

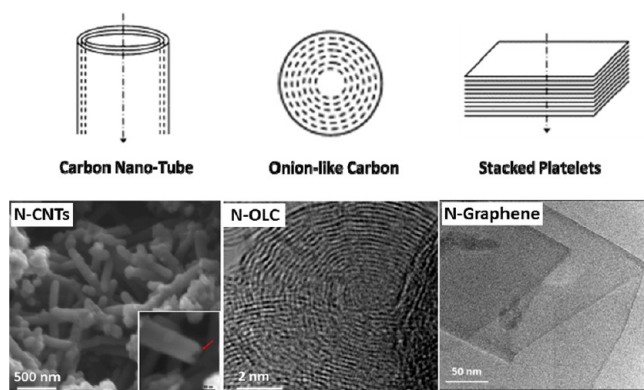
Nanostructured Nonprecious Metal Catalysts for Oxygen Reduction Reaction

GANG WU AND PIOTR ZELENAY*

*Materials Physics and Applications Division, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, United States*

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CONSPECTUS



Platinum-based catalysts represent a state of the art in the electrocatalysis of oxygen reduction reaction (ORR) from the point of view of their activity and durability in harnessing the chemical energy via direct electrochemical conversion. However, because platinum is both expensive and scarce, its widespread implementation in such clean energy applications is limited. Recent breakthroughs in the synthesis of high-performance nonprecious metal catalysts (NPMCs) make replacement of Pt in ORR electrocatalysts with earth-abundant elements, such as Fe, Co, N, and C, a realistic possibility. In this Account, we discuss how we can obtain highly promising M–N–C (M: Fe and/or Co) catalysts by simultaneously heat-treating precursors of nitrogen, carbon, and transition metals at 800–1000 °C. The activity and durability of resulting catalysts depend greatly on the selection of precursors and synthesis chemistry. In addition, they correlate quite well with the catalyst nanostructure. While chemists have presented no conclusive description of the active catalytic site for this class of NPMCs, they have developed a designed approach to making active and durable materials, focusing on the catalyst nanostructure. The approach consists of nitrogen doping, in situ carbon graphitization, and the usage of graphitic structures (possibly graphene and graphene oxides) as carbon precursors. Various forms of nitrogen, particularly pyridinic and quaternary, can act as n-type carbon dopants in the M–N–C catalysts, assisting in the formation of disordered carbon nanostructures and donating electrons to the carbon. The CN_x structures are likely a crucial part of the ORR active site(s). Noteworthy, the ORR activity is not necessarily governed by the amount of nitrogen, but by how the nitrogen is incorporated into the nanostructures.

Apart from the possibility of a direct participation in the active site, the transition metal often plays an important role in the in situ formation of various carbon nanostructures by catalyzing the decomposition of the nitrogen/carbon precursor. We can control the formation of different nanostructures during the synthesis of M–N–C catalysts. For example, in situ formed nitrogen-doped graphene-sheets can only be derived from polyaniline (PANI), probably due to structural similarities between the aromatic structures of PANI and graphene. Highly-graphitized carbon nanostructures may serve as a matrix for the formation of ORR-active groups with improved catalytic activity and durability, containing nitrogen and most probably also metal atoms. In the future, we will likely focus NPMC synthesis approaches on precise control of interactions between precursors of the metal and carbon/nitrogen during the heat treatment. The main purposes will be to maximize the number of active sites, optimize nitrogen doping levels, and generate morphologies capable of hosting active and stable ORR sites.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been generally viewed as one of the most promising energy conversion technologies available today thanks to their high overall fuel conversion efficiency and significant reduction in CO₂ and other emissions. In spite of recent spectacular progress in this technology, a large-scale market introduction of PEFCs continues to face numerous challenges, associated with their high cost and still insufficient performance. Currently, Pt-nanoparticle catalysts, supported on high-surface-area carbonaceous materials, represent state-of-the-art electrocatalysts for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) at the PEFC anode and cathode, respectively. However, the prohibitive price and scarcity of Pt have limited its widespread implementation in PEFCs, especially for the ORR at the cathode that accounts for approximately 80% of the Pt loading in fuel cell electrodes.¹ Alternative nonprecious metal catalysts (NPMCs), synthesized from earth-abundant elements, for example, Fe, Co, N, and C, have the potential to efficiently catalyze the ORR and generate clean energy via a direct electrochemical conversion.^{1,2} In the past decades, some promising NPMCs have been studied, including organometallic components, nonprecious metal chalcogenides, and transition-metals-derived nitrogen-doped carbon catalysts.^{1–4} The best performing NPMCs exhibit ORR activity and stability in alkaline electrolytes that approach or even exceed those of Pt-based catalysts;⁵ however, the NPMC performance in acidic fuel cells is far from sufficient. Thus, the development of high-performance NPMCs for Nafion-based acidic PEFCs continues to be the main challenge for the technology.

Recent advances in the development of high-performance NPMCs at Los Alamos National Laboratory (LANL)^{6–9} and in other research centers^{10–18} show that M–N–C catalysts (M: Fe and/or Co), obtained by simultaneously heat-treating precursors of a transition metal, nitrogen, and carbon at 800–1000 °C, yield the most promising NPMCs for the ORR. The approach has been continuously pursued since the original research of Jasinski¹⁹ and Yeager et al.,²⁰ who heat-treated transition-metal macrocycles at temperatures exceeding 700 °C and demonstrated significantly enhanced ORR activity and stability of the resulting catalysts relative to the performance of unheated macrocycles. In later studies, the expensive macrocycle precursors were replaced with a wide variety of more common and cost-effective nitrogen precursors (ammonia, acetonitrile, amines, etc.), transition-metal salts (sulfates, nitrates, acetates, hydroxides, and chlorides), and carbon supports

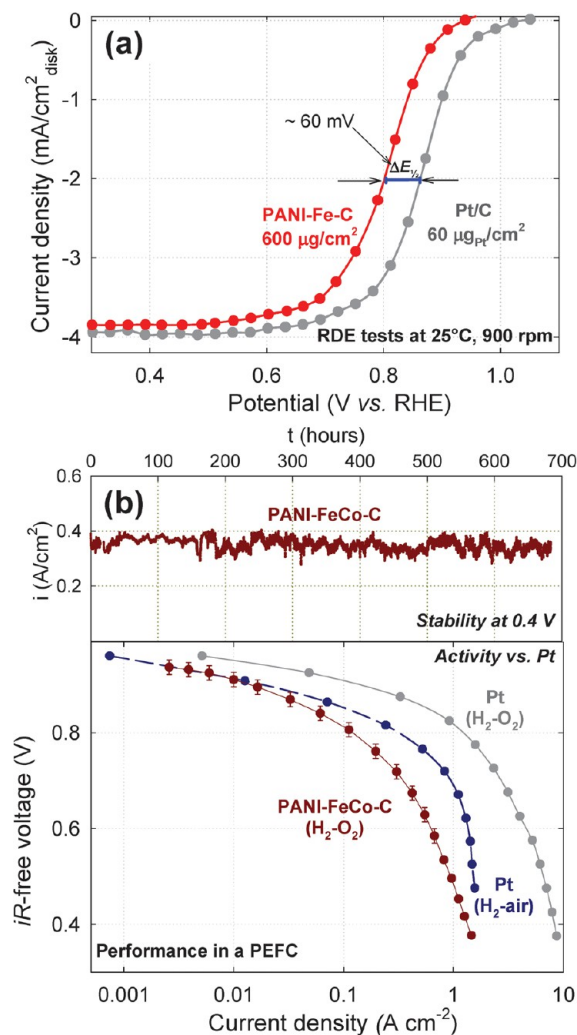


FIGURE 1. Activity and stability of PANI-derived ORR catalysts at LANL: (a) RDE polarization plots recorded at 25 °C and 900 rpm in 0.5 M H₂SO₄ solution (Pt catalyst was tested in 0.1 M HClO₄); (b) fuel cell polarization plots (bottom) and life test data (top). Cell temperature, 80 °C; air/O₂ pressure, 2.8 bar. Reprinted from ref 6 with permission from AAAS.

(Vulcan XC-72, Ketjenblack, Black Pearls, etc.). While it was learned that simultaneous heat treatment of virtually any combination of transition-metal, nitrogen, and carbon precursors can yield materials with certain ORR activity, better-performing catalysts required a careful and creative choice of precursors and supports, and synthesis conditions (control over precursor reactions in solution, heat-treatment temperature and atmosphere, post-treatment conditions, etc.).²¹ As a result of such an approach to NPMC synthesis, an Fe-based catalyst, developed by Dodelet and co-workers, has reached a volumetric activity in PEFC testing of 230 A cm⁻³ at 0.80 V (values extrapolated from Tafel plots).²² Recently, we reported a family of NPMCs that utilized polyaniline (PANI) as a precursor of a carbon/nitrogen template for high-temperature synthesis of Fe- and Co-based catalysts.⁶

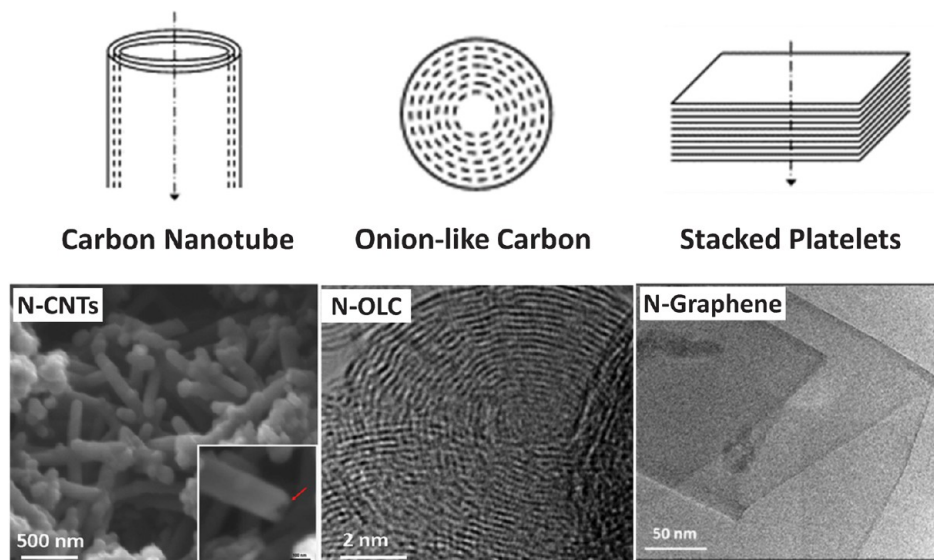


FIGURE 2. Drawings and micrographs of in situ nitrogen-doped carbon nanostructures in M–N–C catalysts: Carbon nanotubes in PANI-derived catalyst (left); onionlike carbon structure in HDA-derived catalyst (middle); and graphene formed in PANI-derived catalyst (right). The drawing and the micrograph (below-middle) reprinted from refs 10 and 28, Copyright 2006 and 2011, respectively, with permission from Elsevier. Micrograph (below-right) reprinted with permission from ref 8. Copyright 2012 American Chemical Society.

PANI-Fe-C tuned out to be the most active and four-electron-selective PANI-derived catalyst, as determined in rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) tests, respectively. The catalyst was shown to catalyze the ORR in acid media at potentials within ca. 60 mV of those delivered by a state-of-the-art carbon-supported Pt catalyst (Figure 1a).⁶ Much improved performance durability was achieved with another catalyst from the PANI family, a binary FeCo catalyst (PANI-FeCo-C) that maintained durable performance for nearly 700 h in a H₂-air fuel cell operated at a constant voltage of 0.4 V. Fuel cell performance of the catalysts was compared with that of a Pt reference cathode operated on both air and oxygen (Figure 1b).⁶

Although catalysts with respectable ORR activity in alkaline media can be prepared without any detectable metal content,^{5,23,24} so far only the presence of Fe and/or Co has been found to generate catalysts with high activity and best durability in acidic environments.^{1,2} The two metals appear to differently contribute to the active-site formation. ORR sites generated in the presence of Co have electrochemical properties similar to those exhibited by metal-free nitrogen-doped carbon (N–C) catalysts, abundant in CN_x moieties (pyridinic and quaternary nitrogen) as potential active sites.¹¹ Unlike Co, there is mounting evidence in support of the hypothesis that Fe species coordinated by nitrogen, such as a Fe–N_x, directly participate in the ORR active site(s) and are responsible for an enhanced intrinsic activity of Fe-based catalysts.^{12,21,25,26} However, the exact nature of the active

site(s) in M–N–C catalysts synthesized using a heat-treatment approach remains unknown. Also lacking is direct evidence of transition-metal participation in the active sites. In either case, while nitrogen species embedded within the carbon structures are likely critical to the active-site performance, the bonding character and structure of active sites are yet to be conclusively identified.

M–N–C catalysts are rich in carbon nanostructures in situ formed during catalyst synthesis. The nanostructures involve for example carbon tubes, onion-like carbon, and platelets (multilayer graphene) shown in Figure 2.^{8,10,27,28} The active ORR catalysts developed at LANL are especially rich in nitrogen-doped graphene, generated directly in the graphitization process of PANI in the presence of transition metal species (Co and/or Fe).^{6–8,21,29} Those highly graphitic structures can serve as a matrix for hosting ORR-active nitrogen or metal moieties.^{6,10} While such efforts are ongoing at LANL and elsewhere, in the present Account, we primarily focus on correlation between ORR performance of M–N–C catalysts and their nanostructures.

2. Nitrogen-Doped Carbons in ORR Catalysts

Nitrogen Doping. Nitrogen doping plays a critical role in modifying carbons, especially due to the comparable atomic size of both elements and five valence electrons in nitrogen available to form a strong covalent bond with carbon atoms. In the case of carbon doping, nitrogen atoms act as n-type dopants assisting in the formation of disordered carbon

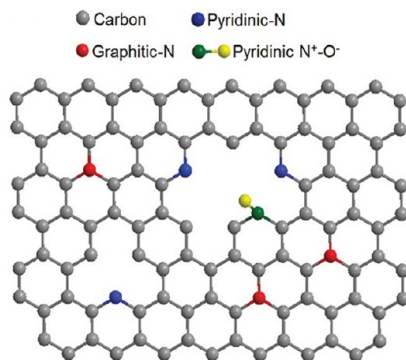


FIGURE 3. Nitrogen functionalities in graphene. Reprinted with permission from ref 18. Copyright 2012 American Chemical Society.

nanostructures and donates electrons to carbon, thus facilitating the ORR.³⁰ It was experimentally found that nitrogen atoms can be readily incorporated into the carbon lattice, replacing carbon atoms at different sites and leading to the formation of defects^{10,18,31} (Figure 3¹⁸). Among different methods of nitrogen doping into carbon structures, heat treatment of a nitrogen–carbon precursor is one of the most effective.^{10,31} The process can be further promoted by the presence of transition metals. Nitrogen doping via heat treatment at high temperatures (800–1000 °C) yields nitrogen atoms with XPS binding energies that can be assigned to pyridinic (398.6 ± 0.3 eV) and quaternary nitrogen (401.3 ± 0.3 eV).³² Pyridinic nitrogen is obtained by doping at the edge of the graphene layer and quaternary nitrogen is the result of in-plane doping. In addition, the pyrrolic form of nitrogen (400.5 ± 0.3 eV) observed at the relatively low heat-treatment temperature (600–700 °C) is assigned to nitrogen atoms in a pentagon structure, which is indistinguishable in XPS from pyridone (pyridinic nitrogen next to an OH group).³¹ Both the pyrrolic and pyridone nitrogen have been shown to decompose at temperatures above 800 °C to either pyridinic or quaternary nitrogen.^{8,31} Nitrogen species with a high binding energy (402–405 eV) can be assigned to oxidized nitrogen, such as a pyridinic N⁺–O[–] species.³¹ One specific type of quaternary nitrogen is “graphitic” nitrogen, which corresponds to nitrogen within a graphene plane, bonded to three carbon atoms.

Nitrogen-doped graphitic nanostructures show enhanced disorder and dislocation in graphene stacking.³³ Using Raman analysis, Stevenson and co-workers³⁰ found that disorder in nitrogen-doped carbon nanotubes (N-CNTs) increase proportionally to the nitrogen content, thus providing direct evidence that the carbon disorder is related to nitrogen doping. A possible disorder mechanism is that nitrogen inclusion facilitates the formation of nanocrystallites and

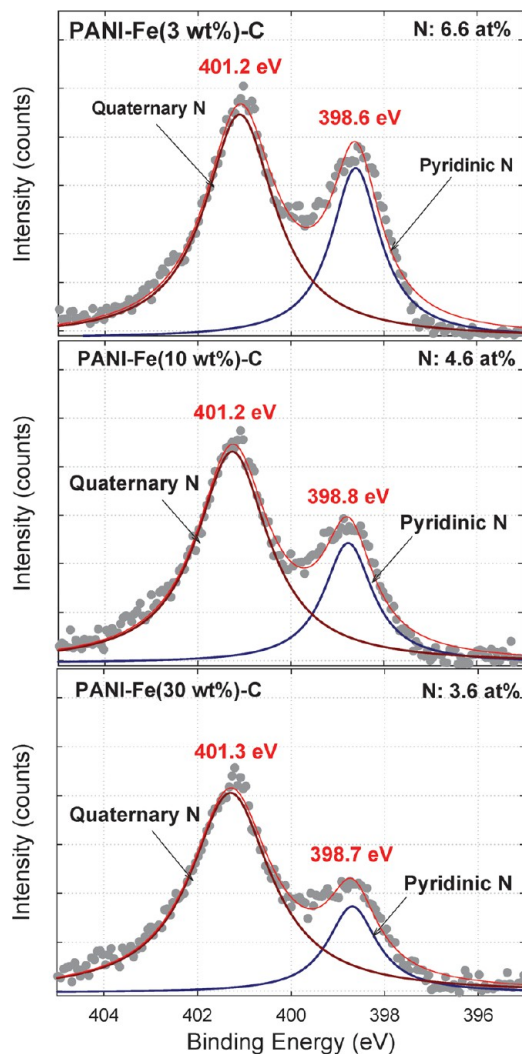


FIGURE 4. N 1s XPS spectra of PANI-Fe-KJ catalysts with different Fe loading in the synthesis.

suppresses surface diffusion of carbon atoms during graphitization.³⁴ The resulting doped-nitrogen defects at the graphene edges and in plane may serve as sites for oxygen adsorption. Pyridinic nitrogen, linked to only two sp^2 carbon atoms, contributes one p_z electron to the graphitic π system. Quaternary nitrogen atom in the in-plane position, where it substitutes carbon atom shared by three adjacent rings, contributes two p_z electrons. Lahaye and co-workers³⁵ confirmed that nitrogen-doped carbons have higher surface polarity than carbons without doped nitrogen. As a result, compared to undoped carbon black, a nitrogen-doped graphitic layer exhibits a faster charge-transfer rate at the electrode/electrolyte interface,^{32,36} favorable to the proton and electron transfer in the ORR.

Effect of Transition Metal on Nitrogen Doping. Gaining some control over N–C structures in nitrogen-doped

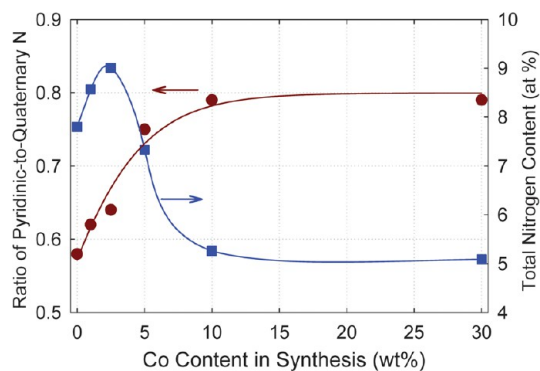


FIGURE 5. Dependence of nitrogen content and the pyridinic-to-quaternary nitrogen ratio on Co loading used in the synthesis of PANI-Co-MWNT catalysts. Reprinted with permission from ref 8. Copyright 2012 American Chemical Society.

M–N–C catalysts was found to be possible by fine-tuning of the synthesis conditions.²¹ Regardless of whether ethylenediamine (EDA) or PANI were used as nitrogen precursors, the XPS shows higher content of quaternary nitrogen in Fe–N–C than Co–N–C catalysts, indicating that in the presence of Fe nitrogen atoms are preferentially doped into the plane rather than at the edges of a graphene layer.²¹ As a general rule, the pyridinic-to-quaternary nitrogen ratio tends to reach “equilibrium” during the heat treatment of carbon/nitrogen precursors.³¹ The addition of Fe seems to shift that equilibrium toward quaternary nitrogen.

Metal Loading versus Nitrogen Doping. The type and content of nitrogen functionalities formed during the doping process depend on the metal loading used in synthesis. Regardless of the metal, that is, Fe versus Co, the total content of the doped nitrogen has been found to consistently decrease with an increase in the loading of metal precursors, even though the change in the metal content itself in the catalyst is often insignificant.^{8,21} Also, the observed decrease in the total content of nitrogen does not lead to a commensurate drop in ORR activity.²¹ These results suggest that ORR activity of M–N–C catalysts does not depend on the quantity of doped nitrogen atoms but more likely on how those atoms are incorporated into carbon. In the case of Fe-based catalysts, the amount of quaternary nitrogen relative to pyridinic nitrogen goes up as Fe loading is increased (Figure 4), the change accompanied by an enhancement in the ORR activity.

In the case of Co-based catalysts, the pyridinic-to-quaternary nitrogen ratio increases from 0.58 in a Co-free sample to 0.79 in the catalyst synthesized from precursor containing more than 10 wt % of Co (Figure 5).⁸ Contrary to iron, cobalt appears to promote the formation of pyridinic

nitrogen functionalities. One likely reason for that is the abundance of graphene sheets in Co-based catalysts, with pyridinic nitrogen functionalities likely forming at their edges. This attests to a different effect of the two metals on the formation of nitrogen functionalities in M–N–C catalysts. Successful replacement of carbon atoms at the edge of graphene layers by the (pyridinic) nitrogen has been often linked to the enhancement in ORR activity.^{10,11} The incorporation of (quaternary) nitrogen in the interior of graphitic sheets has only recently been correlated with ORR activity.¹⁷

Impact of Heat-Treatment Temperature on Nitrogen Doping. The content and relative ratios of different types of doped nitrogen in both Fe- and Co-based catalysts can be controlled by tuning the heat-treatment temperature (Figure 6).^{8,21} In catalysts based on both metals, a raise in the heat-treatment temperature leads to a decrease in the total nitrogen content that does not necessarily result in a drop in the ORR activity. The quaternary-to-pyridinic nitrogen ratio rises with an increase in the heat-treatment temperature from 800 to 1000 °C.^{7,8,21} This data indicates once again that quaternary nitrogen and the optimal C–N_x configuration reflected by the ratio of the two of nitrogen functionalities, may be as important for the ORR activity as the pyridinic nitrogen.¹⁰

3. In Situ Formed Graphitized Carbon Nanostructures

Apart from the obvious advantage of high electronic conductivity and enhanced corrosion resistance, the highly graphitized carbon nanostructures present in the M–N–C may serve as a matrix for hosting nitrogen and metal moieties. As shown in our previous NMPC research, the presence of graphitized carbon appears to enhance stability of the ORR catalysts.^{21,28,37,38} The formation of different carbon nanostructures, which can be correlated to the performance, depends on nitrogen and transition-metal precursors, heat-treatment temperature and the type of support utilized in the catalyst synthesis.^{7,21,28,39}

Carbon/Nitrogen Precursors. The nature of carbon/nitrogen precursor plays a key role in the formation of the catalyst nanostructure in the heat-treatment step. When amine-based nitrogen–carbon precursors, such as EDA¹¹ and hexamethylenediamine (HDA)^{27,28} are used, the morphology of the resulting M–N–C catalysts is dominated by diverse carbon nanostructures, involving nanotubes and onion-like carbon nanoshells (Figure 7).^{11,27,28} Such structures may originate from the carbonization of interlinked [–Co(HDA)₄–]_n complexes. Well-defined

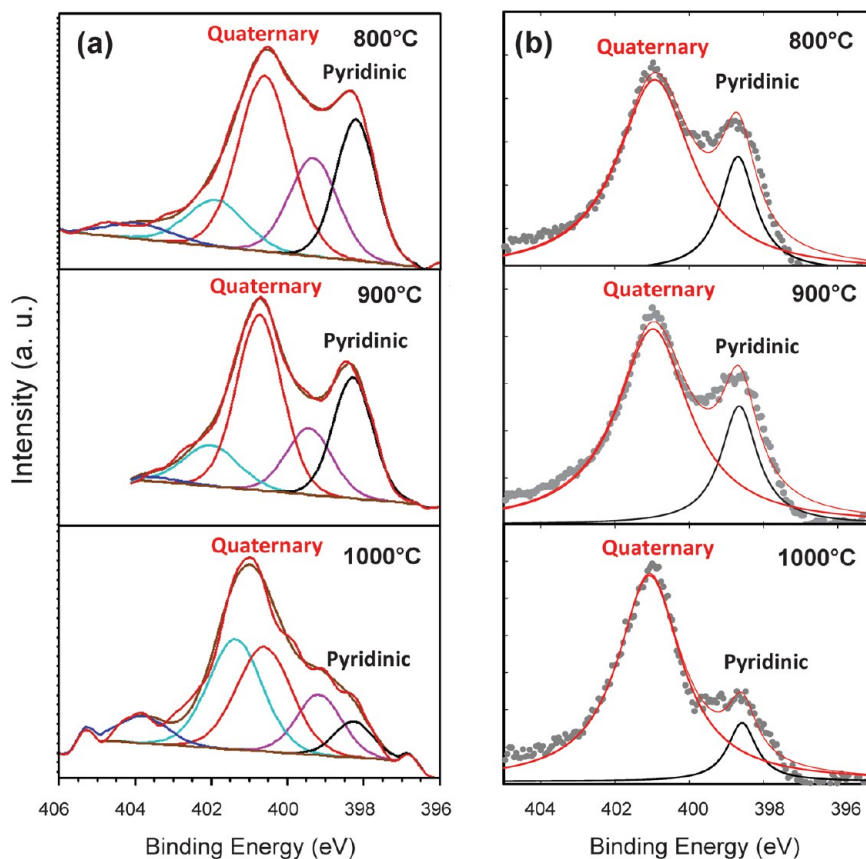


FIGURE 6. N 1s XPS spectra of (a) PANI–Fe–C catalyst and (b) PANI–Co–MWNT catalyst as a function of heat-treatment temperature ranging from 800 to 1000 °C. Panel (a) reproduced from ref 21 by permission of The Royal Society of Chemistry. Panel (b) reprinted with permission from ref 8. Copyright 2012 American Chemical Society.

graphitized carbon shells surrounding metal-rich particles were also observed with iron(III) tetramethoxyphenyl porphyrin chloride (FeTMPP-Cl) when the heat-treatment temperature was raised to 1000 °C.⁴⁰ An increase in the open-circuit ORR potential of the catalysts in oxygen-saturated solution was correlated with the formation of such graphitic shells.

Multilayer graphene sheets were observed only in the Co- and Fe-based catalysts derived from PANI as a carbon/nitrogen precursor (Figure 8),^{7,8} perhaps due to the similarities between the aromatic structures of PANI and graphene. Traditionally, single- and few-layer graphene structures have been grown epitaxially *via* chemical vapor deposition (CVD) of hydrocarbons on the metal substrates or by thermal decomposition of SiC.²³ The new synthesis route of graphene layers from polymers adds a degree of freedom in controlling the catalyst morphology and nitrogen functionalities in M–N–C catalysts with enhanced oxygen reduction activity.

The formation of different carbon structures in M–N–C catalysts have been linked to significant variations in the

ORR activity and durability.^{21,28} Generally, catalysts derived from aromatic precursors, such as PANI, exhibit a better combination of activity and durability than catalysts derived from aliphatic amines, implying that the type of carbon nanostructure formed during the heat treatment may be critical to catalyst performance.

Transition-Metal Precursors. In addition to nitrogen/carbon precursors, transition metal can impact the formation and of carbon nanostructures in M–N–C catalysts. No highly graphitized carbon nanostructures are formed in metal-free catalyst derived from PANI.⁸ When PANI is used as a nitrogen/carbon precursor for metal-based catalysts supported on Ketjenblack, the dominant presence of multilayer graphenesheets can be seen in the PANI–Co–C catalyst, but not in the PANI–Fe–C catalyst.²¹ These significant morphological differences between the two catalysts attest to the effect of the transition metal on the formation of carbon/nitrogen structures during the heat treatment of the polymer. Co appears to be more effective at catalyzing the decomposition of PANI and formation of carbon and nitrogen species that are capable of rearranging and coalescing

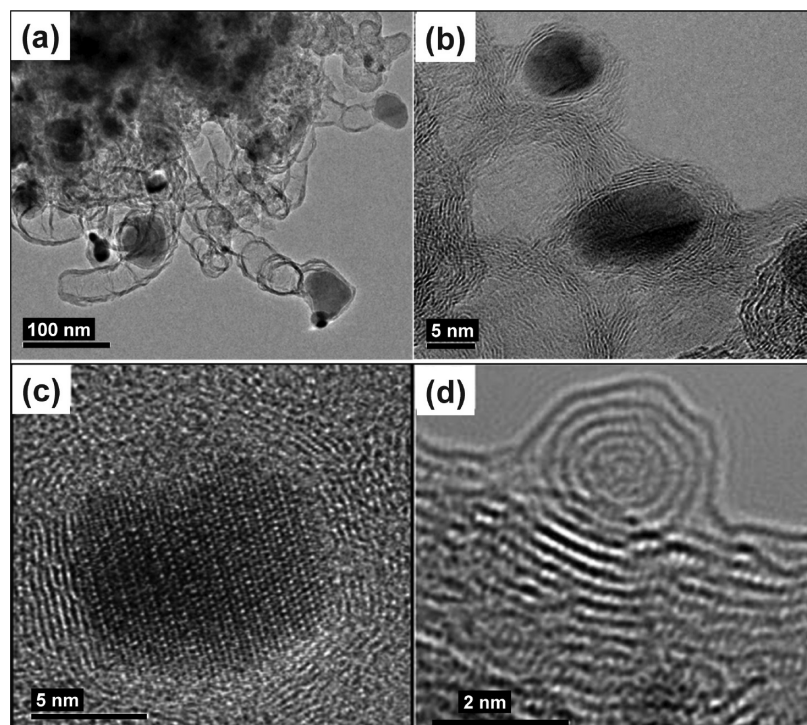


FIGURE 7. Nanoshells and onionlike carbon particles observed in M–N–C catalysts derived from (a, b) EDA and (c, d) HDA. Panels (a) and (b) reprinted with permission from ref 8. Copyright 2012 American Chemical Society. Panels (c) and (d) reprinted from ref 28, Copyright 2011, with permission from Elsevier.

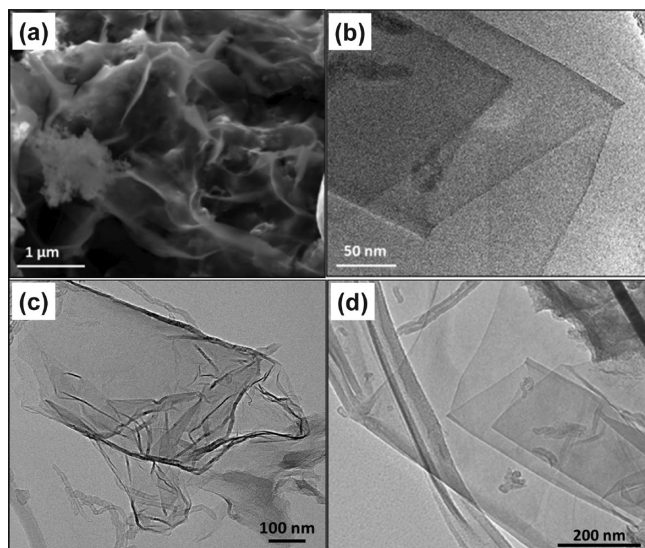


FIGURE 8. Graphene-sheet-like morphology in PANI-derived Co–N–C catalysts: (a) SEM image; (b–d) HR-TEM images. Reprinted with permission from ref 8. Copyright 2012 American Chemical Society.

to yield highly graphitic carbon structures. Contrary to Co, Fe catalyzes the breakdown of PANI into relatively large fragments that are not precursors for graphitic structures.²¹ Although Co species seem to facilitate the formation of graphitized carbon, which can potentially benefit ORR

electrocatalysis via enhancements to the corrosion resistance and electronic conductivity, Co-based catalysts are generally less active in the ORR than the Fe-based materials. This is probably due to the difference(s) in the nature of the ORR active sites formed in catalysts derived, correspondingly, from Co and Fe, with, as already stated above, iron being part of the more active ORR site. Perhaps not surprisingly, the bimetallic catalysts involving both Co and Fe seem to benefit at the same time from the unique graphene-rich morphology due to Co and from the intrinsically active Fe-containing sites.^{6,11,28} Our ORR electrocatalysis research to date has provided strong evidence of a correlation between the appearance of graphene sheets in the catalyst and enhanced performance durability.^{6,13,37}

Multiwalled Carbon Nanotubes as Catalyst Support.

Carbon nanotubes offer several notable advantages over carbon blacks as supports for fuel cell electrocatalysts. Those advantages include improved mass transfer of reagents/products, enhanced electronic conductivity, reduced impurity level, and higher resistance to corrosion.^{41–43} Recently, we introduced multiwalled carbon nanotubes (MWNTs) into the synthesis of M–N–C catalysts derived from PANI and Fe.³⁹ In contrast to the impact of carbon supports on the activity of Pt catalysts,⁴⁴ the ORR activity of PANI–Fe catalysts

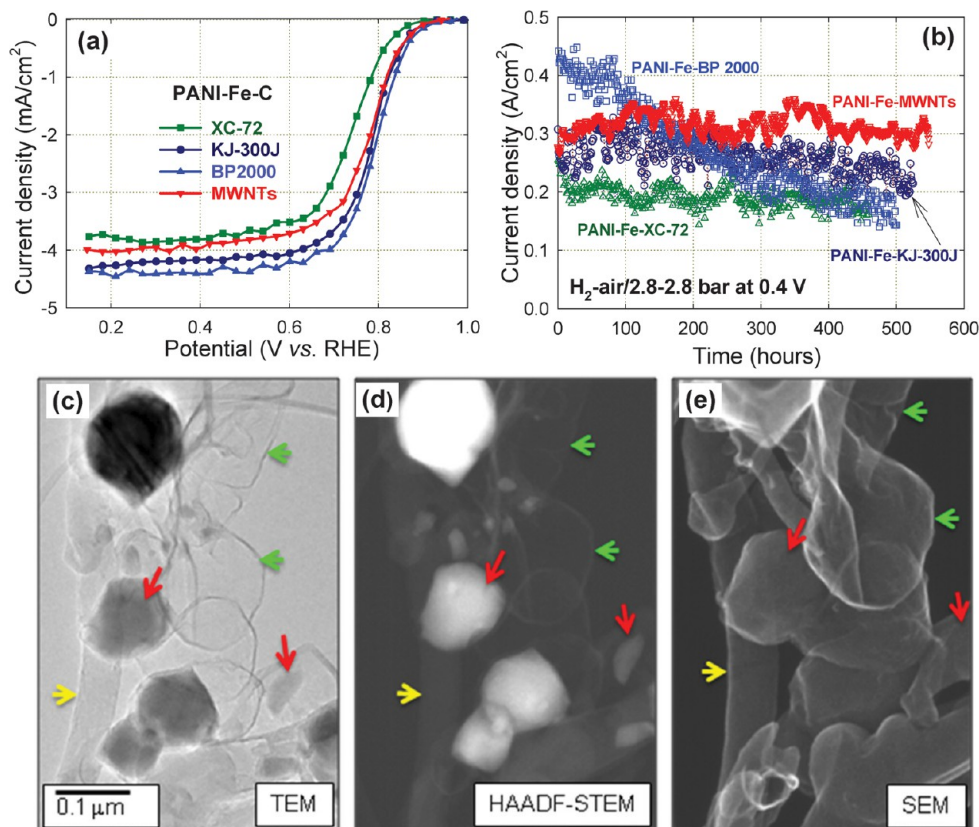


FIGURE 9. ORR performance of PANI-Fe catalyst supported on various carbon materials: (a) steady-state RDE polarization plots; (b) fuel cell life test. Cell temperature: 80 °C. Three images of the same region of PANI-Fe-MWNT catalyst: (c) TEM; (d) HAADF-STEM; (e) SE. Layered-graphene “bubbles”, carbon nanotubes, and FeS_x -rich regions/particles are indicated with the green, yellow, and red arrows, respectively. Reproduced from ref 39 by permission of The Royal Society of Chemistry.

supported on different carbons (Vulcan XC-72, Ketjenblack, Black Pearls, and MWNTs) is virtually the same (Figure 9a).³⁹ At the same time, the durability of the catalyst supported on MWNTs is significantly better than that of catalysts supported on other carbons. MWNTs act in this case as a template for the in situ formation of carbon nanostructures with specific surface area and porosity.^{8,21} As shown in Figure 9b,³⁹ the MWNT-supported Fe-based catalyst shows no performance degradation for more than 500 h of operation at a cell voltage of 0.4 V. By comparison, catalysts supported on carbon blacks exhibit much faster performance loss. Enhanced performance durability of catalysts supported on MWNTs can be linked to the unique carbon nanostructures observed in the catalyst. As shown by the TEM image, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, and secondary electron (SE) image acquired from the same region of the PANI-Fe-MWNT catalyst in Figures 9c, d, and e, respectively, the catalyst contains a large number of layered-graphene “bubbles” (green arrows) that are found to be collocated with carbon nanotubes (yellow arrows) and

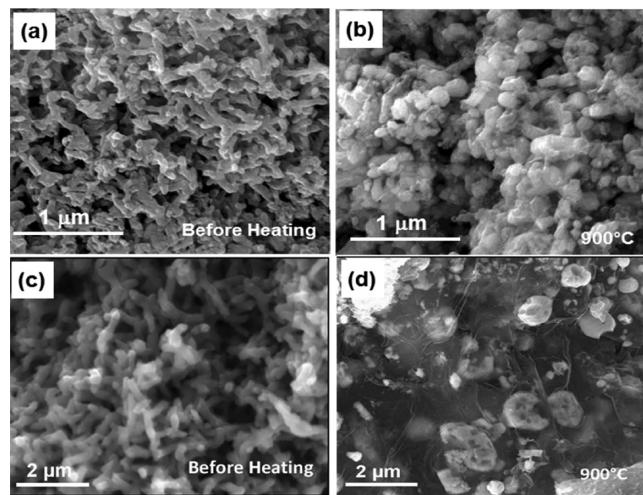


FIGURE 10. SEM images of a PANI-derived Fe–N–C catalyst obtained (a) before and (b) after the heat treatment at 900 °C. (c, d) Corresponding SEM images of Co–N–C catalyst.

the FeS_x regions/particles (red arrows).³⁹ Since MWNTs (yellow arrows in Figure 9d–e) remain abundant in the catalyst after the heat treatment, the graphene sheets are

likely not derived from the carbon nanotubes. Unlike in the PANI-Fe-MWNT catalyst, a very few graphene sheets/bubbles were observed in a PANI-Fe-KJ catalyst, that is, in the catalyst supported on a conventional carbon black rather than nanotubes. The unique properties of the graphene sheets/bubbles, such as their high surface area and electronic conductivity, as well as the presence of sp^2 -conjugated carbon atoms in the basal plane⁸ may all contribute to the much-improved performance durability of the PANI-Fe-MWNT catalyst.³⁹

The Role of Heat-Treatment Temperature. ORR activity of M–N–C catalysts strongly depends on the temperature of the heat-treatment step that also governs the catalyst morphology. As shown in Figures 10a and b for PANI-Fe-C catalysts, the characteristic PANI nanofibers gradually disappear as the heat-treatment temperature increases.²¹ A higher degree of graphitization, evidenced by the formation of graphitic shells covering metal-rich particles, is observed after the heat treatment at 900 °C, the temperature that corresponds to the highest ORR activity.²¹ Heat treatment at even higher temperatures yields catalysts with less uniform morphology, containing particles significantly larger than those present in the original carbon black. The surface area of such catalysts is significantly reduced and ORR activity gradually lost.

As shown in Figure 10c and d for the PANI-Co-MWNTs catalyst, the morphology of Co-based catalysts also depends on the heat-treatment conditions.⁸ The graphene-sheet-like structures grown over the solid metal-rich particles (Co_9S_8 , in this case) are only observed after the heat-treatment temperature is raised to 900 °C. The appearance of graphene-sheet-like morphology is in a good agreement with an increase in the BET surface area (to $278 \text{ m}^2 \text{ g}^{-1}$).⁸ Large differences in the ORR performance resulting from the changes in carbon structures point to the importance of the metal-catalyzed transformation of the precursors into new carbon forms in M–N–C catalysts.²¹

4. Ex Situ Graphene and Graphene Oxide as Potential NPMC Precursor

As discussed above, nitrogen-doped graphene structures are abundant in the most active PANI-derived M–N–C catalysts.^{6–8,21} It is thus possible that high catalytic activity can be accomplished by incorporating metal into nitrogen-doped graphene. Graphene has attracted a great deal of interest since its discovery by Novoselov et al. in 2004.⁴⁵ The unique physical and chemical properties of graphene, such as high surface area (theoretical value of $\sim 2630 \text{ m}^2 \text{ g}^{-1}$),

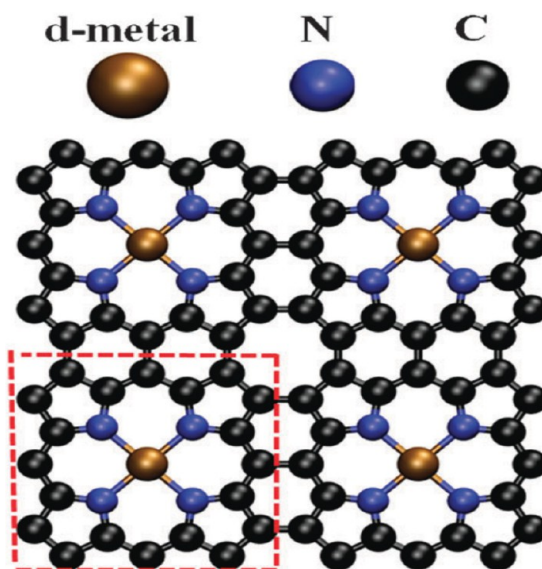


FIGURE 11. DFT-calculated M–N₄ moieties as possible ORR active sites embedded into graphene structure. Reproduced from ref 47 by permission of the Royal Society of Chemistry.

high chemical stability, excellent conductivity, and distinctive structure, as well as the easiness of functionalization make graphene attractive for NPMC research.^{18,23,46} Density functional theory (DFT) calculations imply that a transition-metal site can be stabilized by, for example, four pyridinic nitrogen atoms doped in graphene, creating structures of an M–N_x type, that according to DFT should be active toward ORR (Figure 11).⁴⁷ Incorporating a metal, for example Fe, into a nitrogen-doped graphene can be a key to the ORR activity. In that context, it is of fundamental interest to investigate how nitrogen doping and metal incorporation affect the structure of graphene and how the ensuing chemical structures can be manipulated to maximize the activity.

The number of active sites in M–N–C catalysts, which likely involve metal centers coordinated by nitrogen-containing ligands, is limited by the total number of defects and/or nitrogen-doped sites in the carbon.⁴⁸ As a main precursor of graphene-based materials, graphene oxide (GO) potentially represents a promising catalyst precursor with defects or vacancies tunable by selective chemical oxidation.^{17,49} It was demonstrated that successful reduction of GO can restore the π -conjugated structure and ultimately lead to highly conductive graphene materials (Figure 12).⁵⁰ GO can thus be a useful precursor alternative to graphene, which can be doped with nitrogen and incorporated with transition metals in a controlled manner to obtain graphene-based M–N–C catalysts. In a typical approach, GO samples are treated with various nitrogen precursors (e.g., ammonia,

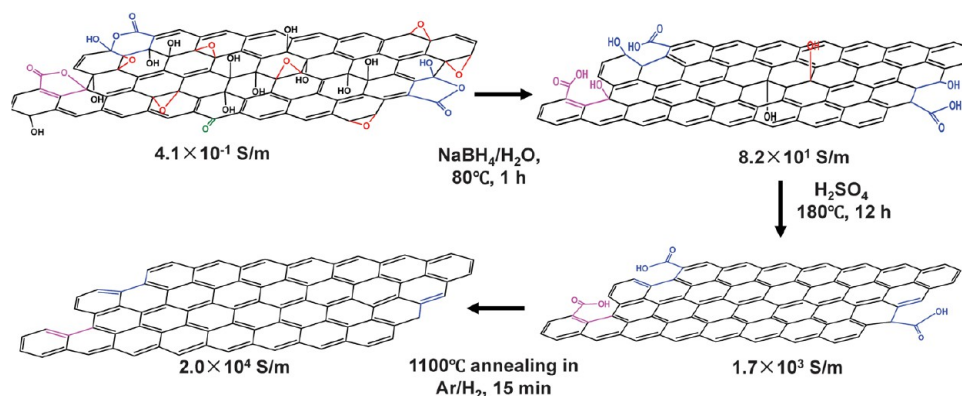


FIGURE 12. Reduction process aimed at restoring π -conjugated graphene structure from GO. Reprinted from ref 50 by permission from Macmillan Publishers Ltd: [Nature Chemistry], copyright 2009.

hydrazine, cyanamide)^{17,18} to form nitrogen-doped GO, followed by chemical reduction to yield reduced GO (rGO). The rGO can then be treated with various metal salt (Co and Fe) solutions to bind metal ions and induce ORR activity. An Fe-N-rGO catalyst, reported by Shao-Horn and co-workers,¹³ exhibits ORR mass activity comparable to that of the state-of-the-art M–N–C catalysts reported to date.^{1,2} The approach offers a pathway toward utilizing the unique order and properties of rGO in creating active sites for the ORR.

5. Conclusion

M–N–C catalysts obtained by simultaneously heat-treating precursors of a transition metal, nitrogen, and carbon (often nitrogen/carbon precursor), typically in the temperature range of 800–1000 °C are the most promising nonprecious metal ORR catalysts for the polymer electrolyte fuel cell cathode. The activity and durability of these catalysts strongly depend on the nitrogen and/or carbon precursor(s), the transition metal, and support as well as on the heat-treatment conditions. The catalyst nanostructure, often correlated with the activity and durability, can be to a certain degree controlled during nitrogen doping and carbon graphitization. Nitrogen-doping of carbon and formation of CN_x groups on the surface, including pyridinic and quaternary nitrogen, play a critical role in inducing ORR activity via structural and electronic modification of the carbon. The location and coordination of doped nitrogen is more important for the activity and durability of M–N–C catalysts than the total nitrogen content. While, in agreement with previous reports, nitrogen doping at the graphene edge appears to be a key to the ORR activity, the importance of quaternary nitrogen cannot be ruled out as well.

Highly graphitic carbon nanostructures formed during the heat treatment of nitrogen/carbon precursor in the presence

of a transition metal represent an important component of M–N–C catalysts. Those structures likely act as a host for the ORR active sites. Their composition and morphology depend on the synthesis conditions, including the nature of all the precursors, type of the support, and heat-treatment temperature.

Future effort in the synthesis of M–N–C catalysts is likely to focus primarily on precise control of interactions between nitrogen/carbon and metal precursors during the heat treatment in order to produce catalysts with optimum chemical composition and morphology, as well as to maximize the population of ORR active sites. Detailed, in-depth knowledge of the active-site and ORR reaction mechanism will be essential for the rational design of nonprecious metal catalysts with the activity, selectivity and stability matching, and ultimately exceeding, those of platinum-based catalysts of oxygen reduction.

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BIOGRAPHICAL INFORMATION

Gang Wu, a scientist at Los Alamos National Laboratory (LANL), completed his Ph.D. studies in 2004 at the Harbin Institute of Technology, concentrating on electrodeposition and electrocatalysis. After postdoctoral trainings at Tsinghua University (2004–2006), the University of South Carolina (2006–2008), and LANL (2008–2010), he became a research scientist at LANL in 2010. Wu is an electrochemist and materials scientist focusing on the development of nanostructured catalysts and electrode materials for energy storage and conversion technologies (e.g., fuel cells, lithium batteries, and supercapacitors). To date, Dr. Wu has authored and coauthored 74 scientific publications with ~2200 citations and 50 presentations in academic conferences.

Piotr Zelenay, a scientist at LANL, received his Ph.D. and D.Sc. ("habilitation") degrees in chemistry from Warsaw University, Warsaw, Poland. He was a postdoctoral research fellow at Texas A&M University, College Station (1983–1986), a visiting professor at the University of Illinois Urbana–Champaign (1988–1992), University of Alicante, Spain (1994), and Colorado State University (1996–1997). Dr. Zelenay was appointed a faculty member in the Department of Chemistry, Warsaw University in 1983 and remained at the University until 1997, when he accepted permanent research position with LANL. He has been associated with Materials Physics and Applications Division (formerly Materials Science and Technology Division) at Los Alamos National Laboratory for the past 15 years. He is currently a Project Leader and Team Leader at LANL focusing primarily on fundamental and applied aspects of polymer electrolyte fuel cell science and technology, electrocatalysis, and electrode kinetics. Dr. Zelenay has published more than 100 research articles in renowned scientific journals, including *Nature* and *Science*, and coauthored nearly 300 presentations, of which approximately 100 have been invited/keynote/plenary lectures.

FOOTNOTES

*To whom correspondence should be addressed. Telephone: 505-667-01976. E-mail: zelenay@lanl.gov.
The authors declare no competing financial interest.

REFERENCES

- Jaouen, F.; Proietti, E.; Lefevre, M.; Chenitz, R.; Dodelet, J. P.; Wu, G.; Chung, H. T.; Johnston, C. M.; Zelenay, P. Recent Advances in Non-Precious Metal Catalysis for Oxygen-Reduction Reaction in Polymer Electrolyte Fuel Cells. *Energy Environ. Sci.* **2011**, *4*, 114–130.
- Chen, Z.; Higgins, D.; Yu, A.; Zhang, L.; Zhang, J. A Review on Non-Precious Metal Electrocatalysts for Pem Fuel Cells. *Energy Environ. Sci.* **2011**, *4*, 3167–3192.
- Rabis, A.; Rodriguez, P.; Schmidt, T. J. Electrocatalysis for Polymer Electrolyte Fuel Cells: Recent Achievements and Future Challenges. *ACS Catal.* **2012**, *2*, 864–890.
- Wu, G.; Cui, G. F.; Li, D. Y.; Shen, P. K.; Li, N. Carbon-Supported $\text{Co}_{1.67}\text{Te}_2$ Nanoparticles as Electrocatalysts for Oxygen Reduction Reaction in Alkaline Electrolyte. *J. Mater. Chem.* **2009**, *19*, 6581–6589.
- Gong, K. P.; Du, F.; Xia, Z. H.; Durstock, M.; Dai, L. M. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, *323*, 760–764.
- Wu, G.; More, K. L.; Johnston, C. M.; Zelenay, P. High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt. *Science* **2011**, *332*, 443–447.
- Wu, G.; Nelson, M. A.; Mack, N. H.; Ma, S. G.; Sekhar, P.; Garzon, F. H.; Zelenay, P. Titanium Dioxide-Supported Non-Precious Metal Oxygen Reduction Electrocatalyst. *Chem. Commun.* **2010**, *46*, 7489–7491.
- Wu, G.; Mack, N. H.; Gao, W.; Ma, S.; Zhong, R.; Han, J.; Baldwin, J. K.; Zelenay, P. Nitrogen-Doped Graphene-Rich Catalysts Derived from Heteroatom Polymers for Oxygen Reduction in Nonaqueous Lithium– O_2 Battery Cathodes. *ACS Nano* **2012**, *6*, 9764–9776.
- Chung, H. T.; Johnston, C. M.; Artyushkova, K.; Ferrandon, M.; Myers, D. J.; Zelenay, P. Cyanamide-Derived Non-Precious Metal Catalyst for Oxygen Reduction. *Electrochem. Commun.* **2010**, *12*, 1792–1795.
- Matter, P. H.; Zhang, L.; Ozkan, U. S. The Role of Nanostructure in Nitrogen-Containing Carbon Catalysts for the Oxygen Reduction Reaction. *J. Catal.* **2006**, *239*, 83–96.
- Nallathambi, V.; Lee, J.-W.; Kumaraguru, S. P.; Wu, G.; Popov, B. N. Development of High Performance Carbon Composite Catalyst for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells. *J. Power Sources* **2008**, *183*, 34–42.
- Lefevre, M.; Proietti, E.; Jaouen, F.; Dodelet, J. P. Iron-Based Catalysts with Improved Oxygen Reduction Activity in Polymer Electrolyte Fuel Cells. *Science* **2009**, *324*, 71–74.
- Byon, H. R.; Suntivich, J.; Shao-Horn, Y. Graphene-Based Non-Noble-Metal Catalysts for Oxygen Reduction Reaction in Acid. *Chem. Mater.* **2011**, *23*, 3421–3428.
- Li, Y.; Zhou, W.; Wang, H.; Xie, L.; Liang, Y.; Wei, F.; Idrobo, J.-C.; Pennycook, S. J.; Dai, H. An Oxygen Reduction Electrocatalyst Based on Carbon Nanotube-Graphene Complexes. *Nat. Nanotechnol.* **2012**, *7*, 394–400.
- Nallathambi, V.; Leonard, N.; Kothandaraman, R.; Barton, S. C. Nitrogen Precursor Effects in Iron-Nitrogen-Carbon Oxygen Reduction Catalysts. *Electrochem. Solid-State Lett.* **2011**, *14*, B55–B58.
- Serov, A.; Robson, M. H.; Artyushkova, K.; Atanassov, P. Templated Non-Pgm Cathode Catalysts Derived from Iron and Poly(Ethyleneimine) Precursors. *Appl. Catal. B: Environ.* **2012**, *127*, 300–306.
- Lai, L.; Potts, J. R.; Zhan, D.; Wang, L.; Poh, C. K.; Tang, C.; Gong, H.; Shen, Z.; Lin, J.; Ruoff, R. S. Exploration of the Active Center Structure of Nitrogen-Doped Graphene-Based Catalysts for Oxygen Reduction Reaction. *Energy Environ. Sci.* **2012**, *5*, 7936–7942.
- Parvez, K.; Yang, S.; Hernandez, Y.; Winter, A.; Turchanian, A.; Feng, X.; Müllen, K. Nitrogen-Doped Graphene and Its Iron-Based Composite as Efficient Electrocatalysts for Oxygen Reduction Reaction. *ACS Nano* **2012**, *6*, 9541–9550.
- Jasinski, R. New Fuel Cell Cathode Catalyst. *Nature* **1964**, *201*, 1212–1214.
- Gupta, S.; Tryk, D.; Bae, I.; Aldred, W.; Yeager, E. Heat-Treated Polyacrylonitrile-Based Catalysts for Oxygen Electroreduction. *J. Appl. Electrochem.* **1989**, *19*, 19–27.
- Wu, G.; Johnston, C. M.; Mack, N. H.; Artyushkova, K.; Ferrandon, M.; Nelson, M.; Lezama-Pacheco, J. S.; Conradson, S. D.; More, K. L.; Myers, D. J.; Zelenay, P. Synthesis-Structure-Performance Correlation for Polyaniline-Me-C Non-Precious Metal Cathode Catalysts for Oxygen Reduction in Fuel Cells. *J. Mater. Chem.* **2011**, *21*, 11392–11405.
- Proietti, E.; Jaouen, F.; Lefevre, M.; Larouche, M.; Tian, J.; Herranz, J.; Dodelet, J.-P. Iron-Based Cathode Catalyst with Enhanced Power Density in Polymer Electrolyte Membrane Fuel Cells. *Nat. Commun.* **2011**, *2*, 1–9.
- Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L. Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells. *ACS Nano* **2010**, *4*, 1321–1326.
- Subramanian, N. P.; Li, X.; Nallathambi, V.; Kumaraguru, S. P.; Colon-Mercado, H.; Wu, G.; Lee, J.-W.; Popov, B. N. Nitrogen-Modified Carbon-Based Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells. *J. Power Sources* **2009**, *188*, 38–44.
- Ferrandon, M.; Kropf, A. J.; Myers, D. J.; Artyushkova, K.; Kramm, U. I.; Bogdanoff, P.; Wu, G.; Johnston, C. M.; Zelenay, P. Multi-Technique Characterization of a Polyaniline-Iron-Carbon Oxygen Reduction Catalyst. *J. Phys. Chem. C* **2012**, *116*, 16001–16013.
- Wu, G.; Chen, Z.; Artyushkova, K.; Garzon, F. H.; Zelenay, P. Polyaniline-Derived Non-Precious Catalyst for the Polymer Electrolyte Fuel Cell Cathode. *ECS Trans* **2008**, *16*, 159–170.
- Wu, G.; Dai, C. S.; Wang, D. L.; Li, D. Y.; Li, N. Nitrogen-Doped Magnetic Onion-Like Carbon as Support for Pt Particles in a Hybrid Cathode Catalyst for Fuel Cells. *J. Mater. Chem.* **2010**, *20*, 3059–3068.
- Wu, G.; Nelson, M.; Ma, S. G.; Meng, H.; Cui, G. F.; Shen, P. K. Synthesis of Nitrogen-Doped Onion-Like Carbon and Its Use in Carbon-Based Coe Binary Non-Precious-Metal Catalysts for Oxygen-Reduction. *Carbon* **2011**, *49*, 3972–3982.
- Wu, G.; Chung, H. T.; Nelson, M.; Artyushkova, K.; More, K. L.; Johnston, C. M.; Zelenay, P. Graphene-Enriched Co_3S_2 -N-C Non-Precious Metal Catalyst for Oxygen Reduction in Alkaline Media. *ECS Trans.* **2011**, *41*, 1709–1717.
- Maldonado, S.; Morin, S.; Stevenson, K. J. Structure, Composition, and Chemical Reactivity of Carbon Nanotubes by Selective Nitrogen Doping. *Carbon* **2006**, *44*, 1429–1437.
- Pels, J. R.; Kapteijn, F.; Moulijn, J. A.; Zhu, Q.; Thomas, K. M. Evolution of Nitrogen Functionalities in Carbonaceous Materials During Pyrolysis. *Carbon* **1995**, *33*, 1641–1653.
- Wu, G.; Li, D. Y.; Dai, C. S.; Wang, D. L.; Li, N. Well-Dispersed High-Loading Pt Nanoparticles Supported by Shell-Core Nanostructured Carbon for Methanol Electrooxidation. *Langmuir* **2008**, *24*, 3566–3575.
- Pollak, E.; Salitra, G.; Soffer, A.; Aurbach, D. On the Reaction of Oxygen with Nitrogen-Containing and Nitrogen-Free Carbons. *Carbon* **2006**, *44*, 3302–3307.
- Fuge, G. M.; Rennick, C. J.; Pearce, S. R. J.; May, P. W.; Ashfold, M. N. R. Structural Characterisation of C_x Thin Films Deposited by Pulsed Laser Ablation. *Diamond Relat. Mater.* **2003**, *12*, 1049–1054.
- Lahaye, J.; Nansé, G.; Bagreev, A.; Strelko, V. Porous Structure and Surface Chemistry of Nitrogen Containing Carbons from Polymers. *Carbon* **1999**, *37*, 585–590.
- Wu, G.; Swaidan, R.; Li, D. Y.; Li, N. Enhanced Methanol Electro-Oxidation Activity of PtRu Catalysts Supported on Heteroatom-Doped Carbon. *Electrochim. Acta* **2008**, *53*, 7622–7629.
- Wu, G.; Artyushkova, K.; Ferrandon, M.; Kropf, A. J.; Myers, D.; Zelenay, P. Performance Durability of Polyaniline-Derived Non-Precious Cathode Catalysts. *ECS Trans.* **2009**, *25*, 1299–1311.
- Chung, H. T.; Won, J. H.; Zelenay, P. Active and Stable Carbon Nanotube/Nanoparticle Composite Electrocatalyst for Oxygen Reduction. *Nat. Commun.* **2013**, *10.1038/ncomms2944*.
- Wu, G.; More, K. L.; Xu, P.; Wang, H.-L.; Ferrandon, M.; Kropf, A. J.; Myers, D.; Johnston, C.; Zelenay, P. Carbon-Nanotube-Supported Graphene-Rich Non-Precious Metal Catalyst of Oxygen Reduction with Enhanced Performance Durability. *Chem. Commun.* **2013**, *49*, 3291–3293.
- Gojkovic, S. L.; Gupta, S.; Savinell, R. F. Heat-Treated Iron(III) Tetramethoxyphenyl Porphyrin Supported on High-Area Carbon as an Electrocatalyst for Oxygen Reduction. *J. Electrochem. Soc.* **1998**, *145*, 3493–3499.

- 41 Shao, Y.; Yin, G.; Gao, Y. Understanding and Approaches for the Durability Issues of Pt-Based Catalysts for Pem Fuel Cell. *J. Power Sources* **2007**, *171*, 558–566.
- 42 Wu, G.; Chen, Y.-S.; Xu, B.-Q. Remarkable Support Effect of Swnts in Pt Catalyst for Methanol Electrooxidation. *Electrochem. Commun.* **2005**, *7*, 1237–1243.
- 43 Wu, G.; Xu, B.-Q. Carbon Nanotube Supported Pt Electrodes for Methanol Oxidation: A Comparison between Multi- and Single-Walled Carbon Nanotubes. *J. Power Sources* **2007**, *174*, 148–158.
- 44 Wang, C.; Waje, M.; Wang, X.; Tang, J. M.; Haddon, R. C.; Yan, Y. S. Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes. *Nano Lett.* **2004**, *4*, 345–348.
- 45 Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.
- 46 Geng, D.; Yang, S.; Zhang, Y.; Yang, J.; Liu, J.; Li, R.; Sham, T.-K.; Sun, X.; Ye, S.; Knights, S. Nitrogen Doping Effects on the Structure of Graphene. *Appl. Surf. Sci.* **2011**, *257*, 9193–9198.
- 47 Calle-Vallejo, F.; Martinez, J. I.; Rossmeisl, J. Density Functional Studies of Functionalized Graphitic Materials with Late Transition Metals for Oxygen Reduction Reactions. *Phys. Chem. Chem. Phys.* **2011**, *13*, 15639–15643.
- 48 Kramm, U. I.; Herranz, J.; Larouche, N.; Arruda, T. M.; Lefevre, M.; Jaouen, F.; Bogdanoff, P.; Fiechter, S.; Abs-Wurmbach, I.; Mukerjee, S.; Dodelet, J.-P. Structure of the Catalytic Sites in Fe/N/C-Catalysts for O₂-Reduction in Pem Fuel Cells. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11673–11688.
- 49 He, Q.; Li, Q.; Khene, S.; Ren, X.; López-Suárez, F. E.; Lozano-Castello, D.; Bueno-López, A.; Wu, G. High-Loading Cobalt Oxide Coupled with Nitrogen-Doped Graphene for Oxygen-Reduction in Anion-Exchange Membrane Alkaline Fuel Cells. *J. Phys. Chem. C* **2013**, *117*, 8697–8707.
- 50 Gao, W.; Alemany, L. B.; Ci, L.; Ajayan, P. M. New Insights into the Structure and Reduction of Graphite Oxide. *Nat. Chem.* **2009**, *1*, 403–408.