

## Platinum Coated Nickel Nanowires as Oxygen Reducing Electrocatalysts

Shaun M. Alia<sup>1</sup>, Brian A. Larsen<sup>1</sup>, Svitlana Pylypenko<sup>2</sup>,  
David A. Cullen<sup>3</sup>, David R. Diercks<sup>2</sup>, K.C.Neyerlin<sup>1</sup>,  
Shyam S. Kocha<sup>1</sup>, and Bryan S. Pivovar<sup>1,\*</sup>

<sup>1</sup> National Renewable Energy Laboratory, <sup>2</sup> Colorado School of Mines, <sup>3</sup> Oak Ridge National Laboratory

National Renewable Energy Laboratory  
Hydrogen Technologies and Systems Center  
1617 Cole Blvd, Golden, CO 80401-3393  
bryan.pivovar@nrel.gov

The commercial deployment of proton exchange membrane fuel cells (PEMFCs) is primarily limited by cost. Carbon supported platinum (Pt) nanoparticles (Pt/C) are typically used in PEMFCs due to their high surface area and thus relatively high ORR mass activity. A reduction in electrocatalyst cost will enable the rapid commercialization of automotive fuel cell vehicles in the near future. In order to meet cost targets through the development of highly active catalysts for ORR, the United States Department of Energy (DOE) has set a 2017 – 2020 mass activity target of  $440 \text{ mA mg}_{\text{PGM}}^{-1}$  for automotive PEMFCs.

Pt nanotubes were previously synthesized to improve the durability and ORR activity of PEMFC catalysts.<sup>3</sup> Pt nanotubes produced a high specific activity in comparison to Pt/C, but lacked the surface area needed to reach the DOE target. Subsequent efforts have been made to improve Pt utilization by adding nanotube porosity and exploring alternative morphologies; palladium and copper templates have further been used to reduce the Pt content.<sup>4-7</sup>

Nickel (Ni) nanowires were used as a template in this case to further improve ORR activity and to avoid template metals that could plate on PEMFC anodes during operation. Pt coated Ni nanowires were synthesized in this study by the partial spontaneous galvanic displacement (SGD) of Ni nanowires. Pt coated Ni nanowires were found to have an outer diameter of 200 – 300 nm and a length of 100 – 200  $\mu\text{m}$ . Electrochemical measurements were conducted in rotating disk electrode (RDE) experiments, with the inks deposited onto the RDE tips with and without the addition of carbon blacks and a Nafion ionomer.<sup>8</sup>

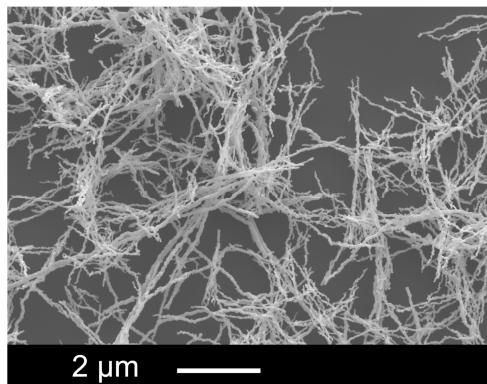


Figure 1. SEM image of PtNi nanowires (7.4 wt. % Pt).

Decreasing the percentage of Pt displacement during the SGD synthesis served to increase Pt utilization and surface area, exceeding  $90 \text{ m}^2 \text{ g}_{\text{PGM}}^{-1}$ . By increasing surface area and maintaining a high specific activity, Pt coated Ni nanowires have been able to produce an ORR

mass activity approaching  $900 \text{ mA mg}_{\text{PGM}}^{-1}$  (in RDEs measured in 0.1 M perchloric acid at 25 °C) that exceeds the DOE target in PEMFCs.

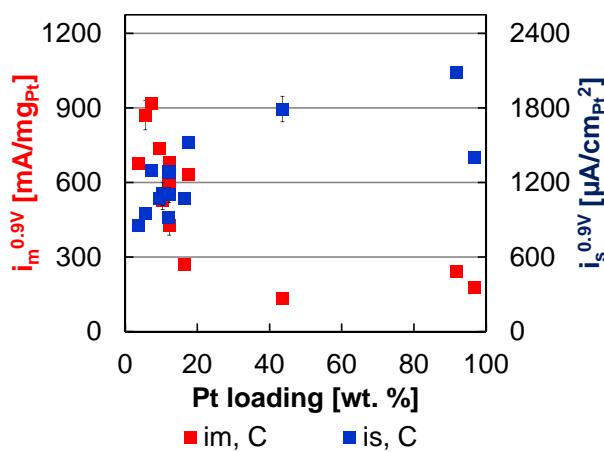


Figure 2. Mass and specific ORR activities of PtNi nanowires at varying Pt loadings. ORR activities were calculated at 0.9 V vs. RHE in an oxygen-saturated 0.1 M  $\text{HClO}_4$  electrolyte at a scan rate of 20  $\text{mVs}^{-1}$  and a rotation speed of 1600 rpm.

Durability testing was further completed to demonstrate the retention of ORR activity following potential cycling. Pt coated Ni nanowires were found to exceed the DOE target for ORR following 30,000 potential cycles (0.6 – 1.0 V vs. RHE). The measurements were carried out using protocols similar to that prescribed by the DOE durability working group.<sup>9,10</sup>

Compared to conventional, supported Pt nanoparticle electrocatalysts and pure Pt nanotubes, Pt coated Ni nanowires appear to provide significant activity and durability advantages as measured in RDE half cells.

## References

1. H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Applied Catalysis B-Environmental* **2005**, 56, 9.
2. P. J. Ferreira, G. J. la O', Y. Shao-Horn, D. Morgan, R. Makharia, S. Kocha, H. A. Gasteiger, *Journal of the Electrochemical Society* **2005**, 152, A2256.
3. Z. W. Chen, M. Waje, W. Z. Li, Y. S. Yan, *Angewandte Chemie-International Edition* **2007**, 46, 4060.
4. S. M. Alia, G. Zhang, D. Kisailus, D. S. Li, S. Gu, Y. S. Yan, *Advanced Functional Materials* **2010**, 20, 3742.
5. B. A. Larsen, K. C. Neyerlin, J. B. Bult, C. Bochert, J. L. Blackburn, S. S. Kocha, B. S. Pivovar, *Journal of the Electrochemical Society* **2012**, 159, F622.
6. S. M. Alia, K. O. Jensen, B. S. Pivovar, Y. S. Yan, *ACS Catalysis* **2012**, 2, 858.
7. S. M. Alia, K. O. Jensen, C. Contreras, F. Garzon, B. S. Pivovar, Y. S. Yan, *ACS Catalysis* **2013**, 3, 358.
8. S. S. Kocha, J. W. Zack, S. M. Alia, K. C. Neyerlin, B. S. Pivovar, *ECS Transactions* **2013**, 50, 1475.
9. M. Uchimura, S. Sugawara, Y. Suzuki, J. Zhang, S. S. Kocha, *ECS Transactions* **2008**, 16, 225.
10. S. S. Kocha, *Electrochemical Degradation: Electrocatalyst and Support Durability*. In M. Mench, E. C. Kumbur, T. N. Veziroglu, *Polymer Electrolyte Fuel Cell Degradation*, pp. 89-185, 2011.