Video Article

Synthesis of Platinum-nickel Nanowires and Optimization for Oxygen Reduction Performance

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Abstract

Platinum-nickel (Pt-Ni) nanowires were developed as fuel cell electrocatalysts, and were optimized for the performance and durability in the oxygen reduction reaction. Spontaneous galvanic displacement was used to deposit Pt layers onto Ni nanowire substrates. The synthesis approach produced catalysts with high specific activities and high Pt surface areas. Hydrogen annealing improved Pt and Ni mixing and specific activity. Acid leaching was used to preferentially remove Ni near the nanowire surface, and oxygen annealing was used to stabilize near-surface Ni, improving durability and minimizing Ni dissolution. These protocols detail the optimization of each post-synthesis processing step, including hydrogen annealing to 250 °C, exposure to 0.1 M nitric acid, and oxygen annealing to 175 °C. Through these steps, Pt-Ni nanowires produced increased activities more than an order of magnitude than Pt nanoparticles, while offering significant durability improvements. The presented protocols are based on Pt-Ni systems in the development of fuel cell catalysts. These techniques have also been used for a variety of metal combinations, and can be applied to develop catalysts for a number of electrochemical processes.

Video Link

The video component of this article can be found at https://www.jove.com/video/56667/

Introduction

Proton exchange membrane fuel cells are partially limited by the amount and cost of platinum required in the catalyst layer, which can account for half of fuel cell costs[1]. In fuel cells, nanomaterials are typically developed as oxygen reduction catalysts, since the reaction is kinetically slower than hydrogen oxidation. Carbon-supported Pt nanoparticles are often used as oxygen reduction electrocatalysts due to their high surface area; however, they have specific selective activity and are prone to durability losses.

Extended thin films offer potential benefits to nanoparticles by addressing these limitations. Extended Pt surfaces typically produce specific activities an order of magnitude greater than nanoparticles, by limiting less active facets and particle size effects, and have been shown to be durable under potential cycling[2,3,4]. While high mass activities have been achieved in extended surface electrocatalysts, improvements have been made primarily through increases in specific activity, and the catalyst type has been limited to Pt with a low surface area (10 m^2 g_{Pt}^{-1})[3,4,5].

Spontaneous galvanic displacement combines the aspects of corrosion and electrodeposition[6]. The process is generally governed by the standard redox potentials of the two metals, and the deposition typically occurs when the metal cation is more reactive than the template. The displacement tends to produce nanostructures that match the template morphology. By applying this technique to extended nanostructures, Pt-based catalysts can be formed that take advantage of the high specific oxygen reduction activity of extended thin films. Through partial displacement, small amounts of Pt have been deposited, and have produced materials with high surface areas (> 90 m^2 g_{Pt}^{-1})[7,8].

These protocols involve hydrogen annealing to mix Pt and Ni zones and improve oxygen reduction activity. A number of studies have theoretically established the mechanism and experimentally confirmed an alloying effect in Pt oxygen reduction. Modeling and correlating Pt-OH and Pt-O binding to oxygen reduction activity suggest that Pt improvements can be made through lattice compression[9,10]. Alloying Pt with smaller transition metals has confirmed this benefit, and Pt-Ni has been investigated in a number of forms, including polycrystalline, faceted electrodes, nanoparticles, and nanostructures[11,12,13,14].

Galvanic displacement has been used in Pt-oxygen reduction catalyst development with a variety of other templates, including silver, copper, and cobalt nanostructures[15,16,17]. The synthesis technique has also been used in the deposition of other metals and has produced electrocatalysts for fuel cells, electrolyzers, and the electrochemical oxidation of alcohols[18,19,20,21]. Similar protocols can also be adapted for the synthesis of nanomaterials with a wider range of electrochemical applications.

Protocol

1. Synthesis of Pt-Ni Nanowires

1. To begin the displacement process, suspend the nickel nanowire template in water and heat it to 90 °C.
    1. Add 40 mg of commercially available, nickel nanowires to 20 mL of deionized water in a 50 mL centrifuge tube. Sonicate it for 5 min.
    NOTE: The nanowires are approximately 150-250 nm in diameter and 100-200 µm in length.
    2. Transfer the suspended nanowires to a 250 mL glass round bottom flask and add 60 mL of deionized water. Heat the flask to 90 °C in a mineral oil bath. Stir the reaction mixture at 500 rpm with a polytetrafluoroethylene paddle connected to a glass shaft and electric stirrer.

2. Form the Pt-Ni nanowires by spontaneous galvanic displacement.
    1. Add 8.1 mg of potassium tetrachloroplatinate to 15 mL of deionized water. Add the solution to a 20 mL syringe with approximately 8 cm of 0.318 cm polyurethane-based tubing attached to the tip. Place the syringe in an automated syringe pump and set the rate to 1 mL/min.
    2. Start the syringe pump and allow the pump to add the solution to the round bottom flask over 15 min. Heat the flask at 90 °C for 2 h.
    3. Centrifuge the solution at 2,500 x g for 15 min, and pour the supernatant into a waste stream. Resuspend the solidswith bath sonication (approximately 10 s) using fresh solution (water or 2-propanol, as specified). Centrifuge the solution again and remove the supernatant. Repeat the washing process three times with deionized water and then once with 2-propanol.
    4. Dry the Pt-Ni nanowires at 40 °C in a vacuum oven overnight (approximately 16 h).

2. Check Composition with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Note: Catalyst composition should be 7.3 ± 0.3 wt. % Pt.

1. Digest 1 mg of sample in 10 mL of aqua regia at room temperature overnight.
2. Dilute to concentrations of 200, 20, and 2 ppb, with a matrix matching of the dilutions to 1.5% hydrochloric and 0.5% nitric acid.
    1. Add 20 µL of digestate into 9.98 mL of stock solution (1.5% hydrochloric and 0.5% nitric acid) for 200 ppb; 2 µL of digestate into 10.00 mL of stock solution (1.5% hydrochloric and 0.5% nitric acid) for 20 ppb; and 0.2 µL of digestate into 10.00 mL of stock solution (1.5% hydrochloric and 0.5% nitric acid) for 2 ppb. Filter the dilutions using a 0.4 µm polytetrafluoroethylene-based filter.

3. Post-synthesis Process of the Pt-Ni Nanowires by Annealing and Acid Leaching.

1. Hydrogen anneal the synthesized Pt-Ni nanowires.
2. Add the entire nanowire sample to a tubular furnace. Apply vacuum to the tube overnight.
NOTE: Since gas flow (hydrogen, oxygen) was used at elevated temperature in the tubular furnace, safety considerations were required. The tube-gas connections were built to ensure that the apparatus could handle vacuum and 500 Torr of back pressure during operation. The tube outlet was vented to exhaust, and the entire furnace was placed in an enclosure vented to an exhaust line.
    1. Feed a low flow rate of hydrogen into the tube with 500 Torr of back pressure.
    2. Heat the sample to 250 °C for 2 h, using a 10 °C/min ramp rate.
    3. Allow for the sample to cool to room temperature naturally.

3. Acid leach the hydrogen annealed Pt-Ni nanowires.
    1. Add 25 mg of the nanowires to 20 mL of deionized water and bath sonicate it. Transfer the suspended nanowires to a 100 mL round bottom flask.
    2. Add room temperature diluted nitric acid to the flask (25 mL of 0.2 M nitric acid to 25 mL of water/nanowire suspension), to bring the flask contents to 50 mL of 0.1 M nitric acid, and shake the flask to ensure a uniform concentration. Add the nitric acid all at once.
    3. Connect the flask to a Schlenk line. Turn on the vacuum for 10 min and then close off the vacuum. Slowly add nitrogen gas into the line and allow the flask to proceed at room temperature for 2 h. Remove the flask from the Schlenk line and wash the products as described in step 1.2.3.
    4. Check the composition with ICP-MS, which should be 15.2 ± 0.3 wt. % Pt.

4. Oxygen anneal the acid leached Pt-Ni nanowires.
    1. Add the nanowires to a commercially available tubular furnace. Apply vacuum to the tube overnight.
    2. Feed a low flow rate of oxygen into the tube with 500 Torr of back pressure.
    3. Heat the sample to 175 °C for 2 h, using a 10 °C/min ramp rate.
    4. Allow for the sample to cool to room temperature naturally.

4. Electrochemically Characterize the Nanowires in Rotating Disk Electrode (RDE) Half-Cells[8]

1. Coat the glassy carbon working electrodes.

1. Add catalyst, which contains 73 µg of Pt, to 7.6 mL of deionized water in a 20 mL scintillation vial, and then add 2.4 mL of 2-propanol. The vial contents are subsequently referred to as the ink. Ice the ink for 5 min and then add 10 µL of a commercially available ionomer.
   NOTE: For the as-synthesized and hydrogen annealed catalyst, 1 mg (7.3 wt. % Pt) should be used. For the acid leached and oxygen annealed catalyst, 480 µg (15.2 wt. % Pt) should be used.
2. Sonicate the ink in ice, 30 s by horn followed by 20 min by bath and 30 s by horn. Add 7.5 mL of the ink to 0.5 mg of graphitized carbon nanofibers.
3. Sonicate the ink in ice, 30 s by horn followed by 20 min by bath and 30 s by horn. Pipette 10 µL of ink onto a glassy carbon working electrode (5 mm outer diameter), with the inverted electrode rotating at 100 rpm. After pipetting the ink, increase the rotation to 700 rpm.
4. Sonicate the ink again (30 s horn, 20 min bath, 30 s horn) while the electrode dries and pipette an additional ink (10 µL) onto the electrode. Continue the coating process to increase the loading to 1.9 µg cm_{elec}^{-2}, five 10 µL drops of ink.

2. Assemble the RDE test station.
   1. Soak the glassware overnight in concentrated sulfuric acid. Then, soak the glassware overnight in a commercially available substitute for chromic acid. Boil eight times in deionized water. Assemble the glassware, by connecting the working, counter, and reference electrodes to the main testing cell.
      NOTE: The RDE half-cells use a three-electrode configuration. The working and counter electrodes were glassy carbon and Pt mesh, respectively. The reference electrode was a reversible hydrogen electrode (RHE), a Pt wire contained in a glass bubbler with 0.1 M perchloric acid electrolyte.
   2. Fill the RDE half-cell with 0.1 M perchloric acid. Connect the working electrode to a commercially available modulated speed controller, and submerge the working electrode tip.
   3. Take electrochemical measurements with a commercially available potentiostat. Purge the electrolyte with nitrogen for 7 min.

3. Take electrochemical surface areas.
   1. Input parameters into an automated cyclic voltammetry file supplied by the potentiostat manufacturer. Set the cycle number to 50, the scan rate to 100 mV s^{-1}, the lower potential to 0.025 V, and the upper potential to 1.4 V. Run the cyclic voltammetry file and discard the electrolyte. Refill with 0.1 M perchloric acid and purge with carbon monoxide.
   2. Input parameters into an automated potential hold file supplied by the potentiostat manufacturer. Set the potential 0.1 V and the time to 20 min, and start rotating the working electrode at 2,500 rpm. Run the potential hold file: for the first 10 min of the program, purge carbon monoxide; for the second 10 min of the program, purge nitrogen. During the last 30 s of the hold, turn off the rotation and set the bubbler to blanket the electrolyte.
   3. Input parameters into an automated cyclic voltammetry file supplied by the potentiostat manufacturer. Set the cycle number to 3, the scan rate to 20 mV s^{-1}, the start potential to 0.1 V, the lower potential to 0.025 V, and the upper potential to 1.2 V. Run the cyclic voltammetry file.

4. Take oxygen reduction polarization curves.
   1. Purge the electrolyte with oxygen for at least 7 min with the working electrode rotating at 2,500 rpm.
   2. Set the oxygen purge to blanket the electrolyte and slow the working electrode rotation to 1,600 rpm.
   3. Input parameters into an automated linear sweep voltammetry file supplied by the potentiostat manufacturer. Set the cycle number to 10, the scan rate to 20 mV s^{-1}, the start potential to -0.1 V, and the end potential to 1.05 V. Run the linear sweep voltammetry file. Discard the electrolyte.
   4. Refill with 0.1 M perchloric acid and purge with oxygen for at least 7 min. Rerun the linear sweep voltammetry file used in step 4.4.3.

5. Run durability tests.
   1. Purge the electrolyte with nitrogen while rotating the working electrode at 2,500 rpm. Set the nitrogen purge to blanket the electrolyte and stop the working electrode rotation.
   2. Input parameters into an automated cyclic voltammetry file supplied by the potentiostat manufacturer. Set the cycle number to 30,000, the scan rate to 500 mV s^{-1}, the lower potential to 0.6 V, and the upper potential to 1.0 V. Run the cyclic voltammetry file.
   3. After durability, take electrochemical surface areas and oxygen reduction polarization curves using the protocols supplied in steps 4.3 and 4.4.

Representative Results

Spontaneous galvanic displacement of Ni nanowires with Pt, using the specified amount, produced Pt-Ni nanowires that were 7.3 wt. % Pt (**Figure 1** and **Figure 2A**). Some modification to the amount of Pt precursor may be required to reach the optimum Pt loading. Pt displacement is sensitive to the thickness of the surface Ni oxide layer, which can vary based on template age (air exposure) and upstream variability[22]. The composition, however, is critical to ensuring high activity and ICP-MS was used to ensure optimum composition. RDE testing protocols have been included, since following these protocols are critical to confirming correct synthesis and processing parameters. Catalysts at this composition (7.3 wt. % Pt) produced peak oxygen reduction mass activity[7]. Higher amounts of Pt deposition resulted in lower electrochemical surface areas, attributed to lower Pt utilization and the formation of thicker Pt layers (**Figure 2b**). Lower amounts of Pt resulted in lower specific activity, potentially due to a particle size effect, although the activity drop was milder than Pt nanoparticle findings[2].

Hydrogen annealing was required to integrate the Pt and Ni zones and compress the Pt lattice[8]. Lattice compression improved oxygen reduction activity and annealing to 250 °C produced optimal mass activity (**Figure 3**). Although the specific activity continued to increase at higher annealing temperatures, the electrochemical surface area decreased potentially due to Pt reordering at the surface.

Although hydrogen annealing produced high oxygen reduction activity, durability testing resulted in large performance losses and high amounts of Ni dissolution. Acid leaching was used to preferentially remove Ni, and oxygen annealing was used to improve durability and minimize Ni dissolution[8,22]. Acid leaching to 15.2 wt. % Pt and oxygen annealing to 175 °C produced optimal activity and durability (**Table 1**). If greater amounts of Ni removal occurred in the acid leaching step, high durability was achieved, but at the cost of initial performance. High Pt composition produced nanowires with lower specific activity (dealloying effect) and the materials were of less interest electrocatalytically. If lower amounts of Ni removal occurred in the acid leaching step, large amounts of Ni still remained on the surface. Oxygen annealing improved the stability of Ni near the nanowire surface, preventing access to Pt sites during electrochemical conditioning. The oxygen annealing temperature of 175 °C provided a balance between the need to stabilize subsurface Ni for durability testing, while still allowing for Pt access during conditioning. For nanowires that were 15.2 wt. % Pt, higher oxygen annealing temperatures produced lower initial activity; conversely, lower oxygen annealing temperatures resulted in higher durability losses and higher degrees of Ni dissolution.

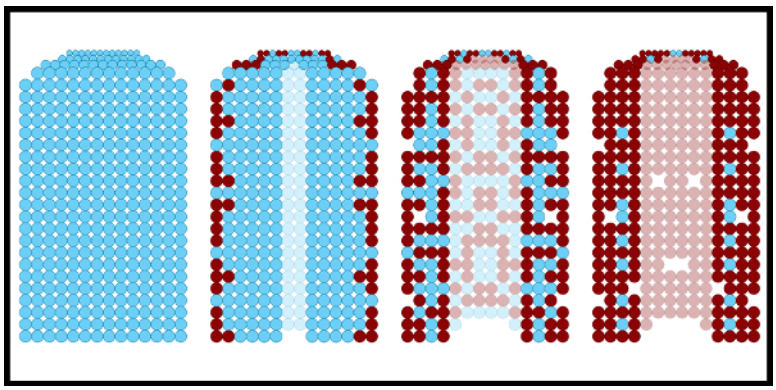

Figure 1. Schematic of spontaneous galvanic displacement process. Schematic of the spontaneous galvanic displacement process, with a nobler metal cation (red) displacing a metal template (blue)[6]. Reprinted (adapted) with permission from S. M. Alia, Y. S. Yan and B. S. Pivovar, Catalysis Science & Technology, 4, 3589 (2014). Copyright 2014 Royal Society of Chemistry. Please click here to view a larger version of this figure.

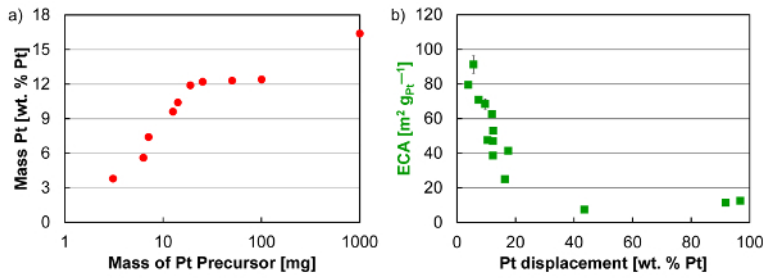

Figure 2. Synthesized Pt-Ni nanowires: their composition and surface area. (**A**) Pt-Ni nanowire composition as a function of the amount of Pt precursor (potassium tetrachloroplatinate) added to 40 mg of Ni nanowires during galvanic displacement. (**B**) Electrochemical surface areas of as-synthesized Pt-Ni nanowires as a function of the level of Pt displacement[7]. The data points denote the average value, while the error bars denote the standard deviation of the measurement. Reprinted (adapted) with permission from S. M. Alia, B. A. Larsen, S. Pylypenko, D. A. Cullen, D. R. Diercks, K. C. Neyerlin, S. S. Kocha and B. S. Pivovar, ACS Catalysis, 4, 1114 (2014). Copyright 2014 American Chemical Society. Please click here to view a larger version of this figure.

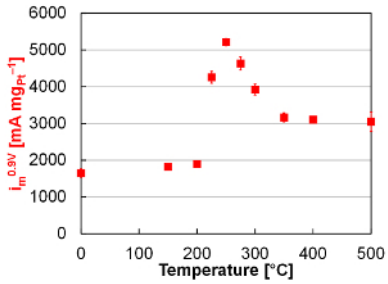

Figure 3. Oxygen reduction mass activity of hydrogen annealed Pt-Ni nanowires as a function of the annealing temperature[8]. The data points denote the average value, while the error bars denote the standard deviation of the measurement. Reprinted (adapted) with permission from S. M. Alia, C. Ngo, S. Shulda, M.-A. Ha, A. A. Dameron, J. N. Weker, K. C. Neyerlin, S. S. Kocha, S. Pylypenko and B. S. Pivovar, ACS Omega, 2, 1408 (2017). Copyright 2017 American Chemical Society. Please click here to view a larger version of this figure.

Catalyst	$i_{m,i}^{0.9V}$ [mA mg_{Pt}^{-1}]	$i_{m,f}^{0.9V}$ [mA mg_{Pt}^{-1}]
Pt-Ni	1653	1339
H_2	5213	3962
Acid	3583	3153
O_2	5414	5305
Pt/HSC	500	375

Table 1. Oxygen reduction mass activities prior to ($i_{m,i}$) and following ($i_{m,f}$) half-cell durability testing. Evaluated catalysts include as-synthesized (Pt-Ni), hydrogen annealed (H_2), acid leached (Acid), and oxygen annealed (O_2) Pt-Ni nanowires. The half-cell performance of carbon-supported Pt nanoparticles (Pt/HSC) was also provided as a reference[8]. Reprinted (adapted) with permission from S. M. Alia, C. Ngo, S. Shulda, M.-A. Ha, A. A. Dameron, J. N. Weker, K. C. Neyerlin, S. S. Kocha, S. Pylypenko and B. S. Pivovar, ACS Omega, 2, 1408 (2017). Copyright 2017 American Chemical Society.

Discussion

These protocols have been used to produce extended surface electrocatalysts with both high surface areas and specific activities in the oxygen reduction reaction[8]. By depositing Pt onto nanostructured templates, the nanowires avoided low coordinated sites and minimize particle size effects, producing specific activities more than 12 times greater than carbon-supported Pt nanoparticles. Using galvanic displacement as the synthesis approach also produced an approximate coating on the Ni template[7]. At low levels of Pt displacement, this process produced electrochemical surface areas in excess of 90 m^2 g_{Pt}^{-1}, a significant breakthrough in extended surface catalysts.

Hydrogen annealing was needed to improve performance[8]. Annealing to elevated temperatures improved the oxygen reduction specific activity, which was rationalized as an alloying effect caused by Pt lattice compression weakening Pt-O chemisorption[9,10]. Although the hydrogen annealing step improved initial activity, the high durability and Ni dissolution losses were a concern. Acid leaching and oxygen annealing were used to minimize these losses. The optimized Pt-Ni nanowires produced oxygen reduction mass activities of eleven times greater than carbon-supported Pt nanoparticles and three times greater than the as-synthesized wires. Significant improvements were also made to the nanowire durability, which lost 3% mass activity (as-synthesized lost 21%) and 0.3% of the catalyst mass to Ni dissolution (as-synthesized lost 7%).

Pt-Ni nanowires have been developed and optimized for their performance in RDE half-cells. RDE testing is often used in catalyst screening, to evaluate the fundamental properties and electrochemical capabilities of a catalyst. RDE activity, however, does not guarantee similar fuel cell performance, and membrane electrode assemblies include activity losses due to mass transport, and electronic and ionic resistance. The Pt-Ni nanowires developed in these protocols demonstrate more than an order of magnitude higher activity to Pt nanoparticles, as well as improved durability. While these results suggest that Pt-Ni nanowires could reduce fuel cell electrode loadings to meet cost-performance metrics, effectively incorporating these materials into membrane electrode assemblies remains a significant challenge.

Disclosures

The authors have nothing to disclose.

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