Pt-Ni Aerogels as Unsupported Electrocatalysts for the Oxygen Reduction Reaction

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The commercial feasibility of polymer electrolyte fuel cells (PEFCs) passes by the development of Pt-based, O₂-reduction catalysts with greater activities and/or lower Pt-contents, as well as an improved stability. In an effort to tackle these requirements, unsupported bimetallic Pt-Ni nanoparticles (NPs) interconnected in the shape of nanochain networks (aerogels) were synthesized using a simple one-step reduction and gel formation process in aqueous solution. The products of this novel synthetic route were characterized by X-ray absorption spectroscopy to elucidate the materials' structure. Using electrochemical experiments, we probed the surface composition of the as-synthesized aerogels and of equivalent materials exposed to acid, and concluded that a Ni-(hydr)oxide side phase is present in the aerogel with a larger Ni-concentration. Regardless of this initial surface composition, the Pt-Ni aerogels feature a ≈ 3 -fold increase of surface-specific ORR activity when compared to a commercial platinum-on-carbon catalyst, reaching the mass-specific requirement for application in automotive PEFCs.

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State-of-the-art polymer electrolyte fuel cells (PEFCs) require large amounts of carbon-supported platinum nanoparticle (Pt/C) catalysts ($\approx 0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2_{\text{electrode}}$)¹ to account for the large overpotential of the oxygen reduction reaction (ORR). Thus, Pt contributes significantly to the fuel cell system cost, and progress to reduce its loading is crucial to meet the long-term PEFC cost target of 40 \$/kW set by the U. S. Department of Energy (DOE).² One approach to reduce this excessive Pt-loading relies on increasing the catalysts' ORR activity, e.g. by alloying platinum with other metals like Ni, Cu and Co, to form materials which show up to one order of magnitude higher mass-specific activity than commercial Pt/C catalysts.³ On the other hand, these carbon-supported materials suffer from significant carbon- and Pt-corrosion during the standard operation of PEFCs, gradually compromising their efficiency and reliability.⁴ To partially overcome stability issues, research focuses on unsupported materials (e.g. Pt-coated Ni, Co or Cu nanowires^{5–7}) besides extended metal surfaces (e.g. 3 M nanostructured thin film catalysts⁸) or alternative supports (e.g. conductive metal oxides^{9–12}). Naturally, those materials should be processable into catalytic layer architectures that provide reactant and product diffusion pathways similar to those in conventional Pt/C electrodes to guarantee high catalyst utilization and PEFC performance.¹³

To meet the requirements mentioned above, unsupported bimetallic electrocatalysts with high surface area (up to $\approx 80 \text{ m}^2/\text{g}_{\text{metal}}$) and nanochain network structure, referred to as aerogels, have been synthesized.^{14–16} The synthetic routes to prepare such materials vary, but generally involve the use of stabilizing surfactants and/or organic solvents^{17–19} that can poison the catalyst's surface and decrease its activity. In contrast to those approaches, our groups have developed a facile one-step synthesis for mono- and bimetallic aerogels based on the reduction of metal salts by NaBH₄ in aqueous solution without addition of stabilizing surfactants.²⁰

On the basis of previous work on Pt-Pd alloy aerogels prepared with the aforementioned method,²⁰ we have adapted our synthetic approach to the combination of a noble and a non-noble metal, targeting a reduced noble metal content while maintaining a high ORR activity. As we will demonstrate in this article, the combination of Pt and Ni yielded materials with a mass-normalized ORR activity ≈ 2 -fold

higher than that of a commercial Pt/C catalyst and that reaches the DOE target for automotive PEFC application.²¹

Experimental

Pt-Ni hydrogels were prepared by a simple co-reduction route in aqueous solution under ambient conditions (room temperature, air). Briefly, Pt and Ni precursors were dissolved in water (18.2 MΩ cm, Millipore) in the Pt⁴⁺:Ni²⁺ molar proportions required to reach the targeted Pt:Ni ratio, and reduced by NaBH₄. Selecting the synthesis of Pt₃Ni hydrogel as an example, 585 μL of a 0.205 M H₂PtCl₆ solution (8 wt% in H₂O, Sigma Aldrich) [final reactant concentration 0.15 mM] and 4 ml of a freshly prepared 10 mM NiCl₂ solution (NiCl₂·6H₂O 99%, Sigma Aldrich) [final reactant concentration 0.05 mM] were dissolved in 790 ml water and stirred until mixing was complete. Subsequently, 7.0 ml of a freshly prepared 0.1 M NaBH₄ solution (granular, 99.99%, Sigma Aldrich) [c(Pt⁴⁺ + Ni²⁺):c(NaBH₄) = 1:1.25] were added under vigorous stirring. Upon addition of NaBH₄, the color of the solution turned immediately from light yellow to dark brown. The solution was kept stirring for another 30 min. Afterwards, the reaction solution was divided and transferred to 100 ml vials. After about four days, black Pt_xNi hydrogel was formed at the bottom of the containers. The hydrogel parts obtained from the same synthesis were collected in a small vial and washed with water. For this, half of the supernatant was removed and replaced cautiously with fresh water. This step was repeated six times. Afterwards, the solvent was exchanged stepwise with acetone. Again, half of the supernatant was removed and replaced by acetone. This step was repeated 11 times. The resulting anhydrous gels were transferred to a critical point dryer (Critical Point Dryer 13200J-AB, SPI Supplies) operating with CO₂.

XAS spectra at the Pt L₃ and Ni K edges were recorded at the SuperXAS beamline of the Swiss Light Source (Paul Scherrer Institut, Villigen, Switzerland), whereby the monochromator energy was calibrated using Pt and Ni foils, respectively. Measurements were performed ex-situ in transmission mode on pouch bags made from conductive Kapton tape that were filled with aerogel powder. The quick-EXAFS (QEXAFS) method was used to increase time resolution;²² 100 and 600 quick-XAS spectra were recorded at the Pt L₃ and Ni K edges, respectively. These XAS data were first analyzed with the JAQ analyzer software which allows averaging of individual XAS spectra into a single spectrum. Subsequently, Athena of the Demeter software

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package was used for normalization and background subtraction.²³ The fit of the EXAFS oscillations was performed with Artemis²³ using a face centered cubic Pt-Ni structure for the paths description. Amplitude reduction terms were calculated from EXAFS fits of Pt and Ni reference foils assuming a coordination number of 12 and amounted to $S_{0,\text{Ni}} = 0.97$ and $S_{0,\text{Pt}} = 0.85$, respectively.

Electrolyte solutions were prepared from $\text{NaOH} \cdot \text{H}_2\text{O}$ pellets (99.995% purity, TraceSELECT, Sigma Aldrich) or 60% HClO_4 (Kanto Chemical Co., Inc.) diluted in ultrapure water (18.2 M Ω cm, Elga Purelab Ultra). High purity N_2 (5.0), O_2 (5.0) and CO (4.7) were purchased from Messer AG, Switzerland. The benchmark catalyst for this study is a Pt/Vulcan XC-72 electrocatalyst with a weight fraction of 30% purchased from E-TEK Inc. (Lot# C0160311). The electrochemical measurements in acid were performed in a house-made three electrode glass cell. A reversible hydrogen electrode was connected to the main cell compartment through a Luggin capillary, and a gold mesh (99.99% metals basis, Alfa Aesar) held in a separate tube in contact with the main cell served as counter electrode (CE). The working electrode (WE) was a PTFE-made, interchangeable rotating ring-disc electrode (RRDE, Pine Research Instrumentation) equipped with a Pt-ring and a mirror-polished, glassy carbon disk insert (5 mm diameter, HTW Hochtemperatur-Werkstoffe GmbH). Before the measurements, the WE was mounted to a polyetheretherketone (PEEK) shaft that was attached to a modulated speed rotator (both Pine Research Instrumentation). A Biologic VSP-300 was used as potentiostat, in combination with the EC-Lab V10.44 software package. The ohmic drop was determined by electrochemical impedance spectroscopy, applying a 5 mV perturbation (100 kHz to 1 Hz) at 0.45 V_{RHE} . The setup for measurements in alkaline electrolyte was described in detail in a previous work.²⁴ In brief, it consisted of a house-made polytetrafluoroethylene (PTFE) cell with a four-necked glass cover. A calomel reference electrode (ALS Co., Ltd.) was kept in a separated glass holder filled with electrolyte connected to the main compartment through a Luggin capillary consisting of a FEP tube closed with a 50 μm thick Nafion membrane (Ion Power, New Castle, DE). The setup was completed by a gas bubbler and a gold mesh counter electrode.

Thin-film electrodes were prepared by dispersing catalyst materials in mixtures of ultrapure water (18.2 M Ω cm, Elga Purelab Ultra) and isopropanol (99.9%, Chromasolv Plus for HPLC, Sigma Aldrich), followed by 10 min sonication in an ultrasonic bath (USC100T, 45 kHz, VWR). Fractions of the inks were pipetted onto the glassy carbon inset of the RRDE to obtain catalyst loadings of 30 and 15 $\mu\text{g}_{\text{Pt}}/\text{cm}^2_{\text{electrode}}$ for Pt-Ni aerogels and Pt/C, respectively. Subsequently, coatings were dried under a gentle N_2 -flux.

Results and Discussion

Bimetallic aerogels with various Pt:Ni atomic ratios were synthesized by the simple co-reduction process of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and H_2PtCl_6 with NaBH_4 in aqueous solution described in the Experimental section.

The composition of the Pt-Ni aerogels produced in this manner was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) and compared to the values expected on the basis of the initial precursor ratios. As Figure SI-1 shows, a decrease in the extent of reduction of the Ni-precursor is observed upon preparation of Pt-Ni aerogels with $x(\text{Ni})_{\text{ICP-OES}}$ -values above 25 at. %. Motivated by this result, two samples were selected for further characterization and analysis: one with a final Ni content ≤ 25 at. % (Pt_3Ni , $x(\text{Ni})_{\text{expected}} \approx x(\text{Ni})_{\text{ICP-OES}} \approx 25$ at. %) and one with >25 at. % Ni ($\text{Pt}_{1.5}\text{Ni}$, $x(\text{Ni})_{\text{expected}} \approx 50$ at. % vs. $x(\text{Ni})_{\text{ICP-OES}} \approx 40$ at. %).

Fig. 1 shows representative transmission electron microscopy (TEM) images of the Pt_3Ni and $\text{Pt}_{1.5}\text{Ni}$ aerogels that look similar to those obtained for aerogels with other Pt-Ni compositions (not shown here). In agreement with previous work,²⁰ the materials consist of a 3D structure of nanochains that are composed of interconnected/fused nanoparticles. The quality of the nanochain network is supported by the fact that no isolated nanoparticles can be observed. Additionally, nanochain diameters from TEM images based on measurement of the

Figure 1. TEM images of Pt_3Ni (A) and $\text{Pt}_{1.5}\text{Ni}$ (B) aerogel; the insets show the corresponding distributions of nanochain diameters and TEM images with lower magnification.

chain's width at different spots are on average ≈ 5 nm for both samples (cf. Table I).

To highlight the reproducibility of our synthesis, the good agreement between nanochain diameter distributions of different batches is illustrated in Fig. SI-2. Moreover, the surface areas of the aerogels were analyzed by N_2 -physisorption measurements (cf. Figure SI-3). Both materials exhibited a type II isotherm and a slight hysteresis indicating the presence of macropores and some mesopores.²⁵ Surface areas were estimated from Brunauer-Emmett-Teller (BET) plots to 55 $\text{m}^2/\text{g}_{\text{Pt}}$ and 58 $\text{m}^2/\text{g}_{\text{Pt}}$ for Pt_3Ni and $\text{Pt}_{1.5}\text{Ni}$, respectively (cf. Table I).

The samples were further characterized by X-ray diffraction (XRD) (see Fig. SI-4) in order to investigate alloy formation between Pt and Ni. The (111) reflections at 2θ -values of 40.73° (Pt_3Ni) and 41.04° ($\text{Pt}_{1.5}\text{Ni}$) present a shift with respect to pure Pt (39.83°).²⁶ These shifts to larger angles, also observed for the (220) reflections at $\approx 67.71^\circ$ (pure Pt), confirm alloy formation between Pt and Ni. The greater 2θ shift for $\text{Pt}_{1.5}\text{Ni}$ compared to Pt_3Ni indicates a larger Ni-concentration in the alloy phase of this aerogel. Analysis of the XRD spectra was concluded by calculating crystallite sizes on basis of the full width at half maximum of the (111) reflections (Scherrer equation); the resulting values tabulated in Table I coincide well with the average nanochain diameters derived from TEM images.

The crystallite sizes and nanochain diameters from XRD and TEM analyses were used to calculate surface areas assuming cylindrical nanowires and compared to the respective values derived from N_2 -physisorption and electrochemical measurements. The latter electrochemical surface areas (ECSAs) were determined by integration of the

Table I. Crystallite size, nanochain diameter and surface area values of the Pt₃Ni and Pt_{1.5}Ni aerogels, derived from XRD, TEM, N₂-physisorption, H_{upd} and CO stripping analysis.

Catalyst	Size [nm]		Surface area [m ² /g _{Pt}]				
	XRD	TEM	XRD _{calc} ¹	TEM _{calc} ¹	H _{upd} ²	CO strip. ³	N ₂ -physis.
Pt ₃ Ni	6.7 ± 1.3	5.6 ± 1.2	35 ± 7	41 ± 9	32 ± 2	30 ± 2	55
Pt _{1.5} Ni	6.0 ± 1.0	5.5 ± 1.1	46 ± 8	51 ± 10	30 ± 1	28 ± 1	58

¹Surface area values based on the assumption of nanowires with a cylindrical geometry of diameter equal to the one averaged from XRD or TEM measurements, along with alloy density values of 19.0 (Pt₃Ni) and 17.3 g/cm³ (Pt_{1.5}Ni).

²Extracted from the integration of H_{upd} desorption peaks (cf. Fig. SI-5) using the double layer current as an extended baseline and averaged on the basis of 3 independent measurements.

³Based on the integration of the charges for the CO oxidation peak using the subsequent CV as a baseline (cf. Fig. SI-5) and averaged on the basis of 3 independent measurements.

charges corresponding to the underpotential deposition of hydrogen (H_{upd}) on Pt²⁷ and the oxidation of a monolayer of carbon monoxide potentiostatically adsorbed on the Pt-surface (CO stripping)^{28,29} (see Fig. SI-5). As summarized in Table I, the ECSAs of both aerogels are similar (≈ 30 m²/g_{Pt}) and ≈ 20 –40% lower than the surface areas obtained from BET plots or estimated from the XRD- or TEM-derived diameters on the basis of a cylindrical geometry approximation. This difference most likely results from the interconnectivity between the nanowires that form the tridimensional network and from the lack of wettability of micropores in the nanostructures, which are accessible to the N₂-adsorbate used in the physisorption measurements.

To elucidate the aerogels' electronic and local structure, X-ray absorption spectroscopy (XAS) at the Ni K edge (8333 eV) was used to characterize the Pt₃Ni and Pt_{1.5}Ni aerogels, as well as a Ni(OH)₂ (β -phase) reference sample.³⁰ The X-ray absorption near edge structure (XANES) region within ± 30 eV of the absorption edge reveals significant differences among the Pt-Ni aerogels (see Fig. 2A). The position of the absorption edge of the Pt_{1.5}Ni aerogel is shifted to higher energy and the white line intensity is increased compared to that of the Pt₃Ni aerogel, suggesting a partial oxidation of Ni in the Pt_{1.5}Ni aerogel.³¹

Considering the resembling nanochain diameters of both materials and the 2-fold larger Ni-concentration of the Pt_{1.5}Ni sample, this difference in the Ni-oxidation states cannot be exclusively assigned to the Ni on the aerogels' surfaces (which would get oxidized upon contact with air). Alternatively, this discrepancy could be additionally related to the formation of Ni-(hydr)oxide sidephase(s) in the Pt_{1.5}Ni

aerogel, implying that only a fraction of the Ni is involved in the alloying with Pt. This hypothesis is further supported by the good agreement between the XANES recorded for the Pt_{1.5}Ni aerogel and the corresponding fit as a linear combination of the Pt₃Ni aerogel and Ni(OH)₂ spectra, displayed in Figure 2B. The best fit was obtained for relative weights of 75% and 25% for Pt₃Ni and Ni(OH)₂ respectively, confirming that a significant amount of the Ni in the Pt_{1.5}Ni aerogel is present in the form of a Ni-(hydr)oxide phase. Surface-sensitive X-ray photoelectron spectroscopy (XPS) in the Ni 2p_{3/2} region (cf. Fig. SI-6) also corroborates this observation. The sharp peak at ≈ 852.6 eV in the spectrum of Pt₃Ni is associated with Ni⁰,^{32–34} whereas the Pt_{1.5}Ni spectrum only contains a minor shoulder at the same energy, pointing at a larger content of Ni⁰ in Pt₃Ni when compared to Pt_{1.5}Ni. Moreover, this finding is in qualitative agreement with previous work by Park et al.,²⁶ who investigated carbon-supported Pt₃Ni and PtNi nanoparticles of 3–4 nm diameter prepared by an aqueous-based approach similar to the one used here.

Next, the local structure of both Pt-Ni aerogels was studied by additionally analyzing the extended X-ray absorption fine structure (EXAFS) spectra collected at both the Pt L₃ (11564 eV) and the Ni K (8333 eV) edge. The outcome of the simultaneous first shell fit of the Pt L₃ and Ni K EXAFS spectra of Pt₃Ni is summarized in Table II, and the Fourier transformed (FT) EXAFS spectra and corresponding fits are shown in Figure 3. The close agreement between the experimental data and the corresponding fits at the Pt L₃ and Ni K edge is discernable from Fig. 3 and confirmed by the low R-factor value.³⁵ Additionally, the properties of our Pt₃Ni aerogel and those reported

Figure 2. (A) X-ray absorption near edge structure at the Ni K edge (8333 eV) for the Pt₃Ni aerogel, the Pt_{1.5}Ni aerogel and a Ni(OH)₂ reference. (B) Fit of the Pt_{1.5}Ni aerogel spectrum as a linear combination of the Pt₃Ni aerogel and Ni(OH)₂ spectra.

Table II. Structural parameters derived from the fitting of the EXAFS (Pt L₃ and Ni K edges) of the Pt₃Ni aerogel. Values in brackets are extracted from Ref. 36 and were determined for a Pt₃Ni/C catalyst of similar particle size. Note that R-factor values below 0.02 are regarded as indicative of a good quality EXAFS fit.³⁵

Coord. shell	Coord. number	Bond length [Å]	σ^2 [10^{-3} Å ²]	R-factor
Pt-Pt	7.5 ± 1.0 (8.0)	2.71 ± 0.01 (2.71)	7 ± 1	0.01
Pt-Ni	2.5 ± 0.7 (2.0)	2.66 ± 0.03 (2.65)	13 ± 1	0.01
Ni-Pt	5.0 ± 1.2	2.66 ± 0.03	13 ± 1	0.01
Ni-Ni	2.8 ± 1.1	2.58 ± 0.03	12 ± 4	0.01

for a Pt₃Ni/C catalyst with a similar particle size in Ref. 36 are very comparable (cf. Table II), as one would expect from the similarities between the individual building blocks of both materials, i.e. Pt₃Ni nanoparticles.

Moreover, the Cowley's short range order parameter (α) which quantifies the homogeneity of bimetallic nanoparticles can be derived from the EXAFS analysis as follow,^{37,38}

$$\alpha = 1 - \frac{CN_{Pt-Ni} / (CN_{Pt-Pt} + CN_{Pt-Ni})}{x_{Ni}}$$

whereby CN_{Pt-Ni} and CN_{Pt-Pt} refer to the Pt-to-Ni and Pt-to-Pt coordination numbers, respectively, and x_{Ni} stands for the molar concentration of Ni in the alloy (i.e. 0.25). This calculation yields a value of 0.0 ± 0.3 that is indicative of a homogeneously random alloy.³⁷ Our attempt at fitting the first shell EXAFS of Pt_{1.5}Ni considering Pt-Pt, Pt-Ni, Ni-Pt and Ni-Ni scattering contributions was unsuccessful (not shown here), possibly due to the sample inhomogeneity caused

Figure 4. Ni K edge EXAFS Fourier transformation (k^3 -weighted) in R-space (uncorrected for phase shifts) for Pt₃Ni and Pt_{1.5}Ni aerogel.

by the presence of a Ni-(hydr)oxide sidephase inferred above. Again, this finding is endorsed upon comparison of the Ni K edge Fourier transformed EXAFS for both aerogels (see Fig. 4), in which Pt_{1.5}Ni displays a first coordination shell between 1.5–1.8 Å indicative of Ni-O scattering³¹ that is only minor for the Pt₃Ni aerogel.

In a final effort to verify the hypothesized presence of two separate phases in the Pt_{1.5}Ni aerogel, the surface compositions of the as prepared Pt₃Ni and Pt_{1.5}Ni aerogels were investigated electrochemically by cyclic voltammetry (CV). Since Ni is thermodynamically prone to dissolution in acid electrolyte,³⁹ the measurements were initially carried out in alkaline medium (0.1 M NaOH) to prevent its leaching from the alloy surface.²⁷ The presence of Pt and Ni on the catalyst surface is indicated by element specific features in the CVs, whereby the peaks between ≈ 0.05 –0.4 V vs. reversible hydrogen electrode (V_{RHE}) are associated to H_{upd} on polycrystalline Pt.⁴⁰ For Ni, the oxidation of Ni(OH)₂ to NiOOH at $\approx 1.4 V_{RHE}$ and its quasi-reversible, subsequent reduction in the negative going scan provides such a characteristic feature.⁴¹

According to the solid curves in Fig. 5 (CVs in alkaline electrolyte between 0.05 and 1.6 V_{RHE}), both aerogels exhibit Pt-related H_{upd} features, but only Pt_{1.5}Ni displays pronounced Ni(OH)₂ oxidation/NiOOH reduction peaks as well. Consequently, the Pt₃Ni surface contains but traces of Ni, as one would expect from the nominal composition (Pt:Ni = 3:1) and alloy homogeneity derived from the XAS-analysis, whereas Pt_{1.5}Ni contains a significant amount of surface Ni possibly in the form of a (hydr)oxide phase, further supporting the hypothesis that not all Ni is present as a Pt-Ni alloy phase.

To probe the stability of this surface Ni species in acid, the experiment was continued by immersing each electrode in a separated electrochemical cell filled with 0.1 M HClO₄ electrolyte, followed by the recording of 25 potential cycles between 0.05 and 1.0 V_{RHE} . Subsequently, CVs were again recorded in 0.1 M NaOH to identify possible changes in the surface. Interestingly, at this point both materials display very similar voltammetric profiles, with a complete absence of redox transitions at $\approx 1.4 V_{RHE}$ that indicates the complete dissolution of the Ni-(hydr)oxide sidephase upon conditioning in acid medium.

After this structural characterization, the ORR activity of both Pt-Ni aerogels in acid medium (0.1 M HClO₄) was determined using rotating disk electrode (RDE) voltammetry, whereby a commercial Pt/C catalyst (30% Pt/Vulcan XC-72) served as benchmark. The ECSA- and mass-specific ORR activities at 0.95 V_{RHE} are shown in Fig. 6. The average ECSA values from H_{upd} and CO stripping analysis summarized in Table I were used for normalization. The potential

Figure 3. EXAFS fit and experimental data (k^3 -weighted) in R-space (uncorrected for phase shifts) for Pt₃Ni aerogel at the Pt L₃ (A) and Ni K edge (B).

of 0.95 V_{RHE} was chosen instead of 0.9 V_{RHE} because the latter was too close to the diffusion-limited regime to allow for accurate correction of mass transport losses (cf. polarization curves in Figure SI-7).⁴² Moreover, mitigating such high currents by reducing the catalyst loading on the electrode was not possible, since minimal loadings of 30 $\mu\text{g}_{\text{Pt}}/\text{cm}^2_{\text{electrode}}$ were required for both aerogels to fully cover the glassy carbon disk.

As displayed in Fig. 6A, both aerogels show a ≈ 3 -fold increase of the ECSA-specific activity vs. Pt/C that can be partially assigned to their larger particle size (cf. average aerogel diameters of 5.5 nm listed in Table I, vs. the 3.4 nm of the 30% Pt/C benchmark estimated in Ref. 43). However, the limited sensitivity of the ORR-kinetics to the Pt particle size within the corresponding range of ECSA-values ($\approx 50 \text{ m}^2/\text{g}_{\text{Pt}}$ vs. $\approx 30 \text{ m}^2/\text{g}_{\text{Pt}}$ for the PtNi-aerogels, see Fig. 6A) implies that the aerogels' larger size can only account for an activity increase of $\approx 20\%$.^{4,27} Thus, the great majority of the observed ≈ 3 -fold activity enhancement can be explained by a down shift of the d-band center through alloying with Ni.⁴⁴ According to literature, this shift decreases the fractional coverage of spectator species at a given potential and increases the number of free sites for O_2 adsorption and subsequent ORR activity.⁴⁵

Upon conversion of these figures into mass-specific ORR activities (Fig. 6B), Pt₃Ni and Pt_{1.5}Ni reach the DOE ORR activity target at 0.95 V_{RHE} that was extrapolated from the reported value²¹ of 440 $\text{A}/\text{g}_{\text{Pt}}$ at 0.9 V_{RHE} assuming a Tafel slope of 60 mV dec^{-1} consistent with our measurements (cf. Fig. SI-7).⁴⁶ Following the same approach, the ORR activity values at 0.95 V_{RHE} for both Pt-Ni aerogels ($\approx 62 \pm 5 \text{ A}/\text{g}_{\text{Pt}}$) can be extrapolated to $\approx 422 \pm 34 \text{ A}/\text{g}_{\text{Pt}}$ at 0.9 V_{RHE} , in good agreement with recent reports on de-alloyed Pt-Ni/C catalysts based on RDE⁴⁷ and fuel cell⁴⁸ tests. The almost identical ECSA and ORR activity values for the two aerogels agree with the above conclusion that their surface compositions become much alike after a few conditioning cycles in 0.1 M HClO_4 (see Fig. 5), in which surface-Ni and $\text{Ni}(\text{OH})_2$ sidephases dissolve into the acid electrolyte.

Figure 6. Pt-ECSA (A) and mass-specific (B) ORR activity values at 0.95 V_{RHE} for Pt-Ni aerogels and Pt/C (averaged from 3 independent measurements). The dotted line represents the DOE ORR activity target at 0.95 V_{RHE} , extrapolated from the benchmark value of 440 $\text{A}/\text{g}_{\text{Pt}}$ at 0.9 V_{RHE} ²¹ assuming a Tafel slope of 60 mV dec^{-1} .⁴⁶ Activity values were extracted from anodic polarization curves in O_2 -saturated 0.1 M HClO_4 electrolyte (5 mV s^{-1}), corrected for IR-drop and mass transport losses (Koutecky-Levich equation). Reported ECSA values are averaged from results for H_{upd} and CO stripping analysis (cf. Table I).

Conclusions

In summary, we have presented a new facile synthesis for the preparation of Pt-Ni bimetallic aerogels. Extensive sample characterization suggested complete alloy formation in the case of Pt₃Ni, along with limited alloying upon targeting larger Ni-contents using this synthetic approach. Electrochemical measurements of the aerogels' catalytic activity toward oxygen reduction revealed a 3-fold ECSA-specific activity increase when compared to commercial Pt/C catalysts that is in agreement with reports in the literature. Additionally, the mass-specific ORR activity of the Pt-Ni aerogels is comparable to that of state-of-the-art, de-alloyed Pt-Ni/C materials, and meets the DOE-target value for automotive FC application. Future work will therefore focus on investigating the stability of these Pt-Ni aerogels under PEFC-relevant working conditions and comparing their behavior to that of commercial Pt/C catalysts, as to verify the stability enhancement expected from the absence of a carbon support in these novel materials.⁴⁹

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Figure 5. Cyclic voltammograms (CVs) in N_2 -saturated 0.1 M NaOH electrolyte at 50 mV s^{-1} of Pt₃Ni (A) and Pt_{1.5}Ni (B) aerogel. CVs before (solid) and after (dotted) 25 conditioning cycles in 0.1 M HClO_4 electrolyte between 0.05 and 1.0 V_{RHE} are shown.

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