

Performance Durability of Polyaniline-derived Non-Precious Cathode Catalysts

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This research has focused on performance durability of the newly-developed polyaniline (PANI)-derived non-precious metal cathode catalysts. These catalysts show high oxygen-reduction activity in electrochemical and fuel cell testing, reflected by the onset and half-wave ($E_{1/2}$) potentials of oxygen reduction in RDE testing of 0.90 V and 0.77 V, respectively. Best-performing catalysts also exhibit insignificant H_2O_2 yield of less than 1%. Catalyst performance in fuel cell testing strongly depends on the choice of nitrogen precursors, transition metals used, and carbon supports. As expected, catalyst stability is affected by the operating voltage of the fuel cell, with more stable performance observed at low operating voltage and open cell voltage, than at intermediate voltages. Physical and electrochemical characterization of the catalysts, also in the presence of hydrogen peroxide, has been carried out to provide insight into the origin of possible degradation mechanisms.

Introduction

The polymer electrolyte fuel cell (PEFC) has been considered an attractive and efficient power source for mobile and stationary applications. However, several performance and economic factors, such as limited lifetime, reliability, and cost, are presently hindering PEFC commercialization. Especially tasking are the lifetime requirements: up to 5000 operating hours for car commercial applications and up to 40,000 operating hours for stationary applications (1). Compared with other key fuel cell components, the durability of catalysts may be of the greatest significance for not only lengthening PEFC operation life, but also enhancing the reliability and reducing the total lifetime cost (gauged in US\$ $kW^{-1} h^{-1}$). In the case of carbon-supported Pt and Pt-alloy catalysts, much work has been done to explore possible degradation paths, which can now be divided into two categories: corrosion of carbon support and degradation of the catalytic site (2). The use of carbon with higher degree of graphitization and alloying Pt with other metals were both found to improve the catalyst durability to some extent.

It is generally believed that the large-scale practical application of fuel cells will be difficult to realize if the expensive platinum-based electrocatalysts for oxygen reduction reaction (ORR) cannot be replaced by other efficient, low-cost, and stable electrodes. As a result, the development of non-precious metal catalysts with high ORR activity and improved durability has become a major focus area for PEFC research as a possible way

of reducing the cost. To date, catalysts obtained by heat-treating precursors of transition metals, nitrogen, and carbon have been widely accepted as promising non-precious alternatives to Pt for the PEFC cathode. In particular, Dodelet and co-workers have invested a great effort in improving ORR performance of such catalysts by heating a ball-milled mixture of carbon support, phenanthroline, and ferrous acetate, first in argon, then in ammonia. Some of the resulting catalysts were found to generate current density equal to that of platinum-based cathode at a loading of $0.4 \text{ mg}_{\text{Pt}}/\text{cm}^2$ at a cell voltage of $\geq 0.9 \text{ V}$ (3). However, the durability of these catalysts has been insufficient for practical use (3). In general, the durability of the novel non-precious cathode catalysts is likely to be key for the viability of these catalysts in practical fuel cell systems (4).

In the past year, we have reported on several new non-precious ORR catalysts derived from heteroatomic polymers, such as polyaniline (PANI) and polypyrrol (PPy). These catalysts were synthesized by heat-treating a hybrid precursor material containing PANI or PPy, *in situ* polymerized onto conventional carbon black (Ketjen black EC-300J) in the presence of transition metals (Fe and/or Co) (5). In rotating disk (RDE) testing, the best performing PANI-derived catalysts give the onset and half-wave ($E_{1/2}$) ORR potentials of 0.90 V and 0.77 V, respectively. At the same time, the rotating ring-disk electrode (RRDE) studies reveal very good selectivity of these catalysts for the four-electron reduction, with H_2O_2 yields often below 1% (0.4% at 0.4 V for some Fe-based catalysts). In the present work, we systematically study the stability of such non-precious metal catalysts in liquid electrolyte (0.5 M H_2SO_4) and in fuel cells as a function of precursors used (nitrogen precursors, transition metals and carbon supporting materials) and cell operating conditions. Possible degradation paths for non-precious metal catalysts are also investigated using advanced surface-analysis and structural characterization methods.

Experimental Details

Catalyst synthesis

Carbon support, typically a commercial Ketjen carbon black EC 300J, with BET surface area of about $950 \text{ m}^2\text{g}^{-1}$ and good corrosion resistance, was treated in an aqueous HCl solution for 24 hours to remove any potential metal impurities. For comparison, commercially available multi-walled carbon nanotubes (MWNTs) (BET surface area: $\sim 230 \text{ m}^2\text{g}^{-1}$, Cheap Tubes Inc, USA) were explored as an alternative support for the synthesis of PANI-derived non-precious metal catalysts.

In a typical approach, carbon support was first ultrasonically dispersed in 0.5 M HCl solution. The suspension was kept below 10°C while the aniline and the oxidant, ammonium peroxydisulfate in 0.5 M HCl, was added drop-wise. After constant stirring for 12 hours to allow aniline to fully polymerize, the transition metal salts, such as FeCl_3 or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, were added to the suspension to form complex with polyaniline or polypyrrole. The suspension containing carbon, polymer and transition metal(s) was vacuum-dried using a rotary evaporator. The subsequent heat-treatment was performed at 900°C in an inert atmosphere of a nitrogen gas for 1 hour. The pyrolyzed sample was then pre-leached in 0.5 M H_2SO_4 at 80°C for 8 hours to remove unstable and inactive species from catalyst, and then thoroughly washed in de-ionized water (6).

RDE/RRDE testing

Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) testing was carried out in 0.5 M H_2SO_4 at a rotating disk speed of 900 rpm and room temperature

using carbon-rod counter electrode and Ag/AgCl (3 M NaCl) reference electrode. Performance data reported in this paper were recorded at a total catalyst loading of 0.6 mg cm^{-2} . As mentioned below, the ring-determined yields of hydrogen peroxide were generally low at the loading used, below 0.5% for the best performing catalysts. Moderate increase in the peroxide yield could be seen at lower catalyst loading, but that increase was significantly less pronounced than usually observed with non-precious metal catalysts. For example, lowering PANI-Fe-C loading from 0.6 mg cm^{-2} to 0.1 mg cm^{-2} led to an increase in H_2O_2 yield from 0.5% to 1.4% at 0.4 V (vs. NHE).

Fuel cell testing

Non-precious metal catalysts were tested at the fuel cell cathode for ORR activity and durability under PEFC operating conditions. Catalyst “inks” were prepared by ultrasonically mixing catalyst powders with Nafion[®] solution for four hours. Cathode “inks” were applied to the gas diffusion layer (GDL, ELAT LT 1400W, E-TEK) by successive brushing until the cathode catalyst loading of $\sim 4 \text{ mg cm}^{-2}$ was reached. The Nafion[®] content in the dry catalyst was maintained at around 30 wt%. A commercially available Pt-catalyzed cloth gas-diffusion layer (E-TEK, 0.25 mg cm^{-2} Pt) was used at the anode without any further processing.

The cathode and anode were hot-pressed onto two separate pieces of a Nafion[®] 1135 membrane, later pressed together to form a two-layer membrane-electrode assembly (MEA). This approach minimized the risk of a possible cross-contamination of the cathode with platinum from the anode and also facilitated *post mortem* characterization of individual fuel cell electrodes. The geometric area of the MEA was 5.0 cm^2 . Fuel cell testing was carried out in a single cell with single-serpentine flow channels. Pure hydrogen and air/oxygen, humidified at 85°C , were supplied to the anode and cathode at a flow rate of 200 and 600/400 mL/min, respectively. Both electrodes were maintained at the same backpressure of 30 psig (~ 40 psi absolute pressure at the Los Alamos altitude). Fuel cell polarization plots were recorded using standard fuel cell test stations (Fuel Cell Technologies Inc.). Polarization data obtained with the two-membrane sandwich were corrected for the excess resistance of one of the membranes, which means that all fuel cell polarization data presented in this paper correspond to an MEA with a single Nafion[®] 1135 membrane. Fuel cell life testing was carried out in the constant voltage mode.

Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed at the University of New Mexico on a Kratos Axis Ultra spectrometer using an Mg $K\alpha$ X-ray source ($h\nu = 1253.6 \text{ eV}$), with emission voltage of 12 kV and emission current of 20 mA. Both low resolution survey spectra and high resolution N 1s spectra were acquired. All XPS data were charge-referenced to aromatic carbon at 284.7 eV. X-ray absorption spectroscopy (XAS) measurements at the energy of Fe K-edge were carried out at Beamline 12 the BM of Advanced Photon Source at Argonne National Laboratory. The X-ray beam was focused through a Pt-coated mirror which also removed higher harmonic fraction of the photons. A multiple-element germanium solid-state detector (Canberra) was used to collect $K\alpha$ X-ray fluorescence signals from Fe in the PANI-derived catalysts.

Results and Discussion

Effect of the nitrogen precursor

While the ORR mechanism on various heat-treated catalysts has been the subject of an ongoing discussion, there is little doubt that the ORR performance of the catalysts is strongly dependent on the structure of the nitrogen precursor. As demonstrated previously (5), catalysts derived from heteroatomic polymers show higher activity than catalysts obtained from simple amines, such as ethylenedimine. In this work, this comparison is extended onto polyaniline (PANI) and polypyrrole (PPy) as nitrogen precursors in the catalyst synthesis. Electrochemical data, obtained using a rotating disk electrode (RDE), show lower onset potential (higher overpotential) for oxygen reduction with PPy-Fe-C (~ 0.85 V vs. NHE) than PANI-Fe-C (~ 0.91 V vs. NHE) (7). Rotating ring-disk electrode (RRDE) results further indicate better selectivity of the PANI-derived catalyst towards the four-electron oxygen reduction. H_2O_2 yield at 0.4 V remains below 1% with the best-performing PANI-derived catalysts.

In good agreement with electrochemical experiments, fuel cell polarization data in **Figure 1a** confirm higher activity of the PANI-Fe-C catalyst at high cell voltages (> 0.55 V). On the other hand, a better dispersion of the PPy-derived catalyst is a likely reason for better performance of PPy-Fe-C at lower voltages, where oxygen reduction becomes mass-transport limited. Long-term fuel cell performance of both catalysts at a constant voltage of 0.4 V is depicted in **Figure 1b**. While PPy-Fe-C shows significantly better activity early in the life test, its performance drops below that of PANI-Fe-C in less than 100 hours. PANI-Fe-C exhibits very good stability during a 200-hour life test shown in Figure 1b. The difference in the two catalysts' durability may be caused by differences in the nature of the active ORR sites, water tolerance and/or other factors. There are indications that the aromatic character of the precursor is beneficial to stabilizing interaction of the metal and nitrogen imbedded in the graphitic carbon structure during the heat-treatment, leading to the formation of more stable active reaction sites (8). This is one possible reason for the much better stability of PANI-derived catalysts.

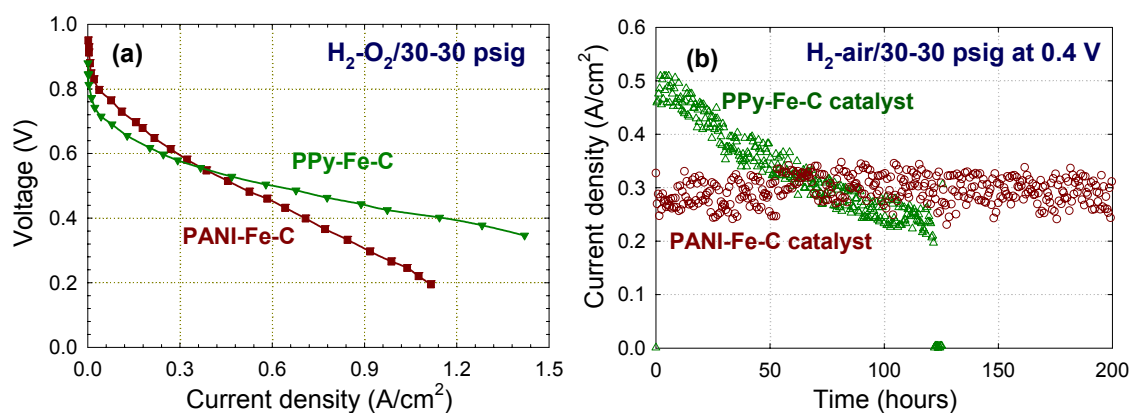


Figure 1. Fuel cell performance of PANI- and PPy-derived catalysts: (a) polarization plots, (b) life tests. Cell temperature 80°C ; anode – 0.25 mg cm^{-2} Pt on a woven-web GDL (E-TEK), 30 psig H_2 ; cathode – catalyst loading 4 mg cm^{-2} ; membrane – Nafion[®] 1135.

Effect of the transition metal

It has been demonstrated that iron and cobalt are more efficient than other transition metals in inducing high activity in ORR catalysts (9). Previously, we have shown the effect of the metal on the activity and four-electron selectivity PANI-derived catalysts using Co, Fe and mixed FeCo (Fe-to-Co ratio of 3:1) precursors (5). While the introduction of nitrogen significantly improves the activity of heat-treated carbons, it is the addition of transition metal precursors that leads to a dramatic enhancement in the catalyst performance, both in terms of the current generated and four-electron selectivity. The RDE half-wave potential measured with PANI-derived catalyst increases from 0.51 V in the absence of Fe to 0.77 V in the presence of the metal. This increase in ORR activity of PANI-Fe-C is accompanied by an approximately 30-fold drop in H₂O₂ yield, from 15% to 0.5% at 0.4 V. The effect of Co, although less pronounced than that of Fe, is also significant, resulting in the half-wave ORR potential of 0.70 V and hydrogen peroxide yield of 5%.

Initial fuel cell performance and performance durability of three different PANI-derived catalysts are shown in **Figure 2**. In good agreement with electrochemical measurements, the addition of Fe results in a much greater improvement in the PANI-C catalyst performance than the addition of Co. It should be noted, however, that the best performing cathode catalyst in fuel cell testing is PANI-Fe₃Co-C that shows the best combination of high activity and long-term performance stability for up to ~650 hours. Unlike PANI-Fe₃Co-C, the PANI-Fe-C catalyst suffers from a gradual performance loss at times longer than 200 hours. In turn, PANI-Co-C shows good stability for 180 hours but significantly lower activity than Fe-containing catalysts. These results indicate that together Fe and Co yield PANI-derived catalysts with the best overall ORR activity and performance stability in fuel cell testing.

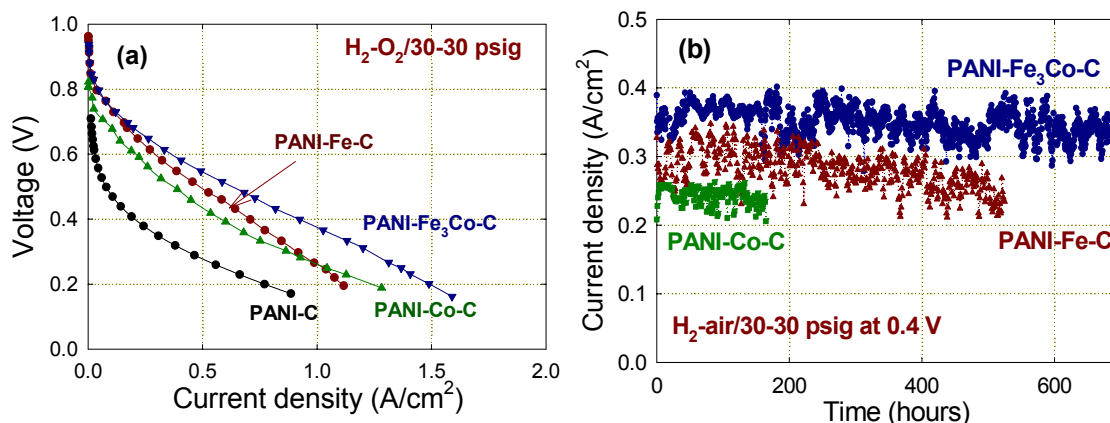


Figure 2. Effect of metals used in the synthesis of PANI-derived non-precious catalysts on fuel cell performance: (a) initial polarization curves, (b) life tests. Cell temperature 80°C; anode – 0.25 mg cm⁻² Pt on a woven-web GDL (E-TEK), 30 psig H₂; cathode – catalyst loading 4 mg cm⁻²; membrane – Nafion[®] 1135.

Effect of carbon support

Thanks to their high electronic conductivity, good corrosion resistance, high specific-surface area, and diminishing price, carbon nanotubes have been considered for a possible replacement of traditional carbon blacks in fuel cells electrocatalysts (10). A

number of earlier studies have shown that Pt, loaded on multi- and single-walled carbon nanotubes, exhibits high activity for methanol electro-oxidation (11) and oxygen reduction (12). In this work, carbon nanotubes have been used as an alternative support for Ketjen carbon black EC-300J in the synthesis of PANI-derived ORR catalysts.

Initial fuel cell polarization plots and life test data obtained with PANI-Fe catalyst supported on Ketjen black and multi-walled carbon nanotubes (MWNTs) are given in **Figure 3a** and **3b**. Fuel cell polarization plots show in both cases nearly identical performance of the PANI-Fe catalyst up to the highest current densities (below 0.35 V), in which range MWNTs offer a noticeable performance advantage. That performance advantage is likely caused by the more open structure of the nanotube support relative to that of carbon black.

In addition to offering mass-transfer benefits at high current densities, MWNT-supported catalyst shows virtually no performance degradation for more than 500 hours at a constant cell voltage of 0.40 V. This represents an improvement over the Ketjen black-supported catalyst that exhibits performance loss at operating times exceeding 200 hours (cf. Figures 2b and 3b).

CNT supports promise to offer an improved fuel cell performance over that of traditional carbon black. There is no energy loss when electrons transfer along the tubes in CNT electrode due to their high electronic conductivity. Since CNTs do not possess micro-porosity, except in the interior of the tube, higher gas permeability is expected, and the active catalytic sites on the nanotubes are likely to be easily accessible (13). Also, water removal within the electrode should be facilitated, an important advantage, especially in the case of non-precious catalyst layers approaching 100 μm in thickness. Higher durability of the MWNT-supported PANI-Fe catalyst may be related to the higher degree of graphitization of MWNTs, leading to enhanced corrosion resistance and improved stability of the ORR active site(s) (14).

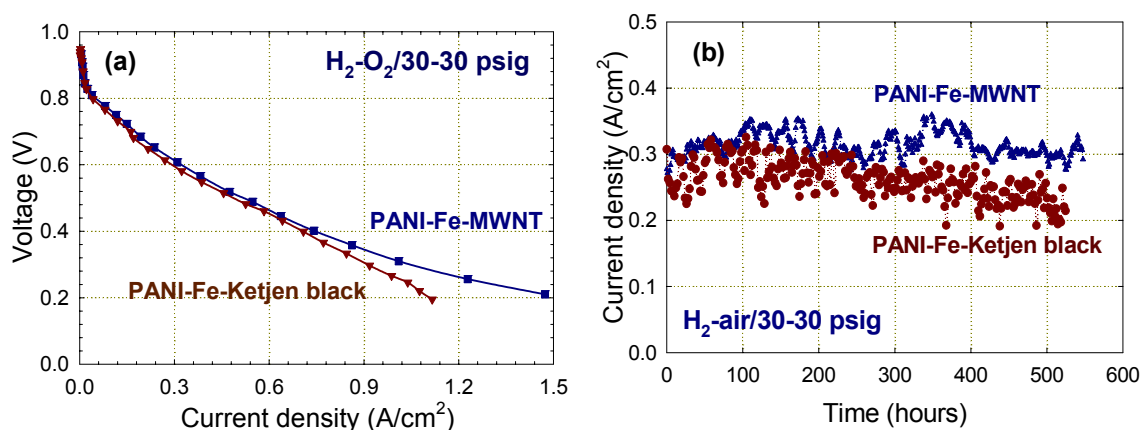


Figure 3. Fuel cell performance of PANI-Fe catalyst obtained using MWNTs and Ketjen black as supports: (a) initial polarization plots, (b) life tests. Cell temperature 80°C; anode – 0.25 mg cm⁻² Pt on a woven-web GDL (E-TEK), 30 psig H₂; cathode – catalyst loading 4.0 mg cm⁻²; membrane – Nafion® 1135.

Catalyst performance at the open cell voltage

Variations in the fuel voltage (cathode potential) are likely to affect several key properties of the cathode catalyst, including the oxidation state of both the active species and carbon, and hydrophilicity/hydrophobicity of the catalytic layer (1). In this work, we

have tested cathode performance at different operating fuel cell voltage, including the open cell voltage (OCV), corresponding to the highest potential experienced by the cathode catalysts under regular fuel cell operation.

A life test of an H₂-air fuel cell operating with PANI-Fe₃Co-C for 100 hours is shown in **Figure 4**. Except from some variations at the beginning and the end of the 100-hour period, the OCV value remains unchanged at 0.90 V, indicating good stability of the catalyst. Higher OCV values, typically close to ~0.95 V, can be reached on pure oxygen in an H₂-O₂ fuel cell. Stability testing of the PANI-Fe₃Co-C catalyst under these conditions is currently in progress, as is long-term performance testing at voltages other than OCV and 0.4 V, shown in Figures 1b, 2b, and 3b above.

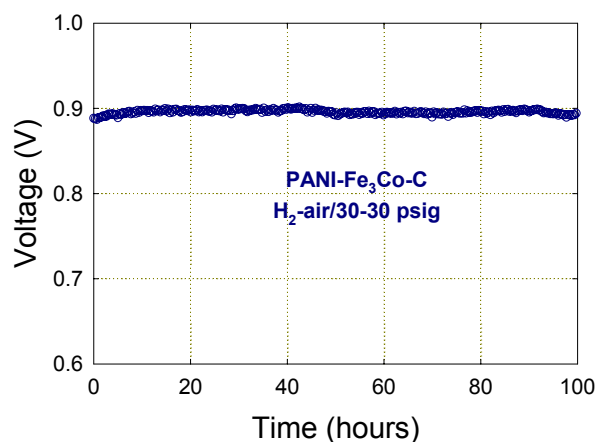


Figure 4. Long-term stability test of a PANI-Fe₃Co-C catalyst at OCV. Cell temperature 80°C; anode – 0.25 mg cm⁻² Pt on a woven-web GDL (E-TEK); cathode – catalyst loading 4.0 mg cm⁻²; membrane – Nafion[®] 1135.

Electrochemical and physical characterization

Cyclic voltammetry.—A pair of redox peaks at *ca.* 0.64 V is the most distinct feature of the cyclic voltammogram of a PANI-Fe-C catalyst in 0.5 M H₂SO₄ shown in **Figure 5**. Once the voltammogram reaches stability after ~10 initial cycles required for full wetting of the catalyst phase, its shape does not change with further cycling for as many as up to 200 cycles. This result indicates a stable nature of the species involved in the redox process. The width of both the anodic and cathodic peaks at half-height is on the order of 100 mV, very close to a theoretical value of 96 mV, expected for a reversible one-electron process involving surface-confined species (15).

The redox peaks at *ca.* 0.50-0.60 V in the voltammograms of carbon-rich materials are often assigned to one-electron oxidation/reduction of the quinone-hydroquinone couple. Because all PANI-Fe-C catalysts in this study were heat-treated at 900°C in nitrogen gas, the quinone groups should have undergone oxidation to CO and CO₂ (16). It is possible, however, that such groups can form later, during electrochemical analysis.

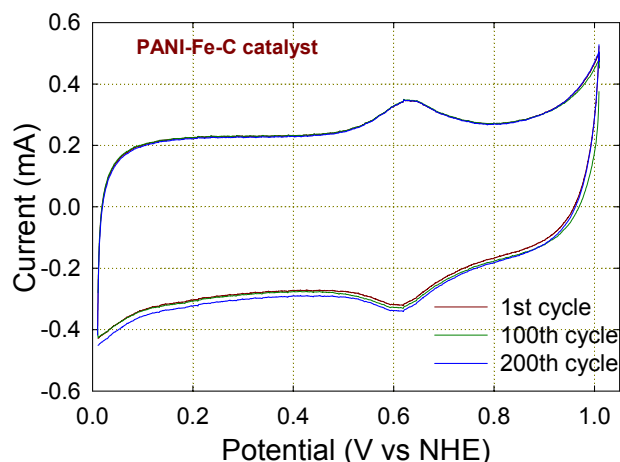


Figure 5. Cyclic voltammetry of a PANI-Fe-C catalyst in N_2 -saturated 0.5 M H_2SO_4 . Sweep rate: 10 mV/s.

Alternatively, the reversible redox couple at 0.64 V could be linked to the Fe^{3+}/Fe^{2+} system. In support of the latter hypothesis, no reversible redox couple is observed with Fe-free catalysts, such as PANI-C and PANI-Co-C, synthesized under the identical thermal treatments as the Fe-containing catalysts.

X-ray absorption.—Iron-containing species in the PANI-Fe-C catalyst were studied *in-situ* in 0.5 M H_2SO_4 using X-ray absorption spectroscopy at the Fe K-edge. The results of experiments conducted during potential scans of the PANI-Fe-C catalyst from 0.87 V to 0.24 V, and back, are shown in **Figure 6**.

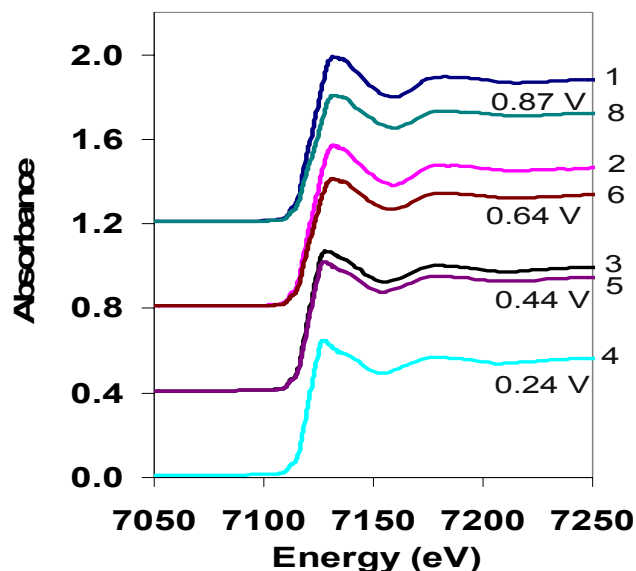


Figure 6. Representative *in-situ* electrochemical XAFS spectra of PANI-Fe-C catalyst in N_2 -saturated 0.5 M H_2SO_4 as a function of potential (vs. NHE). Numbers to the right of spectra indicate sequence in which spectra were taken. (Note: not all scans in the sequence are shown).

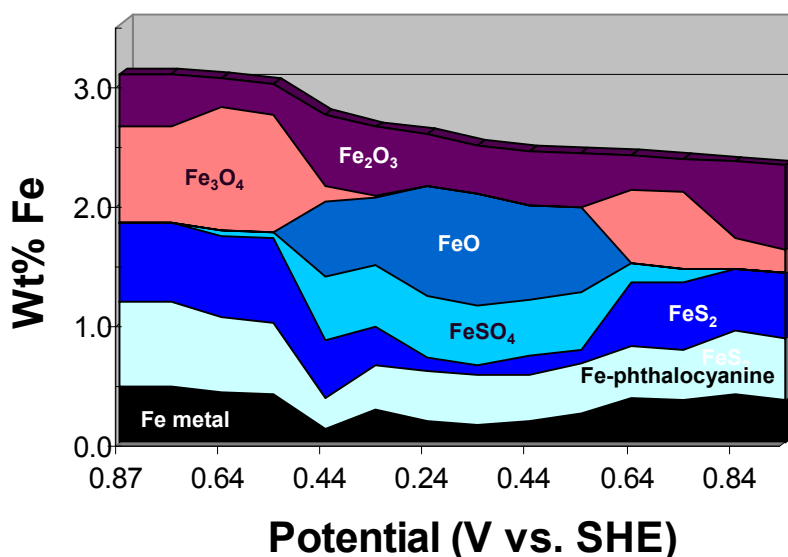


Figure 7. Coordination environment and oxidation state of Fe species in PANI-Fe-C as a function of potential in 0.5 M H₂SO₄, as determined from linear combination fitting of Fe K-edge X-ray absorption spectra to Fe standards.

The near edge region of these spectra (7105 to 7170 eV) were fit, using the linear combination algorithm of the Athena software (17) based on the IFEFFIT code (18), to the spectra for a suite of Fe-containing standards (iron (II) phthalocyanine, Fe₃O₄, Fe₂O₃, FeO, FeSO₄, FeS₂, FeS, and Fe metal). The results of this fitting, as a function of cell potential, are shown in **Figure 7**.

These results show that one of the major components of the as-synthesized, acid-treated catalyst is an Fe species in an Fe phthalocyanine-like coordination environment: Fe coordinated to four nitrogens. The quantity of this catalyst component remains relative constant over the potential range studied. The fitting results also show that a major component of the as-synthesized catalyst is Fe in an Fe₃O₄-like coordination environment and oxidation state (Fe³⁺/Fe²⁺). This species is reversibly reduced to FeO (Fe²⁺ species) at 0.44 V to 0.24 V. This reduction is accompanied by a loss of Fe from the electrode. This loss is consistent with the higher solubility of Fe²⁺ species in acid solutions (19). The species with an Fe₂O₃-like coordination environment appears to be relatively stable against reduction, indicating that it is either protected from the electrolyte or is part of a larger more stable Fe³⁺ complex.

While reversible changes in the oxidation state of Fe with potential correspond well with the reversible voltammetric peak at ~0.64 V (Figure 5), there is no direct evidence that the two features are indeed correlated, as XAFS at the Fe K-edge is not a surface-specific technique. In-situ and ex-situ experiments, involving membrane-electrode assemblies (MEAs) and additional characterization methods, are needed for a deeper insight into the origin of the reversible redox couple, its effect on catalyst performance and, ultimately, the role it may play in the active ORR site itself.

XPS analysis.—XPS analysis was used in this work to determine changes to the composition and oxidation state of PANI-Fe-C during fuel cell operation at a constant voltage 0.4 V for 500 hours (Figure 1b). A summary of changes to the content of all elements except iron (which proved too difficult to assess due to the interference from Fe present in Nafion[®]) are given in **Table 1**. The data in that table attest to significant

increase in the oxygen content during the life test. That increase is almost certainly caused by the oxidation of carbon and or nitrogen functionalities (see below). Oxygen-containing groups, e.g., carboxyl, carbonyl, hydroxyl, and phenol, formed on the carbon surface are likely to both decrease the conductivity of catalysts and weaken the interaction between support and active sites (2).

Table 1: XPS analysis of PANI-Fe-C before and after a 500-hour fuel cell life test

Content, at%:	C	N	O	S
As-prepared	89.4	6.3	2.7	0.7
After life test (Nafion [®] -corrected)	79.2	5.6	10.7	0

While the role of transition metal in the formation and operation of the active catalytic site is subject to an ongoing debate, various nitrogen functional groups, pyridinic, pyrrolic and quaternary nitrogen, attached to the carbon surface, are generally accepted as important to ORR activity in non-precious catalysts. The N 1s XPS spectra of as-synthesized and fuel-cell tested samples of PANI-Fe-C are shown in **Figure 8**. Lorentzian line shape was utilized in the curve fit using individual peaks of constrained width and shape. A linear background subtraction was used for quantification of N 1s spectra.

It has been established that, following heat-treatment at temperatures in excess of 700°C, N 1s peaks can be assigned to four nitrogen species: pyridinic N (398.6 ± 0.3 eV), pyrrolic N (400.5 ± 0.3 eV), quaternary N (401.3 ± 0.3 eV) and N-"O" (402-405 eV) (19,20). Although the exact composition of N-"O" is unclear at this point, the symbol is used here denotes an oxidized nitrogen group (20), most likely pyridine oxide (21).

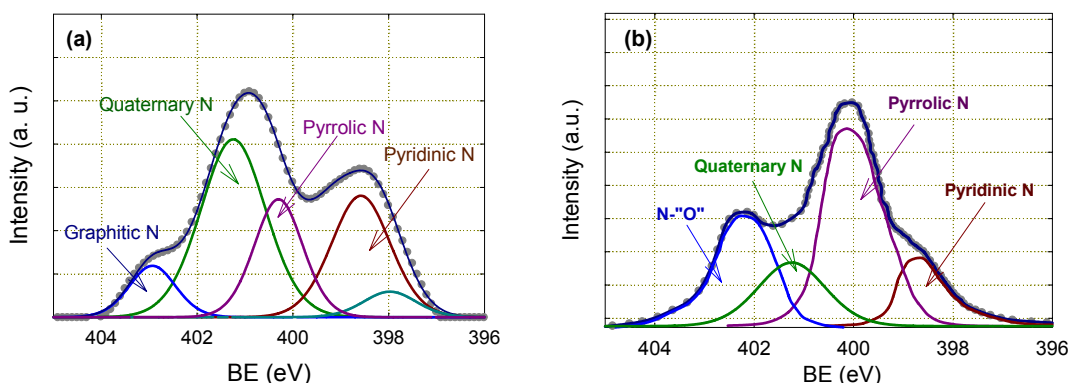


Figure 8. N 1s XPS of PANI-Fe-C catalyst: (a) before and (b) after fuel cell testing for 500 hours.

XPS of an as-synthesized PANI-Fe-C catalyst reveals three dominant peaks at 398.6, 400.5 and 401.3 eV, which can be assigned to the pyridinic, pyrrolic and quaternary nitrogen, respectively. Beside the three main nitrogen species, two minor peaks at 398.0 and 402.9 eV were observed and usually attributed to imine-like structure and graphitic nitrogen, respectively. But, the shift of this imine-like peak to lower BE values in comparison with original PANI sample (22) may indicate a different environment of imine within the pyrolyzed PANI-Fe-C sample. Also, peak at 402.9 eV appears at the same energy spectrum range of N-"O" making the unambiguous identification impossible

(23). Fuel cell operation results in a decrease of the pyridinic nitrogen and increase of the pyridine oxide peak at 402.2 eV. XPS data imply that pyridinic nitrogen is likely involved in the ORR process site, in addition to pyrrolic nitrogen, claimed earlier to be responsible for the unique activity of Fe-containing catalysts (5). It is, however, the pyridinic nitrogen that can be predominantly correlated with the performance loss of the PANI-Fe-C catalyst during prolonged fuel cell operation. That loss appears to be directly related to the oxidation of the pyridinic nitrogen and formation of an inactive oxide. The performance loss thus occurs without a change in the total nitrogen content in the catalyst (Table 1). While fuel cell operation results in little, if any, change in the content of pyrrolic nitrogen, a shift to lower binding energy in the pyrrolic peak (from 400.5 to 400.2 eV) may be indicative of a change in the activity of those ORR sites that involve pyrrolic nitrogen, coordinated to Fe (5).

Peroxide influence.—Despite the generally low H_2O_2 yields measured with PANI-derived catalysts, it is possible that active ORR sites can be affected by hydrogen peroxide (24). Also, H_2O_2 may form locally at large quantities as a result of complex process occurring at the three-phase interface in fuel cell cathode, additionally involving variations of temperature, humidity and O_2 concentration.

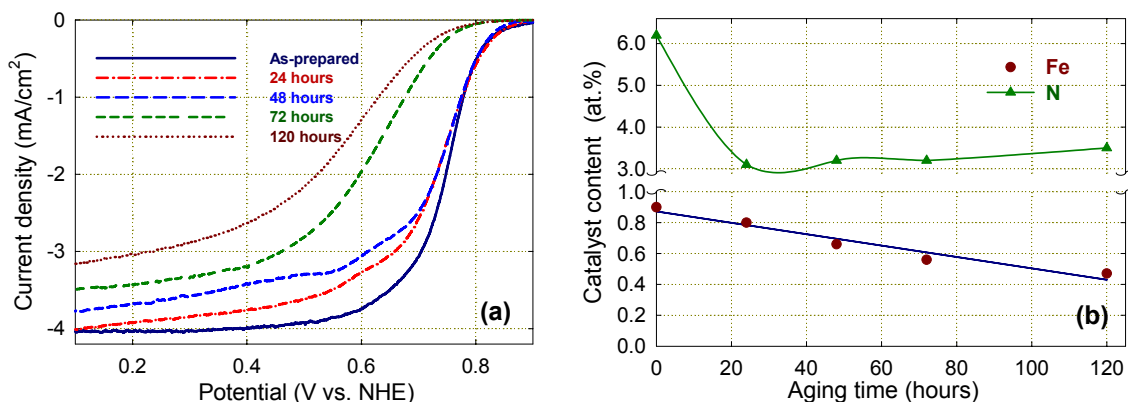


Figure 9 Effect of aging time in 10% H_2O_2 solution on the activity of PANI-Fe-C catalyst: (a) RDE tests and (b) Fe and N content determined by XPS analysis.

The effect of H_2O_2 on catalytic activity of PANI-Fe-C catalyst has been studied as a function of time in 10% H_2O_2 solution at 80°C (**Figure 9a**). Exposure to such large amounts of peroxide leads to significant negative shift in the onset and half-wave potentials in RDE testing. The change in the Fe and N content in the catalyst as a function of time of exposure to H_2O_2 is given in **Figure 9b**. While Fe content steadily decreases with time, the N content stabilizes after a sharp initial drop. The difference in the behavior of the two elements may be indicative of a better stability of nitrogen than iron in the bulk of the catalyst particles. In either case, the results show that the highly-active ORR sites cannot survive in the peroxide-rich environment.

Conclusions

In the present work, performance durability of PANI-derived non-precious catalysts for oxygen reduction was studied as a function of nitrogen precursors, transition metal precursors and carbon materials used in the catalyst synthesis. Also studied was the effect of the fuel cell voltage (0.4 V vs. OCV).

PANI offers obvious advantage over PPy in the synthesis of more durable ORR catalyst. The unique properties of PANI-derived catalysts may be caused by the aromatic character of polyaniline, resulting in a stronger bond between the catalytically active species and the carbon support. Combining Fe and Co leads to further improvement in the catalyst stability, highlighted by a 650-hour life test of a PANI-Fe₃Co-C catalyst without any significant performance loss.

The use of carbon nanotubes instead of carbon black as a catalyst support results in a better fuel cell performance at high current densities. This is likely related to more effective mass transport of oxygen and water in a thick cathode catalyst layer. In turn, the durability improvement observed with MWNT-supported catalyst may be caused by higher degree of graphitization of nanotubes relative to carbon blacks.

A reversible redox process was identified in voltammetric experiments involving Fe-containing catalysts. The potential of that process correlates well with the potential of a change in state of Fe detected in the in-situ electrochemical X-ray absorption experiments. Although insufficient for directly assigning the redox process to the surface Fe, this correlation provides strong indication that iron may be involved in the ORR site.

Degradation of non-precious catalysts was explored using advanced surface-analysis and structural-characterization methods. Performance loss of PANI-derived catalyst, observed at high fuel cell voltages, may be related to the oxidation of pyridinic nitrogen. Experiments in the presence of peroxide show that exposure to H₂O₂ has a detrimental effect on long-term performance stability of PANI-derived catalysts.

Acknowledgments

The authors are grateful to Dr. Jerzy Chlistunoff for very helpful discussions. Financial support of the DOE-EERE Hydrogen, Fuel Cells and Infrastructure Technologies Program as well as Los Alamos National Laboratory through Laboratory-Directed Research and Development program (LDRD) is gratefully acknowledged.

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