Enhancement of the Oxygen Reduction on Nitride Stabilized Pt-M (M = Fe, Co, and Ni) Core-Shell Nanoparticle Electrocatalysts

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Abstract

Given the harsh operating conditions in hydrogen/oxygen fuel cells, the stability of catalysts is one of the critical questions affecting their commercialization. We describe a distinct class of oxygen reduction (ORR) core-shell electrocatalysts comprised of nitride metal cores enclosed by thin Pt shells that is easily synthesized. The synthesis is reproducible and amenable to scale up. Our theoretical analysis and the experimental data indicate that metal nitride nanoparticle cores could significantly enhance the ORR activity as well as the durability of the core-shell catalysts as a consequence of combined geometrical, electronic and segregation effects on the Pt shells. In addition to its fuel cells application, this class of catalysts holds promise to significantly contribute in resolving the problem of platinum scarcity and furthermore indicates the guidelines for future research and development.

Key words: Core-shell nanoparticle, Nitride, Oxygen reduction, Electrocatalysis, Fuel cell, DFT.

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Graphical Abstract

Introduction

The slow kinetics of the oxygen reduction reaction (ORR) is one of the main obstacles hindering the commercialization of proton exchange membrane fuel cells (PEMFCs) [1-3]. Platinum is by far the most effective elemental catalyst for the ORR. However, besides high price, it has several drawbacks including insufficient activity and instability due to Pt dissolution and agglomeration during harsh operating conditions [4-6]. Thus, the existing fuel cell technology requires relatively high platinum content at the cathode that increases the cost seriously, and the development of more efficient electrocatalysts with lower cost is crucial for commercial use of PEMFCs.

Several efforts have been made to alleviate these problems; one particularly attractive approach is to design and synthesize core-shell structured catalysts comprising layers of Pt on various nanoparticle cores. The core-shell structure can be obtained by several methods, including (i) Pt monolayer catalysts synthesized by galvanic replacement of an underpotentially deposited metal on a substrate surface by Pt,[7] [8] and (ii) Pt “skin” catalysts, in which a layer of Pt is formed by surface segregation of Pt during thermal annealing[9, 10], or by de-alloying through etching of a less noble metal from Pt bimetallic alloys [11, 12].

It has been known that Pt alloys (mostly with transition metals as Co, Ni, and Fe) are more active for ORR than pure Pt [13-16]. However, the Pt loading in these alloys is still high and moreover the non-noble metals in these alloys are etched easily in the acid environment of the PEMFC. Therefore, it is necessary to design catalysts that have higher ORR activity, lower Pt loading, and better stability.

Recently, we have reported a new route to the development of PtNiN core-shell catalysts consisting of inexpensive Ni nitride cores covered with very thin Pt shells;[17] despite substantial reduction in Pt loading the catalysts retained high ORR activity and stability. The nitride core improves the performance of the Pt shell by inducing both the geometric and electronic effects. The synthesis procedure is facile and applicable to large-scale synthesis. Here, we focus on the performance of various nitride-stabilized Pt-metal electrocatalysts (PtMN) and draw a relationship between various nitrides lattice parameters and their effect on binding energy of oxygen using DFT calculations.

Experimental

Material synthesis

The carbon-supported PtFe core-shell nanoparticles were prepared by using K_2PtCl_4 (51.9 mg) and $\text{FeCl}_6 \cdot 6\text{H}_2\text{O}$ (115.4 mg) salts with a 1:3 molar ratio mixed with high-area Vulcan XC72R carbon black (105.8 mg) to obtain a loading of 30 wt.% total metal. The mixture was dissolved in Millipore water and purged with Ar in an ultrasonic bath for an hour. The salts were then reduced by adding NaBH_4 while simultaneously purging the mixture with Ar. The mixture obtained was washed and rinsed with Millipore water, and then dried. The dried powder was annealed at 510 °C under NH_3 gas for 2 hours in a tube furnace and then cooled down to room temperature under NH_3 flow. The sample was then washed in 0.1 M H_2SO_4 to dissolve Fe precipitates on the carbon support surface, and rinsed and dried again. The carbon-supported PtCo core-shell nanoparticles were prepared in the same manner except for using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt. Both the mean mole ratios of Pt to Fe ($x_{\text{Pt}}/x_{\text{Fe}}$) and Pt to Co ($x_{\text{Pt}}/x_{\text{Co}}$) was determined to be 1.

Characterizations

Hitachi aberration-corrected scanning transmission electron microscope (HD-2700C) at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory (BNL) equipped with a cold field emission electron source and a high resolution Gatan Enfina energy-loss spectrometer was used for this study. We performed STEM imaging and EELS using a 1.3 Å electron probe with a probe current ~50 pA. The STEM convergence angle is around 28 mrad while the collection angle is from 114 to 608 mrad. In this experimental condition, the contrast of images directly related with atomic number (Z-contrast). The energy resolution for EELS is about 0.4 eV estimated from the half-width of zero loss peaks. The carbon-supported nanoparticles were dispersed in water and then deposited on a lacy-carbon TEM grid (EMS, Hatfield, PA).

XRD experiments were performed at Beamline X18A at the National Synchrotron Light Source (NSLS) at BNL. The XRD spectra were recorded using a 2D detector (Perkin Elmer XRD 1621 N ES) at 12.4 keV and subsequently processed using standard data processing software. The dark current and the diffraction pattern were collected over 40 seconds (10 exposures at 4 s per exposure) and the diffraction pattern was recorded over 400 seconds (100 exposures at 4 s per exposure). The wavelength of X-ray used was 1.000 Å.

Electrochemical Measurement

For both PtFeN/C and PtCoN/C catalysts, an aqueous dispersion (1 mg/mL) was prepared and sonicated for 5 min. A thin film of the electrocatalyst was prepared on a glassy carbon rotating disk electrode (area: 0.196 cm²) for electrochemical measurements using the dispersion.

The electrode was then covered by a small amount of a Nafion solution (5 μL of 4 $\mu\text{g}/10 \mu\text{L}$) and dried in air before rotating disk electrode measurements. Solutions were prepared from Optima perchloric acid obtained from Fisher and MilliQ UV-plus water (Millipore). Commercial Pt/C (10 wt. % of 3.2 nm Pt nanoparticles on Vulcan XC-72 carbon support) from E-TEK was used for comparison.

Cyclic Voltammetry (CV) characterization of the catalysts in the absence of oxygen was typically carried out in the potential range from 0.0 to 1.1 V at a sweep rate of 20 mV/s in Ar-saturated 0.1 M HClO_4 electrolyte. ORR polarization curves using rotating disk electrode (RDE) were recorded in O_2 -saturated electrolyte at various rotation rates from 225 to 2500 rpm at a sweep rate of 10 mV/s. Stability tests for the catalyst were conducted in air saturated 0.1 M HClO_4 in the potential range from 0.6 to 1.05 V at a sweep rate of 50 mV/s at room temperature. An Ag/AgCl/KCl(3M) electrode was used with a double-junction chamber as a reference and all potentials, E , are quoted with respect to reversible hydrogen electrode (RHE).

DFT calculations

Plane-wave-based density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP) code [18, 19]. Similar to the previous studies,[20-22] the projector augmented wave method (PAW)[23] with the generalized gradient approximation (GGA) using the revised Perdew-Burke-Ernzerhof (RPBE) functional [24] was applied. The bulk calculations of Pt and M_4N ($\text{M} = \text{Fe}$ or Co) were performed with a $(3 \times 3 \times 3)$ Monkhorst-Pack k-point grid. The space group of cubic M_4N is Pm-3m. All of calculations were carried out with the spin-polarized method with a 400 eV plane-wave cut off. The Γ point for $\mathbf{k}$ sampling was used for nanoparticle calculations. All atoms were fully relaxed without constraint.

The ORR activity of the electrocatalysts was approximated by means of the binding energy of atomic oxygen (BEO) on the (111) plane of a nanoparticle [22]. The binding energy is defined as $BEO = E[O-NP] - E[NP] - E[O]$, where $E[O-NP]$, $E[NP]$, and $E[O]$, respectively, are the calculated electronic energies of an adsorbed oxygen atom on a nanoparticle, a clean nanoparticle, and a triplet oxygen atom. Furthermore, a geometric effect was examined by computing surface strains of Pt atoms linked an oxygen atom according to $(a - a_0)/a_0$. a and a_0 are an averaged Pt-Pt distance and the calculated Pt-Pt distance of bulk Pt (2.82 Å), respectively. For the nanoparticle calculations, the core-shell nanoparticles ($Pt_{ML}M_4N$; Pt is a shell and M_4N is a core) consisting of 182 Pt, 19 M, and 4 N atoms ($N/M = 0.21$; two Pt monolayers) or 122 Pt, 79 M, and 20 N atoms ($N/M = 0.25$; one Pt monolayer), a sphere-like nanoparticle model with ~1.7 nm were prepared.

Results and discussion

Morphology and structure

STEM-EELS observations were made on several PtFeN and PtCoN nanoparticles. Fig. 1 shows (A) a high angle annular dark field (HAADF) image of a single PtFeN nanoparticle and (C) comparison of the EELS intensities from the Pt M-edge (2122 eV) and Fe L-edge (708 eV) obtained by moving the electron probe along the line indicated in Fig. 1(A) (we note the arbitrary scales of the Y axes). It is evident from the EELS line profile that Pt is enriched (Fe is depleted) at both edges of the nanoparticle while few Pt atoms along with enriched Fe atoms are coexisting around the center of nanoparticle. The measured thickness of the Pt shells on various nanoparticles is around 0.5 to 1 nm, which corresponds to approximately 2 to 4 monolayers of Pt. A two-dimensional image overlapping Fe EELS signals (blue) on Pt signals (red) from the

same nanoparticle (Fig. 1(B)) also clearly demonstrates the formation of core-shell structure with Pt shell on PtFe core. Fig. S1 (ESI†) exhibits an EELS spectrum of the nitrogen K edge from a single PtFeN nanoparticle, illustrating the incorporation of nitrogen in the nanoparticles. We consider that segregation of Pt on the surfaces takes place while Fe nitride cores are formed during thermal annealing in NH_3 as the nitrogen precursor.

A low-resolution STEM image of the PtFeN/C catalyst is depicted in Fig. S2 (ESI†). Most particles have round, sphere-like shapes, although some are slightly semi-rounded. The average particle size is 4.2 nm, which is fairly in line with the value determined by the XRD experiments. STEM-EELS observations on the PtCoN/C samples (Fig. S3, ESI†) also showed a core-shell structure consisting of Pt-rich top layers on the surfaces of Co nitride cores.

Synchrotron XRD patterns of the PtFeN/C and PtCoN/C catalysts are shown in Fig. 2. Three major peaks are shown on the XRD pattern from PtFeN/C; these peaks are located at slightly higher positions than those of Pt (dashed lines in the figure), indicating that there is slight contraction in the Pt-Pt bonds that are caused by the formation of Fe_4N . The average particle diameter was calculated to be 4.3 nm. No individual peaks for α -Fe (bcc) (JCPDS PDF 06-0696) are observed. A small peak as indicated by blue-solid triangle (26.92°) suggests the presence of iron nitrides such as Fe_4N (fcc) (PDF 83-0875), Fe_3N (hcp) (PDF 83-0879), and Fe_2N (hcp) (PDF 73-2102). It is reported that iron nitrides such as Fe_3N and Fe_2N decompose above 476°C , while Fe_4N is thermally more stable because it does not decompose up to 640°C [25]. The annealing temperature in the present study was 510°C , and it is most likely that Fe_4N is formed and alloyed with Pt during the annealing in NH_3 environment. We envisage that the PtFeN catalyst comprises of Pt shell with a core of Fe_4N nitride, in which Fe atoms are partially

substituted by Pt. The PtFeN/C catalyst structure is analogous with the PtNiN catalyst that consists of Ni₄N-based core and 2-4 monolayer-thick Pt shell.

The XRD pattern from PtCoN/C shows a couple of noticeable features; three major peaks shift toward much higher angles compared with those of PtFeN/C, representing greater contraction in the Pt-Pt bonds as a consequence of the formation of Co nitride cores. A small peak designated by a red-solid square (27.95°) may represent the formation of Co₄N (fcc) [26-28]. Considering the STEM-EELS and XRD patterns, the catalyst comprises of a Pt shell with a Co₄N core and with some regions having Co atoms partially substituted by Pt atoms. The average diameter was estimated to be 3.1 nm.

Electrochemical ORR activity and stability

Fig. 3 illustrates the RDE measurements of the ORR on the PtFeN/C and commercial Pt/C electrocatalysts in a 0.1 M HClO₄ solution purged by O₂ at a rotation rate of 1600 rpm. The half-wave potential measured from the PtFeN core-shell catalyst was 892 mV which was 42 mV higher than that of Pt/C catalyst. The kinetic current was calculated from the ORR polarization curves by using the Koutecky–Levich equation at different rotation speeds in O₂-purged 0.1 M HClO₄ solution (as shown in the inset of Fig. 3). Likewise, we measured the ORR polarization curves and obtained the kinetic currents at 0.9 V for the PtCoN/C catalyst and used for comparison earlier obtained results of PtNiN/C [17] catalysts. The kinetic currents were normalized to the amount of Pt on the electrodes to obtain the mass activity, and were normalized to the electrochemically active surface area by measuring the charge in the hydrogen adsorption/desorption region to obtain the specific activity. Fig. 4 (and Table S1, ESI†) depicts the mass and specific

activities of PtFeN/C, PtCoN/C, and PtNiN/C together with those of commercial Pt/C for comparison. The PtMN catalysts showed 3 to 4 times higher mass activities and 3 to 7 times higher specific activities than those of Pt/C.

The long-term durability of ORR electrocatalysts is another important requirement for their application in fuel cells. Fig. 5 displays the accelerated stability tests for PtCoN/C by applying triangle sweeps between 0.6 and 1.05V with a scan rate of 50mV/s in air-saturated 0.1M HClO₄ solution at room temperature. As shown in Fig. 5, after 10,000 cycles the ORR polarization curve showed only a 5 mV decrease in its half-wave potential and the voltammetry exhibited nearly no loss in hydrogen adsorption/desorption peaks. In contrast commercial Pt/C showed a negative shift of 40 mV in half-wave potential and a considerable loss in surface area, approximately 45% [29-31]. The same stability tests were performed on PtFeN/C and PtNiN/C [17], and the decreases in half-wave potential were 11 and 5 mV, respectively. The results demonstrated that nitride cores improved the stability of the core-shell catalysts. Our previous DFT study [17] proposed that the presence of N atoms in cores facilitates the segregation of Pt atoms from inner shells to defective sites on surfaces, leading to the filling of the sites and accordingly, improving the stability of the electrocatalysts. Such a mending action can prevent further dissolution of Pt and transition metals from the cores.

The order of increase in ORR activity for nitride based core is PtNiN/C > PtFeN/C > PtCoN/C > Pt/C. In a previous study, Watanabe et al. had explained the enhanced ORR activity based on the lattice parameter changes by alloying non-precious metals to Pt. Their results showed that the ORR activity increased in the order of PtFe/C > PtCo/C > PtNi/C, whereas the calculated lattice parameter decreased in the order of PtFe/C <

PtCo/C < PtNi/C [13]. However in the present study nitriding the non-precious metal completely changes the trend in the ORR activity. From the (111) diffraction profiles in Fig. 2 and previous study,[17] the changes in lattice constant a relative to bulk Pt a_{Pt} can be estimated according to $(a - a_{Pt})/a_{Pt}$; these were -0.5, -2.3, and -6.4% for PtNiN/C, PtFeN/C, and PtCoN/C, respectively. The lattice parameters for the catalysts are smaller than that of Pt, and so they are compressively strained. An intriguing feature is that the order of the decrease in Pt-Pt distance observed is PtNiN/C < PtFeN/C < PtCoN/C, which is in the reverse sequence of the increase in the ORR activity (Fig. 4). We assume that the strain at the shell surface has the same tendency since the Pt shells on PtMN/C are very thin.

Fig. 6 shows the ORR specific activities for PtNiN/C, PtFeN/C, PtCoN/C, and Pt/C plotted as a function of the strain determined by the XRD profiles. It has been known that ORR activity of Pt shell (or Pt monolayer) can be enhanced or decreased by the configuration of the substrate-induced strain in combination with the electronic (ligand) effect. Strain-induced d-band center shifts apparently are a major factor determining the catalysts' activity [32]. It has been demonstrated that with an increase in compressed strain in a Pt surface, the ORR activity is enhanced by down-shifting d-band center and therefore lowering the binding energy of intermediate oxygenated adsorbates;[11, 33] however, beyond a certain strain, the binding becomes too weak and the ORR starts to decline because breaking O-O bond is more difficult. We predict that the NiN core gives a slight but moderate compressive strain to the Pt shell, thereby attaining the highest ORR activity among the catalysts, whereas the FeN and CoN cores impart comparatively higher compressive force to the Pt surfaces, resulting in lower activities than the NiN core. Electronic effects reflecting the electronic coupling between the overlayer and

its supporting substrate play another role in determining the activity. Mukerjee et al. investigated the enhancement mechanism on some PtM alloys for the ORR by using XANES and EXAFS [34]. Based on the d-band calculations that decreased in the order of PtFe/C < PtCo/C < PtNi/C, the ORR activity increased in the order of PtFe/C > PtCo/C > PtNi/C. The electronic effect on the ORR activity for the present nitride-based systems was calculated using DFT techniques.

DFT calculations

Periodic DFT calculations were executed to theoretically understand the experimental trend of the ORR activity for nitride-stabilized PtMN electrocatalysts (PtNiN/C > PtFeN/C > PtCoN/C). Fig. 2 suggests that the cores of PtFeN/C and PtCoN/C can be approximated as Fe₄N and Co₄N, respectively, similar to the Ni₄N core of PtNiN/C.[17] As summarized in Table S2 and Fig. S4 (ESI[†]), the calculated lattice parameters of Fe₄N and Co₄N (3.801 Å and 3.749 Å, respectively) are in line with the experimental results (3.795 Å and 3.740 Å, respectively), confirming the validity of our computational approach. We first constructed the nanoparticle models (Fig. 7a) with two Pt monolayers (Pt_{2ML}MN; 182 Pt, 19 M, and 4 N atoms). We calculated the BEO that serves as a descriptor for scaling the ORR activity [22] (Table S3), where a volcano-like relationship between the ORR activity and the BEO was observed. The performance of Pt can be improved by slightly weakening the O-Pt interaction. However, the trend in the calculated BEOs (Pt (−4.09 eV) > Pt_{2ML}NiN (−3.94 eV) > Pt_{2ML}CoN (−3.83 eV) > Pt_{2ML}FeN (−3.71 eV)) does not follow that of the observed ORR activities. The inconsistency seems primarily associated with the fact that the BEO of the Pt_{2ML}CoN NP is too strong using the two-monolayer model. Thus, we took into account two hypotheses to adjust the strong

BEO of $\text{Pt}_{2\text{ML}}\text{CoN}$; a slightly thinner Pt shell layer and higher N/Co ratio than 0.21, which can possibly lead to weaken its BEO. Accordingly, $\text{Pt}_{1\text{ML}}\text{CoN}$ (122 Pt, 79 M, and 17 N atoms) with one Pt layer was constructed to corroborate the scheme. It is noted that the total number of metal atoms was kept constant to maintain the nanoparticle size (~ 1.7 nm), while the N/M ratio in the core was set close to that of $\text{Pt}_{2\text{ML}}\text{CoN}$. It was found that varying the N/M ratio from 0.22 (79 Co and 17 N atoms) to 0.25 (79 Co and 20 N atoms) only slightly weakens the BEO on $\text{Pt}_{1\text{ML}}\text{CoN}$ by 0.06 eV, which is much smaller than that introduced by decreasing the Pt shell from $\text{Pt}_{2\text{ML}}$ to $\text{Pt}_{1\text{ML}}$. As summarized in Table S3, $\text{Pt}_{1\text{ML}}\text{CoN}$ exhibits a weaker BEO than the $\text{Pt}_{2\text{ML}}\text{CoN}$ model (-3.34 eV versus -3.83 eV, respectively). Correspondingly,[20] its surface strain becomes more compressive from -4.35% to -5.67% . $\text{Pt}_{1.5\text{ML}}\text{CoN}$ was considered to represent PtCoN in consideration of the possible coverage of Pt between 1ML and 2ML, where the BEO, surface strain, and d-band center were simply averaged over $\text{Pt}_{1\text{ML}}\text{CoN}$ and $\text{Pt}_{2\text{ML}}\text{CoN}$. Fig. 7b and Table S3 show that the nitride M cores weaken the BEO compared to Pt's ($\text{Pt} > \text{PtNiN} > \text{PtFeN} > \text{PtCoN}$), and introduces more contraction therein ($\text{Pt} < \text{PtNiN} < \text{PtFeN} < \text{PtCoN}$). Fig. 7c displays the BEO against the d-band center, exhibiting that the variation of M_4N cores shifts the d-band center of Pt atoms connected to oxygen atom away from the Fermi level ($\text{Pt} > \text{PtNiN} > \text{PtFeN} > \text{PtCoN}$) so that it weakens the BEO. The replacement of Ni with Fe or Co causes a weaker BEO (-3.94 eV, -3.71 eV, and -3.59 eV, correspondingly). Fig. 7d plots the calculated BEOs against the specific activities for Pt/C, PtNiN/C, PtFeN/C, and PtCoN/C. It illustrates a volcano-like trend at the maximum near PtNiN for the ORR activity. It markedly demonstrates that pure Pt binds oxygen too strongly, while the nitride cores with non-precious Fe and Co metals introduce too much strain. The nitriding

of Ni tunes the Pt-Pt bond length and therefore the ORR activity, being able to promote the dissociation of O₂, and remove O efficiently under the ORR conditions at low overpotentials. Furthermore, we successfully verified the bulk strain from the synchrotron based XRD of PtNiN/C, PtFeN/C, and PtCoN/C (−0.5, −2.3, and −6.4%, respectively) are qualitatively in excellent agreement with the surface strain from the DFT data (−3.7, −4.4, and −5.0%, respectively). Overall, we demonstrated that both the electronic and geometric effects under the fuel cell conditions are essential in rationalizing the increase in the ORR activity of nitride core PtMN/C compared to Pt/C.

Conclusions

Core-shell catalysts have possibility of reducing in simple manner the precious metal content in the ORR catalysts, while increasing their activity by combined geometric and electronic effects. Thus, they are promising choice for the future fuel cell vehicles. It is known that addition of Ni, Co or Fe in Pt alloys increases the ORR activity in the order of PtFe/C > PtCo/C > PtNi/C, but adding nitride metal in the core increases the ORR activity in the order of PtNiN/C > PtFeN/C > PtCoN/C. Improving the non-precious core by making it more stable using nitrogen bonds changes the geometric and electronic structure of these PtMN/C catalysts compared to their non-nitrided counterparts. DFT calculations have shown a volcano type behavior with PtNiN/C at the top of the curve revealing the fact that, among the catalysts investigated, it has the best combination of both the surface strain and d-band center shifts.

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Figure Captions

Figure 1. STEM- EELS analysis of core-shell nanoparticles (a, c) HAADF-STEM image of a single PtFeN nanoparticle and (b, d) two-dimensional EELS mappings of Fe L-edge signal (blue) on Pt M-edge signal (red) from (a) and (c) respectively. (e) EELS line scan profiles of Pt (red) and Fe (blue) from the nanoparticle along the scanned line as indicated in (c).

Figure 2. Synchrotron XRD patterns of PtFeN and PtCoN catalysts. Wavelength: 1.000 Å. ▲: Fe₄N, ■: Co₄N.

Figure 3. Comparison of polarization curves for the ORR on PtFeN/C and commercial Pt/C electrocatalysts at a rotation rate of 1600 rpm. The Pt loadings of the PtFeN/C and Pt/C electrocatalysts are 4.8 μg/cm² and 7.7 μg/cm², respectively. The inset shows a Koutecky-Levich plot of PtFeN/C at 0.9 V at different rotation speeds. Electrolyte: O₂-saturated 0.1 M HClO₄. Sweep rate: 10 mV/s.

Figure 4. Mass and specific activities for PtCoN/C, PtFeN/C, and PtNiN/C along with commercial Pt/C.

Figure 5. ORR polarization and voltammetry (inset) curves of PtCoN core-shell nanoparticles before and after 10,000 cycle test between 0.6 and 1.05 V in 0.1 M HClO₄. Pt loading: 5.31 μg/cm².

Figure 6. ORR specific activities for PtNiN/C, PtFeN/C, PtCoN/C, and Pt/C at 0.9 V plotted as a function of the lattice strain determined by the XRD patterns.

Figure 7. DFT modelling (a) Schematic of a PtMN model representing $\text{Pt}_{\text{ML}}\text{M}_4\text{N}$ ($\text{M} = \text{Ni}, \text{Fe}, \text{or Co}$). Binding energy of oxygen (BEO) of PtMN and Pt nanoparticles against (b) surface strain of Pt and (c) d-band center. (d) specific activities of Pt/C and PtMN/C.

Bio-sketch

<p>Dr. Kurian Kuttiyel received his Ph.D. in Material Science and Engineering from Stony Brook University in 2011. He is currently working as a post-doctoral research associate at Brookhaven National Laboratory under the supervision of Dr. Radoslav Adzic. Apart from synchrotron-based characterization of materials, his research interests include synthesis of nanostructured materials for energy conversion which include core-shell structured nanoparticles and structurally ordered intermetallic nanoparticles.</p>
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<p>Dr. Sun-Mi Hwang received her Ph.D. in Chemical and Biological Engineering from Seoul National University, Republic of Korea in 2011. She worked at the National Institute of Standards and Technology (NIST), U.S as a research associate from 2007 to 2010. Since 2012, she has been working at the Fuel Cell Laboratory of Korea Institute of Energy Research (KIER) as a post-doctoral research associate. Her present research focuses on the evaluation and development of nanostructured electrocatalyst materials for polymer electrolyte fuel cells (PEFCs).</p>
<p>Dr. Gu-Gon Park is a principal researcher in Fuel Cell Research Laboratory at the Korea Institute of Energy Research (KIER, since 1999) and an adjunct professor of Advanced Energy Technology in University of Science and Technology (UST, since 2009). He received his Ph.D. in Energy and Hydrocarbon Chemistry from Kyoto University, Japan. He is presently working as a visiting scientist at Brookhaven National Laboratory. His research interests is focused on the polymer electrolyte fuel cells; electrocatalysts, membrane and electrode assembly (MEA) and water management issues. He has authored and coauthored over 50 publications and 80 patents.</p>

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Dr. Radoslav Adzic is a senior chemist at the Brookhaven National Laboratory. He graduated from the University of Belgrade in 1974 with a Ph.D. in chemistry. He is a Fellow of the Electrochemical Society and of International Society of Electrochemistry and correspondent member of the Serbian Academy of Arts and Sciences. He has more than 295 scientific publications in the field of electrochemistry and 20 U.S. patents. He has won numerous awards, including the SciAm 50 Award in 2007 and the U.S. Department of Energy's Hydrogen R&D Award in 2008 and in 2012. Lately his group won the "R&D 100" for Pt Monolayer catalyst.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7