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A Surface Modification Route to Nonprecious Metal Fuel Cell Catalysts

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Nonprecious metal oxygen reduction reaction catalysts have been prepared via a simple chemisorption-based methodology. First, an aminosilane was chemically attached to a carbon surface, followed by coordination of iron and subsequent high temperature pyrolysis. Catalysts were prepared from a series of mono, di, and triaminosilanes. Physical and electrochemical properties of these catalysts were studied using inductively coupled plasma optical emission spectroscopy, X-ray photoelectron spectroscopy, and rotating ring-disk electrode cells. Maximum catalytic activity was achieved for samples prepared from the triaminosilane combined with a more disordered carbon black. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3283100] All rights reserved.

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Platinum is presently the best catalyst available for the reduction of oxygen at the fuel cell cathode. As a consequence of the slow reaction kinetics surrounding the oxygen reduction of platinum, a large active catalytic area of platinum is required to maintain high current densities. Impregnating a high surface area carbon support with platinum nanoparticles significantly reduces the amount of platinum needed, though this still constitutes 40% of the cost of a fuel cell.¹ Not only is platinum expensive, but it is also rare. Platinum reserves are likely to deplete in the event that the world energy economy begins a large-scale shift toward polymer electrolyte membrane fuel cells. If the technology is to be made materially sustainable, platinum will have to be replaced with more readily available metals.

Iron-nitrogen complexes have been investigated toward a possible activity in oxygen reduction. There have been numerous papers about the synthesis of Fe–N/C catalysts, with the synthetic methods falling into two main categories. The first and most common method is the physisorption of iron (or cobalt) and nitrogen-containing precursors on a carbon support, followed by pyrolysis at temperatures between 600 and 1000°C. A vast number of metal precursors, carbon supports, and nitrogen sources have been investigated and are summarized in a couple of recent reviews.^{2,3} The other category is physical vapor deposition, which has been used primarily by Dahn's group.^{4,9} In this method, Fe (or Co) and carbon is cosputtered in a reactive nitrogen plasma magnetron onto variable substrates, which are subsequently heat-treated to induce catalytic activity. The catalytic activity is highly dependent on the nitrogen content achieved after heat-treatment, regardless of the synthetic method.

The exact structure of the catalytically active site is not exactly known. However, it is presently believed to be Fe (or Co) coordinated to pyridinic-type and pyrrolic-type nitrogen sites that are embedded into the carbon support at the edge of the basal planes,¹⁰ with the pyridinic type believed to be associated with the highest activity. More recent work from Dodelet's group further suggests that iron actually bridges two graphitic sheets via nitrogen coordination.¹¹⁻¹³

Surface modification of electrode structures using organosilane derivatives has been extensively used to endow an electrode surface with desired functionalities.¹⁴ High surface area carbon blacks possess surface oxygen functional groups on their surface through which organosilanes can chemisorb, forming robust linkages. Such methodologies have been employed in applications such as sensors, chemically modified electrodes, and modified fuel cell supports.¹⁵⁻¹⁷

Here we have grafted nitrogen-containing functional groups to a carbon black surface via a series of aminosilanes shown in Fig. 1. After coordination of iron, samples were pyrolyzed to induce cata-

lytic activity. One major advantage of this method is that chemisorption is more specific than physisorption, thereby allowing the attachment to occur at the end of the basal plane. This places the nitrogen and iron in the location where active sites can form, as opposed to in the middle of the graphitic sheets where active sites are not believed to form. The impact of carbon black properties, heat-treatment temperature, and aminosilane selection has been investigated and was related to the oxygen reduction reaction (ORR) activity.

Experimental

Catalysts synthesis.- Modification was performed by using a combination of two carbon blacks and three aminosilanes. The carbon blacks used in this study were Vulcan XC72 and Black Pearls 2000 (Cabot) and are hereafter referred to as V and BP, respectively. According to the manufacturer, the specific surface areas of V and BP carbons were 250 and 1500 m^2/g , respectively. The three aminosilanes used for individual modifications were 3-aminopropyltrimethoxysilane (97%, Sigma), N-[3-(trimethoxysilyl)propyl]ethylenediamine (97%, Sigma), and N'-[3-(trimethoxysilyl)-propyl] diethylenetriamine (technical grade, Sigma), referred to hereafter as N1, N2, and N3, respectively. Carbon black was modified with an aminosilane using a procedure similar to that reported by Easton and Pickup.¹⁸ Approximately 500 mg of dry carbon black was placed in a 200 mL round bottom flask. The system was sealed with a septum and placed under an inert nitrogen atmosphere. To this, 50 mL of anhydrous dichloromethane (Sigma Aldrich) and 5 mL of aminosilane were added via a syringe. Keeping the system under inert atmosphere, the mixture was allowed to stir for 2 h, after which the modified carbon was collected via suction filtration, washed several times in dichloromethane, and finally dried for 30 min at 110°C.

Iron coordination.— Approximately 400 mg of the dried surfacemodified carbon was ground to a powder with a mortar and pestle and placed in a conical flask along with 20 mL of 10 mM FeCl₃ (aq). This suspension was allowed to sit for 48 h to allow time for the iron to coordinate to the amino functional groups. After 2 days, the suspension was filtered over a sintered glass funnel, washed with deionized water, and collected. This material was then dried at 110°C for 1 h and ground to a fine powder via a mortar and pestle. The complete uptake of Fe from the solution would result in a final product with a maximum Fe content of ca. 2 wt %.

Heat-treatment procedure.— Approximately 75 mg of catalyst material was placed in an alumina boat and inserted into a tube furnace (Barnstead/Thermolyne 21100). Samples were heated under flowing argon at a rate of 20° C/min up to the annealing temperature where they were held for 2 h.

Sample nomenclature.— To clearly refer to the specific combinations of carbon support, aminosilane, Fe, and heat-treatment temperatures, a short hand nomenclature was developed. For example, BP-N2-Fe-850 refers to a catalyst produced using a Black Pearls carbon modified with N2, with Fe coordinated that has been heat-

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Figure 1. (Color online) The chemical structures of the N1, N2, and N3 aminosilanes used in this work.

treated at 850°C. Similarly, V-N3-Fe-700 refers to a catalyst produced using a Vulcan XC72 carbon modified with N3, with Fe coordinated that has been heat-treated at 700°C.

Electrochemical measurements.— Catalyst ink preparation.— Electrochemical measurements were obtained through the creation and analysis of electrode inks. A series of inks were prepared by dispersing ca. 10 mg of catalyst in 500 μ L of solution containing Nafion, water, and isopropyl alcohol. Ink (4 μ L) was deposited onto the glassy carbon disk surface (5 mm in diameter) of a rotating ring-disk electrode (RRDE) using a microsyringe. The deposited ink was allowed to air-dry for 30 min before electrochemical measurements were performed.

The electrocatalytic behavior of each deposited ink was studied using cyclic voltammetry (CV) with an RRDE. The RRDE consisted of an ink-coated glassy carbon disk (5 mm diameter) surrounded by a Pt ring (7.5 and 8.5 mm inside and outside diameters, respectively). Measurements were made in a one-compartment cell equipped with a Pt wire counter electrode and a saturated calomel electrode (SCE) reference electrode. The potential of the SCE reference electrode was calibrated vs the reversible hydrogen electrode (RHE). All the data presented in this work were corrected to the RHE potential. Measurements were made at room temperature using 0.5 M H₂SO₄ (aq) as the electrolyte.

All the electrochemical measurements were made with the Pine Instruments AFCBP1 bipotentiostat controlled using the PineChem software. The electrolyte was purged with nitrogen and the disk electrode was cycled from 0 to 1 V vs RHE at a sweep rate of 100 mV/s until a steady-state CV was obtained. After a steady state was obtained, a final CV at 10 mV/s was obtained to determine the nonfaradaic current. Afterward, the electrolyte was purged with oxygen and subjected to the same sweep conditions as the nitrogen purge. The electrode was then rotated at various rotation rates to determine limiting currents. While under rotation, the ring was held at a potential of 1.2 V vs RHE to oxidize any generated peroxide.¹⁹

The %H₂O₂ produced was determined from the following equation¹⁹⁻²¹

$$\% H_2 O_2 = \frac{200 I_R}{N I_D + I_R}$$
[1]

where $I_{\rm R}$ is the current obtained from the ring, $I_{\rm D}$ is the current obtained from the disk, and N is the collection efficiency, which was determined to be 0.1933 for our RRDE system by a ferricyanide calibration.

Kinetic current densities (i_k) for each catalyst were determined using the Koutecky–Levich theory, which expresses the disk current density (i_d) as

Table I. Weight percent iron in ORR catalysts as determined by ICP-OES.

Sample	Fe (wt %)
Pure Vulcan	0.03
V-N1-Fe-650	2.20
V-N2-Fe-650	1.24
V-N3-Fe-650	0.35
Pure Black Pearls	0.02
BP-N1-Fe-700	1.05
BP-N2-Fe-700	0.80
BP-N3-Fe-700	0.89

$$\frac{1}{i_{\rm d}} = \frac{1}{i_{\rm k}} + \frac{1}{i_{\rm dl}}$$
[2]

where i_{dl} is the diffusion-limited current density, which is given by

$$i_{\rm dl} = 0.62 n F C_{\rm O_2} D_{\rm O_2}^{3/2} \nu^{-1/6} \omega^{1/2}$$
[3]

where *n* is the number of electrons, *F* is Faraday's constant, C_{O_2} is the concentration of oxygen, D_{O_2} is the diffusion coefficient of oxygen, ν is the kinematic viscosity, and ω is the rotation rate of the electrode. Thus, plots of $1/i_d$ vs $\omega^{-1/2}$ yield an intercept of $1/i_k$. The values of C_{O_2} and D_{O_2} employed here were 8.263 mg/L and 2.20 $\times 10^{-5}$ cm²/s, respectively.

Material characterization.— Inductively coupled plasma-optical emission spectrometry (ICP-OES) was utilized for a quantitative determination of iron content in synthesized catalysts. A Varian Vista-MPX CCD simultaneous ICP-OES was set to an analytical wavelength of 238.204 nm to look for the characteristic iron emission line. The sample preparation was similar to that reported by Sirk et al. and involved refluxing ca. 15 mg of catalyst in 10 mL of 10% HNO₃ for 24 h.²² Subsequent gravity filtration over Whatman 42 ashless filter paper and volumetric dilution yielded a solution of sufficient purity to be analyzed by ICP-OES. Standardization was performed with four iron(III) chloride external standards ranging from approximately 1–10 ppm. These standards contained approximately 2% nitric acid to ensure the complete dissolution and keep both sample and standard matrices equivalent.

X-ray photoelectron spectroscopy (XPS) was performed using an Omicron EA-125 energy analyzer and a multichannel detector equipped with a monochromatic Mg K α X-ray source ($h\nu$ = 1253.6 eV). The N 1s peaks were fitted using a mixed Gaussian–Lorentzian-shaped profile with a Shirley background. Identical parameters were used for all the observed N 1s peaks. The peak broadening was constrained to a maximum of 2 eV.

Results

Material characterization.— ICP-OES was used to quantitatively determine the amount of iron present in all the samples. The results are compiled in Table I. For the Vulcan-based samples, a trend is observed in which iron content decreases as nitrogen content increases. Nevertheless, these values are still above the minimum 0.2 wt % Fe that is necessary for the activity.²³ The iron content of Black-Pearls-based catalysts were all quite similar, ranging between 0.8 and 1.0 wt %, showing no dependence on the nitrogen content of the aminosilane.

XPS data.— Figure 2 compares the N 1s XPS spectra obtained for V-N3-Fe, V-N3-Fe.650, and BP-N3-Fe-700 catalysts. The spectra obtained from V-N3-Fe can be fitted well with two peaks centered on 400.0 and 401.2 eV, which we attribute to the secondary and primary amine groups, respectively, that originated from the N3-aminosilane. The atomic ratio of the secondary to primary amines was determined to be ca. 2.3, which is close to the expected value. As expected, the heat-treatment induces significant structural



Figure 2. (Color online) XPS N 1s narrow scan spectra obtained for (a) V-N3-Fe, (b) V-N3-Fe-650, and (c) BP-N3-Fe-700 catalysts.

changes, as shown in Fig. 2b and c. The data sets for both heattreated catalysts were fit with three peaks that are known to originate from pyridinic (398 eV)-, pyrrolic (400 eV)-, and graphene (402 eV)-type nitrogen.¹⁰ The relative contribution of each are listed in Table II. Pyrrolic N is the largest component of the V-N3-Fe-650 catalyst, almost twice that of pyridinic N. Pyrrolic N is also the largest component of the BP-N3-Fe-650 catalyst, although it is only slightly larger than the pyridinic content. Both heated catalysts have a surprisingly large signal due to the graphene-type N.

Electrochemical characterization: Vulcan-based samples.— A survey of the RDE behavior for V-N3-Fe catalysts at various heattreatment temperatures was conducted to determine the optimum temperature for further investigation. The onset potential for the reduction of oxygen, V_{ORR} , is defined as the potential at which the current for ORR is first observed²⁴ and is the commonly used parameter to gauge the catalytic activity. V_{ORR} was determined from the intersection of the lines tangential to the baseline and steepest part of the ORR wave in the RDE voltammogram. Figure 3 plots V_{ORR} as a function of the heat-treatment temperature for the

Table II. The relative concentration of nitrogen species present as determined by XPS.



Figure 3. Variation in $V_{\rm ORR}$ with heat-treatment temperature for V-N3-Febased catalysts.

V-N3-Fe catalyst system. This clearly shows that the ideal pyrolysis temperature is 650° C for this system, with a sharp decline in activity occurring at higher (and lower) temperatures.

To separately evaluate the electrochemical activity before and after the addition of iron, Vulcan-based catalyst systems were characterized at various stages of development in the absence of iron. Figure 4 shows the oxygen reduction current produced by a pure Vulcan, V-N3, and V-N3-650 (no iron). This clearly demonstrates that the ORR activity is quite poor in the absence of iron.

Given the clear importance of both the presence of iron and heat-treatment temperature in producing catalysts active toward the ORR, the influence of aminosilane precursor on the ORR activity was investigated. Figure 5 compares the ORR activity achieved with V-N1-Fe-650, V-N2-Fe-650, and V-N3-Fe-650. The percent of H_2O_2 produced as a function of disk potential for the catalysts are shown in Fig. 6. The ORR activity increases with increasing nitrogen content, with maximum activity achieved with the N3-based catalyst system. This agrees with the trend of catalytic activity depending upon nitrogen content as reported by others.^{6,10} Furthermore, peroxide production decreased as the nitrogen content increases. The V-N3-Fe-650 catalyst, in particular, demonstrated a very low percent peroxide production (ca. 3% at 0.3 V).

To further investigate the electrochemical kinetics, Koutecky– Levich plots were constructed for V-N2-Fe-650 and V-N3-Fe-650 catalysts systems, which are shown in Fig. 7 (these plots could not be constructed reliably for V-N1-Fe-650 as its ORR activity was too low.). This allowed for the determination of the kinetic current densities (i_k) for each catalyst system, which are listed in Table I. The maximum kinetic current density was achieved for the V-N3-Fe-650 catalyst, which was substantially larger than that for V-N2-Fe-650.

Figure 8 shows the oxygen-free voltammograms obtained for V-N3-based catalysts at various stages of development. The CVs are featureless, with no discernable peaks in the absence of Fe. How-



Figure 4. (Color online) Disk current densities for the Vulcan-based catalysts at different stages of development in the absence of iron. Measurements were made at a sweep rate of 10 mV/s in O_2 -saturated 0.5 M H_2SO_4 at room temperature.



Figure 5. (Color online) Comparison of the disk current densities obtained for V-N1-Fe-650, V-N2-Fe-650, and V-N3-Fe-650 catalysts. Measurements were made at a sweep rate of 10 mV/s in O_2 -saturated 0.5 M H₂SO₄ at room temperature while the electrode was rotated at 900 rpm.

ever, a stable and well-defined redox wave centered around 0.6 V vs RHE was observed after heat-treatment in the presence of Fe. This corresponds to the only V-N3-based catalyst with a high ORR activity and may possibly be related to the formation of the active site as waves at higher potentials are sometimes (but not always) observed in Fe–N/C-based catalysts.² Thermal treatment has led to a significant increase in the double-layer capacitance of the sample in both the presence and absence of Fe. This is somewhat surprising because we would expect the surface area of carbon, and hence its double-layer capacitance,²⁵ to decrease upon heating in the presence of a graphitization catalyst such as Fe.

Electrochemical characterization: Black-Pearls-based samples.— As with the Vulcan-based ORR catalysts, the temperature dependence of the BP-N3-Fe catalysts system was first surveyed, which is shown in Fig. 9. Unlike the Vulcan-based samples, the Black-Pearls-based samples displayed a much broader temperature range under which the optimal activity could be achieved. This can be attributed to the higher surface area and more disordered nature of Black Pearls compared to Vulcan.



Figure 6. (Color online) Percent of H_2O_2 produced as a function disk potential for V-N1-Fe-650, V-N2-Fe-650, and V-N3-Fe-650 catalysts. Measurements were made at a sweep rate of 10 mV/s in O_2 -saturated 0.5 M H_2SO_4 at room temperature while the electrode was rotated at 900 rpm.



Figure 7. (Color online) Koutecky–Levich plot for V-N2-Fe-650 and V-N3-Fe-650 catalysts at 0.3 V vs RHE. Measurements were made in O_2 -saturated 0.5 M H_2SO_4 at room temperature.

A preliminary analysis was performed on BP-N3-based catalysts before the addition of iron to gauge the ORR activity of the asreceived and aminosilane-modified carbon blacks, which is shown in Fig. 10. Even before heat-treatment, the as-received Black Pearls carbon black shows a mild ORR activity. Modification with N3 leads to a small increase in activity before heat-treatment. However, heat-treating the N3-modified Black Pearls leads to a substantial



Figure 8. (Color online) Steady-state CVs obtained for the Vulcan-based catalysts at different stages of development (a) in the absence and (b) in the presence of iron. Measurements were made at a sweep rate of 100 mV/s in N_2 -saturated 0.5 M H₂SO₄ at room temperature.



Figure 9. Variation in $V_{\rm ORR}$ with heat-treatment temperature for BP-N3-Febased catalysts.



Figure 10. Disk current densities for the Black-Pearls-based catalysts at different stages of development in the absence of iron. Measurements were made at a sweep rate of 10 mV/s in O_2 -saturated 0.5 M H_2SO_4 at room temperature.

increase in the ORR activity ($V_{ORR} = 576 \text{ mV}$), which is comparable to other results in the literature for metal-free ORR catalysts.²⁶ However, because the as-received Black Pearls do contain a measurable quantity of Fe (0.02 wt %), these are not truly metal-free but are certainly below the point of Fe saturation of active sites.²³ Further enhancements in the iron-free activity may be achievable by varying the heat-treatment conditions.

The influence of aminosilane precursor on the ORR activity was investigated for Black-Pearls-based catalysts with adsorbed iron, followed by heat-treatment at the optimal conditions (700°C). Figure 11 compares the ORR activity achieved with BP-N1-Fe-700, BP-N2-Fe-700, and BP-N3-Fe-700 catalysts. The percent of H_2O_2 produced as a function of disk potential for these catalysts are shown in Fig. 12. This clearly shows that the N3-based catalysts have higher activity than either the N1- or N2-based catalysts, although it did produce slightly higher amounts of H_2O_2 than the N2-based catalyst (ca. 9 vs 13% at 0.3 V).

Koutecky–Levich plots were constructed for BP-N1-Fe-700, BP-N2-Fe-700, and BP-N3-Fe-700 catalysts systems, which are shown in Fig. 13. Kinetic current densities were found to increase with the amount of nitrogen in the aminosilane precursors, with the N3-based catalyst having a substantially larger $i_{\rm K}$ than the N1- and N2-based catalysts.

Figure 14 shows the oxygen-free voltammograms obtained for BP-N3-based catalysts at various stages of development. Much like the Vulcan-based samples, the CVs are featureless, with no discern-



Figure 11. (Color online) Comparison of the disk current densities obtained for BP-N1-Fe-700, BP-N2-Fe-700, and BP-N3-Fe-700 catalysts. Measurements were made at a sweep rate of 10 mV/s in O_2 -saturated 0.5 M H_2SO_4 at room temperature while the electrode was rotated at 900 rpm.



Figure 12. (Color online) H_2O_2 produced as a function disk potential for BP-N1-Fe-700, BP-N2-Fe-700, and BP-N3-Fe-700 catalysts. Measurements were made at a sweep rate of 10 mV/s in O₂-saturated 0.5 M H₂SO₄ at room temperature while the electrode was rotated at 900 rpm.

able peaks except for the catalyst heat-treated in the presence of Fe. This corresponds to the most active BP-N3-based catalyst with a high ORR activity.

Comparing the Black-Pearls- and Vulcan-based samples.- A summary of the key electrochemical parameters for the Vulcan- and Black-Pearls-based catalysts are complied in Table III. The results above show that the N3-based catalysts on both Vulcan and Black Pearls are the most active, with the Black-Pearls-based catalysts significantly more active. The best Vulcan-based catalysts have an onset potential that is ca. 100 mV less than that obtained with the best Black-Pearls-based catalysts. Furthermore, the kinetic current densities determined for the most active Black-Pearls-based was ca. 3 times that of the most active Vulcan-based catalyst. This is not surprising given the fact that Black Pearls have a much higher surface area and a higher content of disordered carbon, the latter of which has been shown to yield more active catalysts.¹³ Such differences in activity between Vulcan- and Black-Pearls-based catalysts have also been observed by others.²⁷ In addition, the XPS data show that the BP-N3-Fe-700 catalyst has a significantly higher ratio of pyridinic- to pyrrolic-type N compared to V-N3-Fe-650 (0.88 vs



Figure 13. (Color online) Koutecky–Levich plot for BP-N1-Fe-700, BP-N2-Fe-700, and BP-N3-Fe-700 catalysts at 0.3 V vs RHE. Measurements were made in O_2 -saturated 0.5 M H_2SO_4 at room temperature.



Figure 14. (Color online) Steady-state CVs obtained for the Black-Pearlsbased catalysts at different stages of development (a) in the absence and (b) presence of iron. Measurements were made at a sweep rate of 100 mV/s in N₂-saturated 0.5 M H₂SO₄ at room temperature.

0.54). This is of note because high pyridinic-N contents have been related to more active catalysts.²¹ Furthermore, (semiquantitative) XPS survey scans indicate that the surface nitrogen-to-carbon ratio of BP-N3-Fe-700 was more than double that of the V-N3-Fe-650 (1:8 vs 1:20). Assuming that a complete monolayer of aminosilane was achieved for both Vulcan- and Black-Pearls-based catalysts, the Black Pearls would adsorb ca. 6 times the amount of aminosilane per gram of carbon due to its higher specific surface areas. Samples with higher initial nitrogen content have been shown to retain more nitrogen after heat-treatment, which is likely one of the main reasons for the higher activity.⁶,

The differences in activity may also be related to the higher iron content in the Black-Pearls-based catalysts compared to the Vulcanbased samples. For example, both the exchange current density and the Fe content obtained for BP-N3-Fe-700 was ca. 3 times that obtained for V-N3-Fe-650. Thus, the activity of each sample was very similar on the basis of Fe loading.

Although the ORR activity of these catalysts report here are respectable, their activity is less than the best Fe-N/C catalysts reported, such as that reported in Ref. 21. One major reason for this difference is that our catalysts were not heat-treated in the presence of ammonia. Heat-treatment in an ammonia atmosphere is commonly used to increase nitrogen content, which significantly improves the ORR activity. In this work, we have intentionally chosen not to employ ammonia so that the impact of the organosilane structure could be clearly demonstrated. Future work on this topic will revolve around both characterizing and increasing the nitrogen content of the catalyst through both ammonia treatment and surface modification. For example, attachment of a species that contained pyridinic functional groups (like the ones believed to be in the active site) via a chemisorbed linkage may prove interesting.

Table III. Summary of the electrochemical properties of the Fe-N/C catalysts in this study.

Sample	V _{ORR} (mV vs RHE)	$i_{\rm k} \ ({\rm mA/cm^2})$ at 0.3 V	% H ₂ O ₂ at 0.3 V (900 rpm)
V-N1-Fe-650	237.6	N/A	N/A
V-N2-Fe-650	454.7	5.68	41.1
V-N3-Fe-650	603.9	11.01	3.5
BP-N1-Fe-700	639.2	11.62	26.4
BP-N2-Fe-700	644.8	16.57	9.3
BP-N3-Fe-700	701.2	29.52	13.4

Conclusions

A chemisorption approach to nonprecious metal fuel cell catalysts was successful in producing catalysts with a decent ORR activity. Many variables were manipulated to produce the most highly active catalysts, including nitrogen content, carbon type, and heattreatment temperature. The results showed that the catalysts prepared with organosilanes with higher nitrogen content produced more highly active catalysts. Heat-treatment temperature played a significant role with an optimum temperature being critical to obtaining a highly active catalyst. However, one of the most substantial changes in activity came from the choice of carbon black. Black Pearls, due to its significantly higher surface area, more oxidized surface, and more disordered nature, possessed significantly more activity toward the ORR than Vulcan even before heat-treatment with iron.

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