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The development of aligned PtNi NW electrodes for PEMFCs

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CDT Fuel Cells and their Fuels

University of Birmingham



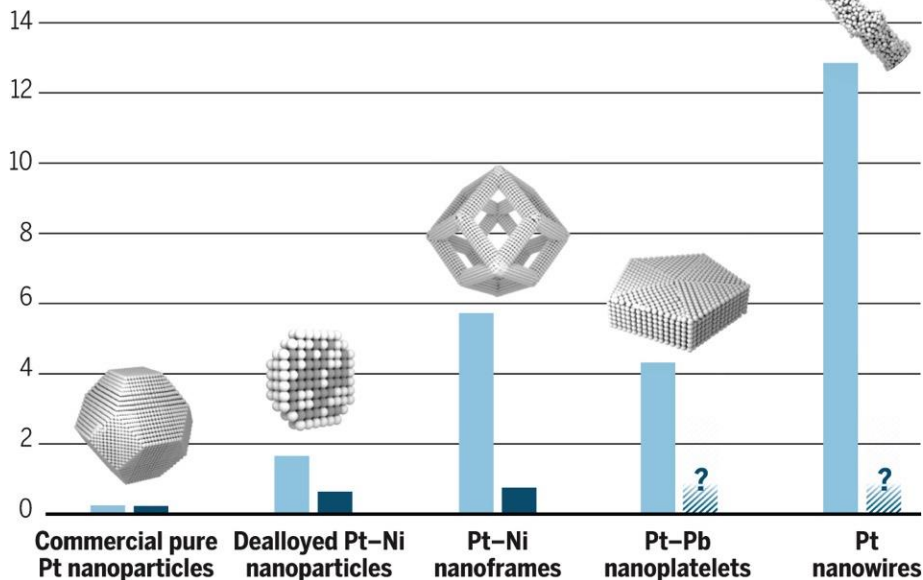
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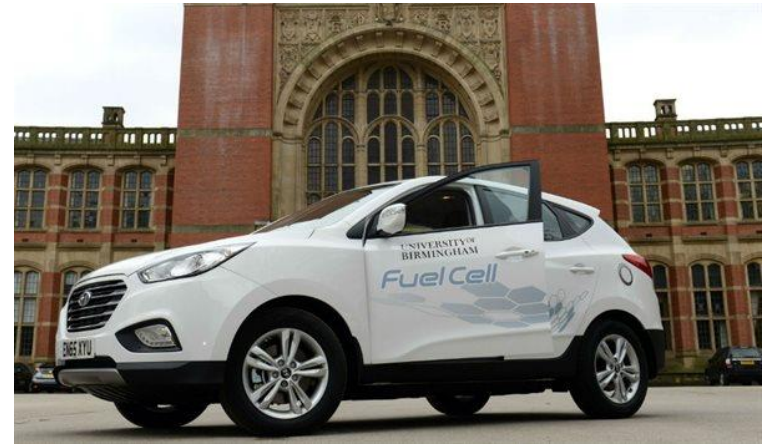
Current challenges of PEMFC catalysts

Mass activity (A/mg Pt)

● Liquid half cell ● Fuel cell



I.E.L Stephens, J. Rossmeisl and I. Chorkendorff, 2016. Science, 354, 1378-1379 with permission from The American Association for the Advancement of Science. Copyright (2016).



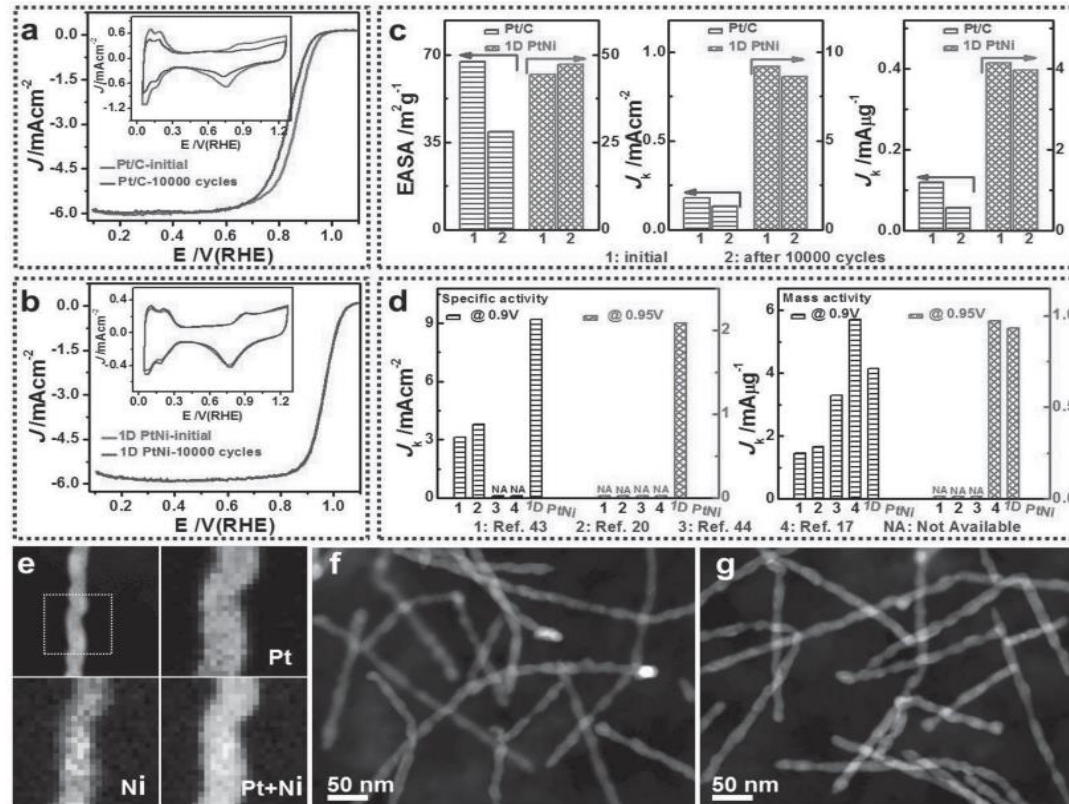
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A great catalyst - PtNi nanowires



Bu, L, Ding, J, Guo, S, et al. 2015. Advanced Materials, 27, 7204-7212 with permission from John Wiley and Sons. Copyright (2015).



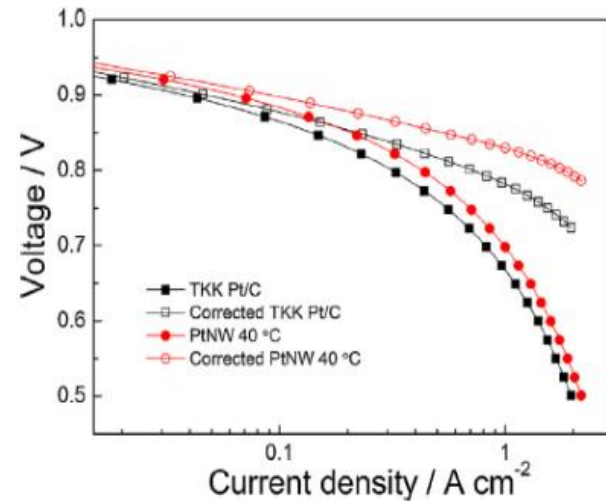
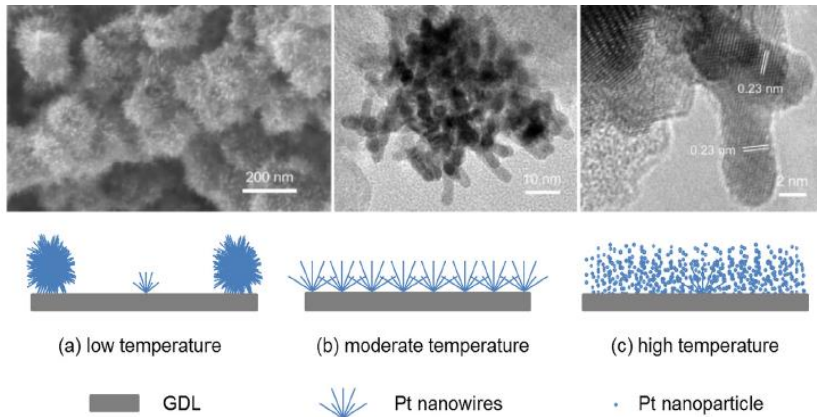
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A good electrode – Aligned Pt nanowire arrays



Figures copied from Lu, Y., Du, S., and Steinberger-Wilckens, R., 2015, Applied Catalysis B: Environmental 154, 389-395, with permission from Elsevier. Copyright (2015).

- High catalytic activity from the single crystal nanowires.
- Aligned nanowire arrays show increased fuel cell performance, notably at high current densities.



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The goal – Aligned PtNi nanowire array electrodes

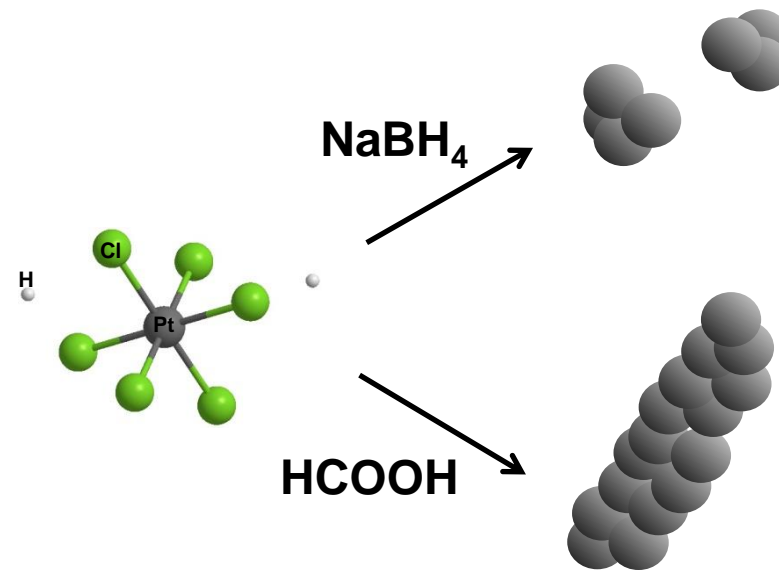
~~PtNi NW Array~~



- If similar nanowire array electrode can be made with PtNi rather than pure Pt, further performance enhancements can be expected:
 - A simple idea but not so easy to achieve.



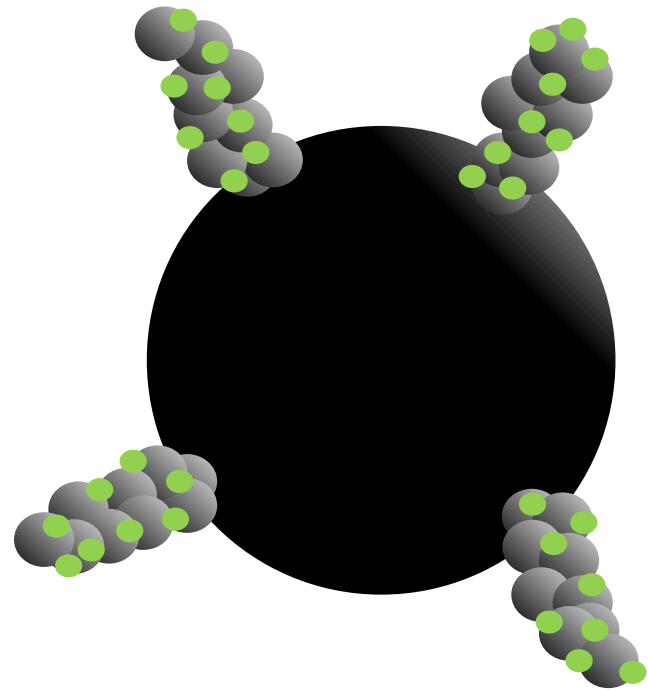
Pt nanowires by formic acid reduction



Ni impregnation

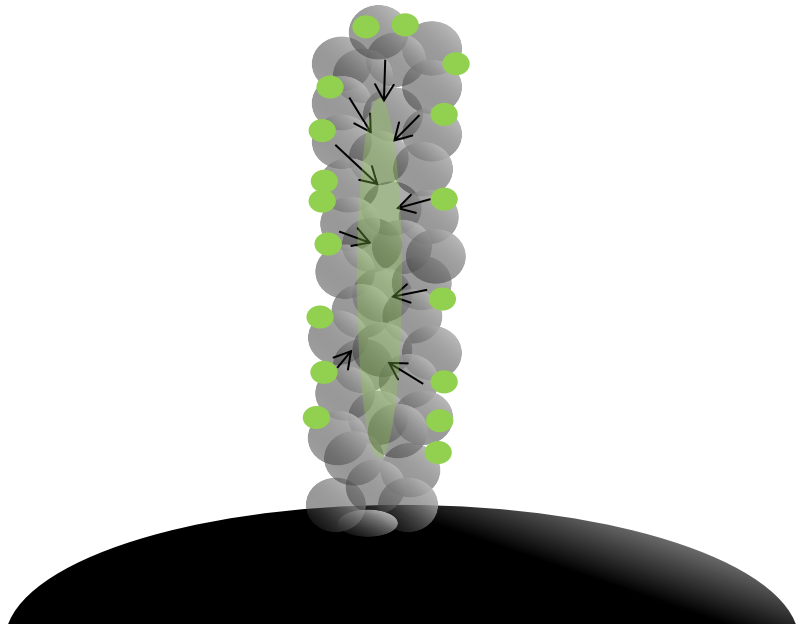
□ Synthesis method

1. Growth of Pt NWs on carbon using HCOOH.
2. Impregnation of Ni on the Pt NWs using NaBH_4 .



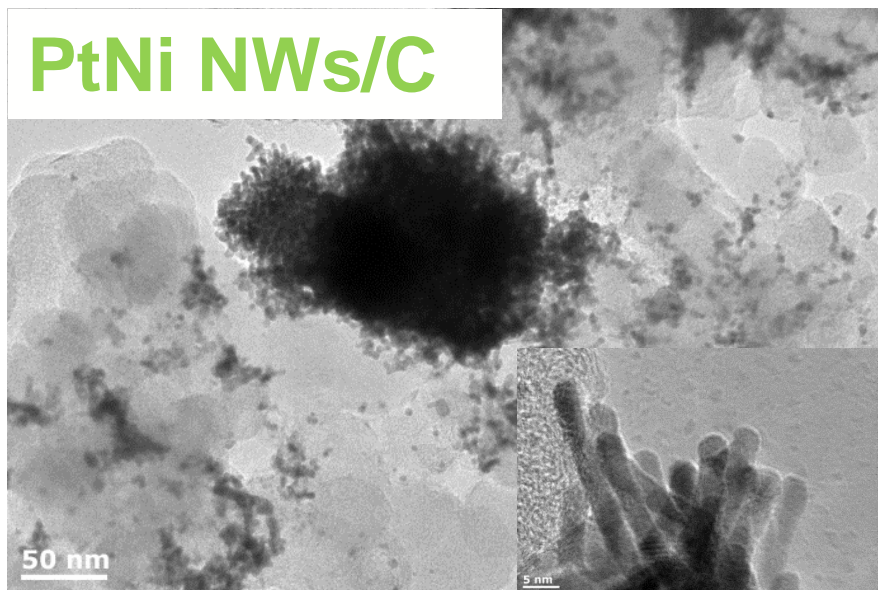
Thermal annealing of PtNi

3. Thermal annealing under a flow of H_2/Ar for 24 hrs.

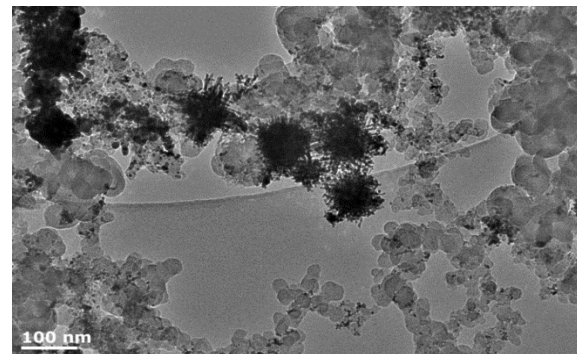


Effect of annealing temperature on morphology

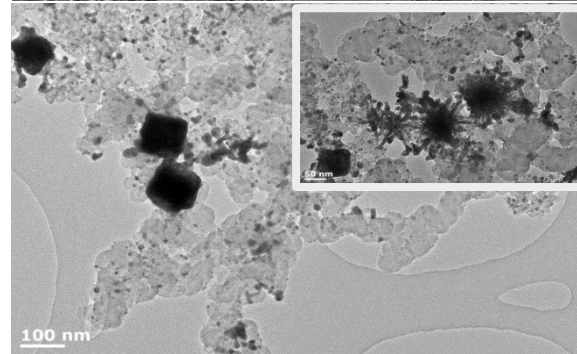
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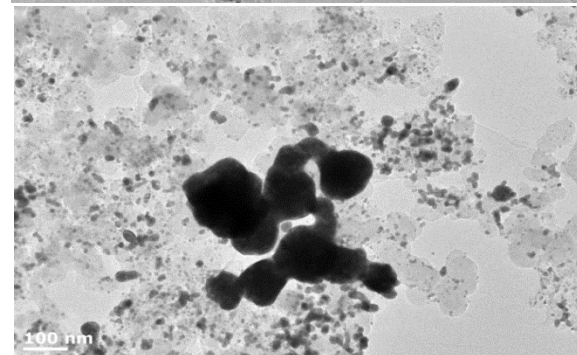
150 °C



250 °C



350 °C



- Conventional annealing temperatures of up to 900 °C cannot be used if NW morphology is to be retained.



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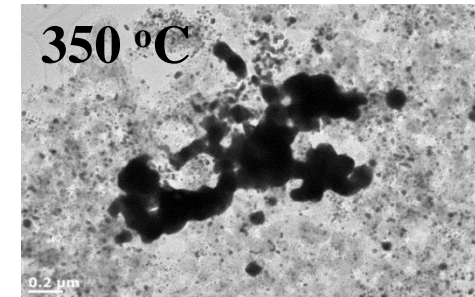
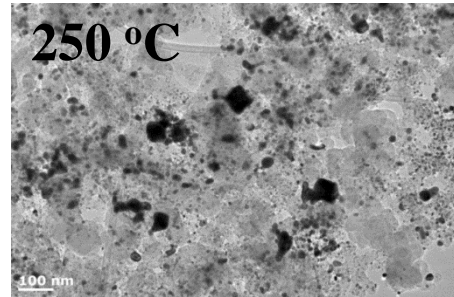
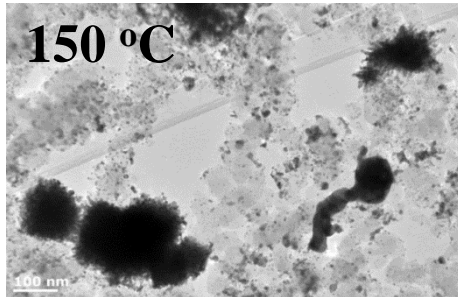
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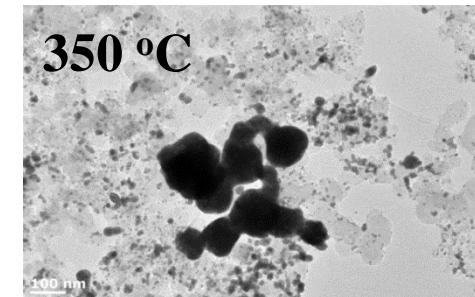
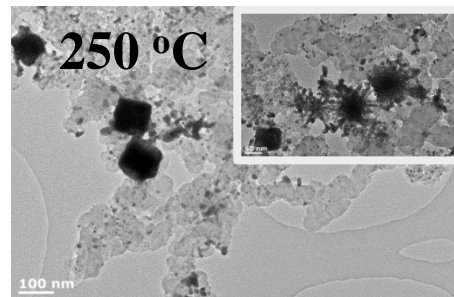
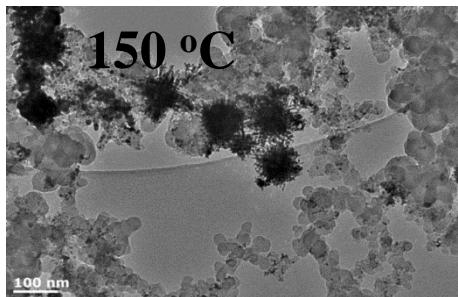
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Effect of composition on coarsening

Pt NWs/C



PtNi NWs/C

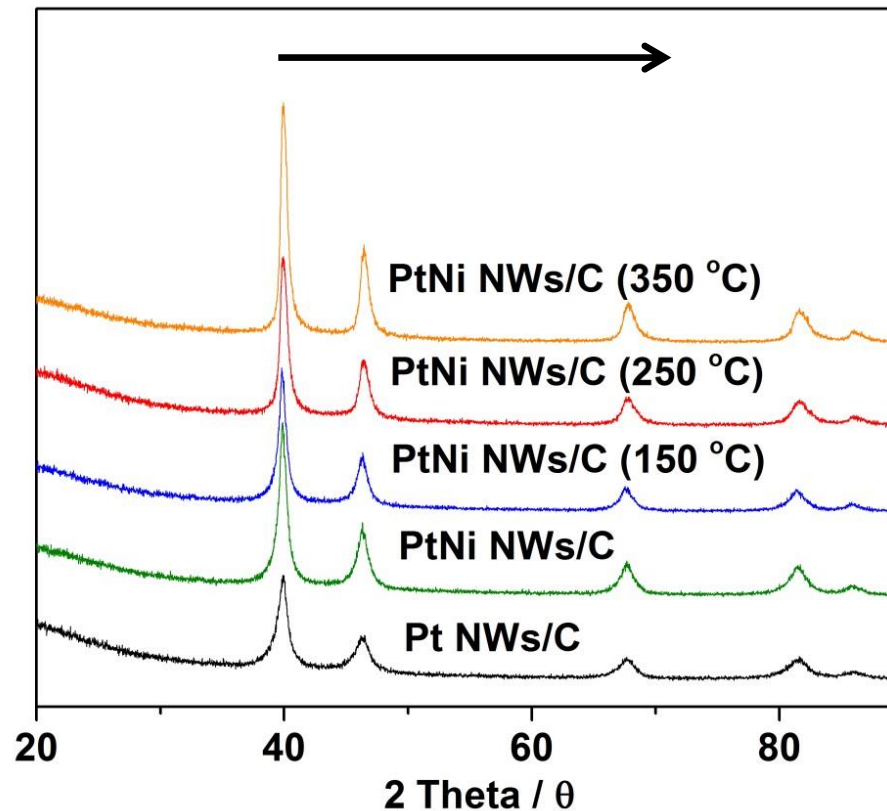


- Samples impregnated with Ni are more resistant to coarsening than the samples of pure Pt.



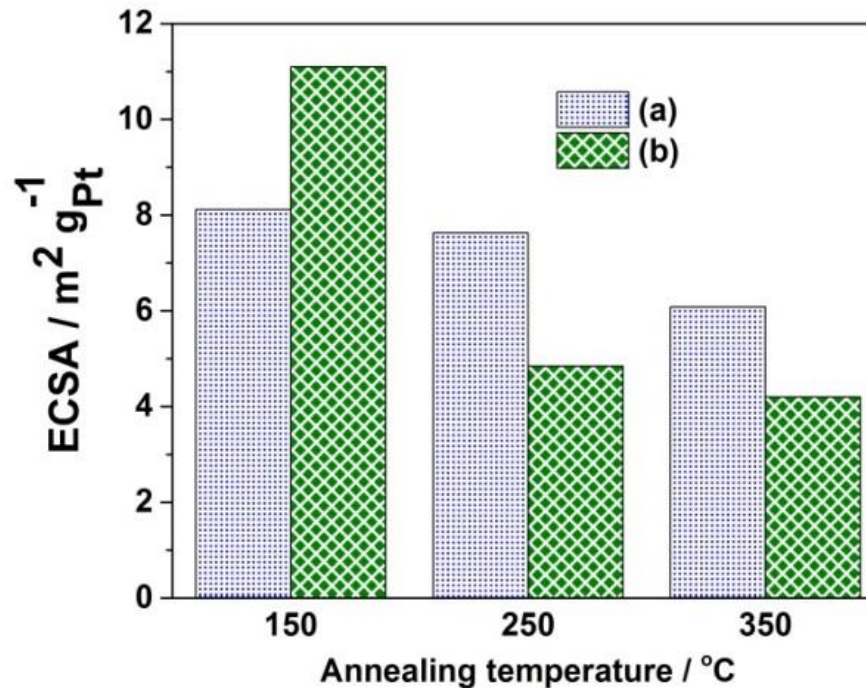
Degree of annealing – XRD

- Positive peak shift with higher annealing temperatures = Increase in degree of alloying.



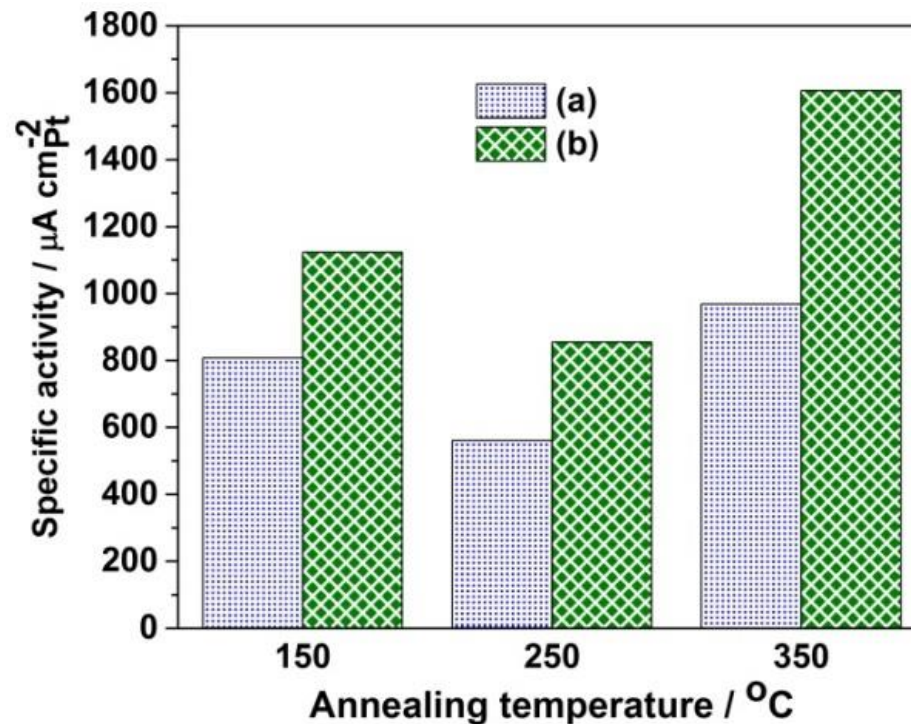
Rotating Disk Electrode - ECSA

- (a) Pt NWs/C
- (b) PtNi NWs/C



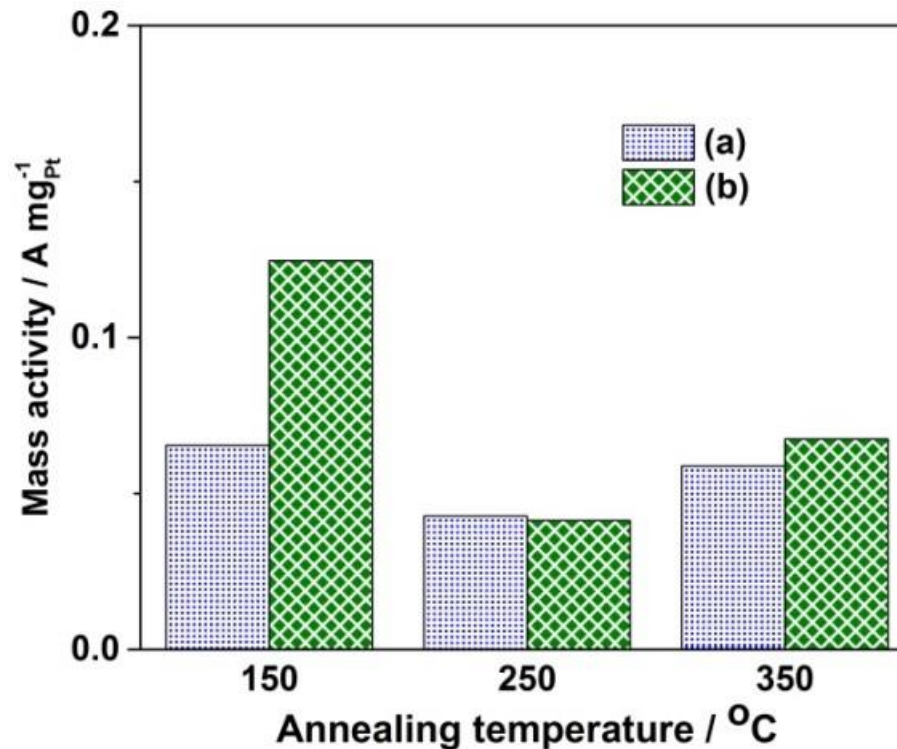
Rotating Disk Electrode – Specific activity

- (a) Pt NWs/C
- (b) PtNi NWs/C

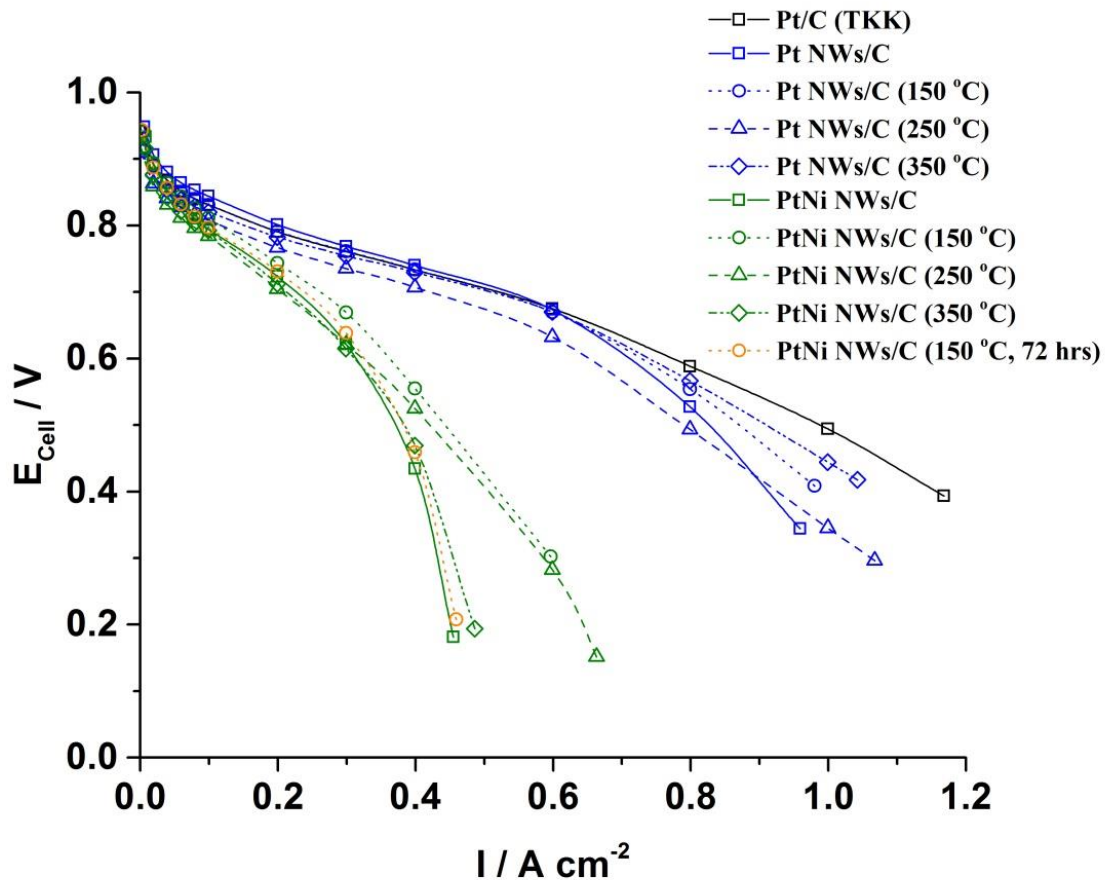


Rotating Disk Electrode – Mass activity

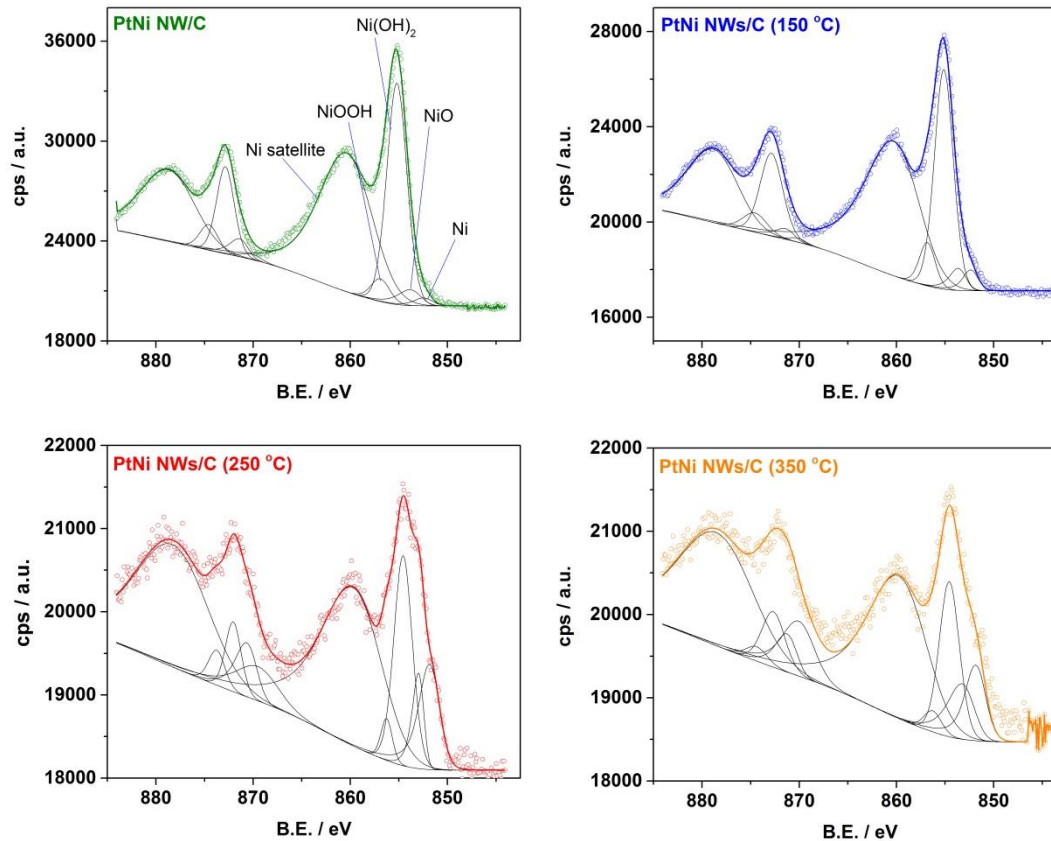
(a) Pt NWs/C
(b) PtNi NWs/C



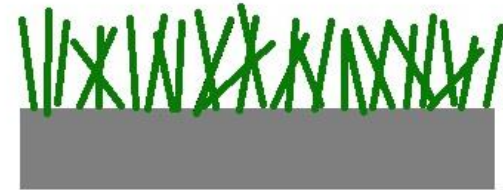
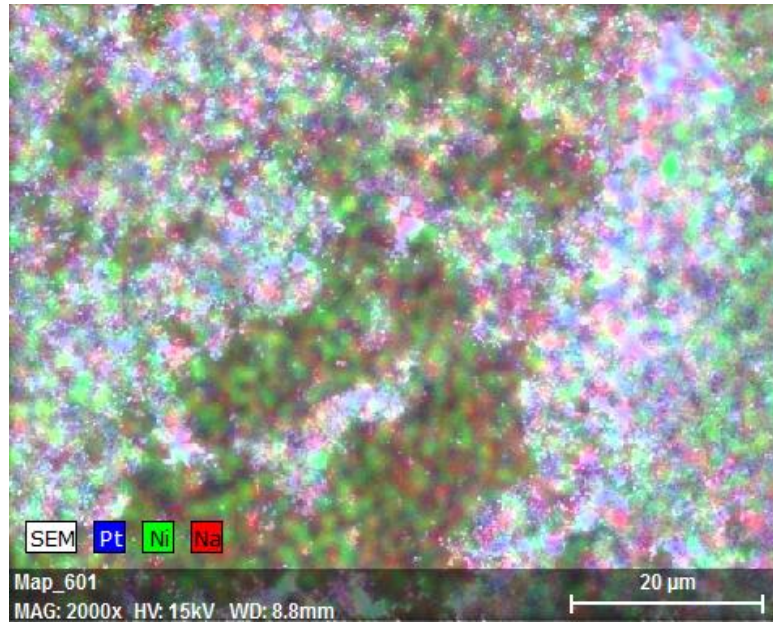
Single Cell Tests of PtNi NW/C catalysts



Why does PtNi perform badly? – XPS



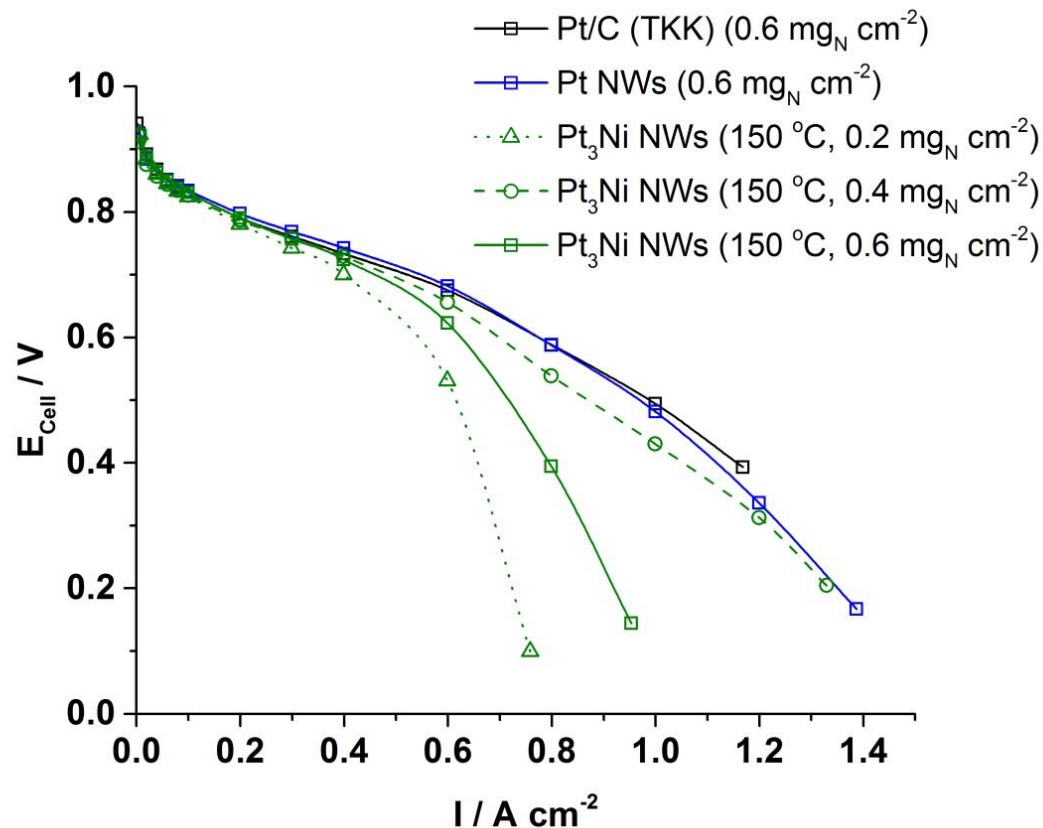
Moving on to PtNi NW arrays



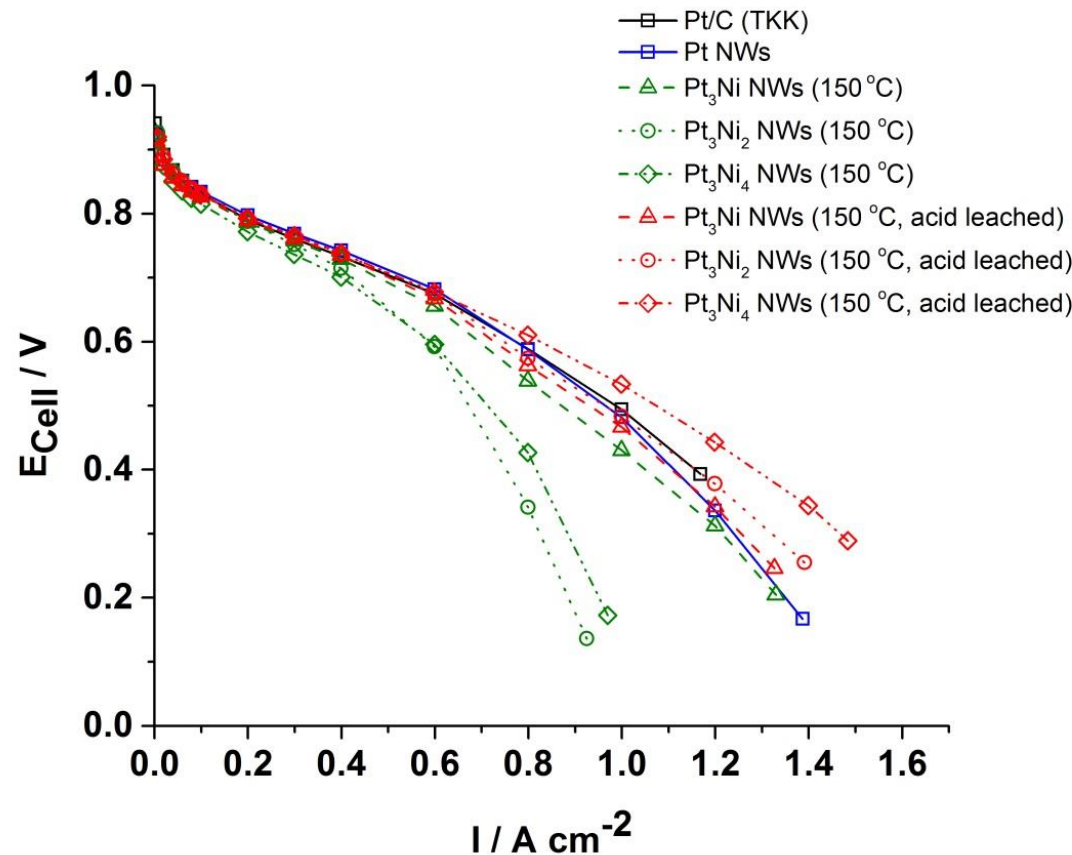
- An analogous Ni impregnation method can be used...however Ni does not impregnate selectively.
- Na is also present after use of NaBH_4 and cannot be simply washed away.



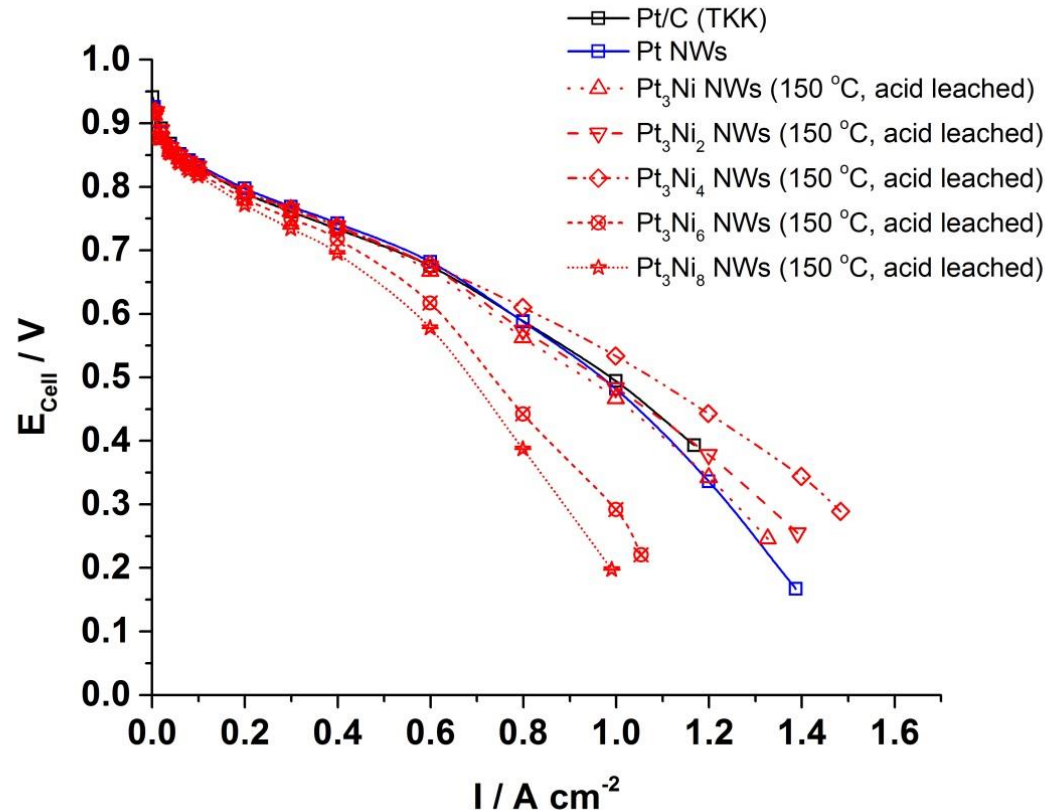
PtNi NW arrays - Ionomer content



PtNi NW arrays – Acid leaching



PtNi NW arrays - Ni content

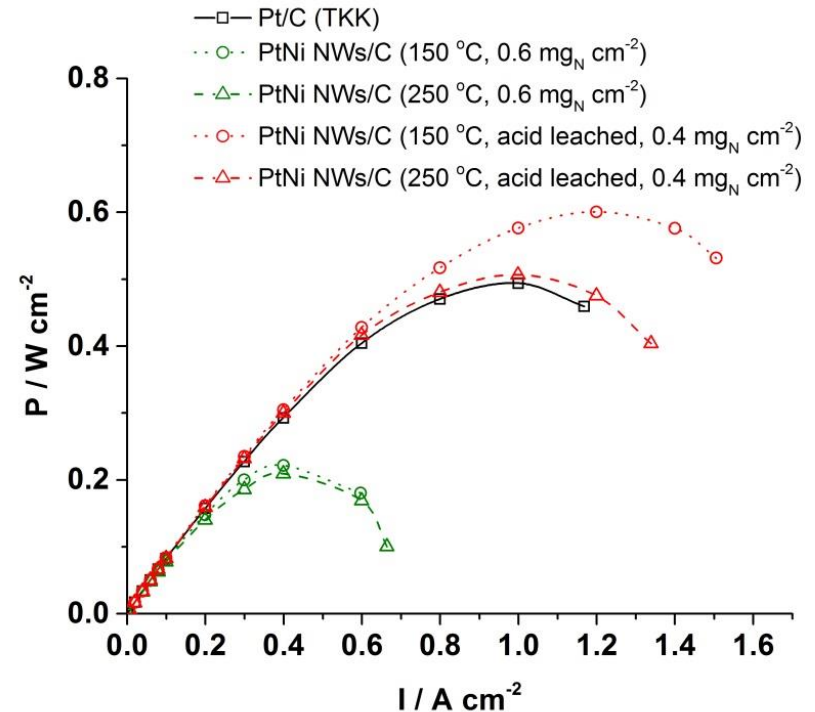
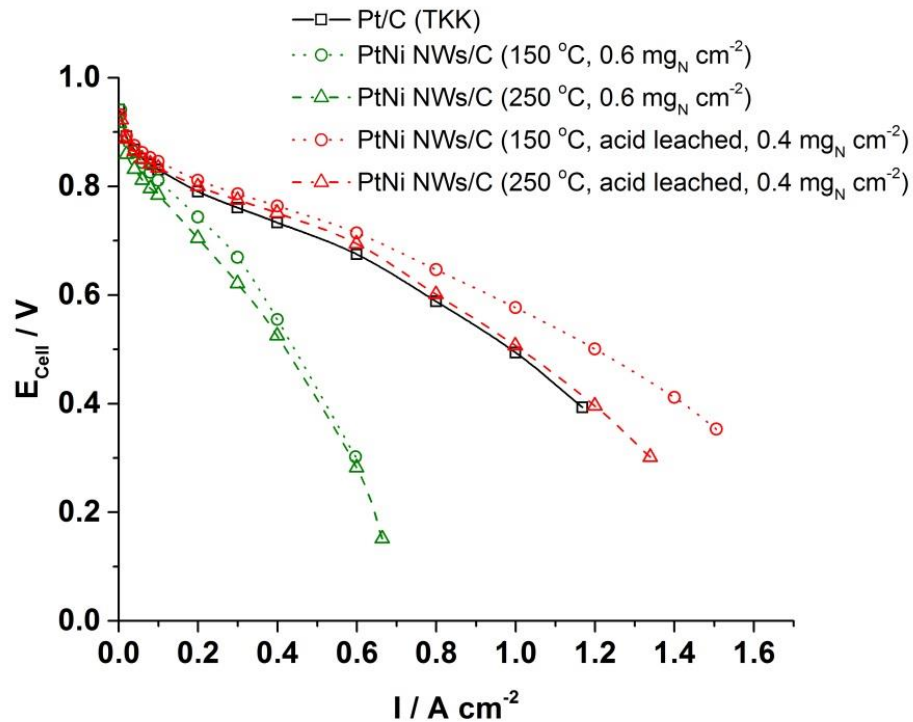


Two simple solutions to improve PtNi performance in PEMFCs

1. Use less ionomer (Ni contamination causes crosslinking, inhibiting O₂ diffusion).
2. Employ acid leaching to remove surface Ni.



Using this on PtNi NWs/C



Conclusions

- PtNi nanowires can be synthesised using an impregnation / annealing method.
- Loss of morphology at higher annealing temperatures limits the degree of alloying achievable.
- Control of other such as ionomer content, Ni content and use of acid leaching can be used to achieve a high performance electrode.
- While adjustments increase overall performance, catalytic activity remains unchanged.



Acknowledgements



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Johnson Matthey



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Thanks for Listening!



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