Exceptional Oxygen Reduction Reaction Activity and Durability of Platinum–Nickel Nanowires through Synthesis and Post-Treatment Optimization

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Supporting Information

ABSTRACT: For the first time, extended nanostructured catalysts are demonstrated with both high specific activity (>6000 μA cm⁻² at 0.9 V) and high surface areas (>90 m² g⁻¹). Platinum–nickel (Pt–Ni) nanowires, synthesized by galvanic displacement, have previously produced surface areas in excess of 90 m² g⁻¹, a significant breakthrough in and of itself for extended surface catalysts. Unfortunately, these materials were limited in terms of their specific activity and durability upon exposure to relevant electrochemical test conditions. Through a series of optimized postsynthesis steps, significant improvements were made to the activity (3-fold increase in specific activity), durability (21% mass activity loss reduced to 3%), and Ni leaching (reduced from 7 to 0.3%) of the Pt–Ni nanowires. These materials show more than a 10-fold improvement in mass activity compared to that of traditional carbon-supported Pt nanoparticle catalysts and offer significant promise as a new class of electrocatalysts in fuel cell applications.

1. INTRODUCTION

The commercial impact of proton-exchange membrane fuel cells (PEMFCs) is limited in part by the catalyst cost, as the catalyst layer can account for as much as half of the fuel cell cost.¹,² Catalyst development typically focuses on the oxygen reduction reaction (ORR) at the cathode, as ORR in acidic environments is 6 orders of magnitude slower kinetically than the hydrogen oxidation reaction. PEMFCs typically use carbon-supported platinum nanoparticles (Pt/HSC) as the ORR catalyst. Pt/HSC is commonly used due to its high surface area but has limitations in site-specific activity and durability. In durability, Pt nanoparticles are prone to surface area loss through aggregation, Ostwald ripening, and dissolution, whereas the carbon support is susceptible to corrosion/particle detachment.³⁻⁵ Extended surface catalysts offer the potential to dramatically improve both site-specific activity and durability, key limitations for the current commercial catalysts.

To guide ORR catalyst development, the United States Department of Energy (DOE) has a 2020 target for mass activity of 440 mA m⁻² at 0.9 V (Pt group metal, PGM, basis). The DOE target is intended for activity determined in fuel cells. Activities measured in fuel cells are susceptible to losses from mass transport and resistance (electronic and ionic); therefore, rotating disc electrode (RDE) measurements are used as screening tools to determine the inherent catalyst activity. The evaluation of activity in RDE half-cells, however, by itself does not ensure similar performance in fuel cells. This study relies on RDE experiments to show the potential of materials in an effort to focus on their fundamental electrocatalytic properties without the complicating factors of fuel cell performance through optimized membrane electrode assemblies (MEAs).

A number of researchers have correlated Pt-ORR activity to Pt—OH and Pt—O binding, suggesting that Pt alloys can offer ORR performance improvements beyond Pt-only catalysts.⁶⁻⁹ Alloying Pt with other elements has been found to offer activity improvements, and Pt-nickel (Ni) has been investigated in a number of forms, experimentally confirming the modeled alloy benefit.⁹⁻¹⁸ Work within Pt—Ni has included nanoparticle development by a variety of methods, alloyed and dealloyed, to produce Pt skins and skeletons.¹⁹⁻²⁴ In several cases, developed electrocatalysts have produced ORR activities significantly.
higher than Pt nanoparticles and the DOE-MEA target in RDE half-cells.

Extended thin films generally offer high site-specific activities, often an order of magnitude greater than nanoparticle catalysts.\textsuperscript{25–27} Extended nanostructures have also shown improved long-term durability when exposed to potential cycling. A highly recognized example of extended surface Pt-ORR catalysts is 3M’s nanostructured thin films, which have shown high activity and durability.\textsuperscript{28,29} Although improvements to ORR mass activity have occurred through large increases in site-specific activity, extended surface catalysts have traditionally been limited by low surface areas, on the order of 10 m\textsuperscript{2} g\textsuperscript{-1}.\textsuperscript{32,33} Although extended surface electrocatalysts show great promise, they have been limited by the low surface areas they have achieved.

We have previously used galvanic displacement to deposit thin Pt layers onto extended nanostructures and demonstrated a dramatic increase in the Pt surface areas of extended surface electrocatalysts (\textgtrsim 90 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{27,34–37} These materials, however, suffered from moderate specific activity and were prone to performance loss and Ni dissolution. Postsynthesis processing parameters, including thermal treatment under reducing and oxidizing conditions and acid leaching to selectively remove Ni, have been optimized to significantly improve the site-specific activity without appreciably impacting the surface area. The resulting materials also minimized durability performance losses, including activity and Ni dissolution. The results of these studies represent the first example of extended surface materials with both exceptionally high specific activity (>6000 \(\mu\)A cm\textsuperscript{-2}) and exceptionally high surface area (>90 m\textsuperscript{2} g\textsuperscript{-1}).

2. RESULTS AND DISCUSSION

2.1. Hydrogen Anneal. Pt—Ni nanowires were annealed in hydrogen at select temperatures in an attempt to improve incorporation of Ni into the Pt phase, thereby offering site-specific activity advantages due to alloying effects.\textsuperscript{8,11} Compared with the as-synthesized catalyst, annealing in hydrogen to 250 °C produced a 3-fold specific activity increase in RDE half-cells (Figures 1 and S1–S3). The largest increase in specific activity was observed between 200 and 250 °C; at higher temperatures, more incremental improvements were found. Although increasing the annealing temperature improved the specific activity, the ORR mass activity reached a peak value of 5200 mA mg\textsubscript{Pt}\textsuperscript{-1} at 250 °C and decreased at higher annealing temperatures (Figure 1). This decline was due to surface area loss, which could be rationalized in terms of reordering and aggregation of Pt at the surface, and a loss of surface roughness was observed in microscopic analysis (Figures 2 and S4–S6).

Incorporation of Ni in the Pt phase was confirmed with X-ray absorption spectroscopy at the near-edge (XANES) and the extended region (EXAFS, Figure 3a,b). The Pt L\textsubscript{3} absorption edge corresponded to core electron transitions from the 2p\textgtrsim1/2 orbital to unoccupied states. Hydrogen annealing decreased the area, likely due to alloyed Ni contributing electrons to the
previously unoccupied Pt orbitals. Parameters derived from the first-shell fitting of the Fourier-transformed Pt L\textsubscript{3} EXAFS spectra provide quantitative structural information (Figure 3b,c). For the as-synthesized Pt—Ni nanowires, the best fit was achieved with only Pt in the first shell. After hydrogen annealing to 250 °C, equivalent amounts of Ni and Pt in the first shell and a compressed Pt—Pt interatomic distance (−0.05 Å, relative to the as-synthesized nanowires) were required for the fit. Only Pt—Ni bonding is evident from the fit for the nanowires annealed at 400 °C, with Ni being the only scattering element in the best fit of the first shell. The EXAFS results demonstrated incorporation of Ni into the Pt first shell and established that hydrogen annealing increases mixing of the Pt and Ni phases. X-ray photoelectron spectroscopy (XPS) further confirmed changes in the surface composition, consistent with migration of Pt into the Ni core. Although no major changes were observed in the Pt 4f spectra, there is substantial growth of the peak at approximately 852.5 eV due to an increase in the metallic Ni species near the nanowire surface (Figure 3d,e).

The specific activities of the Pt—Ni nanowires were more than 10 times larger than those of Pt/HSC. Pt—Ni nanowire catalysts offer potential advantages in site-specific activity, by the extended surface avoiding low coordinate surface sites and/or reduced particle size effects.\textsuperscript{25,26} The increase in specific activity observed with the hydrogen annealing temperature can be rationalized as an increased alloying effect, with Ni-induced Pt lattice compression weakening Pt—O chemisorption.\textsuperscript{8,11} As discussed above, the improved mixing of the Pt and Ni phases with the annealing temperature was confirmed with XANES and EXAFS (Figure 3). Pt lattice compression was probed directly by X-ray diffraction (XRD), where examination of the Pt(111) reflection revealed a gradual shift from a characteristically Pt lattice into a shoulder on the Ni(111) reflection at 500 °C (Figures 4a and S7). Through Rietveld refinement of the XRD patterns, the average Pt lattice constant compressed from

Figure 2. STEM-HAADF of Pt—Ni nanowires (7.3 ± 0.3 wt % Pt): as-synthesized; annealed in hydrogen to 250 and 400 °C; annealed in hydrogen to 250 °C and ex situ acid-leached (A1, N1, N3); and annealed in hydrogen to 250 °C, ex situ acid-leached (N1), and annealed in oxygen to 175 °C.
3.911 Å in the as-synthesized material to 3.551 Å after annealing to 500 °C (Figure S8). Differences in the exposed Pt facets may have influenced activity but likely did not provide a significant benefit for the Pt—Ni nanowires. Studies on the redox of adsorbed germanium and tellurium confirmed a wide distribution of surface Pt facets; a majority (50−65%), however, were in the {100} set, previously found to be less active for Pt—Ni alloys (Pt3Ni, Figures 4 and S9).38−42 The distribution of Pt facets was generally consistent for all Pt—Ni nanowires examined and did not significantly change with the annealing temperature. In contrast, Pt/HSC contained more Pt{111} (46.3%) than {100} (26.1%) in comparable tests. The observed Pt facet distribution may not have improved the ORR activity. Understanding why the Pt—Ni nanowires contained a high proportion of Pt{100}, however, was of significant interest, and density functional theory (DFT) calculations were performed to examine the relative stabilities of the Pt facets and lattices found in the Pt—Ni nanowires.

DFT calculations were completed on a Pt skin on the Pt—Ni alloys (Ni3Pt and Pt3Ni), on the relevant facets of (100), (110), and (111, Figures 4, S10, and S11, and Tables S1−S3). Calculations were completed on Ni3Pt and Pt3Ni substructures, on a single and three Pt overlayers, to give a range of Pt lattices and bracket the range found in the XRD patterns. Calculations confirmed that (111) is the most stable surface for the alloys, with >99% of exposed facets being (111, Boltzmann distribution). The presence of a Pt skin, however, resulted in a reordering of facet stabilities. Specifically, the (100) facet of Ni3Pt with a Pt skin of three layers was stabilized with cohesive energies comparable to those of the (111) facet. A lattice constant of 3.62 Å resulted in cohesive energies of $E_{\text{coh}}(100) = -4.98$ and $E_{\text{coh}}(111) = -5.01$ eV/atom; likewise, a lattice of 3.77 Å resulted in $E_{\text{coh}}(100) = -5.03$ and $E_{\text{coh}}(111) = -5.06$ eV/atom. The alloying effect of Ni3Pt was more pronounced than that of Pt3Ni as the Ni-enriched alloy particularly stabilizes both (100) ∼ (111) over (110) with a compressed lattice constant ca. 3.77 Å. This effect may become more pronounced as the Pt skin grows thicker and may have far-reaching effects on the electrocatalytic activity exhibited by the high-performer. Stabilization of the Pt skin on Ni3Pt varied depending on both skin thickness and the size of the lattice—a single Pt layer was more stabilized on a sublayer of Ni, whereas a thicker Pt layer was more stabilized on a sublayer of mixed Pt—Ni. Although (111) is the most stable surface of face-centered cubic metals in vacuum, the competitive stability of a Pt skin on (100) Ni3Pt appears to explain how the Pt—Ni nanowires can contain a high amount of Pt(100) on the surface with a compressed lattice. The DFT calculations addressed the synthesized catalyst by focusing on the extended surface and the Ni3Pt substructure to induce Pt lattice compression. A three-layer Pt skin on (100) Ni3Pt was representative of the high-performing nanowires (hydrogen-annealed, 250 °C), as the lattices approximately matched, and the (100) facet was dominant electrochemically.

As discussed above, the hydrogen-annealed samples showed very high initial activity. Their durability, however, was a concern. Durability testing was completed in RDE half-cells, by performing 30,000 potential cycles in the range of 0.6−1.0 V versus a reversible hydrogen electrode (RHE) at 500 mV s$^{-1}$. For the less-active Pt—Ni nanowires, as-synthesized or annealed to low temperatures, durability losses were generally

| Sample               | N | R  | $\Delta\sigma^2 \times 10^3$ | R-factor |
|----------------------|---|----|-----------------------------|----------|
| As-synthesized       |   |    |                             |          |
| H2 250°C             |   |    |                             |          |
| H2 400°C             |   |    |                             |          |
| H2 250°C, Acid (N1), O2 175°C |   |    |                             |          |

Figure 3. (a) XANES spectra of the Pt—Ni nanowires. (b) Fourier transform of the k3-weighted EXAFS data (solid line) and first-shell fits (dashed line) of the Pt—Ni nanowires. (c) Pt and (d) Ni XPS spectra of the Pt—Ni nanowires. Pt—Ni nanowires as-synthesized (gray), hydrogen-annealed to 250 °C, ex situ acid-leached (N1), and oxygen-annealed to 175 °C, purple. (e) Parameters derived from the EXAFS fits for the Pt—Ni nanowires, including the coordination numbers ($N$), absorber-scattering atoms, interatomic distance ($R$), sigma squared ($\sigma^2$), and the R-factor.
modest (Figures 1 and S3). These losses increased at higher annealing temperatures, however, due to a combination of ECA and specific activity losses and corresponded to elevated levels of Ni dissolution (Figure S12). XPS data confirmed that annealing in hydrogen increased the presence of Ni metal (relative to Pt or Ni hydroxide) near the nanowire surface (Figure 3). The prevalence of the Ni metal likely resulted in the susceptibility of the nanowires to corrosion and contributed to higher specific activity losses in durability testing. Although significant amounts of Ni dissolved during electrochemical conditioning and durability, microscopic analysis found solid, in-tact nanowires that remained after electrochemical testing (Figure S13).

The Ni dissolution rates observed were higher than typical for Pt—Ni nanoparticles. The primary difference between these systems was the amount of Ni available and the location of Pt and Ni at the beginning of the annealing process. The nanowires were Ni dominant (92.7 wt % Ni), with Pt at the outer layer. Conversely, Pt—Ni nanoparticles were typically more homogeneous with a lower Ni composition. Although Pt may have a surface preference over Ni, the Ni/Pt atomic ratio and the initial location of Pt on the nanowire surface potentially overwhelmed this preference. Intermixing of Pt and Ni may also have created Ni-dissolution routes, exposing the Ni nanowire core.

2.2. Acid Leach. As Ni leaching in durability testing was found to be a concern, ex situ acid exposure was used to explore the potential impacts of Ni leaching on performance and durability following the hydrogen annealing step. Annealed Pt—Ni nanowires were exposed to different acid types, concentrations, and temperatures to create catalysts with a variety of compositions (Table S4). The results of these studies exposed general trends on the basis of the acid type (Figures 2 and S14). First, exposure to acetic acid caused low amounts of Ni removal, primarily small Ni pockets near the nanowire surface, but did not significantly impact catalyst morphology. Second, exposure to nitric acid resulted in moderate amounts of Ni removal, including the partial removal of the nanowire core. Higher nitric acid concentrations resulted in higher degrees of Ni removal; many nanowires were broken into shorter segments (0.5–1 μm), and all of the Ni metal that was not incorporated within the Pt layers was removed. Third, exposure to sulfuric acid resulted in the highest degree of Ni removal. A significant portion of the catalyst was broken into fragments, with few nanowires maintaining their original morphology.

Ex situ acid leaching of the hydrogen-annealed Pt—Ni nanowires proved to be effective in improving durability; these improvements, however, came at the expense of activity (Figures 5 and S15). This trend can be divided into two groups. Small amounts of Ni removal, using acetic acid or dilute (0.1 M) nitric acid, maintained Pt lattice compression and high
site-specific activity, but did not dramatically reduce activity losses or Ni dissolution in durability testing. Large amounts of Ni removal (using more concentrated nitric acid or sulfuric acid) significantly improved catalyst durability and minimized Ni dissolution, but resulted in much lower initial specific activity and was of less interest from an electrocatalyst standpoint (Figure S16). This drop in initial site-specific activity could be rationalized as being caused by a dealloying effect, and XRD confirmed that ex situ acid leaching resulted in a shift of the Pt lattice from relatively compressed to characteristic Pt

2.3. Oxygen Anneal. Annealing in oxygen was pursued since the approach had previously improved the durability of as-synthesized Pt—Ni nanowires. All acid-treated catalysts were annealed in oxygen at 175 °C, which was found to provide a balance between durability and initial activity. Trends in the oxygen annealing step can be divided into three groups. At one extreme, for catalysts with low Pt compositions, annealing in oxygen dramatically reduced the Pt-ECA and ORR performance. Although the intent was to reduce Ni dissolution and durability losses, large amounts of Ni persisted at the nanowire surface. Oxygen annealing stabilized Ni, which prevented Pt surface cleaning during electrochemical conditioning and resulted in low activity. At the other extreme, for catalysts with high Pt compositions, little Ni was present, and oxygen annealing had minimal impact. Although these materials were highly durable, they were of less interest electrocatalytically. Between these two extremes, Pt—Ni nanowires (15.2 wt % Pt) were found that produced high initial activity, a high degree of durability, and low amounts of Ni dissolution (Figures 6, S18, and S19, and Table S5).

Oxygen annealing minimized activity losses in durability testing and decreased Ni dissolution, attributed to the increased prevalence of Ni oxide (NiO) near the nanowire surface. High-resolution XPS of the optimized nanowires (15.2 wt % Pt, Ni 2p spectrum) showed a substantial decrease in the amount of Ni metal (peak at 852.5 eV) near the nanowire surface, accompanied by the appearance of NiO (peak at 854.2 eV, Figure 3). Without oxygen annealing (as-synthesized or hydrogen-annealed), Ni hydroxide species, and not oxides, were observed. In RDE half-cells, the optimized Pt—Ni nanowires (15.2 wt % Pt) exceeded the initial ORR mass activity of the as-synthesized material by 3 times and Pt/HSC by 11 times (Figure 6). After durability testing (30 000 cycles, 0.6–1.0 V vs RHE), the optimized catalyst also lost less than 3% of its initial ORR mass activity and less than 0.5 wt % of its mass (Pt and Ni) due to dissolution.

A summary of the Pt—Ni nanowire electrochemical properties, before and after durability, is provided in Figure 6e. This figure separates ECA (x axis) and specific activity (y axis) as the source of mass activity. As-synthesized Pt—Ni nanowires (Pt—Ni) produce higher specific activity than Pt/HSC due to the extended surface, and hydrogen annealing (H2) further improves the specific activity. Acid leaching (acid) slightly improved the durability but at the cost of initial specific activity, and oxygen annealing (O2) provided the optimum in activity (ECA and specific activity) and durability.

3. CONCLUSIONS

Pt—Ni nanowires were previously demonstrated with surface areas in excess of 90 m2 g−1, a significant breakthrough in and of itself for extended thin-film electrocatalysts. These
materials, however, lacked exceptional site-specific activity and durability. Through a series of post-synthesis optimization steps, Pt—Ni nanowires were developed with dramatically improved specific activity, durability, and stability (Ni dissolution). The optimized nanowires demonstrated ORR activities 3 times greater than the as-synthesized nanowires and 11 times greater than Pt/HSC. After durability testing, the optimized Pt—Ni nanowires lost less than 3% of their initial mass activity and less than 0.3 wt % of Ni due to dissolution, a significant improvement to the as-synthesized material (21% loss in activity, 7% Ni to dissolution). The electrochemical properties of these catalysts are summarized in Figure 6. To date, no study has produced extended surface, Pt electrocatalysts for ORR with the high surface areas, specific activities, and durability reported here. Although these materials offer significant performance advantages when tested in RDE, a major challenge remains in incorporating them effectively into high-performance electrodes and devices.

In RDE half-cell tests, Pt—Ni nanowires offer greater than a 10-fold improvement in performance and significant durability benefits to Pt nanoparticles. These results suggest that much lower loadings could potentially be used in PEMFC electrodes and that Pt—Ni nanowires can become a critical element for enabling the broader commercial deployment of fuel cells.

4. EXPERIMENTAL SECTION

Pt—Ni nanowires were synthesized by the spontaneous galvanic displacement of Ni nanowires with Pt.36 Ni nanowires (40 mg, as-received PlasmaChem GmbH) were dispersed by sonication in 80 mL of water in a 250 mL round bottom flask. The flask contents were heated in an oil bath to 90 °C and
stirred at approximately 500 rpm by a Teflon paddle (glass shaft). After a 15 min wait period, the Pt precursor (8.1 mg of potassium tetrachloroplatinate in 15 mL of water) was added dropwise by a syringe pump over a period of 15 min. After the addition of the Pt precursor, the reaction continued for 2 h at 90 °C, at which point it was cooled to room temperature. Pt—Ni nanowires were washed in water and 2-propanol and collected by centrifugation.

Post synthesis annealing of the Pt—Ni nanowires was completed in a Lindberg/Blue M split-hinge tubular furnace, equipped with a 2 in. quartz tube. Samples were inserted into the tube and vacuumed overnight to ensure adequate drying, using a Pfeiffer Vacuum Duo 2.5 and a Pfeiffer HiCUBE pumping station connected to a MKS Type 146 vacuum gauge measurement and control system. After vacuuming, a low flow rate of gas (hydrogen or oxygen, depending on the experiment) was fed to the tube. Annealing was completed on samples to a variety of temperatures, with a 10 °C min⁻¹ ramp rate and a 2 h run time. After the annealing was complete, the furnace cooled to room temperature naturally. The glass blowing of the quartz tube and the fitting to account for vacuum and gas flow were completed in-house.

Annealing of the Pt—Ni nanowires in hydrogen (10%, balance nitrogen) was completed with low gas flow, 500 Torr of back pressure, a 10 °C min⁻¹ ramp rate, and a 2 h run time. Acid leaching of Pt—Ni nanowires occurred in acetic, nitric, or sulfuric acid, with exposure to different concentrations, temperatures, and times, to create materials with a variety of compositions. The conditions and compositions produced are summarized in Table S4. All acid leaching experiments were conducted in a nitrogen environment by way of a Schlenk line. Annealing of the Pt—Ni nanowires in oxygen (50%, balance nitrogen) was completed with low gas flow, 500 Torr of back pressure, a 10 °C min⁻¹ ramp rate, and a 2 h run time.

Material compositions were determined by ICP-MS, taken on a Thermo Scientific iCAP Q. Samples were digested in aqua regia and diluted to total sample concentrations of 200, 20, and 2 ppb. The dilutions were matrix matched to 1.5% hydrochloric acid and 0.5% nitric acid and filtered to 0.4 µm. The instrument was calibrated to a blank, an internal standard, and three Pt Ni standards. Measurements of each dilution were taken three times at a dwell time of 0.15 s. After the analysis of every five dilutions, the ICP-MS was checked to a Pt Ni standard.

ICP-MS was also completed on electrolytes (0.1 M perchloric acid) after electrochemical conditioning and durability testing. Electrolytes were filtered but not diluted for analysis as the Pt Ni concentrations were on a ppb level, above the detection limit but well below a concentration to flood the detector. Standards and the blank were matrix matched to 0.1 M perchloric acid. ICP-MS accounted for Pt or Ni that dissolved from the electrode but could not account for spurious interaction between periodic images. Surface calculations occurred under a k-point sampling of 4 × 4 × 1 for (100) and (111) and 2 × 3 × 1 for (110). Because of the size of the supercell, the (111) surface composed of a Pt skin of three layers on an alloy utilized a grid of 2 × 2 × 1. Reference atomic energies were calculated at the Γ point in a box of volume >1000 Å³ with the symmetry of the cell broken to replicate appropriate spin states. Cohesive energies (Ecoh) were determined with the equation:

\[ E_{\text{coh}} [\text{eV/atom}] = \frac{E_{\text{tot,surf}} - n_{\text{Pt}}E_{\text{Pt}} - n_{\text{Ni}}E_{\text{Ni}}}{n_{\text{Ni}} + n_{\text{Pt}}} \]

where \( E_{\text{tot,surf}} \) is the total energy in VASP of the surface, \( E_{\text{Ni}} \) (\( E_{\text{Pt}} \)) are reference atomic energies, and \( n_{\text{Pt}} \) (\( n_{\text{Ni}} \)) are the number, \( n \), of Pt (Ni). Reported cohesive energies follow the convention of negative energies indicating attraction between atoms for stabilization.

DFT calculations were performed to understand relative stabilities of a Pt skin on Pt—Ni alloys, both on Ni₃Pt and Pt₃Ni, and on the relevant facets of (100), (110), and (111) of these alloys (Figures 4, S8, and S9, and Tables S1–S3). Appropriate lattice constants were chosen to consider conditions such as the alloy’s compressed lattice, a lattice midway between the alloy and Pt, and the lattice of pure Pt. For a Pt skin on Ni₃Pt, lattice constants of 3.62, 3.77, and 3.92 Å were explored, and for Pt₃Ni, 3.82, 3.87, and 3.92 Å were
explored. These lattice constants represent a sampling of the range of surface phenomena that would be present on the nanowires. Moreover, the stability of the Pt skin on these alloys was further explored by modeling a Pt skin composed of a single layer and of three layers on Pt—Ni alloys. This provides a first-order approximation of the stability of Pt-skin growth on the faceted alloy. On the (100) and (110) surfaces of Ni,Pt, the alloy alternates between a layer of Ni and a layer of Pt and Ni atoms. The Pt skin was evaluated on both to consider the Ni-enrichment, sublayer effect on Pt—Ni. More details are provided in Supporting Information regarding the construction of these surfaces.

Electrochemical testing was completed in RDE half-cells in 0.1 M perchloric acid. The RDE half-cell contained a glassy carbon working electrode, a platinum mesh counter electrode, and a RHE reference electrode. The RHE reference consisted of a glass bubbler containing hydrogen-saturated 0.1 M perchloric acid, connected to the main cell by a Luggin capillary. Electrochemical measurements were taken with an Autolab potentiostat (Eco Chemie, Metrohm Autolab B.V.), and rotation of the working electrode was controlled by a modulated speed controller (Pine Instrument Company).

Pt—Ni nanowire inks were prepared by adding 7.6 mL of water and 2.4 mL of 2-propanol to 1 mg of the catalyst. The ink was iced for 5 min, then 10 μL of Nafion (5 wt %, Sigma-Aldrich) was added, and the ink was horn sonicated for 30 s, bath sonicated for 20 min, and horn sonicated for 30 s. The sonicated ink (7.5 mL) was then added to 0.5 mg of graphitized carbon nanofibers, and the sonication process (30 s horn, 20 min bath, 30 s horn) was repeated. Ink (10 μL) was pipetted onto an RDE working electrode, inverted on a test stand. After ink application, the electrode rotation speed was increased to 700 rpm, and the ink was sonicated (20 min bath, 30 s horn) while the working electrodes dried. Reapplication of the nanowire inks, necessary to increase the ORR diffusion-limited current, continued until 50 μL of ink had been pipetted and dried onto the electrode.

The as-synthesized Pt—Ni nanowires were evaluated in a previous publication and served as the starting point for the materials developed here. The activity of as-synthesized Pt—Ni nanowires was previously reported as 917 mA mgPt−1, compared with 1653 mA mgPt−1 reported here. The improvement in activity was due to optimized electrode-coating methods, that is, using a rotational electrode-coating method and making changes to the ink, including a reduction in the catalyst concentration and Nafion/carbon content optimization. The rotational coating method also improved the Pt/HSC performance from 300 to 500 mA mgPt−1.

Pt/HSC (46 wt % Pt, Tanaka Kikinzoku Kogyo) was used as a benchmark catalyst in this study. Pt/HSC inks contained 7.6 mg of catalyst, 7.6 mL of water, 2.4 mL of 2-propanol, and 40 μL of Nafion. After sonication (20 min bath), 10 μL of ink was dispensed onto the working electrodes and dried in air at 700 rpm.

ECAs were determined by carbon monoxide oxidation voltammograms and verified by charges due to hydrogen underpotential deposition. In the oxidation of an adsorbed carbon monoxide layer, the working electrodes were held at 0.1 V versus RHE for 20 min in 0.1 M perchloric acid. For the first 10 min, carbon monoxide was bubbled into the electrolyte to adsorb a layer onto the catalyst. For the second 10 min, nitrogen was bubbled into the electrolyte to remove excess carbon monoxide. Because of the location of the bubbler, rotation of the working electrode at 2500 rpm was required. Electrode rotation and gas bubbling were turned off 30 s before the end of the 20 min hold. A linear sweep was immediately run at 20 mV s−1 anodically to 1.2 V versus RHE, then cathodically to 0.025 V versus RHE. Cyclic voltammograms (0.025−1.2 V vs RHE) were run thereafter to ensure that excess carbon monoxide had been removed from the RDE half-cell before the end of the potential hold. ECAs were calculated from the carbon monoxide oxidation voltammograms assuming a Coulombic charge of 420 μC cmPt−2. ECAs were verified by the charge associated with hydrogen adsorption, assuming a Coulombic charge of 210 μC cmPt−2.

Germanium and tellurium adsorption was used to quantify the amount of Pt{100} and {111} facets present on the catalyst surfaces. All electrodes underwent electrochemical conditioning (potential cycling up to 1.2 V) before metal adsorption. To adsorb germanium, a drop of 1 M sodium hydroxide containing 0.01 M germanium(IV) oxide (483 001, Sigma-Aldrich) was added to the electrode surface. With the drop coating the working electrode, it was submersed into 0.5 M sulfuric acid at 0.1 V versus RHE and immediately scanned at 50 mV s−1 in the potential range of 0.025−0.6 V versus RHE. The charge due to germanium redox was normalized to the ECA from Pt{100} by the conversion factor. To adsorb tellurium, the electrode tips were submersed for 10 min in 0.5 M sulfuric acid containing 10−5 M tellurium dioxide (435 902, 99.9995%, Sigma-Aldrich) and then rinsed with water. After tellurium adsorption, the working electrodes were scanned at 50 mV s−1 in 0.5 M sulfuric acid in the potential range of 0.025−0.9 V versus RHE.

ORR polarization curves were taken anodically at 20 mV s−1 in the potential range of −0.01−1.05 V versus RHE at 1600 rpm in an oxygen-saturated 0.1 M perchloric acid electrolyte. The diffusion-limited currents for ORR (4.7−4.9 mA cmHSC−2) were lower than those typically found at the sea level, due to the elevation where the experiments were completed (83.2 kPa at 5674 ft elevation). These diffusion-limited currents, however, were typical for the elevation and were predicted by the Levich equation, in which the diffusion-limited current is linearly proportional to the partial pressure of oxygen. The diffusion-limited currents were not corrected in the linear polarization curves. ORR activities, however, were corrected for mass transport (by the Koutecky−Levich equation), the internal resistance of the electrolyte (18–25 Ω, depending on the electrode), and the partial pressure of oxygen (a reaction order of 0.75 at 0.9 V vs RHE). As a reference point, polycrystalline Pt produced ORR site-specific activities of 2500 and 445 μA cmPt−2, respectively, at 0.9 and 0.95 V versus RHE.

The ORR activities reported here have been corrected for mass transport. With the high performances reported here, it was possible that the kinetic ORR activities were overcorrected by the Koutecky−Levich equation. To ensure that the ORR activities were not overestimated, activities at 0.95 V were included in the Supporting Information section (Figures S2, S11, and S14). Activities at 0.9 V, however, were used in the main text because the DOE-MEA target is at that potential and because the activity benefit of Pt—Ni nanowires (compared to Pt/HSC) was similar at 0.9 and 0.95 V.

Durability testing was completed by potential cycling (30 000 cycles) in the range of 0.6−1.0 V versus RHE in a nitrogen-saturated 0.1 M perchloric acid electrolyte. Full cyclic voltammograms were taken every 1000 cycles until 5000 and every 5000 cycles thereafter to monitor catalyst ECA by
hydrogen underpotential deposition. ORR polarization curves and carbon monoxide oxidation voltammograms were taken after durability testing.

**ASSOCIATED CONTENT**

* Supporting Information

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Electrochemical, modeling, diffraction, and microscopy results (PDF)

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**Notes**

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