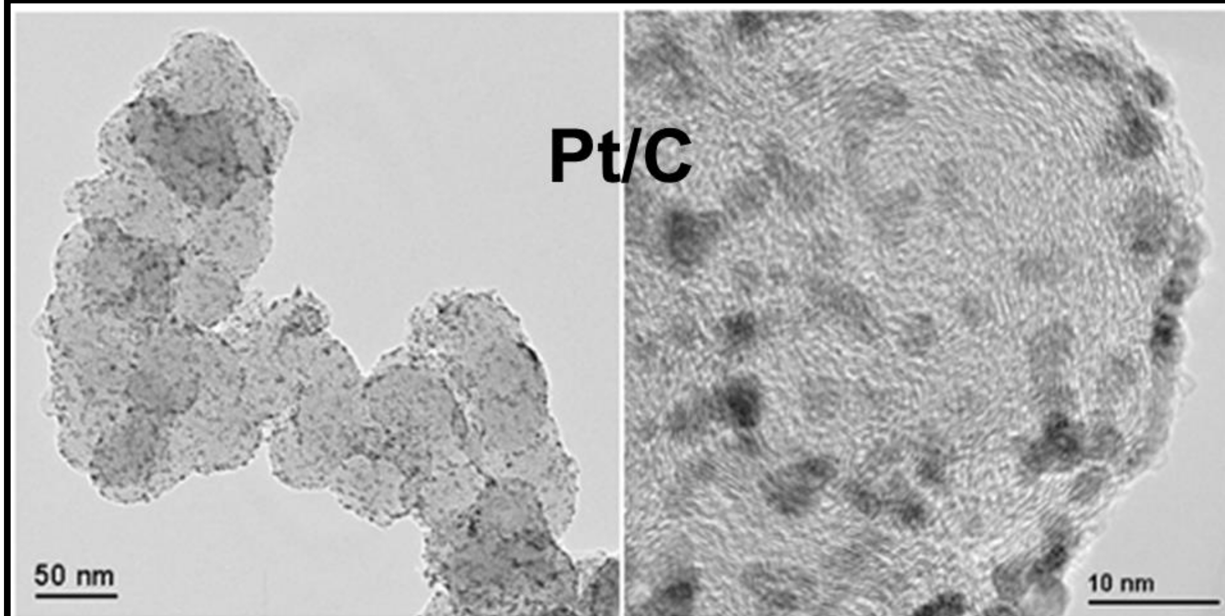
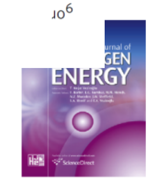
ADVANCED ENERGY MATERIALS www.advenergymat.de

Materials Views www.MaterialsViews.com

Mixed-PtPd-Shell PtPdCu Nanoparticle Nanotubes ...nt



Sigma-Aldrich, http://www.sigmaaldrich.com/materials-science/renewable-alternative-energy/pem-fuel-cells.html



...ire ...on reaction

...ue Wang [a],

...19-K22 (2012) ...mical Society

...on Carbon Nanotubes

Mark C. Elvington and Héctor R. Colón-Mercado*

...ne

Fuel Cells**

By *Shuhui Sun,* Frédéric Jaouen,* and *Jean-Pol Dodelet**

Binghong Han,[ac] Christopher E. Carlton,[ac] Anusorn Kongkanand,*[d] Ratandeep S. Kukreja,[d] Brian R. Theobald,[e] Lin Gan,[f] Rachel O'Malley,[e] Pet... Frederick T. Wagner[d] and Yang Shao-Horn*[abc]

Pt_{ML}/Pd/C core-shell electrocatalysts for the ORR in PEMFCs

B. C. Tessier[a], A. E. Russell[b], B. Theobald[a], D. Thompsett[a]

Mu Li [a], Yanhua Lei [a, b, *], Nan Sheng [a, b], Toshiaki Ohtsuka [a]

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...ciences

...Research Council

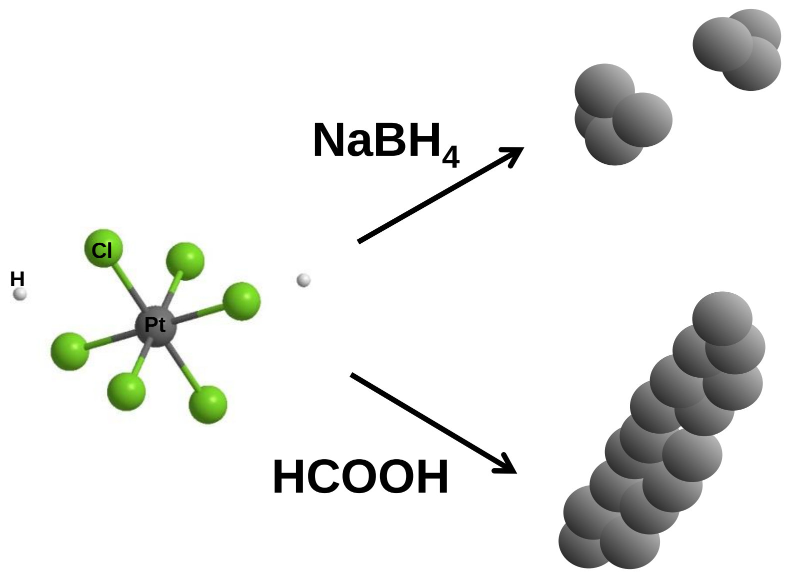
Why is Pt/C still used?

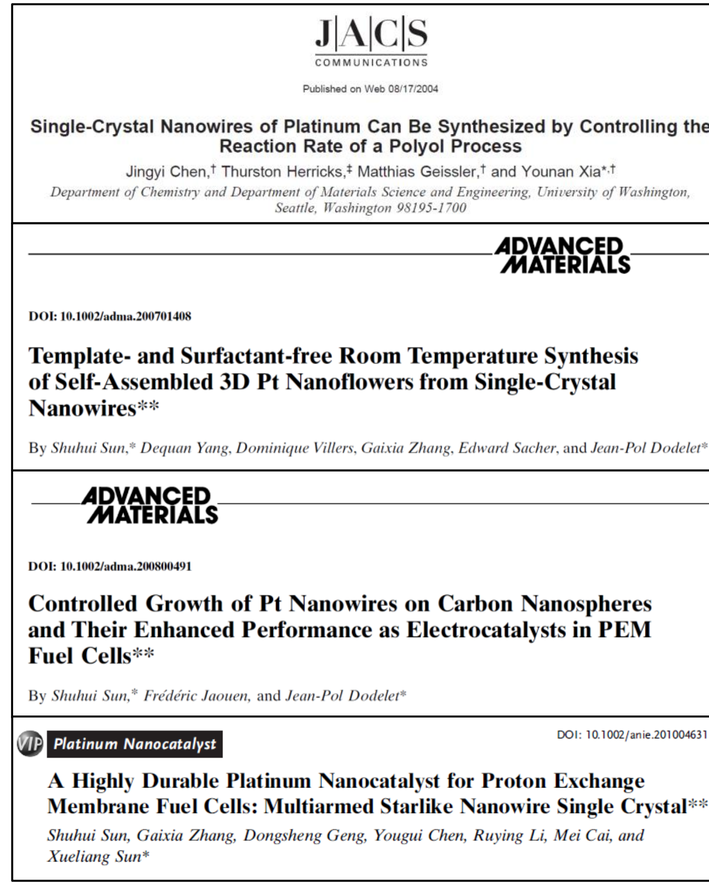
- A good catalyst does not necessarily make a good electrode.

Need to consider not just the activity but the effect of the catalyst on:

- Water transport
- Gas transport
- Ionomer distribution in the catalyst layer.
- Durability from coarsening at temperature.
- Effect of catalyst materials on component durability.
- Scalability of synthesis.

Pt Nanowire Arrays – The Inspiration





J|A|C|S COMMUNICATIONS

Published on Web 08/17/2004

Single-Crystal Nanowires of Platinum Can Be Synthesized by Controlling the Reaction Rate of a Polyol Process

Jingyi Chen,† Thurston Herricks,‡ Matthias Geissler,† and Younan Xia*,†

Department of Chemistry and Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195-1700

ADVANCED MATERIALS

DOI: 10.1002/adma.200701408

Template- and Surfactant-free Room Temperature Synthesis of Self-Assembled 3D Pt Nanoflowers from Single-Crystal Nanowires**

By *Shuhui Sun,* Dequan Yang, Dominique Villers, Gaixia Zhang, Edward Sacher,* and *Jean-Pol Dodelet**

ADVANCED MATERIALS

DOI: 10.1002/adma.200800491

Controlled Growth of Pt Nanowires on Carbon Nanospheres and Their Enhanced Performance as Electrocatalysts in PEM Fuel Cells**

By *Shuhui Sun,* Frédéric Jaouen,* and *Jean-Pol Dodelet**

VIP Platinum Nanocatalyst

DOI: 10.1002/anie.201004631

A Highly Durable Platinum Nanocatalyst for Proton Exchange Membrane Fuel Cells: Multiarmed Starlike Nanowire Single Crystal**

*Shuhui Sun, Gaixia Zhang, Dongsheng Geng, Yougui Chen, Ruying Li, Mei Cai, and Xueliang Sun**

Intrinsic catalyst improvement:

- Preferential exposure of crystal facets.
- Increase in electrical conductivity in one dimension.

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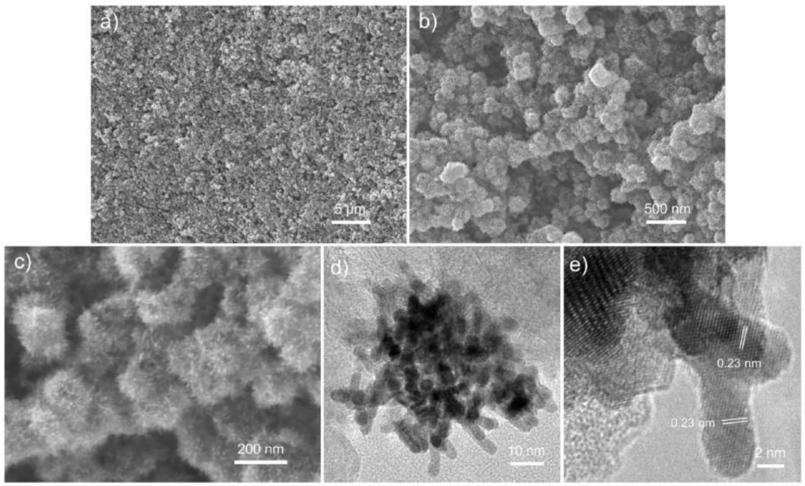
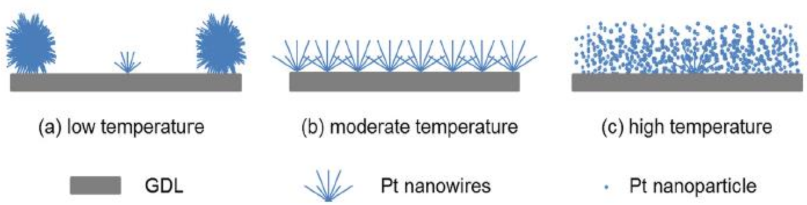
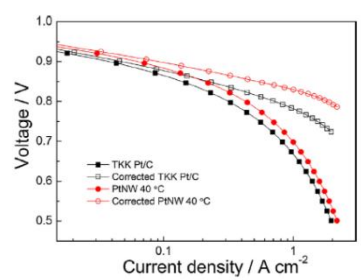
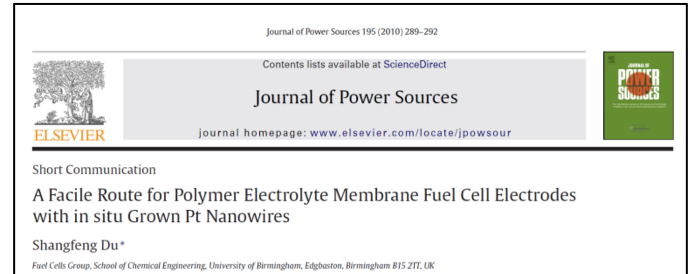
Pt Nanowire Arrays





Not just high catalytic ability, but good electrode performances shown.





Journal of Power Sources 195 (2010) 289–292
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Journal of Power Sources
journal homepage: www.elsevier.com/locate/jpowsour
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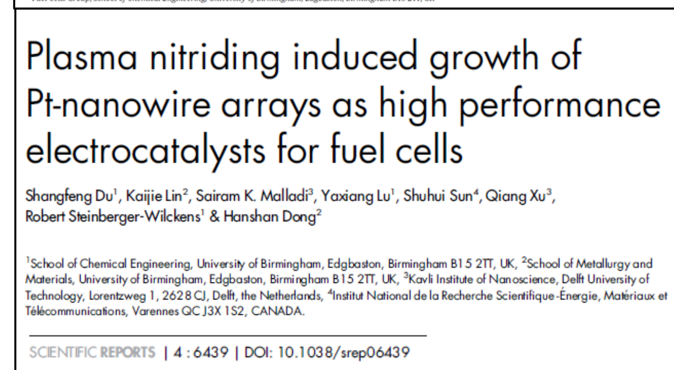
Short Communication

A Facile Route for Polymer Electrolyte Membrane Fuel Cell Electrodes with in situ Grown Pt Nanowires

Shangfeng Du*
Fuel Cells Group, School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK



Plasma nitriding induced growth of Pt-nanowire arrays as high performance electrocatalysts for fuel cells

Shangfeng Du[1], Kaijie Lin[2], Sairam K. Malladi[3], Yaxiang Lu[1], Shuhui Sun[4], Qiang Xu[3], Robert Steinberger-Wilckens[1] & Hanshan Dong[2]

[1]School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK, [2]School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK, [3]Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ, Delft, the Netherlands, [4]Institut National de la Recherche Scientifique-Énergie, Matériaux et Télécommunications, Varennes QC J3X 1S2, CANADA.

SCIENTIFIC REPORTS | 4 : 6439 | DOI: 10.1038/srep06439

Applied Catalysis B: Environmental 164 (2015) 389–395
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journal homepage: www.elsevier.com/locate/apcatb
ELSEVIER

Temperature-controlled growth of single-crystal Pt nanowire arrays for high performance catalyst electrodes in polymer electrolyte fuel cells

Yaxiang Lu, Shangfeng Du*, Robert Steinberger-Wilckens
School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Towards NiPt NW Arrays

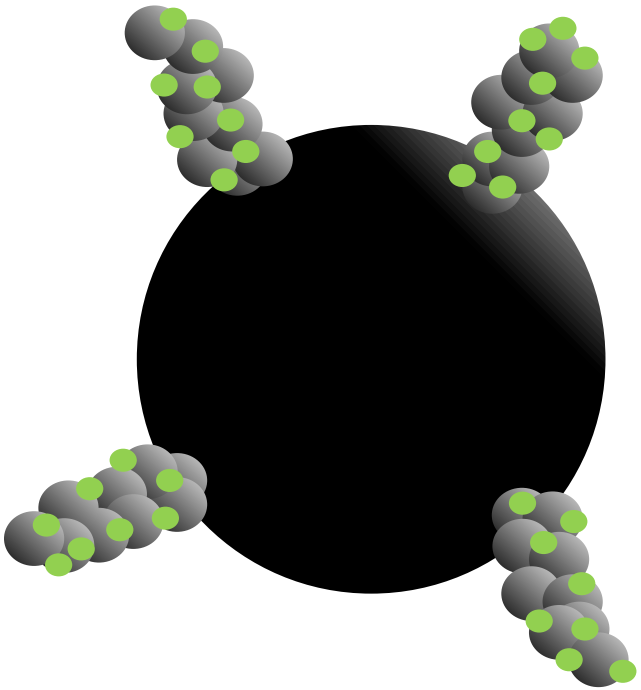
□ Synthesis method

1. Growth of Pt NWs on carbon.

$3\ H_2PtCl_{6(aq)} + 6\ HCOOH_{(aq)} \rightarrow Pt_{(s)} + 18\ HCl_{(aq)} + 3\ CO_{2(g)}$

2. Impregnation of Ni on the Pt NWs.

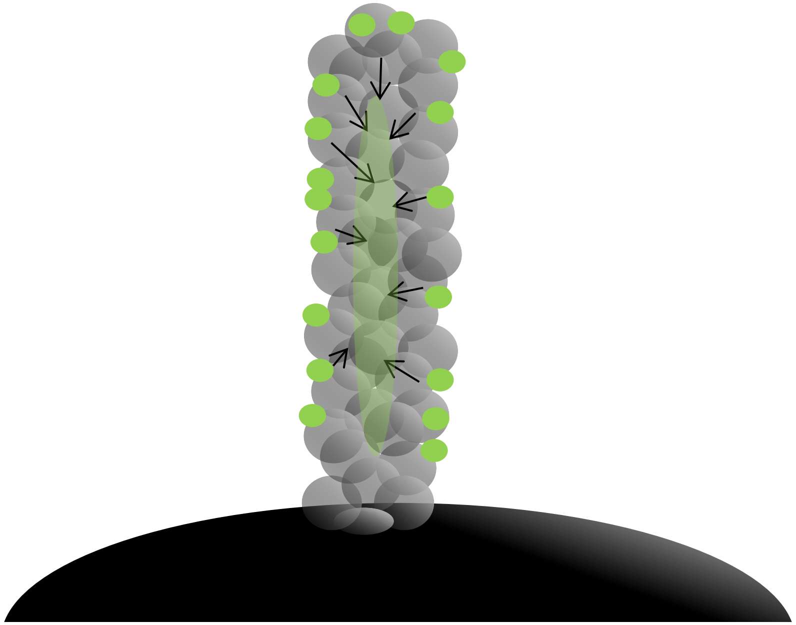
$2\ NiCl_{2(aq)} + NaBH_{4(aq)} + 3\ H_2O_{(l)} \rightarrow 2\ Ni_{(s)} + H_3BO_{3(aq)} + 3\ HCl_{(aq)} + NaCl_{(aq)} + 2\ H_{2(g)}$



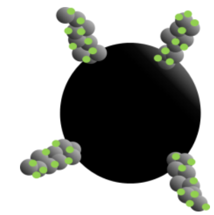
Towards NiPt NW Arrays

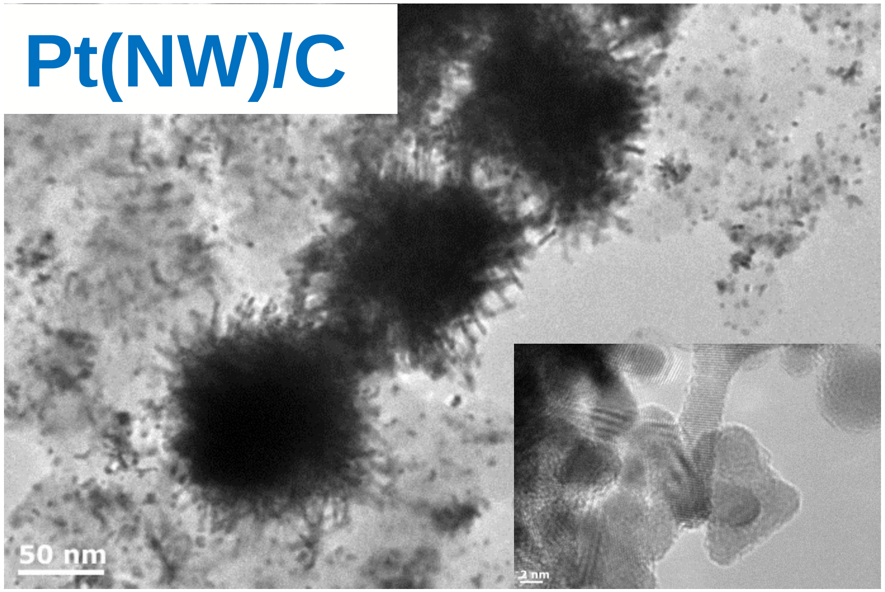
3. Thermal annealing

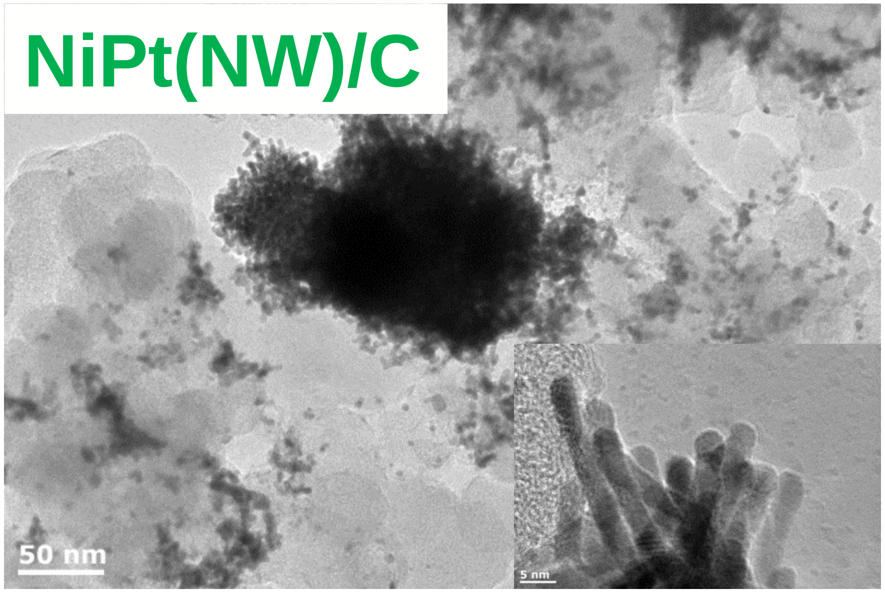
Anneal NiPt(NW)/C for 24 hours under a flow of 4 % H_2/Ar to promote surface segregation and alloying.

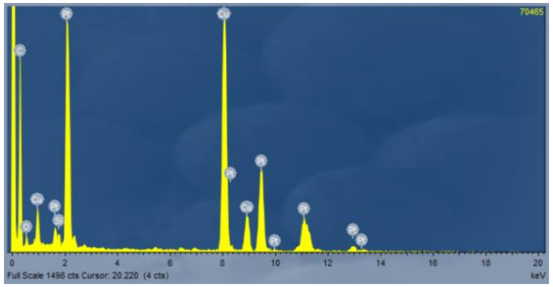


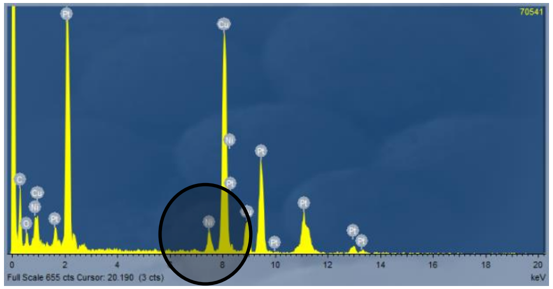
TEM before and after Ni impregnation











Pt:Ni atomic ratio 8:1

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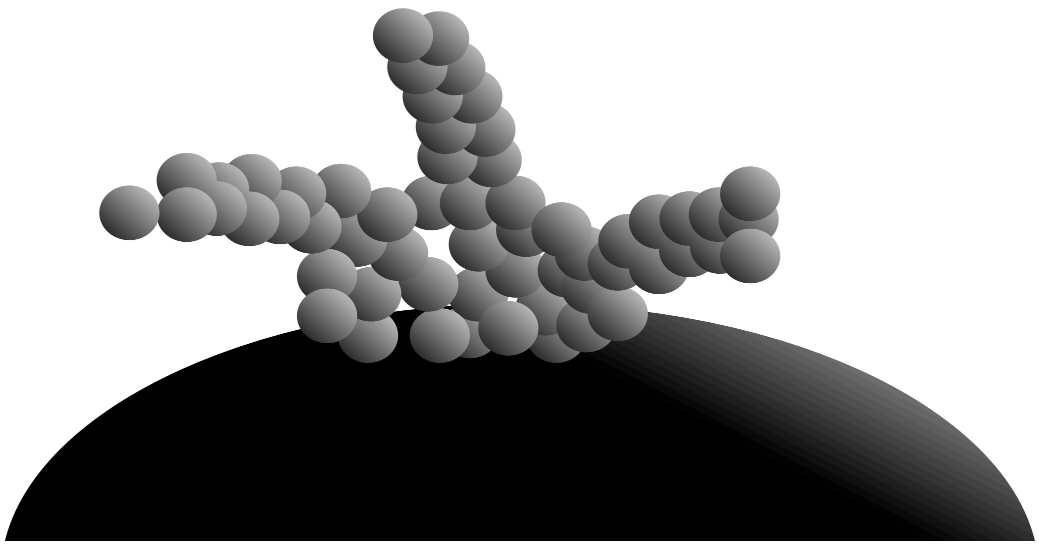
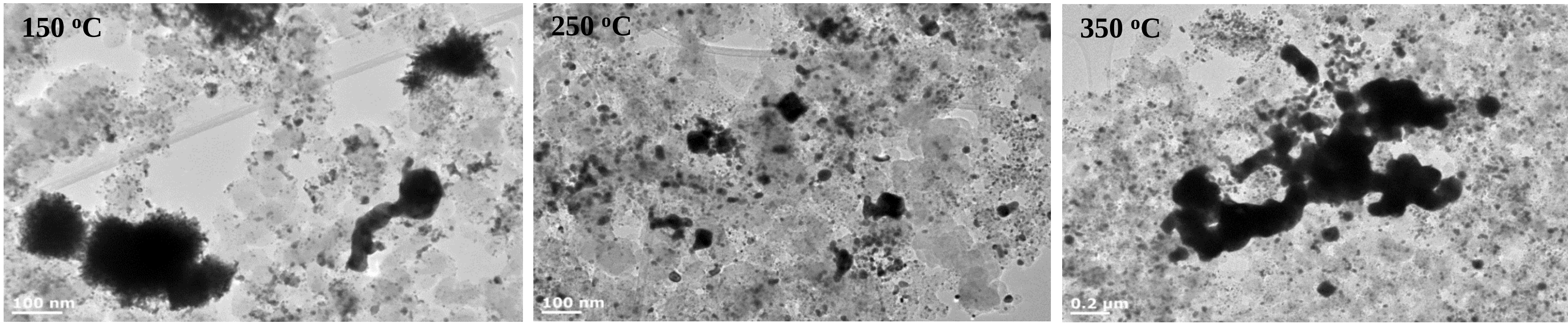
PtNW agglomeration – A Hypothesis



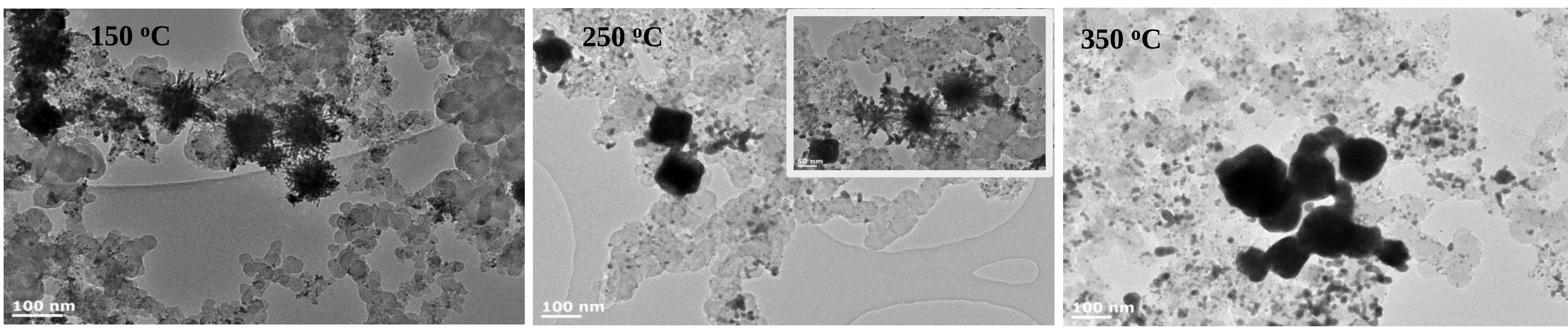
Reactant concentration: LOW / HIGH

After annealing

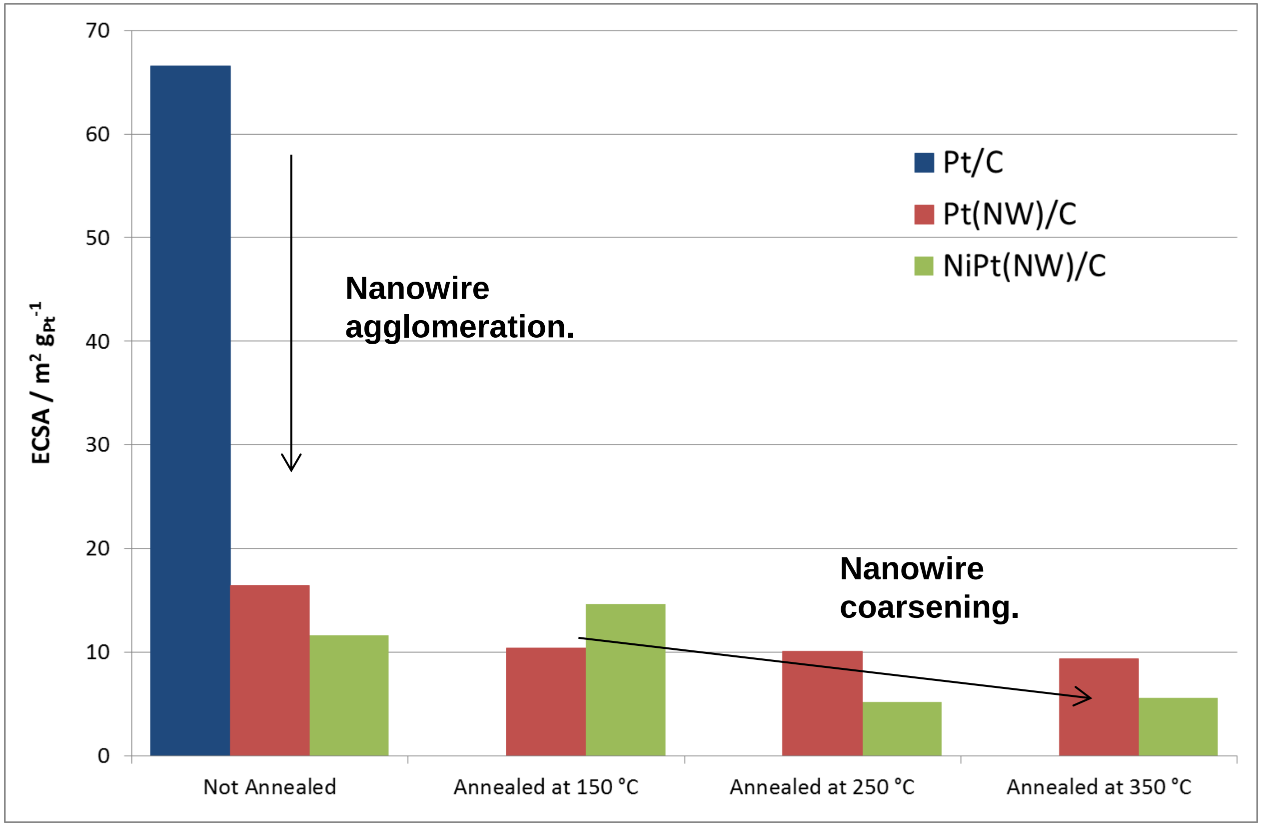
Pt(NW)/C



NiPt(NW)/C



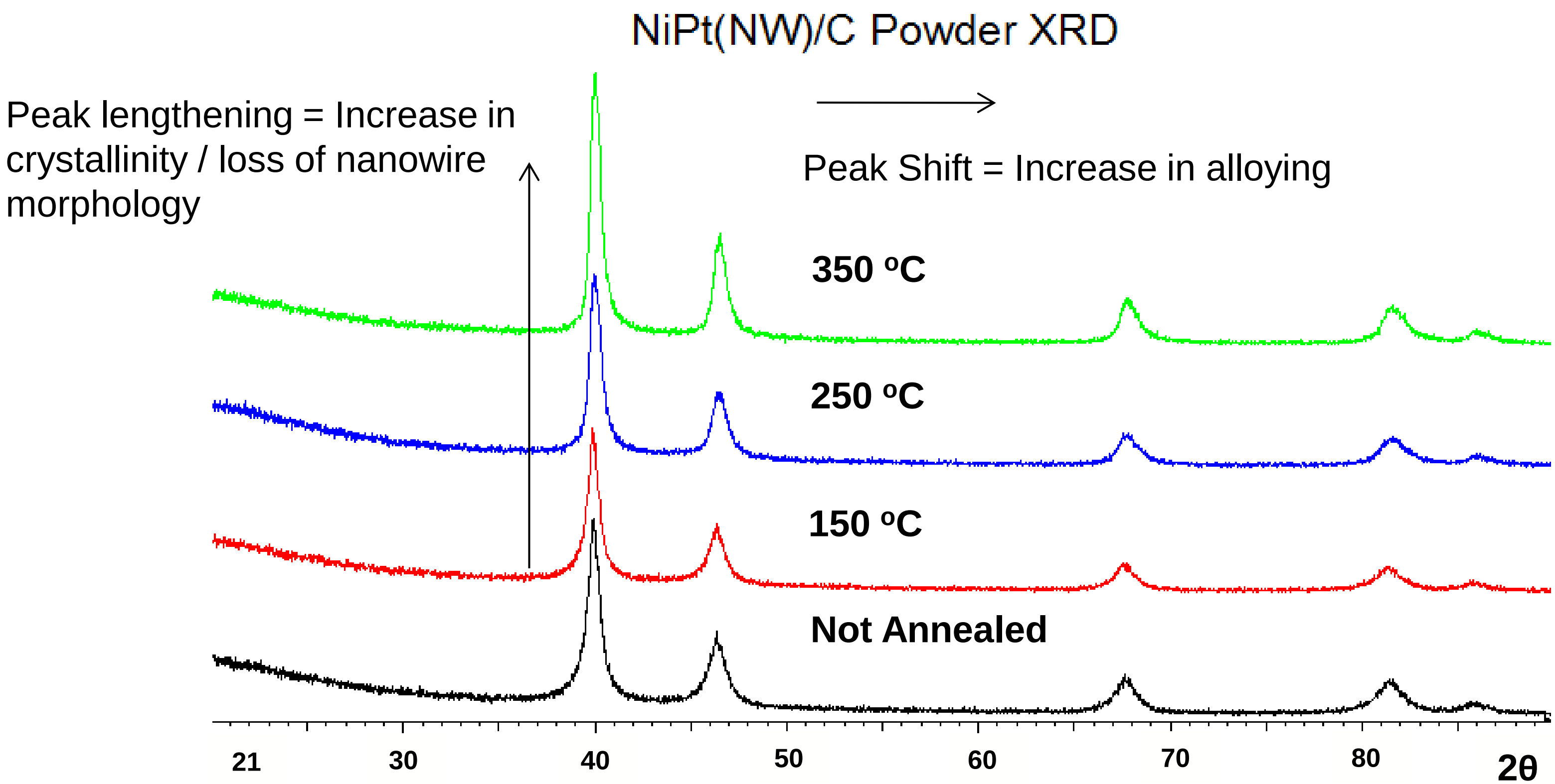
Electrochemically Active Surface Area (ECSA) – Ex-Situ



- 25 µg catalyst on 0.196 cm^2 GCE
- RHE reference electrode
- Pt gauze counter electrode
- 0.1 M $HClO_{4(aq)}$ electrolyte
- Temperature maintained at 25 ^oC via water jacket
- The H_{des} region from a CV (0.05-1.2 V vs. RHE, 100 mV s^{-1}) in N_2 saturated environment was used to obtain the ECSA.

ECSA = Surface area electrochemically active per unit mass of Pt metal. i.e. Pt utilisation.

Degree of annealing – XRD and Specific activity



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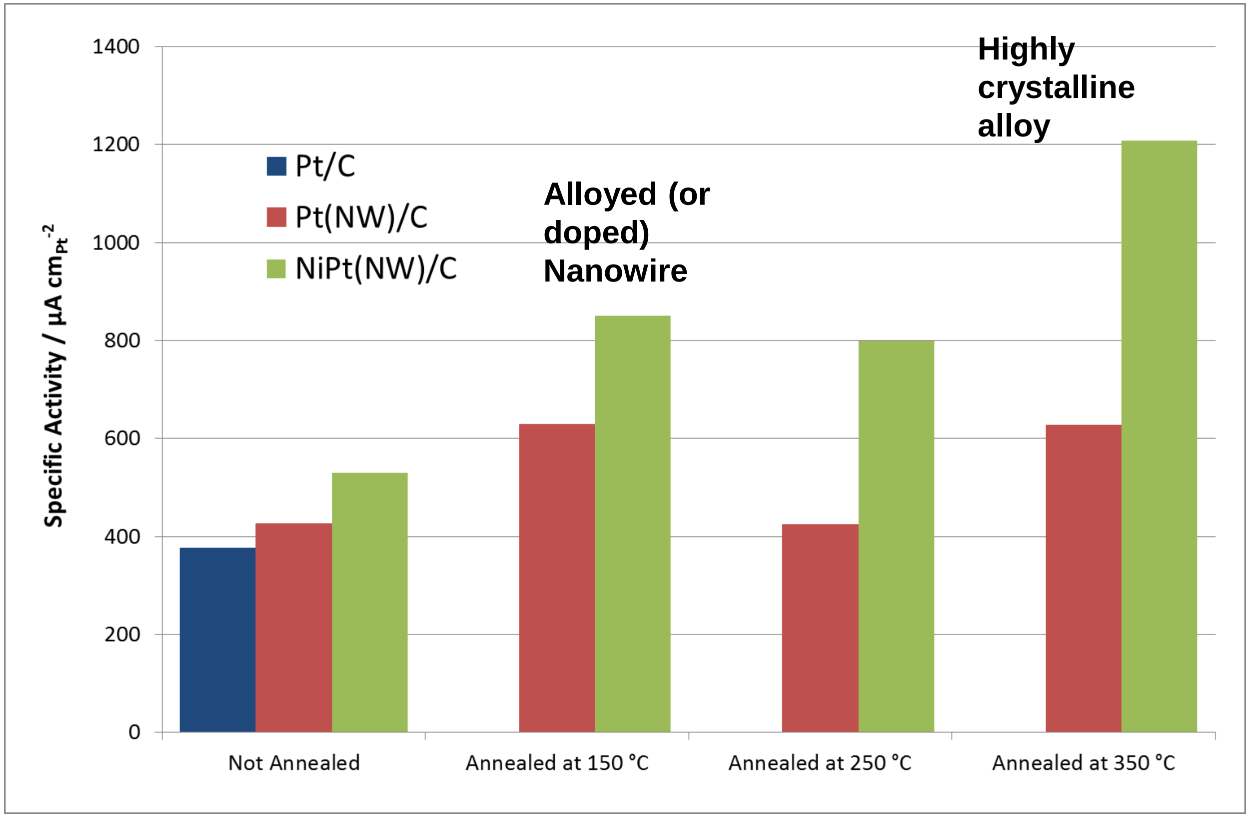
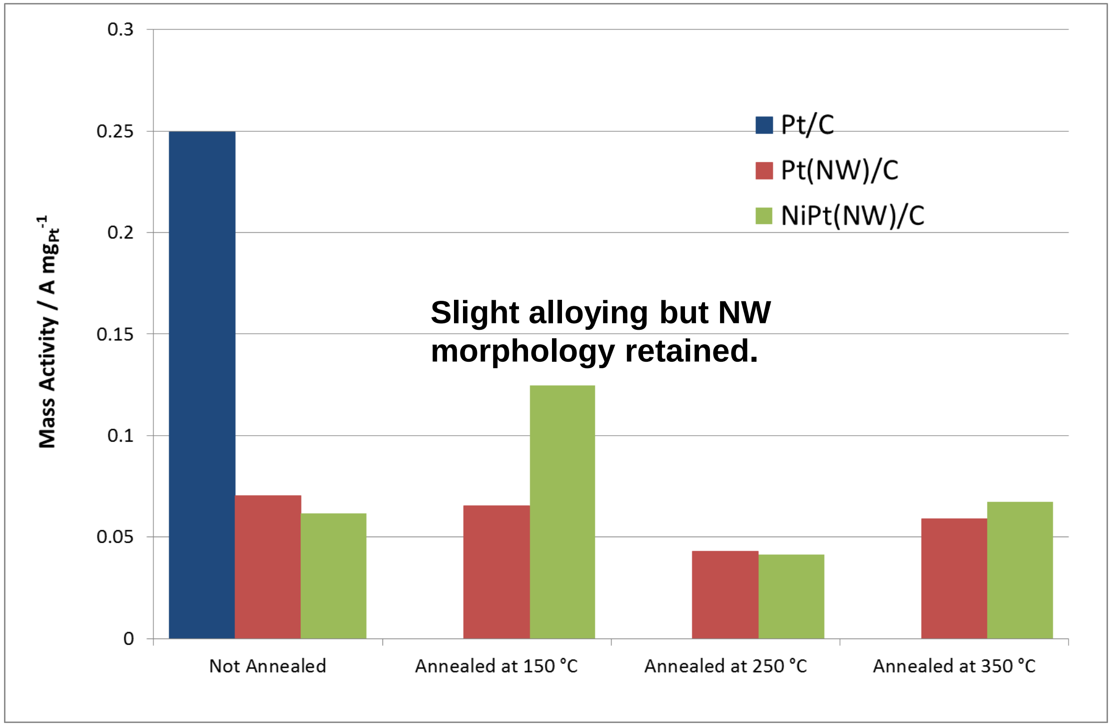
Surface Specific Activity– Ex-Situ



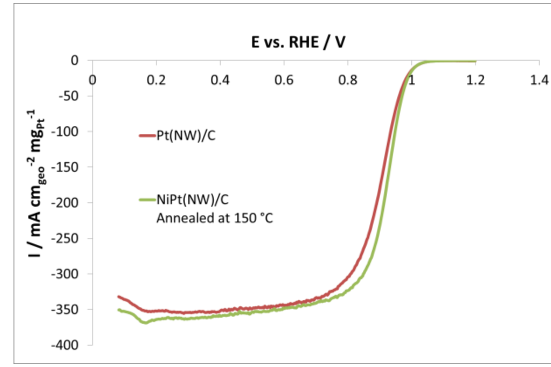
- 25 µg catalyst on 0.196 cm^2 GCE
- RHE reference electrode
- Pt gauze counter electrode
- 0.1 M $HClO_{4(aq)}$ electrolyte
- Temperature maintained at 25 ^{o}C via water jacket
- Koutecky-Levich analysis at 0.9 V vs. RHE (based on LSVs from 0.05 – 1.2 V vs. RHE, 20 mV s^{-1}) was run at rotation rates 400, 800, 1200, 1600 and 2000 rpm to obtain the kinetic currents.

Specific activity = The intrinsic catalytic activity of a material’s surface.

Mass activity (RDE testing)



Mass activity = Catalytic activity per unit mass of Pt i.e. how much bang for your buck.



Above is the representative LSV from 0.05-1.2 V vs. RHE at a rotation rate of 1600 rpm.

RDE screening indicates NiPt(NW) annealed at 150 °C **could** make more active electrodes than Pt(NW)/C.

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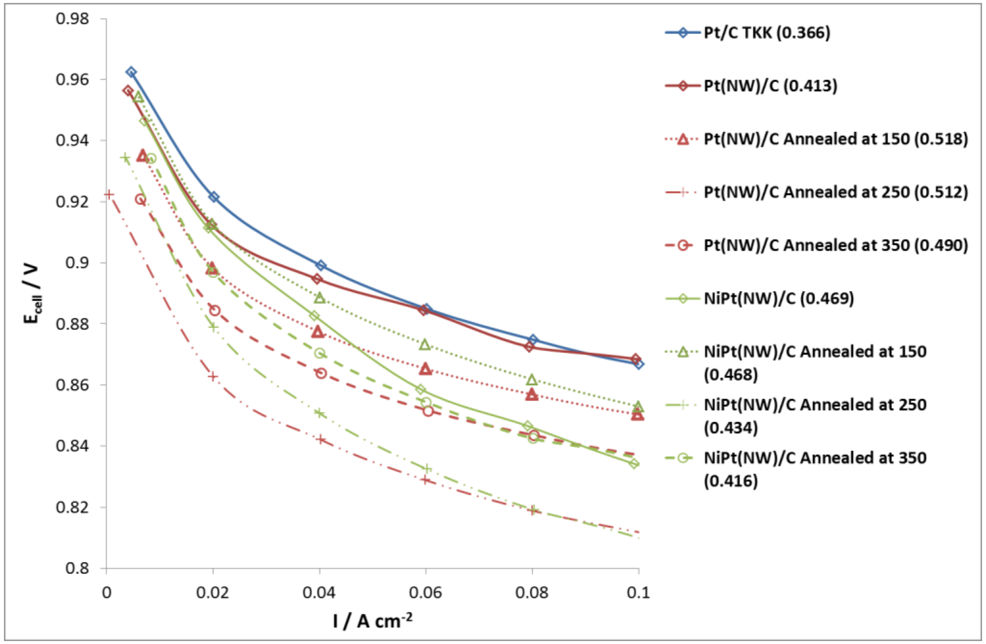
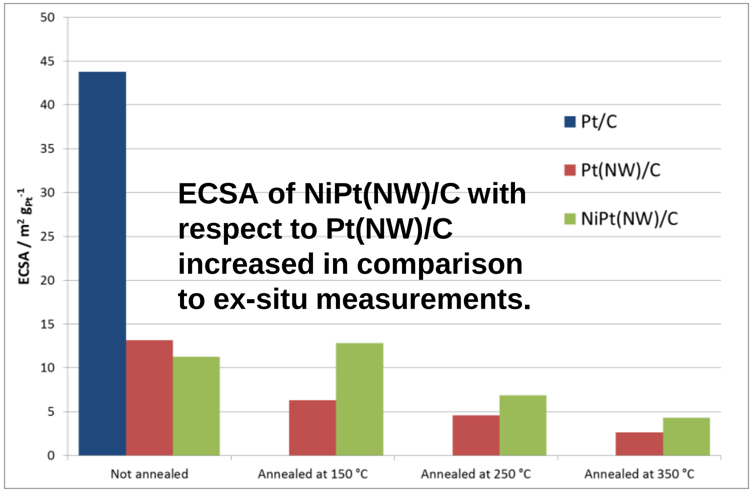
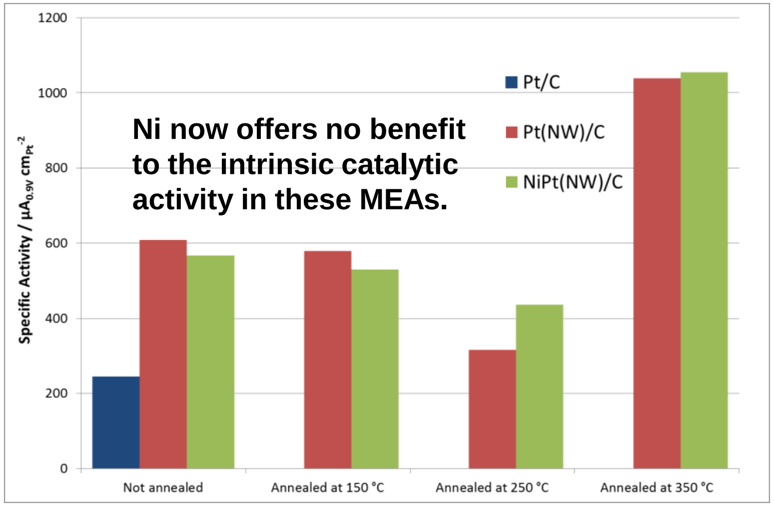
MEA Testing – Catalytic Activity

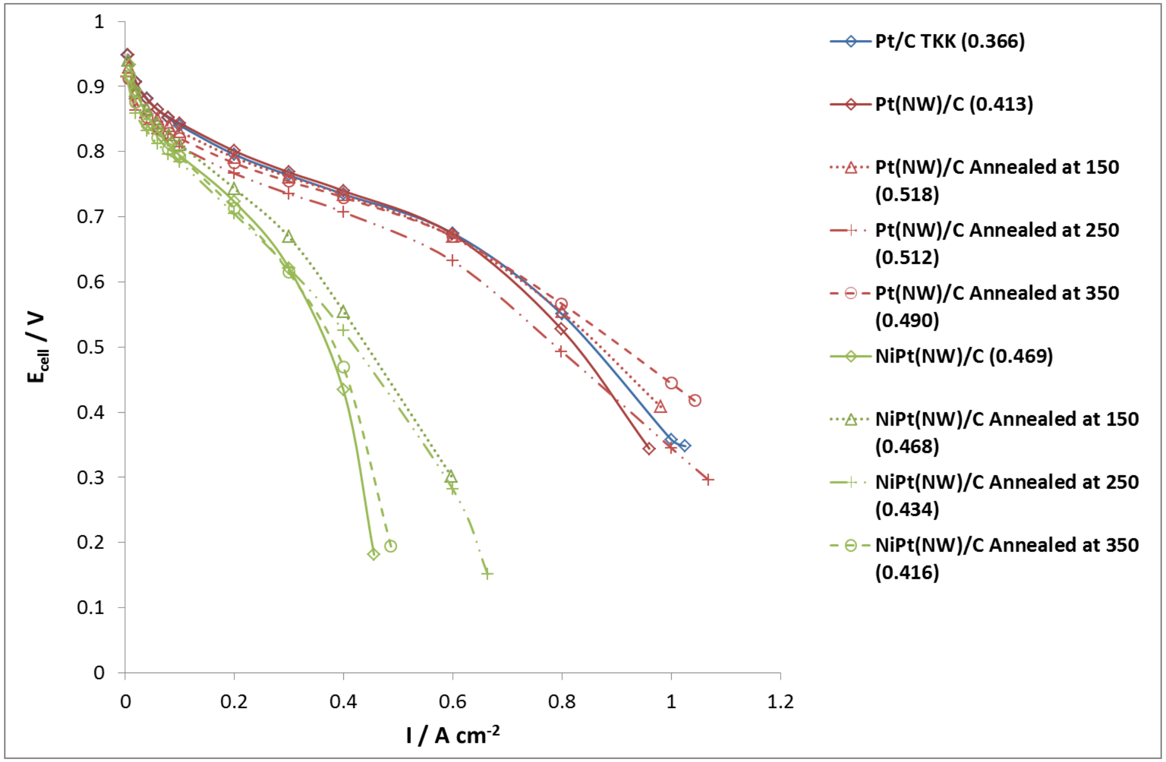






- Electrode area 16 cm^2 (Pt loading in mg_{Pt} cm^{-2} given in brackets)
- Nafion content 0.6 mg cm^{-2}
- Nafion 212 membrane
- JM Pt/C electrode (0.4 mg_{Pt} cm^{-2}) used as the anode
- H_2/O_2 stoichiometry 2/9.5 respectively at 1.5 bar absolute pressure
- The cell temperature was 80 ^{o}C

MEA Testing – Full Polarisation Curves



- H_2/Air stoichiometry 1.3/1.5 at 2.5/2.3 absolute pressure respectively, with humidity 50%/30%
- The cell temperature was 80 °C

- One hypothesis is that the NiPt(NW)/C is more hydrophilic than Pt(NW)/C.
- As a result the catalyst layer is more hydrated -> can explain the larger ECSAs.
- Gas transport could be inhibited by an overly hydrated catalyst layer.
- Ionomer content needs to be investigated.

Conclusions and perspectives

- I am trying to synthesise high performance electrodes using NiPt NWs.
- Issues of NW agglomeration in this work need to be addressed – Move onto modifying NWs grown on the gas diffusion layer.
- Compared to conventional methods, much lower annealing temperatures must be adopted for 1D catalysts.
- As an example in this work, an annealing temperature of 150 ^{o}C should be used to alloy Ni and retain NW morphology. Higher catalytic activities can be obtained ex-situ.
- Ionomer content in the alloy catalyst layers will be investigated.

Acknowledgements

- This work was funded by the EPSRC Centre for Doctoral Training in Fuel Cells and their Fuels (EP/L015749/1).
- For the TEM images I thank Dr Michael Fay and Rhys Lodge at the NMRC, University of Nottingham as well as the CEM at the University of Birmingham.
- Johnson Matthey for helping me with RDE experiments.

Thanks for Listening!