Mesoporous platinum nickel thin films with double gyroid morphology for the oxygen reduction reaction

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KEYWORDS: Fuel cell, Platinum, Nickel, Mesoporous, Double gyroid, Oxygen reduction.

Abstract

Improving both the activity and stability of the cathode catalyst in platinum-based polymer electrolyte fuel cells is a key technical challenge for next-generation sustainable-energy conversion technologies. Here, we synthesize a high surface area supported meso-structured Pt_xNi alloy thin film with a double gyroid morphology that both exhibits high activity and stability for the oxygen reduction reaction.

1. Introduction

Electrocatalysis is widely believed to play a key role in next-generation technologies for sustainable-energy conversion. In particular, the oxygen reduction reaction (ORR: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) is crucial for several energy conversion and storage technologies, such as fuel cells[1, 2] and metal–air batteries[3, 4]. A major technical challenge for these electrochemical systems is the sluggish kinetics of the ORR. Currently, dispersed Pt nanoparticles (NPs) on amorphous high-surface-area carbon supports are typically used for this reaction, see e.g. Sun's paper in this Electrocatalysis Special Issue. However for large-scale deployment of these renewable energy technologies, a substantial improvement in catalyst activity and stability is needed, due to the high cost and limited resource of Pt.[5, 6] Alloying Pt with transition metals (Ni, Co, Fe, Cu, Sc, Y etc.) has been shown to be an effective route to increase the activity relative to that of pure Pt.[6-9] The enhancement is caused by changes in the electronic structure of the surface Pt atoms induced by the neighboring transition metal atoms which leads to an improved interaction strength with oxygenated ORR intermediates.[8-10] In particular Pt_xNi alloys have been intensely studied. However, whereas the activity can be greatly enhanced over that of pure Pt, it is often on the expense of the durability of the catalyst. Leaching of Ni in the corrosive ORR environment can lead to rapid performance losses from e.g. collapse of nanostructured catalysts.[11, 12] Hence, developing Pt alloy ORR catalysts with both high catalytic activity and stability remains an important challenge.

Several strategies have been employed to control the structure, size, shape and composition of catalytically active materials, see e.g. Stamenkovic's paper in this Electrocatalysis Special Issue. In this work we aim at controlling the nanostructure of a Pt_xNi alloy ORR catalyst by directing the structure into an ordered mesoporous thin film. We have previously shown that a supported

mesoporous platinum thin film exhibit improved stability over platinum nanoparticles.[13] A mesoporous ORR catalyst could potentially show several advantages over nanoparticle based systems. A mesoporous thin film is one contiguous material that is effectively pre-sintered which minimizes losses of electrochemical surface area, ECSA, due to agglomeration. Furthermore, it is anchored to the integrated structure at numerous interfacial sites (orders of magnitude more sites than those of a supported nanoparticle) and as such active sites will likely retain electrical contact with the integrated structure due to the interconnected contiguous nature of the film itself, even if some corrosion occurs. In fact, as a mesoporous thin film has inherently high surface area, such films eliminate the need for high surface area carbon supports which can themselves degrade quickly under certain operating conditions.[14] Omitting the high surface area carbon support from the catalyst layer may further reduce the thickness of the catalyst layer and reduce the interfacial resistance in a practical device since only the catalyst layer, only mesoporous Pt or Pt-alloy, would be in direct contact with the gas diffusion layer (GDL).[15]

Similar to our previous study of mesostructured Pt films, for Pt_xNi we chose to pursue an extended three dimensional mesoporous network structure with a double gyroid (DG) morphology, illustrated in Figure 1. This particular mesostructure exhibits a diffusivity that is higher by an order of magnitude compared to other mesoporous structures.[16, 17] This will presumably allow facile transport of reactants (O_2 and H^+) and products (H_2O) through the structure.

We successfully synthesized a DG Pt_xNi structure, which to our knowledge is the first ever reported fully contiguous large area supported thin film of a highly ordered mesoporous metal alloy.[18, 19] Our studies of ORR catalysis on these thin films show that the DG meso-structure remains intact and maintains good activity even after intensive accelerated stability testing,

which shows the promise of controlling the morphology of Pt-based ORR catalyst materials in the form of mesoporous thin films.

2. Experimental section

The DG Pt_xNi alloy structure was synthesized by co-electrodeposition of Pt and Ni into a mesoporous silica film that served as a template on top of a glassy carbon (GC) disk (see Figure 1 and Supplementary material). Before electrodeposition of the metals, the silica templates were examined by small angle XRD to ensure that they exhibited the DG structure (see Figure S1, Supporting material). The silica films are highly oriented with their (211) planes parallel to the substrate as indicated by the main peak located at $2\theta = 2.0^\circ$. The three smaller peaks at lower 2θ with increasing 2θ values from the $(12\bar{1})$, $(2\bar{1}1)$ and (121) planes, constitute an important fingerprint pattern used to distinguish the DG structure from hexagonal or lamellar phases.[20] Pt and Ni were electrodeposited at different potentials into the DG silica template using a standard three electrode electrochemical setup (see Figure 1 and Supplementary material). Lastly, the silica template was removed by etching with hydrofluoric acid leaving a supported thin film of a bicontinuous inverse double gyroid Pt_xNi alloy.

3. Results and discussion

3.1. Structure and morphology of DG Pt_xNi

Small angle XRD spectra of a mesoporous DG Pt_xNi thin film after the etch procedure is shown in Figure S1. The electrodeposited Pt_xNi alloy fills the 3D bicontinuous network pore structure of the silica DG template, and thus represents the negative of the silica morphology. Accordingly, the peak pattern matches that of the template confirming the DG nature of the Pt_xNi

alloy in accordance with Babinet's principle.[21] The intensity of the diffraction peaks of the DG Pt_xNi alloy is lower relative to those from the silica template since the electrodeposited alloy films underfilled the silica template.

The thin film nature of the mesoporous double gyroid Pt_xNi was further investigated by SEM. Figure S2 shows SEM images of the mesoporous Pt_xNi DG structures deposited at different voltages. The DG Pt_xNi structure is stable after removal of the silica and maintains the interlocked, twisted network structure, as evidenced in the SEM images. As nickel is not stable in hydrofluoric acid solutions, we expect that the DG Pt_xNi structure is Pt terminated after the HF etch, see also the review by Strasser and Köhl on dealloyed Pt-based core-shell structures in this Electrocatalysis Special Issue. We further observed that the more nickel rich alloys deposited at more cathodic potentials show slightly less order, possibly due to a greater extent of Ni leaching during the etch procedure leading to some degree of structural collapse.

The TEM image in Figure 2a shows a higher magnification image of the Pt_xNi DG mesoporous structure and illustrates the high porosity and ordered structure of these thin films. The average pore-to-pore distance is ~7 nm and the pore width is 3-4 nm. The elongated hexagonal pattern as indicated by the dashed box is indicative of the [311] projection, as shown in Figure 2b which shows a simulated TEM image (top) and model (bottom) of the [311] projection. To confirm uniform dispersion of Pt and Ni in the alloyed DG Pt_xNi structure, we further used energy-dispersive spectroscopy (EDS) to identify the elements present in the DG structure. Figures 2d-f show elemental maps taken in scanning TEM (STEM) mode of the region indicated in the TEM image in Figure 2c. The Ni signal is shown in red (Figure 2d) and the Pt signal in blue (Figure 2e). A composite of the two images is shown in Figure 2f where the red and blue signals combine to form magenta pixels in the RGB color spectrum. From the combined

image it is clear that both Pt and Ni are distributed throughout the DG structure. We furthermore performed high angle XRD in both symmetric and grazing incidence mode on the DG Pt_xNi (deposited at -0.3 V vs Ag|AgCl), see Figure S4. The two main peaks corresponding to the (111) and (200) peaks are significantly shifted relative to those of pure Pt and pure Ni indicating an alloy phase. Using Vegard's law [22] on the (111) peak from the GIXRD gives Ni to Pt ratio of Ni/Pt = 21 %. The chemical nature of the DG Pt_xNi samples was further investigated by X-ray photoelectron spectroscopy (XPS). Figure S5 shows that we deposit both Pt and Ni at all deposition potentials (-0.3 V, -0.4 V and -0.5 V vs Ag|AgCl). Deconvolution of the Pt 4f region and the Ni 2p region by peak fitting revealed a predominant doublet in both regions at positions indicative of Pt and Ni in a metallic state (Pt 4f: 71.5, 74.5 eV and Ni 2p: 853.5, 869.7 eV). The magnitude to the Ni 2p doublet increases with more cathodic deposition potentials. By XPS the atomic Ni to Pt ratio of the DG Pt_xNi alloy was determined to be: Ni/Pt = 15 %, 22 % and 24 % for deposition potentials of -0.3 V, -0.4 V and -0.5 V vs Ag|AgCl, respectively. Likely XPS underestimates the bulk ratio due to the Pt surface terminated DG structure. For instance, by inductively coupled plasma mass spectrometry (ICP-MS) we find the total Ni to Pt ratio to be Ni/Pt = 21 % for samples deposited at -0.3V vs Ag|AgCl, in good agreement with the ratio found from XRD.

3.2. ORR activity of DG Pt_xNi

Catalytic activity for the ORR of the as-prepared DG Pt_xNi was evaluated in a rotating disk electrode configuration (RDE) using 0.1 M HClO₄ (aq) electrolyte and a homebuilt RHE reference electrode. Initial ORR experiments showed that the more Ni-rich DG Pt_xNi thin films deposited at -0.4 V and -0.5 V vs Ag|AgCl showed higher activity initially (see Figure S6) but exhibited poor stability. This instability is likely due to leaching of nickel from the alloy (see

XPS before and after ORR in Figure S5) which can lead to a considerable structural degradation of the DG structure even after just several hundred cycles (see SEM images in Figure S2). Hence throughout the rest of this paper we will focus on the DG Pt_xNi thin films deposited at -0.3 V vs Ag|AgCl, that showed no visible sign of degradation or activity loss. In fact, these thin films even showed slightly improved activity after cycling (see Figure S6).

Cyclic voltammetry in N₂-purged 0.1 M HClO₄ (aq) electrolyte showed typical Pt characteristics and served to evaluate the electrochemical surface area (ECSA). Assessing the ECSA by both hydrogen underpotential deposition (HUPD) and CO stripping has been well-established for pure Pt catalysts, methods that have also been extended to Pt alloys.[23, 24] The use of HUPD has in some cases been observed to underestimate the ECSA, but the limitations of HUPD depends on the detailed nature of the Pt alloy and the testing protocol.[24] To validate the use of HUPD for the DG Pt_xNi, we compared with CO stripping experiments and confirmed that the two methods gave consistent ECSA values, see Figure S7 in supplementary materials. The heat-treated GC introduces a large background most noticeable by the broad features between +0.4 to +0.8V vs RHE. To correct for this carbon background we scaled a cyclic voltammogram (CV) of a blank heat-treated GC disk to the CV of the DG Pt_xNi in the region around +0.45 V vs RHE. This scaled CV, shown in shaded gray in Figure 3a, was subtracted from the CV of the DG Pt_xNi in order to estimate the ECSA was estimated by means of charge passed in the hydrogen adsorption/desorption region (between 0.05 and 0.4 V, the red-shaded region in Figure 3a) and assuming a value of 210 $\mu\text{C cm}^{-2}$ for the adsorption of a hydrogen monolayer.[2, 25] The ECSA was determined to be: $43 \pm 2 \text{ m}^2 \text{ g}_{\text{Pt}}$, which is on par with Pt nanoparticles supported onto high surface area carbon ($\sim 30\text{-}90 \text{ m}^2 \text{ g}_{\text{Pt}}$).[2]

The ORR polarization curves in the anodic direction for a DG Pt_xNi sample (Pt loading: 31 µg cm⁻²) and a DG Pt sample (Pt loading: 40 µg cm⁻²) for comparison are shown in Figure 3b. The polarization curves have two distinguishable potential regions: a diffusion limited region below 0.7 V and a mixed kinetic/diffusion control region between 0.7 and 1.1 V. Both DG Pt_xNi and DG Pt reach the expected mass transport-limited current density,[2] and despite having a lower Pt loading we observe an earlier onset and a more positive half-wave potential for the DG Pt_xNi sample indicating higher ORR activity as compared to DG Pt. However, both onset and half-wave potentials are generally sensitive to parameters such as the loading and surface area of the catalyst and a more accurate quantitative comparison of the catalysts is needed beyond that which can be ascertained directly from the linear sweep voltammograms. To facilitate a direct comparison of the catalysts, we extract the kinetic current density using the following equation:

$$\frac{1}{i} = \frac{1}{j_k A_{real}} + \frac{1}{j_d A_{geo}}$$

where A_{real} is the catalytically active surface area (unit: cm²_{Pt}) approximated by ECSA found from hydrogen underpotential deposition (HUPD) on the DG Pt_xNi and DG Pt samples, A_{geo} is the projected geometric area of the electrode (0.2 cm²) and j_k and j_d are the kinetic and diffusion-limited current densities, respectively. The kinetic current densities for both specific activity and for mass activity are displayed as Tafel plots in Figure 3c and 3d, respectively. For comparison we added a state-of-the-art commercial platinum catalyst (Pt/C from TKK, Pt: 14 µg cm⁻²). The mass loadings were determined by dissolving the sample in aqua regia and using an ICP-MS to measure the Pt and Ni concentration. The intrinsic kinetic current density at 0.9 V vs. RHE is a standard metric for evaluating the specific activities of ORR catalysts. More recently, 0.95 V has also been used as a basis for comparison, due to more active catalysts where the close proximity

of current values measured at 0.9 V to the diffusion limited current can result in larger errors.[26] The specific and mass activities of the DG Pt_xNi, DG Pt and Pt/C at both 0.90 and 0.95 V vs. RHE are displayed in Figure 3e. The mass activities are displayed as Tafel plots in Figure 3d and the values at both 0.90 and 0.95 V vs RHE are shown in Figure 3e; by both metrics the DG Pt_xNi outperforms the pure DG Pt and Pt/C.

3.3. Stability of DG Pt_xNi

Stability is a critical concern for ORR catalysts. To investigate the electrochemical durability of the DG Pt_xNi and DG Pt catalysts we performed accelerated stability test by cycling the potential between 0.6 and 1.0 V vs RHE in O₂-saturated 0.1 M HClO₄ (aq) at a scan rate of 50 mV s⁻¹. The potential cycling causes alternating surface oxidation/reduction of the catalyst which is particularly vigorous due to the dynamic nature of the surface changes.[27, 28] The catalytic ORR activity and the ECSA of DG Pt_xNi catalyst were evaluated initially and immediately following 100, 1,000 and 10,000 accelerated stability test cycles, using the conditions described above. Before every ORR activity and ECSA measurement, the solution was replaced with fresh electrolyte and the sample was cleaned by electrochemical cycling in N₂-saturated electrolyte from 0.05 to 1.1 V vs RHE at 500 mV/s and 0 rpm to condition the electrode until stable CVs were obtained (typically 20-100 cycles).

The cyclic voltammograms displaying the hydrogen underpotential deposition (HUPD) region are shown in Figure S8a for the DG Pt_xNi and the DG Pt, respectively. The ECSA was determined by the method described above. Even after 10,000 stability cycles both DG Pt and DG Pt_xNi maintain a high ECSA with 75% and 82% of the initial values, respectively (Figure S8b). The excellent stability of the Pt-based double gyroid systems is further highlighted by a

nearly unchanged specific activity for both the DG Pt_xNi and the DG Pt as shown in Figure 3f. Overall the minimal changes in ECSA and specific activity lead to negligible changes in the ORR activities upon accelerated stability cycling as measured by linear sweeps, Figure S8c.

To further evaluate the physical condition of the DG Pt_xNi and DG Pt after the accelerated stability tests, we performed SEM and TEM imaging. Figure S9 shows SEM images of the DG Pt_xNi and DG Pt sample after 10,000 cycles with no significant degradation in both cases. Similarly, Figure S10 shows TEM images of the DG Pt_xNi after 10,000 cycles where the double gyroid structure is still clearly visible. We suggest the origin of the excellent stability is the mesostructured nature of the DG Pt-based catalysts which inhibits the activity losses associated with the higher fraction of low-coordinated surface atoms present in e.g. nanoparticulate-based catalysts. [13, 29] Overall, the DG meso-structure remains intact and maintains good activity even after intensive accelerated stability testing which shows the promise of controlling the morphology of Pt-based ORR catalyst materials in the form of mesoporous thin films.

4. Conclusion

In summary, we have directed the morphology of a Pt_xNi alloy to develop an oxygen reduction reaction catalyst with high specific and mass activity and excellent stability. To our knowledge the DG Pt_xNi represents the first ever reported contiguous large area supported thin film of a highly ordered mesoporous metal alloy. Our studies of ORR catalysis on these thin films show that the DG meso-structure remains intact and maintains high activity even after intensive accelerated stability testing demonstrating the potential of directing the morphology of Pt-based ORR catalyst materials in the form of mesoporous thin films.

Future work could involve doping the DG Pt_xNi with small amounts of other transition metals, e.g. molybdenum.[11] Furthermore expanding to DG films of platinum lanthanide intermetallics would also be interesting given the high performance of these materials for the ORR in polycrystalline and nanoparticle form.[30, 31] A core-shell DG structure would be another interesting structure to pursue; e.g. that based on core-shell Ru@Pt.[32, 33] Similar to the previously investigated Ru@Pt nanoparticles, the binding energies of oxygen reaction intermediates could be tuned on a core-shell DG structure by taking advantage of two opposing effects: strengthening of oxygen binding energies through nano-scale effects and weakening of oxygen binding energies due to thin-film overlayer, in order to achieve optimal surface properties.[33]

Finally, we note that the concept of using meso-structured double gyroid alloy materials as active and durable catalysts is not limited to the ORR. There are a number of other electrochemical reactions where sintering, dissolution or detachment of the electrocatalyst is problematic. The contiguous nature of a DG mesoporous thin film helps to ensure that active sites will likely retain electrical contact with the support due to the extensive network of connections within the film itself, even if some corrosion occurs. The morphological control of a catalyst, as shown in this work, can be of general use in developing improved catalyst materials for a variety of reactions.

FIGURES:

Figure 1. Synthesis procedure and structural model for mesoporous double gyroid (DG) platinum nickel alloy. The SEM image shows the interlocked, twisted network structure of a DG Pt_xNi deposited at -0.3V vs Ag|AgCl.

Figure 2. (a), TEM image of the DG Pt_xNi structure (deposited at -0.3 V vs Ag|AgCl). The elongated hexagonal pattern as indicated by the dashed box is indicative of the [311] projection, as shown in (b) which shows a simulated TEM image (top) and structural model (bottom) of the [311] projection. (c), The elements present in DG structure were probed by energy-dispersive spectroscopy (EDS) within the dashed box. (d)-(f), Elemental maps taken in scanning TEM (STEM) mode show that both Pt and Ni are distributed throughout the DG structure.

Figure 3. (a), Base cyclic voltammograms (CV) of DG Pt_xNi (Pt: 31 μg cm⁻² and 13.8 cm² cm²_{Pt}/cm²_{geo}). Conditions: N₂-purged 0.1 M HClO₄ (aq), 23 °C, sweep rate 20 mV/s, 1600 rpm. (b), ORR polarization curves for DG Pt_xNi and DG Pt. The insert shows a zoom-in of the mixed kinetic/diffusion control region. Conditions: O₂-saturated 0.1 M HClO₄ (aq), 23 °C, sweep rate 20 mV/s, 1600 rpm. (c), Tafel plot of the kinetic current density from O₂ reduction for the DG Pt_xNi and DG Pt samples from (b). (d), Mass activity of the DG Pt_xNi and DG Pt samples from (b). A

state-of-the-art commercial platinum catalyst (Pt/C from TKK, Pt: 14 μg cm⁻²) has been added to (c) and (d) for comparison. (e) Specific and mass activities of the DG Pt_xNi and DG Pt samples measured at 0.90 and 0.95 V vs RHE. (f), Initial and post potential cycling Tafel plot of the

kinetic current densities of DG Pt_xNi (Pt: 17 $\mu\text{g cm}^{-2}$ and 6.5 $\text{cm}_{\text{Pt}}^2/\text{cm}_{\text{geo}}^2$) and DG Pt (Pt: 40 $\mu\text{g cm}^{-2}$ and 15.9 $\text{cm}_{\text{Pt}}^2/\text{cm}_{\text{geo}}^2$).

Acknowledgments

J.K., A.J. and T.F.J. acknowledge support from the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. DE-SC0008685. J.K and T.F.J. acknowledge financial support from the U.S. Department of Energy (DOE), Office of Basic Energy Sciences to the SUNCAT Center for Interface Science and Catalysis. The authors would like to thank Dr. Yelena Gorlin for helpful discussions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at

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