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13. ABSTRACT (Maximum 200 words)

This one-year feasibility study was designed to examine the thermal, chemical, and electrochemical properties of novel nitrogen-rich carbon nitride (C_3N_{4+x}) network materials for use as catalysts in proton exchange membrane (PEM) fuel cell electrodes. We have produced carbon nitride materials and carbon composites thereof; particularly we discovered a rapid, facile method to make carbon nitride - carbon black composites in a single step. This *in-situ* method is an effective strategy to produce homogeneous electrically conducting composite materials. As expected, the electrical conductivity of the semiconducting carbon nitride greatly improves when it is mixed with conducting carbon black. We have determined that carbon nitride and its composites with carbon black are electrochemically inert in neutral and acidic environments and do not impede oxidation-reduction reactions. Catalytically active metals were deposited onto the carbon nitride powders using solution and hydrogen reduction strategies. Platinum metal containing carbon nitrides showed appreciable electroactivity in O_2, CO and methanol aqueous environments. In some cases, the current densities achieved for these Pt-carbon nitride composites exceed those observed for Pt on carbon obtained from commercial sources. Other metal catalysts such as Ni also showed promising electrochemical events in O_2, CO, and methanol environments.

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Final Report for Grant # DAAD19-03-1-0274

**Investigation of Nitrogen-Rich Carbon Nitride Networks
as Redox-Active Metal Catalyst Support Materials**

Principle Investigator: Edward G. Gillan, Department of Chemistry, University of Iowa

co-Investigator: Johna Leddy, Department of Chemistry, University of Iowa

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Scientific Progress and Accomplishments

Investigation of Nitrogen-Rich Carbon Nitride Networks
as Redox-Active Metal Catalyst Support Materials

Principle Investigator: Edward G. Gillan, Department of Chemistry, University of Iowa

co-Investigator: Johna Leddy, Department of Chemistry, University of Iowa

1. Overview

This one-year feasibility study is designed to examine the thermal, chemical, and electrochemical properties of novel nitrogen-rich carbon nitride (C_3N_{4+x}) network materials for use in the catalyst layer of proton exchange membrane (PEM) fuel cell electrodes. These lone pair rich solid networks can modify the local coordination environment around individual metal catalyst sites, influencing catalytic efficiency and stability. As a component of fuel cell electrodes, the nitrogen sites in C_3N_{4+x} may coordinate and modify the local electronic and chemical bonding environment of metal catalyst particles to a greater degree than conventional carbon support materials.
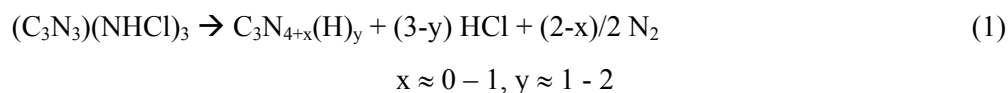
Our recent investigations have answered several questions posed in the original proposal and provide promising directions for utilizing these semiconducting nitrogen-rich materials in electrocatalytic environments. Preliminary electrochemical stability examinations were conducted and indicate that these carbon nitrides are robust and inert under conditions that are representative of fuel cell environments. Several metal incorporation strategies were examined, including metal salt adsorption and reduction by chemical means at either ambient temperatures (hydrazine) or elevated temperatures (H_2), with the latter method being more universally successful. Incorporated metals include Pt, Ni, Cu, Co, Mn, V, and Ag.

Several of the metal impregnated carbon nitride materials were mixed with conducting carbon black and electrochemically examined in a carbon paste electrode test system. Preliminary tests focused on Pt and Ni systems. The conducting composites were studied by cyclic voltammetry in Na_2SO_4 solutions purged with N_2 (control), saturated with either O_2 or CO gases, or dosed with methanol. Several of the metal impregnated carbon nitride/carbon black electrodes performed either equivalently or better than control electrodes, including commercial Pt on carbon and Pt disks.

2. Production and thermal investigation of carbon nitride materials

2.1. Synthesis of nitrogen-rich carbon nitride networks

The nitrogen-rich carbon nitride materials used for this study were produced by the rapid heating ($\sim$ 150 ºC/hr) of an inexpensive, commercially available (Aldrich Co.) molecular triazine (C_3N_3) precursor, trichloromelamine [TCM, $(C_3N_3)(NHCl)_3$]. The precursor decomposition process was performed in a 125 ml stainless steel Parr reactor using a custom-made Glas-Col heating mantle and an Omega Engineering temperature controller. Several experiments were performed using TCM precursor amounts on the order of 5 g (22 mmol). When the Parr reactors internal temperature reached $\sim$ 185 ºC, the analog pressure gauge attached to the reactor recorded a rapid pressure jump (300 psi for 5 g of precursor). Based on our previous work, most of the evolved gas consists of HCl and nitrogen (Equation 1),[1] although for mass balance there may be trace amounts of chloramines or chlorine gas also produced.

$$(C_3N_3)(NHCl)_3 \rightarrow C_3N_{4+x}(H)_y + (3-y) \ HCl + (2-x)/2 \ N_2 \qquad (1)$$
$$x \approx 0 - 1, y \approx 1 - 2$$

There is residual hydrogen in the product, likely present as N-H bonds, regardless of decomposition method, indicating that the hydrogen arises from the TCM precursor. The isolated carbon nitride products were vacuum annealed at 250 ºC to ensure any reactive or dangling bonds were stabilized or removed. The amount of isolated tan-orange product in these large-scale reactions corresponds to a 25 - 30 wt % yield based on precursor starting mass, which is equivalent to a near quantitative conversion of triazine rings into the product structure. We have also performed this TCM decomposition using 10 g of precursor, leading to larger scale carbon nitride production.

Important note: It is significant to realize that the carbon nitride (C_3N_{4+x}) materials are *formed* under very hot and corrosive acidic conditions, facts that bode well for its chemical stability in acidic fuel cell environments.

2.2. Attempted graphitization of C_3N_{4+x} materials

Our previous thermal investigations on loose powders of C_3N_{4+x} in a heated system under continuous inert gas flow, resulted in complete powder evaporation by 650 – 700 ºC and downstream deposition of carbon nitride ($\sim C_3N_5$) films.[2,3] These pale yellow to light-orange coatings show improved local carbon nitride structural order by IR spectroscopy and are visibly luminescent under UV light.

In an effort to convert the nitrogen-rich semiconducting solids to more graphitically ordered and conjugated, electrically conducting materials, several thermal conversion experiments were conducted using cold-pressed pellets of C_3N_{4+x} (10,000 psi with a 13 mm die). The carbon nitride powders formed into coherent, but brittle pellets with poor integrity. Two-probe electrical measurements on these tan-colored pellets verified that their resistance is greater than 10^{+6} Ω. Pelletized C_3N_{4+x} was subjected to several thermal conversion processes, namely heating under inert conditions including:

a) in a dynamic horizontal Ar flow system (100 sccm)

> result: material transport begins at ~ 450 ºC, pellet completely vaporizes by 650 ºC

b) in a static evacuated (30 mTorr) system

> result: material transport to cooler regions of reactor begins at ~625 ºC, pellet completely
> vaporizes by 675 ºC.

c) in a static 1 - 2 atm N_2 pressure system

> result: material transport began at ~ 625 ºC, pellet's edges blacked slightly at 700 ºC, but pellet
> also completely evaporated after several hours at 700 ºC.

In all thermal methods investigated thus far, pure C_3N_{4+x} exhibits a strong tendency towards either molecular or macromolecular fragmentation instead of graphitization when heated. This is likely a consequence of the high nitrogen content, because thermally induced multiple bond formation between C and N is very common. Note that previously reported nitrogen-doped graphite films produced at 750 ºC or above generally contain less than 20 at % nitrogen.[4]

2.3. Production of carbon nitride – carbon black composites

2.3.1. Physical mixtures of C_3N_{4+x} and carbon black (Vulcan XC-72)

To improve the electrical conduction of nitrogen-rich carbon nitride, several experiments were performed using conducting carbon additives. It was initially assumed that percolation limits (16 wt % of a conductive material mixed with a non-conducting phase) would be applicable to composites formed from physical mixtures of semiconducting carbon nitride with conducting carbon black (Vulcan XC-72, Cabot ~200 nm aggregate size). Two-probe electrical resistance measurements were performed on cold-pressed pellets of intimately ground physical mixtures of C_3N_{4+x} and carbon black. These composite pellets had fairly poor integrity, similar to the pure C_3N_{4+x} pellets. As is shown in Table 1, the electrical resistance of the physical mixtures approaches that of pure carbon black by a 25 wt % addition level.

Table 1. Comparison of electrical resistance of physically prepared C_3N_{4+x} – carbon composites

Pellet composition (wt % ratio) C_3N_{4+x} : carbon black	2-probe electrical resistance (Ω)	Pellet appearance/homogeneity
0 : 100	30	black homogeneous, brittle/fragile
50 : 50	80	black and yellow – heterogeneous, brittle
75 : 25	60	black and yellow – heterogeneous, brittle
90 : 10	~1000	black and yellow – heterogeneous, brittle
100 : 0	$> 10^5$	tan-orange, homogeneous, moderate pellet integrity

All of the samples listed above were hand-mixed using a mortar and pestle. Further improvements in homogeneity and mixing in these physically combined systems are possible using ball-milling or other high energy mixing techniques.

2.3.2. Rapid *in-situ* formation of C_3N_{4+x} - carbon black composites

One significant advantage of the method utilized to form the carbon nitride materials in this study, is that their formation is rapid (a few seconds) and exothermic (temperature elevation to ~400 ºC).[1] Previous electron microscopy evidence suggests that there is some gas phase recondensation and melting that occurs during synthesis. In order to produce submicron scale mixing of C_3N_{4+x} with carbon black, the decomposition of the TCM precursor was conducted in the presence of varying amounts of carbon black. The precursor was intimately ground with the carbon black and then rapidly decomposed using a home-built heated wire ignition reactor.[1] This reactor allows both a quick survey of various TCM:carbon black ratios and preparation of composites on small (~ 0.5 g) initial scales. The products from this *in-situ* composite formation reaction are noticeably distinct from the physical mixtures in Section 2.3.1. The *in-situ* products are visibly homogeneous even under an optical microscopic (200x) examination. Cold-pressed pellets of these *in-situ* produced composites also have significantly better integrity and higher electrical resistance (Table 2) than observed for equivalent physical mixtures. The pure carbon black and pure carbon nitride results listed in Table 1 are listed again in Table 2 for ease of comparison and trends.

Table 2. Comparison of electrical resistance of *in-situ* prepared C_3N_{4+x} – carbon composites
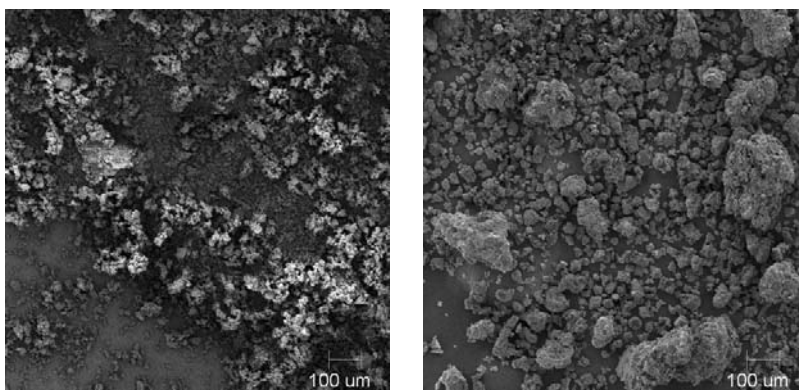
Pellet composition (wt %) C_3N_{4+x} : carbon black*	Composition (wt %) and overall formula based on elemental analysis*	2-probe electrical resistance (Ω)	Pellet appearance/homogeneity
0 : 100	99+ % C	30	black homogeneous, brittle/fragile
50 : 50	50 [$C_3N_{7.47}H_{6.07}$] : 50 [C] or $C_3N_{1.33}H_{1.09}$	60	black, slightly iridescent, homogeneous, excellent integrity
75 : 25	75 [$C_3N_{5.12}H_{3.3}$] : 25 [C] or $C_3N_{2.45}H_{1.53}$	3000	black iridescent, homogeneous, excellent integrity
90: 10	not analyzed	$> 10^5$	iridescent black with yellow and brown spots, excellent integrity
100 : 0	$C_3N_{4.19}H_{2.38}$	$> 10^5$	tan-orange, homogeneous, moderate pellet integrity

*based on amount of product isolated, assuming no carbon black loss.

To produce a composite with resistance comparable to pure carbon black, it was necessary to raise the amount of conducting carbon black to 50 wt %. This contrasts with the physical mixtures (Table 1) that only required a 25 wt % carbon black addition to achieve the same conduction threshold. These resistance results suggest that the carbon black particles are efficiently coated and sequestered by semiconducting carbon nitride coatings.

As expected, the microstructure and morphology of the 50:50 wt % C_3N_{4+x} – carbon black composite is markedly different than that of the pure carbon nitride. Figure 1 shows a comparison of scanning electron microscopy images for these two materials. The ground pure carbon nitride is a fine particulate powder (Figure 1 left). The *in-situ* composite reaction process results in carbon black particles that are fused together into larger masses nearly 1 mm in size that are held together by carbon nitride "glue". These masses are easily ground to a fine homogeneous powder (Figure 1 right), which still has larger aggregate sizes than the pure carbon nitride.

Figure 1. SEM comparison of particle morphologies of ground pure carbon nitride materials (left) and *in-situ* composites formed between carbon nitride and carbon black (right).
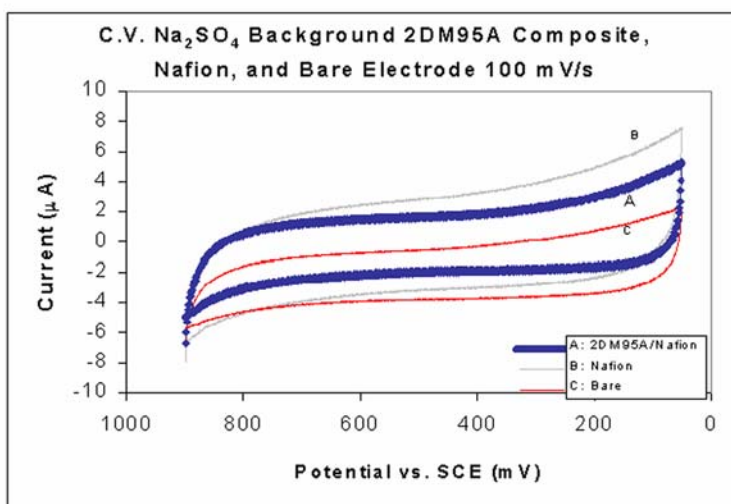
Several efforts were made to improve the conductivity of poorly conducting *in-situ* mixed 75:25 sample using thermal processing similar to that described in Section 2.2. Since the C_3N_{4+x} material is in intimate contact with the carbon black particle surface, the inherent carbon nitride volatilization should decrease due to enhanced carbon nitride reaction with the dangling bonds on the carbon black surface. This would result in more intimate electrical contact between the particle and surface coating, leading to an increase the electrical transport through the composite. Initial annealing attempts on *in-situ* 75:25 pellets shows that conductivity improved to ~200 Ω after prolonged heating at 600 ºC under dynamic vacuum, but this was accompanied by an unacceptable degree of carbon nitride volatilization, as observed visually and by sample weight loss.

3. Examination of electrochemical characteristics of carbon nitride materials

3.1. Pure C_3N_{4+x} network materials

The electrochemical stability of the pure carbon nitride material was investigated by affixing it to a carbon disk electrode using Nafion (perfluorosulfonic acid polymer). The experiments were run with 15 wt % C_3N_{4+x} dispersed in a solution of Nafion dissolved in aliphatic alcohol and cast onto the electrode surface (0.45 cm^2). The electrodes were carefully dried to avoid film cracking. The carbon nitride material shows no significant electrochemical events over the 0.05 to 0.9 V range (vs SCE) in 0.1 M Na_2SO_4 (Figure 2). It showed similar stability characteristics when the same cycling was performed in a 0.1 M HNO_3 solution. In either solution, the cyclic voltammetry was qualitatively similar to that of a Nafion-coated carbon disk electrode.

Figure 2. Comparison of electroactivity of pure C_3N_{4+x} (2DM95a) versus pure Nafion films in 0.1 M Na_2SO_4 solution. Note that the bare electrode trace is offset by 2 μA for clarity.

3.2. Physical mixture of C_3N_{4+x} with carbon black

Due to the visible heterogeneity of physically mixed composites, it seemed likely that these systems would show electrochemical stability similar to that of the pure carbon nitride materials (Section 3.1). Preliminary testing and analysis showed that physical composites with a 50:50 weight ratio of carbon nitride and carbon black (Vulcan XC-72) were acceptably electrically conducting to carry out further electrochemical measurements.

3.3. *In-situ* mixture of C_3N_{4+x} with carbon black

The electrochemical stability of the homogeneous *in-situ* generated mixture of C_3N_{4+x} with carbon black (50:50 wt % ratio based on product ratio, pellet resistance = 60 Ω) was initially examined using a glassy carbon disk electrode. The experiments were run with 15 wt % of the C_3N_{4+x}/carbon black composite dispersed in a Nafion matrix. The cyclic voltammetry of this material in 0.1 M Na_2SO_4 and 0.1 M HNO_3 showed no events other than those observed for pure Nafion-coated carbon electrode.

3.4. Examination of C_3N_{4+x} and carbon black composites in presence of redox processes

After determining that the carbon nitride materials are electrochemically stable in acidic solution, their electroactivity in the presence of a redox test sample was investigated. A series of electrodes (bare carbon, Nafion only, Nafion with 15 wt % carbon black [XC-72], Nafion with C_3N_{4+x} [2DM95a], and Nafion with 15 wt % of the *in-situ* C_3N_{4+x}/carbon black mixture [2DM112a]) were exposed to a solution of 1.0 mM tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate in 0.1 M HNO_3 for 12 – 18 hrs to ensure complete exchange of the Ru^{2+} complex into the Nafion film on the electrode. Cyclic voltammetry (50, 75, and 100 mV/s) was performed to investigate the Ru^{2+}/Ru^{3+} redox behavior in the presence of the various electrode constituents. Representative CV scans for this redox process are shown in Figure 3 (next page) for the 5 different electrodes compositions noted above.

These scans show that the carbon black containing electrodes have the highest current flow of all samples. The pure carbon nitride containing electrodes (2DM95a) do not enhance or significantly hinder the ruthenium redox process relative to the pure Nafion coated electrode. There is a slightly lower current maximum observed for the pure carbon nitride containing electrodes relative to Nafion that can be explained based on a semiconducting filler (C_3N_{4+x}) hindering conduction of the ruthenium complex. The electrodes containing the 50:50 wt % *in-situ* C_3N_{4+x} – carbon black additive (2DM112a) show slightly less current flow than the pure carbon black containing electrode, consistent with the presence of the semiconducting carbon nitride filler (nominally 7.5 wt %).
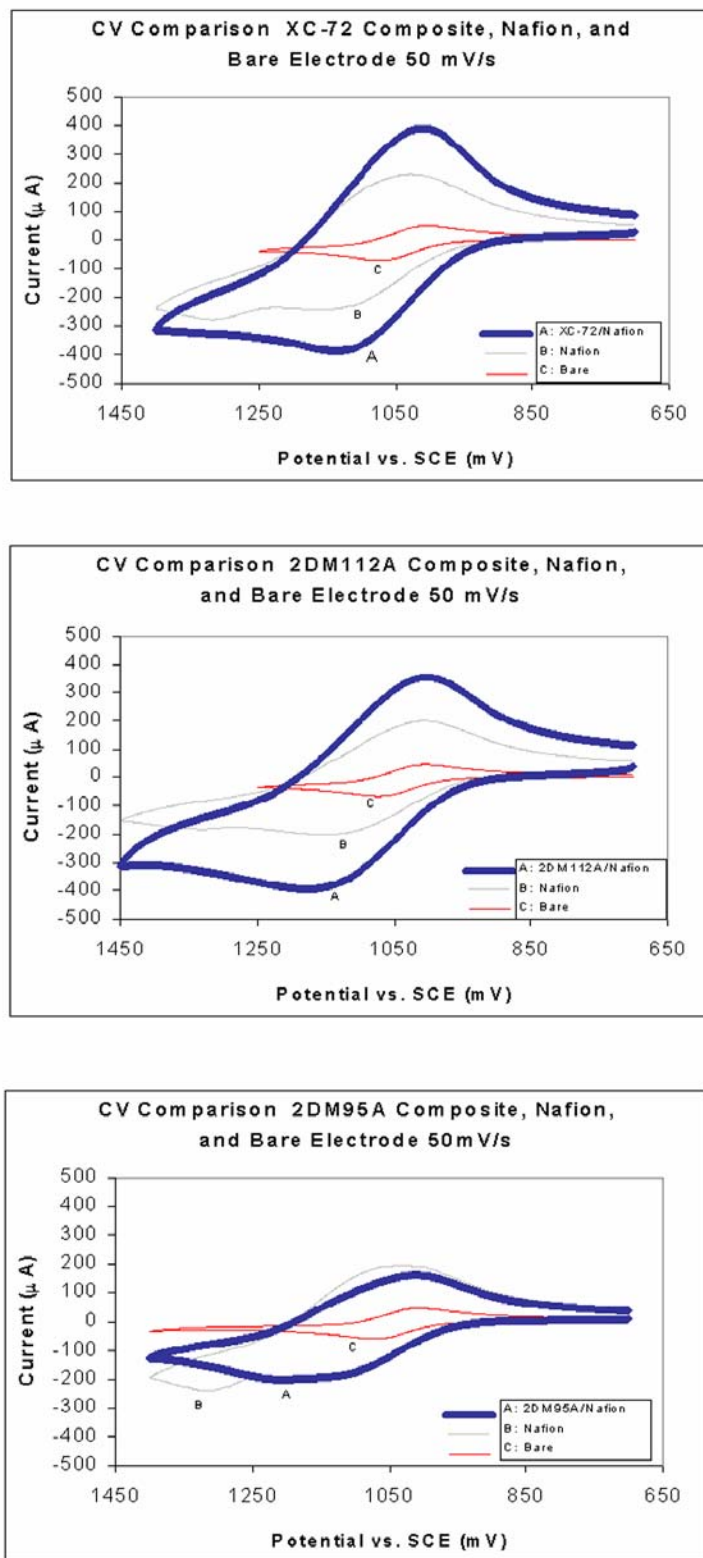
Figure 3. Comparison of cyclic voltammetry of a redox active component [Ru(bpy)$_3$$^{2+}$] using various modified carbon electrodes in 0.1 M HNO$_3$.

Figure 4 plots the slopes of peak current versus square root of the scan rate ($\upsilon^{1/2}$) obtained from the CV data (*c.f.* Figure 3) for a set of 4 electrodes used in a series of 3 replicates. Each experiment included a bare carbon electrode, a carbon electrode coated with Nafion, and duplicate electrodes coated with Nafion containing 15 wt % of a filler material (CN1 and CN2: filler was pure carbon black - XC-72, pure C_3N_{4+x} - 2DM95A, or the *in-situ* mix of C_3N_{4+x} with carbon black - 2DM112A).
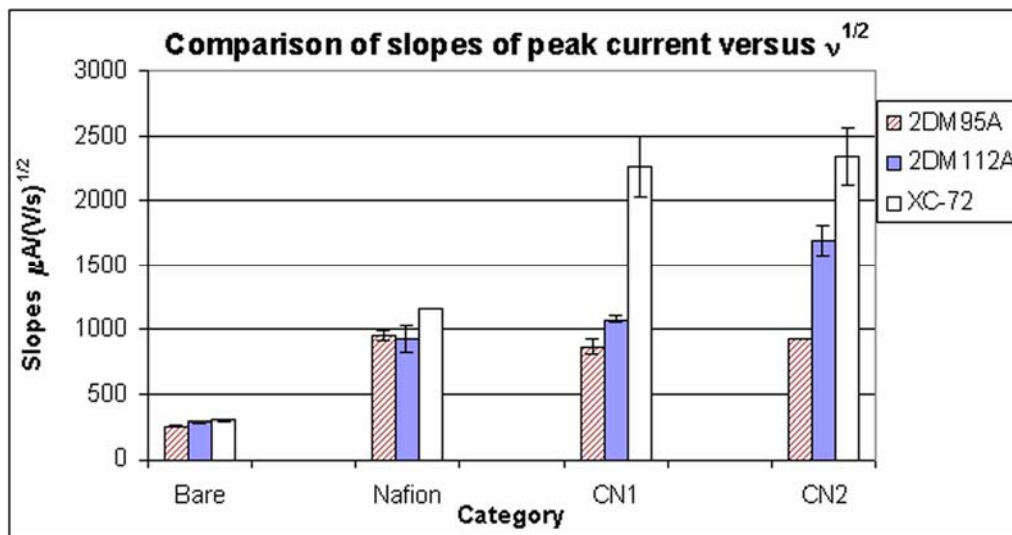
Figure 4. A comparison of slopes of peak current versus $v^{1/2}$ for carbon disk electrode with Nafion coatings containing carbon black (white), carbon nitride (red), or *in-situ* carbon nitride/carbon black composite material (blue).

Assuming that diffusion and concentration of redox species is constant, the slope reflects a change in apparent electrode area and is roughly proportional to the amount of carbon black added to the electrode. These results are consistent with the presence of a filler containing semiconducting carbon nitride along with an electrically active carbon black. Notably, adding the carbon nitride filler to Nafion does not appreciably alter the peak current achievable by Nafion alone.

4. Synthesis and electrochemistry of metal containing carbon nitride-carbon black composites

4.1. Chemical preparation of metal-C_3N_{4+x} composite structures

The chemical reduction and surface binding of several metals onto the carbon nitride framework was investigated by several methods. Initial ambient temperature solution reductions of the several metal salts with hydrazine in the presence of carbon nitrides were only partially successful. The lack of crystalline metal peaks by powder X-ray diffraction and observed halide residues indicated that hydrazine was not a strong enough reducing agent. Self-reduction of H_2PtCl_6 in methanol at 60 °C did produce a black coating on suspended tan carbon nitride powder, but powder XRD analysis showed it to primarily consist of PtO_2. Metal salts were combined with TCM and carbon nitride formation performed in the heated filament reactor. These resulted in partially reduced salts mixed in the carbon nitride network with moderate heterogeneity and were not investigated further.

A more successful iteration involved the creation of slurries of the C_3N_{4+x} powders (from the large scale Parr reactor decomposition) with a dissolved metal salt in methanol. The solution was evaporated to dryness under vacuum, yielding an intimate mixture of a metal salt and the carbon nitride network. This dried metal salt/C_3N_{4+x} mixture was placed in a Pyrex tube and subjected to flowing 10 % H_2 (balance N_2) at 350 °C for 24 hrs. In many cases, this produced crystalline metal after reduction (see Table 3). This method was the preferred preparation method for metal/C_3N_{4+x} composite formation. The samples listed in Table 3 represent a small fraction of those synthesized and analyzed. Specifically the data are for samples produced from pyridine pretreated carbon nitride materials (see next section).

Table 3. Comparison of several metal - carbon nitride incorporation experiments
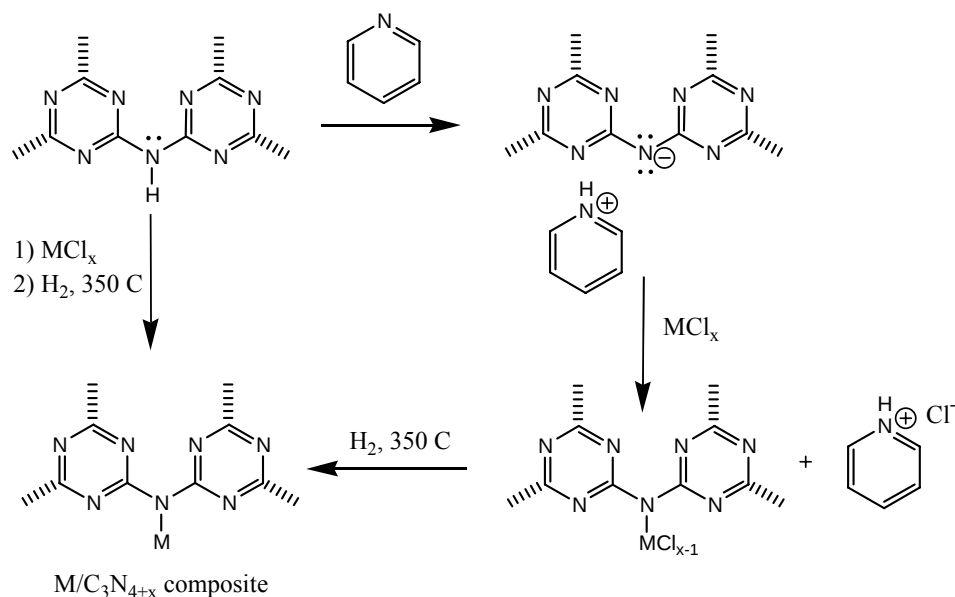
Metal salt (M:C_3N_{4+x} target weight ratio)	Color after H_2 at 350 °C	XRD result after H_2 reduction	Metal residue after TGA in Ar to 1000 °C (wt %)*
H_2PtCl_6 (10 : 90)	grey	Pt metal	10.8 (Pt)
H_2PtCl_6 (50 : 50)	grey	Pt metal	34.8 (Pt)
$CuCl_2 \cdot 2H_2O$ (10 : 90)	red-brown	amorphous	8.2 (CuO)
$NiCl_2 \cdot 6H_2O$ (10 : 90)	grey-green	Ni metal	12.6 (Ni, NiO)
$CoCl_2 \cdot 6H_2O$ (10 : 90)	grey-green	amorphous	9.4 (Co)
$MnCl_2$ (10 : 90)	orange-tan	amorphous	6.2 (Mn_3O_4)
VCl_3 (10 : 90)	grey	amorphous	≤ 10 (VO_x)
$AgNO_3$ (10 : 90)	grey	Ag metal	9.1 (Ag)

* XRD identified material in TGA residue is noted in parentheses

4.2. Effect of pyridine pretreatment on metal binding to carbon nitride materials

In preliminary experiments examining metal salt binding to carbon nitride, we observed that dissolved metals appear to adsorb more readily or "stick" to C_3N_{4+x} powders that were pretreated with a strong organic base (pyridine, C_5H_5N, py) as compared to the as-synthesized products. Because the as-synthesized carbon nitride materials contain residual hydrogen, likely present as amine moities (>NH or -NH$_2$), the pyridine may activate the carbon nitride nitrogen surface states, with the pyridinium cation (pyH$^+$) serving as a placeholder near the activated nitrogen site until the metal salt replaces it and binds to the nitrogen site, releasing py-HCl into solution (Scheme 1). Several experiments described in Table 3 were performed under identical metal salt incorporation conditions with and without pyridine pretreatment of the carbon nitride. Scheme 1 shows how these two routes may lead to metal incorporation in the C_3N_{4+x} network. One potential advantage of the pyridine pretreatment is that the metals may be more intimately associated with the carbon nitride network structure, as compared to the process without pretreatment.

Scheme 1. Proposed mechanism for base-enhanced metal binding to carbon nitride network

M/C$_3$N$_{4+x}$ composite

There is evidence that pyridine species remain strongly associated with the carbon nitride network after the pyridine wash process. The pyridine treated C_3N_{4+x} powders were isolated and washed with methanol, but when they were resuspended in metal salts, e.g., $CuCl_2$ or H_2PtCl_6, dissolved in methanol, there is solution evidence for the formation of (pyridine)$_2$MCl$_x$. Specifically, when the solutions are recovered after exposure to the pyridine treated carbon nitride and evaporated to dryness, the

repreciptated solids contains powder XRD evidence for pyridine metal salts such as (pyridine)$_2$CuCl$_2$ and (pyridine)$_2$PtCl$_4$. Other related Lewis basic amines were examined for carbon nitride pretreatment chemistry, specifically triethylamine and ethylenediamine. Preliminary results suggest that ethylenediamine may activate the nitride surface similarly to pyridine, but additional studies are needed to verify these initial results. A potential advantage of ethylenediamine is its lower cost relative to pyridine.

The *in-situ* generated C$_3$N$_{4+x}$ – carbon black composite materials were also metal impregnated in a manner similar to that described above, but preliminary electrochemical studies did not show distinct advantages associated with these carbon black composites ("co-mingled" materials) as compared to M/C$_3$N$_{4+x}$ products (described above) that were physically mixed with carbon black ("blended" materials) after metal impregnation. In the interest of rapid facile survey of several metal-carbon nitride materials, most of the electrochemical studies described below focus on M/C$_3$N$_{4+x}$ powders that were intimately mixed with ~50 wt % of Vulcan XC-72 carbon prior to electrochemical analysis. Because the *in-situ* generated C$_3$N$_{4+x}$ – carbon black composites are inherently conductive, they provide an additional degree of chemical tuning that can be exploited in future studies on these systems.

4.3. Preliminary electrochemical examinations of metal-carbon nitride composites

4.3.1. Preparation of composite carbon paste electrodes

For simplicity and rapid screening reasons, the metal-carbon nitride composite electrochemical studies were conducted using carbon paste electrodes. A majority of the metallated carbon nitride materials used in carbon paste electrodes consisted of pure metal-carbon nitride composites described in Section 4.1 and 4.2 that involved hydrogen reduction of metal salts impregnated into pure carbon nitride solids. These electrodes consisted of a ground mixture of the material of interest with typically 50 wt % of carbon black (Vulcan XC-72) to achieve consistent electrical conduction. This dry mixture was converted to a thick paste with mineral oil (~ 60 wt % of the sample). Because all of the metal containing carbon nitride samples were diluted by 50 wt % XC-72, the final amount of Pt in the dry mixture (prior to mineral oil mixing) was 5 wt %. After mixing these samples with mineral oil, Pt was ~2 wt % of the total paste electrode weight. A similar procedure was used with a commercial standard 10 % Pt on XC-72 (E-tek, Inc.).

The composite paste mixture was transferred to a 2 ml disposable polyethylene transfer pipet that was cut at the 0.25 ml mark to provide a tapered cylinder approximately 1.75" long and open at both ends. The

end of the tapered cylinder with the larger opening is considered the "top" of the completed electrode. A Pt wire was inserted into the top end of the electrode assembly to provide electrical contact between the carbon nitride-carbon black carbon paste electrode (CN-CPE) and the potentiostat.

4.3.2. Electrochemical data collection and analysis

A Bioanalytical Systems (BAS) 100B Electrochemical Workstation with a saturated calomel electrode (SCE) reference electrode and Pt wire mesh counter electrode was used for all analyses. A 0.10 M aqueous Na_2SO_4 electrolyte solution was used to measure the capacitive background of all electrodes. These measurements provide a means to estimate the electroactive area of carbon paste electrodes. The solution was vigorously purged with N_2 for 10 to 15 minutes prior to any electrochemical measurements and a blanket of N_2 gas was maintained above the solution while measurements are taken. Capacitive backgrounds were taken at three scan rates (100, 300, and 500 mV/s). First, the BAS potentiostat measures the rest potential of an electrode. The potentiostat then scans negatively from the rest potential to -700 mV. The second segment consists of a scan from -700 mV to +1200 mV. The third segment scans from +1200 mV to -700 mV and the fourth segment from -700 mV to 1200 mV. The width of the capacitive envelope measured at +400 mV using segments 2 and 3 is proportional to the electrode area and was used to estimate the carbon paste electrode area relative to a Pt disk electrode of known dimensions. The reported relative current densities were calculated using these approximate electrode areas. Note that this estimate of electrode area may contain errors as great as 30 % and greater errors are possible for systems containing metals other than platinum. Several controls were examined under similar conditions, including commercial 10% Pt on XC-72 (E-tek, Inc.), pure XC-72 (Cabot Corp.), and a Pt disk electrode.

Cyclic voltammetry was used to measure the electroactivity of the control and carbon paste electrodes towards several dissolved gaseous species that are relevant to fuel cell technology. In separate experiments, either carbon monoxide (CO) or oxygen (O_2) gas were vigorously bubbled through a 0.10 M Na_2SO_4 electrolyte solution for at least 10 to 15 minutes prior to electrochemical measurements. A blanket of gas was maintained over the solution while electrochemical measurements are taken. Electrodes are preconditioned under both gases prior to collecting data. Preconditioning consists of cycling the electrode between -700 mV and +1200 mV (vs. SCE) 100 times at 500 mV/s. Cyclic voltammograms were then recorded in a similar manner as described above for capacitive background analysis.

The electrochemical studies involving methanol (MeOH) utilized an aqueous solution consisting of 0.10 M Na_2SO_4 and 0.02 M MeOH. The MeOH solution was vigorously purged with N_2 gas for 10 to 15 minutes prior to making any electrochemical measurements. A blanket of N_2 gas was maintained over the solution while electrochemical measurements are taken. Electrode preconditioning and cyclic voltammogram recording were conducted as described above.

Representative scans in N_2 saturated solutions are shown in Figure 5. Figure 5 compares the background CV in N_2 for electrodes made from either a 50:50 physical mixture of Pt/C_3N_{4+x} or a commercial Pt on carbon sample mixed with carbon black (both are 2% Pt in bulk paste electrode). All electrodes exhibit similar morphologies.

Data tables describing the electrodes and sample conditions are compiled in the Appendices. Each table is ordered in descending order by ratio of sample current density ratio relative to that recorded for a platinum disk control electrode.
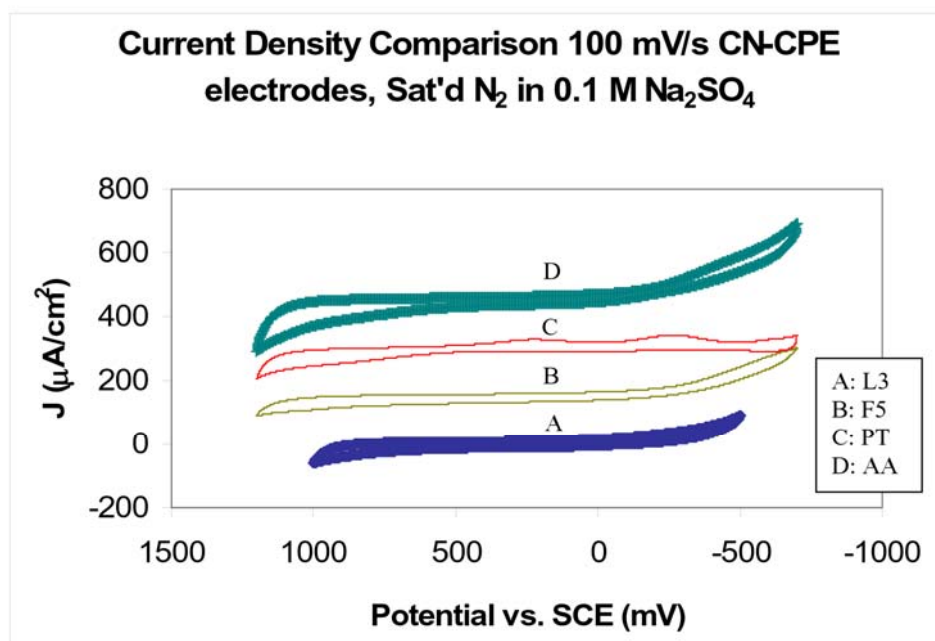
Figure 5. Cyclic voltammetry comparison in N_2 purged 0.10 M Na_2SO_4 of carbon paste electrodes containing 50:50 weight % carbon black mixtures with (A, D) Pt/C_3N_{4+x} (pyridine pretreated samples), (B) commercial Pt on carbon black, or (C) a Pt disk electrode. The CV scans are offset for clarity.

4.3.3. O$_2$ electrochemical results

A key catalytic process that occurs at the cathode of a fuel cell structure is reduction of O$_2$. The metal containing carbon nitride/carbon black paste electrodes were examined in an O$_2$ saturated solution and their redox activity was compared to pure Pt disk electrodes and to an electrode made with commercial Pt on carbon black (XC-72). In general, most platinum containing carbon nitride samples exhibited faradaic response with an onset near -270 mV vs. SCE with a thin and somewhat sigmoidal shape, in contrast to the more well-defined waves observed for a 50:50 mixture of commercial 10 % Pt on carbon with carbon black (2% Pt in the carbon paste electrode). Figure 6 shows a comparison of CV data for these materials in a saturated O$_2$ solution.
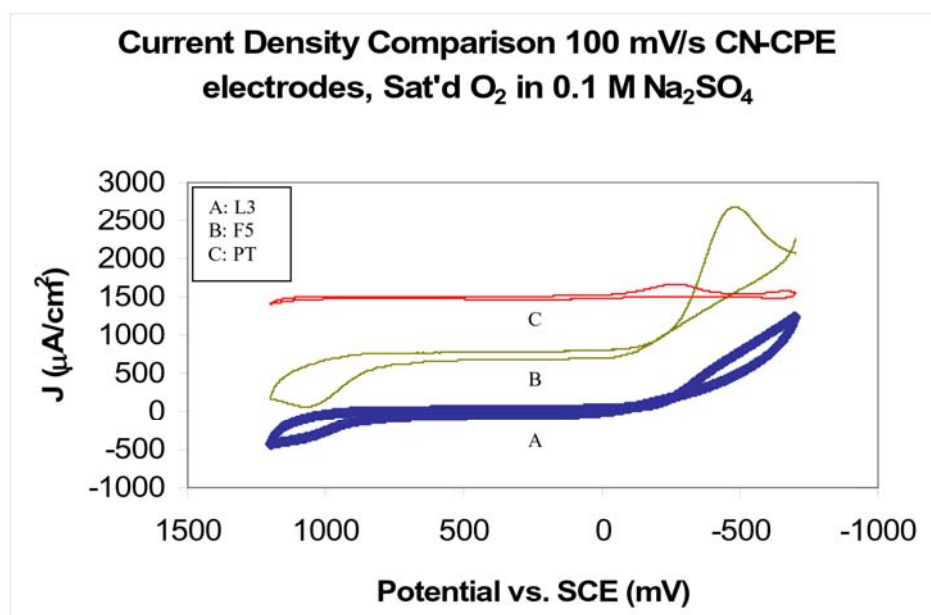
Figure 6. Cyclic voltammetry comparison in O$_2$ purged 0.10 M Na$_2$SO$_4$ of carbon paste electrodes containing 50:50 weight % carbon black mixtures with (A) Pt/C$_3$N$_{4+x}$ (pyridine pretreated sample), (B) commercial Pt on carbon black, or (C) a Pt disk electrode. The CV scans are offset for clarity.

This electrochemical events in O$_2$ were observed both for Pt samples based on the co-mingled (carbon black incorporated during C$_3$N$_{4+x}$ synthesis) and blended (carbon black added when preparing final electrode) materials (see Appendix 2). Similar to the Pt samples, nickel impregnated carbon nitrides also show thin and sigmoidal response near -270 mV. In addition, the Ni-carbon nitride electrodes show what

appears to be a quasi-reversible redox couple with an E_o near 600 mV under O_2. These waves appear during electrode preconditioning and more investigation is necessary to determine their source. The Pt-carbon nitride composites have comparable current densities (J in $\mu A/cm^2$) to those observed for the blended commercial Pt on carbon electrodes. For comparison, the commercial Pt standard recorded current densities 4 to 18 times greater than the Pt disk electrode, while several carbon nitride composites containing Pt registered current densities 2 to 24 times greater than the Pt disk control. The highest value of 65 for a Ni on carbon nitride sample is a bit uncertain because the surface area of the Ni electrodes is less well determined than the Pt electrodes, but there is still enhanced current density for the Ni systems, as well.

4.3.4. CO electrochemical results

Carbon monoxide is a recognized problematic constituent of reformate hydrogen and is a byproduct of several hydrocarbon fuel oxidations processes. CO is a well-established strongly binding Lewis basic ligand for many transition metals, particularly platinum. CO passivates reactive Pt metal catalytic sites, resulting in degradation of its catalytic properties. Typically, adsorbed CO is removed from a Pt or other metal surface by sweeping to a positive potential (> + 500 mV vs. SCE), which generates a CO stripping wave in the CV scan. In contrast to the Pt disk electrode standards, which show well-defined stripping waves, the Pt/C_3N_{4+x} samples generally displayed broader CO response waves (Figure 7A), similar to those displayed by some of the commercial Pt on carbon control electrodes (Figure 7B). Figure 7 shows representative CV scans for several platinum based catalytic systems.
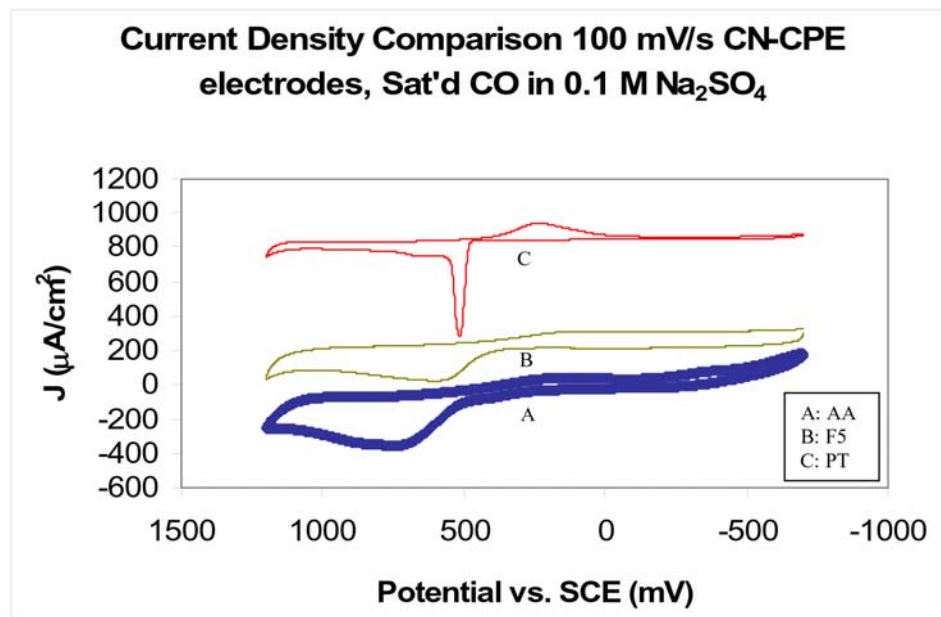
Figure 7. Cyclic voltammetry comparison in CO purged 0.10 M Na_2SO_4 of carbon paste electrodes containing 50:50 weight % carbon black mixtures with (A) Pt/C_3N_{4+x} (pyridine pretreated sample), (B) commercial Pt on carbon black, or (C) a Pt disk electrode. The CV scans are offset for clarity.

In contrast to the O_2 data, the relative current densities recorded for the observed CO peaks are lower for all carbon paste electrodes relative to the Pt disk electrode value. Notably, the pyridine treated Pt/ Pt/C_3N_{4+x} based electrodes show values similar to those prepared from commercial Pt on carbon black. These samples had current densities in the range of 50 - 70 % of that observed for the Pt disk electrode. The entire range of Pt samples had relative current densities from 10 to 70 % relative to the Pt disk value and Ni impregnated samples showed small CO waves, corresponding to ~15 % relative current densities to that of Pt disks. Ratios of peak current densities relative to Pt disks are listed in Appendix 3. In all cases, the ratio is less than 1. This result is a bit deceiving in that the Pt disk wave yields to a stripping wave and the other systems do not. Note that the Ni value may be low due to errors in the calculated electrode area. Appendix 3 tabulates data and observations for several carbon paste electrode preparations involving CO electrochemistry. Overall, there are significant electrochemical events observed for both Pt and Ni impregnated carbon nitride materials in CO saturated solutions, relative to those observed in N_2 saturated solutions. Copper and other metal impregnated carbon nitride samples also show several observable electrochemical events in CO versus N_2 solutions, but the source of these events is still unclear.

4.3.5. Methanol electrochemical results

In methanol solution, the Pt disk control electrodes show distinct wave onsets around +300 mV vs. SCE. The pyridine pretreated Pt/C_3N_{4+x} carbon paste electrodes exhibited similar responses with consistently greater peak current densities (2 - 5 times greater) relative to the Pt disk value. In contrast, the commercial Pt on carbon black carbon paste electrodes showed weak or unobservable events near 300 mV, with only 90 % or less current density relative to the Pt disk value. A Ni/C_3N_{4+x} sample showed more complex electrochemistry and well-defined peaks near 600 mV. Figure 8 shows a CV comparison of several Pt containing samples in methanol containing electrolyte. Appendix 4 lists more extensive information on a wide range of Pt and Ni based carbon nitride and control electrode experiments. The pyridine washed Pt/C_3N_{4+x} samples all yield current densities several times that of a Pt disk electrode. The lone Ni electrode is also pyridine washed and also performed well.
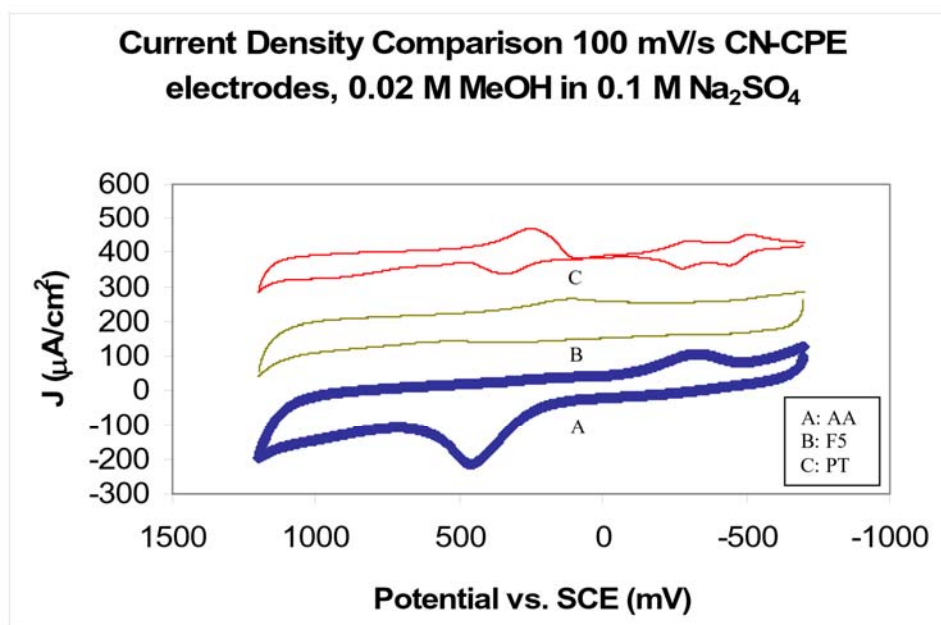

Figure 8. Cyclic voltammetry comparison in a N_2 purged solution of 0.10 M Na_2SO_4 and 0.20 M MeOH of carbon paste electrodes containing 50:50 weight % carbon black mixtures with (A) Pt/C_3N_{4+x} (pyridine pretreated sample), (B) commercial Pt on carbon black, or (C) a Pt disk electrode. The CV scans are offset for clarity.

5. Summary

The general goals for this one-year feasibility study as stated in the original proposal are:

1) Produce carbon nitride materials and carbon composites with and without metal components.

2) Determine the electrical conductivity and redox characteristics of C_3N_{4+x} powders, thermally graphitized products, and carbon composites with and without metals additions.

3) Conduct preliminary experiments on the feasibility of utilizing carbon nitrides as components of modified electrodes for use in redox processes relevant to fuel cell technology.

We have made significant progress in all of the listed areas, particularly with respect to examining the thermal and electrochemical stability of the pure carbon nitride materials and carbon composites, and depositing several transition metals onto the carbon nitride network surface.

- Initial experiments support the contention that the nitrogen-rich carbon nitride materials can be incorporated into a conducting composite system.

- The *in-situ* generated C_3N_{4+x} – carbon black composite formation method is a promising strategy to produce homogeneous electrically conducting systems.

- The C_3N_{4+x} materials are inert under acidic and neutral electrochemical environments and do not impede oxidation-reduction reactions.

- The carbon nitride solids were impregnated with metal species using hydrogen reduction methods, with pyridine sample pretreatment appearing to improve metal salt adsorption, which may yield a more homogeneous distribution of metal on the surface.

- Physical mixtures of the M/C_3N_{4+x} materials with carbon black show electrochemical activity toward O_2, CO, and methanol solutions.

- In the oxygen and methanol cases, the calculated current densities of metal - carbon nitride materials comparable to or greater than those observed for commercial Pt on carbon black standards.

References

1.   Miller, D. R.; Wang, J.; Gillan, E. G. "Rapid, facile synthesis of nitrogen-rich carbon nitride powders", *J. Mater. Chem.* **2002**, *12*, 2463-2469.

2.   Gillan, E. G. "Synthesis of nitrogen-rich carbon nitride networks from an energetic molecular azide precursor", *Chem. Mater.* **2000**, *12*, 3906-3912.

3.   Wang, J.; Miller, D. R.; Gillan, E. G. "Photoluminescent carbon nitride films grown by vapor transport of carbon nitride powders", *Chem. Commun.* **2002**, 2258-2259.

4   Kroke, E.; Schwarz, M. "Novel group 14 nitrides", *Coord. Chem. Rev.* **2004**, *238*, 493-532.

Dissemination of Project Results and Listing of Project Personnel

1) At this time, no publications based on this research have been published or submitted. It is anticipated that a paper on the synthesis of M/C_3N_{4+x} materials and a report on their electrochemical characteristics will be submitted for publication in the near future.

2) No patent applications have yet been filed based on the results of this study. A disclosure will be filed, pending more data that confirms the preliminary results.

3) Two senior personnel conducted all of the research in this study.
a) All of the synthetic work, including chemical synthesis of carbon nitrides and metal impregnation and reduction was conducted by Dale Miller (Gillan group), who is currently writing his Ph.D. dissertation for a December 2004 graduation. His efforts in this study are contained in one chapter of his dissertation.

b) All of the electrochemical characterization, including carbon paste electrode preparation and data analysis was conducted by Dr. Drew Dunwoody (Leddy group), who is currently a postdoctoral associate.

Appendix 1: Main Inventory of Electrode Materials

Pine = Pt disk electrodes

GC = glassy carbon electrode

2DM materials = carbon nitride solids

XC72 = conductive carbon black additive

blended = metal salts are condensed on to carbon nitride then reduced with hydrazine or H_2

co-mingled = metal salts are present during the carbon nitride formation reaction

pyr = pyridine was pretreatment of the carbon nitride powder

I.D.	Material	% metal in electrode
PT	PINE Pt 10095 (small)	100
GC	GC 10222	-
G	PINE Pt 3489	100
H	GC 10222	-
A	2DM127a 10 wt% Cu BLENDED N_2H_4	2.0
B	2DM127b 10 wt% Pt BLENDED N2H$_4$	1.7
B2	2DM127b 10 wt% Pt BLENDED N_2H_4	1.9
C	2DM127c 10 wt% Cu BLENDED N_2H_4 w/pyr. wash	1.9
D	2DM127d 10 wt% Pt BLENDED N_2H_4 w/pyr. wash	2.0
D2	2DM127d 10 wt% Pt BLENDED N_2H_4 w/pyr. wash	2.0
E	2DM96C NO METAL BLENDED	-
F	XC72 10 wt% Pt BLENDED	2.0
F2	XC72 10 wt% Pt BLENDED	2.0
F3	XC72 10 wt% Pt BLENDED	2.0
F4	XC72 10 wt% Pt BLENDED	1.9
F5	XC72 10 wt% Pt BLENDED	2.0
I	2DM138a 10 wt% Cu BLENDED H_2	1.9
J	2DM138c 10 wt% Cu BLENDED H_2 w/pyr. wash	1.8
J2	2DM138c 10 wt% Cu BLENDED H_2 w/pyr. wash	1.9
K	2DM138d 10 wt% Pt BLENDED H_2	2.0
K2	2DM138d 10 wt% Pt BLENDED H_2	2.0
L	2DM138f 10 wt% Pt BLENDED H_2 w/pyr. wash	1.9
L2	2DM138f 10 wt% Pt BLENDED H_2 w/pyr. wash	2.0
L3	2DM138f 10 wt% Pt BLENDED H_2 w/pyr. wash	1.9
M	2DM145a co-ming. 10 wt% Pt NEAT H_2	4
M2	2DM145a co-ming. 10 wt% Pt NEAT H_2	4
N	2DM145b co-ming. 10 wt% Pt NEAT H_2 w/pyr. wash	4
N2	2DM145b co-ming. 10 wt% Pt NEAT H_2 w/pyr. wash	4
O	2DM145c co-ming. 10 wt% Cu NEAT H_2	4
P	2DM145d co-ming. 10 wt% Cu NEAT H_2 w/pyr. wash	4
Q	2DM145e co-ming. NEAT NO METAL	-
V	Fe_3O_4/CB-10% Pt NEAT	3.0
W	10 wt% Pt XC-72 NEAT	3.9
W2	10 wt% Pt XC-72 NEAT	4.0
W3	10 wt% Pt XC-72 NEAT	3.8
W4	10 wt% Pt XC-72 NEAT	4.0
W5	10 wt% Pt XC-72 NEAT	4.0
X	20% Pt/Ru BLENDED [50% XC-72]	3.9
Y	Fe_3O_4/20% Pt/Ru NEAT [20% mags]	6.6
Z	20% Pt/Ru BLENDED [20% XC-72]	6.5
	All 2DM194 samples were reduced using H2 at 350 C	
AA	2DM194a 10 wt% **Pt** BLENDED w/pyr. wash (variant of "L")	1.9
AB	2DM194b 10 wt% **Pt** BLENDED w/ethylenediamine wash (variant of "L")	1.9
AC	2DM194c 10 wt% **Pt** BLENDED w/triethylamine wash (variant of "L")	2.0
AD	2DM194d 50 wt% **Pt** BLENDED w/pyr. wash (variant of "L")	9.9
AE	2DM194k 10 wt% **Ni** BLENDED w/MeOH wash	2.0
AF	2DM194l 10 wt% **Ni** BLENDED w/pyr. wash	2.0
AG	2DM194m 10 wt% **Ag** BLENDED w/MeOH wash	2.0
AH	2DM194n 10 wt% **Ag** BLENDED w/pyr. wash	2.0
AI	XC72 (**no Pt**) 10 wt% **Pt** BLENDED w/pyr. wash	2.0
AJ	2DM194e 10 wt% **V** BLENDED w/MeOH wash	2.0
AK	2DM194f 10 wt% **V** BLENDED w/pyr. Wash	2.0
AL	2DM194g 10 wt% **Mn** BLENDED w/MeOH wash	2.0
AM	2DM194h 10 wt% **Mn** BLENDED w/pyr. wash	2.0
AN	2DM194i 10 wt% **Co** BLENDED w/MeOH wash	2.0
AO	2DM194j 10 wt% **Co** BLENDED w/pyr. wash	2.0

Appendix 2: Comparison of Oxygen (O₂) CV Data

J_{O2} ratios are relative to Pt disk value and are arranged in decreasing order

ID		metal	Blend	Neat	control	wash	-270 mV response	Ratio J_{O2} to Pt m	
AF	40% solids [50.3 CN & 49.7 XC72]	Ni	X			pyr.	X?	65	couple around 600 mV / thin and sigmoidal (-) range
AB*	38% solids [49.8 CN & 50.2 XC72]	Pt	X		ethylenediamine			24	thin and sigmoidal
AE	40% solids [49.2 CN & 50.8 XC72]	Ni	X			MeOH	X?	21	couple around 600 mV / thin and sigmoidal (-) range
F4	39% solids [49.3 10 wt% Pt on XC72 & 50.7 XC72]	Pt	X		X	-		18	well defined waves
L3	39% solids [49.7 CN & 50.3 XC72]	Pt	X			pyr.	X	15	thin and sigmoidal
F5	39% solids [50.1 10 wt% Pt XC72 & 50.0 XC72]	Pt	X		X	-		14	well defined waves
AA*	39% solids [49.2 CN & 50.8 XC72]	Pt	X			pyr.	x	5	thin and sigmoidal
W5	40 % solids [10 wt% Pt XC72]	Pt		X	X	-		4	well defined waves
K2	40% solids [50.0 CN & 50.0 XC72]	Pt	X			-	X	3	thin and sigmoidal
N2	39% solids [CN co-ming Pt H2 w/pyr. wash]	Pt		X		pyr.	X	3	thin and sigmoidal
AC*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			triethylamine	X	3	thin and sigmoidal
AD*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			pyr.		2	thin and sigmoidal
W4	40 % solids [10 wt% Pt XC72]	Pt		X	X	-		2	well defined waves
PT 7/29	PINE Pt 10095	Pt			X	-	X	1	well defined wave
PT 8/02	PINE Pt 10095	Pt			X	-	X	1	well defined wave

* = variant on L series samples

Appendix 3: Comparison of CO CV Data

J_{CO} ratios are relative to Pt disk value and are arranged in decreasing order

ID	Description	metal	Blend	Neat	control	wash	CO Response		N2 bckgrd height (cm)	CO Peak height (cm)	Ratio	Ratio J_{CO} to Pt m
PT 7/29	PINE Pt 10095	Pt			X	-	X	stripping	0.75	9.2	12.3	1
PT 8/02	PINE Pt 10095	Pt			X	-	X	stripping	0.45	9.3	20.7	1
AA*	39% solids [49.2 CN & 50.8 XC72]	Pt	X			pyr.	X		1.55	13.5	8.7	0.69
L3	39% solids [49.7 CN & 50.3 XC72]	Pt	X			pyr.	X	narro neck wave	0.6	6.5	10.8	0.66
W4	40 % solids [10 wt% Pt XC72]	Pt			X	-			5.7	45	7.9	0.62
N	40% solids [CN co-ming Pt H2 w/pyr.]	Pt		X		pyr.	X	narrow wave	0.7	7.1	10.1	0.62
N2	39% solids [CN co-ming Pt H₂ w/pyr. wash]	Pt		X		pyr.	X	narrow wave	0.8	7.3	9.1	0.55
K2	40% solids [50.0 CN & 50.0 XC72]	Pt	X			-	X	narrow wave, traces cross	0.9	8.2	9.1	0.55
F5	39% solids [50.1 10 wt% Pt XC72 & 50.0 XC72]	Pt	X		X	-			1.4	8.4	6.0	0.47
K	40% solids [49.4 CN & 50.6 XC72]	Pt	X				X	narrow wave	1	7.5	7.5	0.45
AB*	38% solids [49.8 CN & 50.2 XC72]	Pt	X			ethylenediamine	X		0.8	4.1	5.1	0.40
L	39% solids [49.2 CN & 50.8 XC72]	Pt	X			pyr.	X	narrow wave	1.2	7.4	6.2	0.37
F	40% solids [49.4 10 wt% Pt CB & 50.6 XC72]	Pt	X		X	-	X	narrow wave	1	6	6.0	0.36
AD*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			pyr.	X	not as strong akin to AC	6.3	28.2	4.5	0.35
AC*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			triethylamine	X	not as strong akin to AD	8.2	35.3	4.3	0.34
W5	40 % solids [10 wt% Pt XC72]	Pt		X		-			3.2	11.2	3.5	0.28
G	PINE Pt 3489	Pt		X	X	-	X		2.2	8.9	4.0	0.25
W	39% solids [CB-10% Pt]	Pt		X	X	-	X	narrow wave, with 2 bumps	1.9	6.5	3.4	0.21
D	40% solids [50.0 CN & 50.0 XC72]	Pt	X			pyr.	X	narrow neck	2	6.1	3.1	0.19
AF	40% solids [50.3 CN & 49.7 XC72]	Ni	X			pyr.	x	small wave	0.07	0.15	2.1	0.17
AE	40% solids [49.2 CN & 50.8 XC72]	Ni	X			MeOH	x	small wave	0.32	0.6	1.9	0.15
D2	40% solids [49.6 CN & 50.4 XC72]	Pt	X			pyr.	X	narrow neck	2.7	5.4	2.0	0.12
L2	40% solids [50.3 CN & 49.7 XC72]	Pt	X			pyr.	X	Not as well defined as "L"	2.7	5.4	2.0	0.12
M2	40% solids [CN co-ming Pt H2]	Pt		X		-	X		2.3	4.5	2.0	0.12
X	39% solids [50.1 20% Pt/Ru & 49.9 XC72]	Pt/Ru	X			-	X	well defined wave	2.8	4.3	1.5	0.09
M	40% solids [CN co-ming Pt H2]	Pt		X		-	X		3.4	5	1.5	0.09
F4	39% solids [49.3 10 wt% Pt on XC72 & 50.7 XC72]	Pt	X		X	-			1.3	1.2	0.9	0.07
B2	38% solids [50.3 CN & 49.7 XC72]	Pt	X			-	?	small possible wave	2	0.8	0.4	0.024
J	37% solids [48.0 CN & 52.0 XC72]	Cu	X			pyr.	X	minor response ON Cu	1.9	0.4	0.2	0.01
Z	39% solids [82.9 20% Pt/Ru & 17.1 XC72]	Pt/Ru	X			-	X	small wave	3.3	0.35	0.1	0.01

* = variant on L series samples

J_{MeOH} ratios are relative to Pt disk value and are arranged in decreasing order

ID		Blend	Neat	control	wash	Ratio J_{MeOH} to Pt m	cycling build	+ 300 mV response
AA*	39% solids [49.2 CN & 50.8 XC72]	Pt	X			pyr.	5.08	++	+++	well formed wave around 300 mV
AD*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			pyr.	4.95	+++	+++	CV morphology more complex
L	39% solids [49.2 CN & 50.8 XC72]	Pt	X			pyr.	4.20	++	++	sharp Triangular stripping wave (+100 mV r)
AF	40% solids [50.3 CN & 49.7 XC72]	Ni	X			pyr.	2.73	+	+?	small shoulder around +600 mV
L3	39% solids [49.7 CN & 50.3 XC72]	Pt	X			pyr.	1.76	++	++	sharp Triangular stripping wave
PT 7/29	PINE Pt 10095	Pt			X	-	1.00	+++	+++	well formed wave around 300 mV
PT 8/02	PINE Pt 10095	Pt			X	-	1.00	+++	+++	well formed wave around 300 mV
K	40% solids [49.4 CN & 50.6 XC72]	Pt	X			-	0.96	++	+?	waves~ (+400 mV o) (+150 mV r)
AC*	40% solids [50.1 CN & 49.9 XC72]	Pt	X			triethylamine	0.93	++	++	CV morphology more complex
G	PINE Pt 3489	Pt			X	-	0.90			
F4	39% solids [49.3 10 wt% Pt on XC72 & 50.7 XC72]	Pt	X		X	-	0.81			small wave
M	40% solids [CN co-ming Pt H2]	Pt		X		-	0.66	++	+?	waves (-200 mV o) & (+225 mV r)
W4	40 % solids [10 wt% Pt XC72]	Pt		X	X	-	0.66			small wave
N2	39% solids [CN co-ming Pt H2 w/pyr. wash]	Pt		X		pyr.	0.54	++	+	small wave (+100 mV r)
AB*	38% solids [49.8 CN & 50.2 XC72]	Pt	X			ethylenediamine	0.39	+	+	small wave near 300 mV
F5	39% solids [50.1 10 wt% Pt XC72 & 50.0 XC72]	Pt	X		X	-	0.36			very small waves
N	40% solids [CN co-ming Pt H2 w/pyr.]	Pt		X		pyr.	0.11	++	+?	waves +400mV
L2	40% solids [50.3 CN & 49.7 XC72]	Pt	X			pyr.	0.10	+	+	smaller wave, but is there
W	39% solids [CB-10% Pt]	Pt		X	X	-	0.08	++	++	
K2	40% solids [50.0 CN & 50.0 XC72]	Pt	X			-	0.03	++	+	wave ~ (+300 mV o); very small

* = variant on L series samples