Novel dual templating approach for preparation of highly active Fe-N-C electrocatalyst for oxygen reduction

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Abstract:

A highly active, stable Fe-N-C electrocatalyst with unique 3D porous graphene “nano-stack” morphology is synthesized using a novel, facile and a direct process that involves a sodium salt templating of a small organic molecule benzimidazole carboxylic acid. We synthesize different combinations of the precursor with sodium salt templates and silica sacrificial support method, followed by their pyrolysis to generate Fe-N-C catalysts. The oxygen reduction reaction catalytic performance of such benzimidazole derived catalysts is studied in the alkaline media using rotating ring disk electrode and in alkaline exchange membrane fuel cell. The electrocatalytic performance of the best catalyst shows an improvement over the commercial Pt/C catalyst in the Rotating Ring-Disk Electrode tests along with excellent stability (as performed under the Department of Energy- Durability Working Group protocols). This work offers intriguing future avenues to the direct synthesis of Fe-N-C catalysts from tuning small molecule organic precursors for high temperature pyrolysis.

Keywords: *Benzimidazole carboxylic acid, Dual-templating, Graphene nano-stack, Active-electrocatalyst, Stable*

1. Introduction

The question of environmentally sustainable growth is increasingly being addressed with significant research efforts in the area of clean energy devices like fuel cells, batteries, ultracapacitors, etc. Of all such sources, fuel cells are one of the most environmentally friendly alternatives which do not require recharging as long as a continuous supply of the fuel is provided. They have diverse applications ranging from automotive propulsion to portable electronic systems. Unfortunately, though, the high cost of commercial platinum-based catalyst for the hydrogen electrooxidation and oxygen reduction reaction (ORR) is a serious limiting factor in the widespread deployment of this technology, e.g. the estimated cost of the fuel cell vehicle *Toyota Mirai* in North America is ~\$57,000. [1] The development of platinum group metal-free (PGM-free) catalysts has however renewed interest in fuel cell research, and there has been a fierce development in the synthesis of Metal-Nitrogen-Carbon (M-N-C) systems that have clearly emerged as promising alternatives for the cathode. [2-6] Such catalytic systems have been obtained by pyrolysis/carbon grafting of precursors ranging from porphyrins and phthalocyanines, [7-10] polymers, [11-13] metal organic frameworks (MOF), [14-19] zeolitic imidazolate frameworks (ZIF), [20-24] use of sacrificial support with small organic molecule precursors and naturally occurring materials. [25-28] The process of producing high surface area of these PGM-free catalysts and active materials involves the use of soft (organic molecules) and hard (silica and salts) templates. Previously a hard templating approach has been used in various ways by our group (SSM), [29, 30] Joo and coworkers, [31] Antonietti and coworkers [32] and several other researchers. [33] Ogale and coworkers recently demonstrated a process of sodium salt templating of polymer precursors to generate pyrolyzed high surface area carbons for ultracapacitors. [34, 35] Owing to the unique properties of graphene-based systems (high electrical and thermal conductivity, tunable surface area, corrosion resistance etc.), efforts have also been in place to generate graphene-based electrocatalysts using graphene oxide (GO) as the starting material followed by various reduction strategies. [36-38] This however has been a cumbersome process and not readily scalable at the current level of technology mainly due to tedious protocols and limitations of GO synthesis by the standard Hummers method. [39]

In this work, we demonstrate a facile, one-step synthesis of a Iron-Nitrogen-Carbon (Fe-N-C) catalytic system comprising of a unique 3D porous graphene nano-stack- morphology, using

1 a novel template generated by formation of sodium salt of carboxylic acid groups of the small
2 organic molecule- benzimidazole carboxylic acid, in combination with the University of New
3 Mexico patented silica sacrificial support method. This Platinum Group Metals-free (PGM-
4 free) cathode catalyst exhibits high electrochemical performance and stability in the alkaline
5 media with potential use in alkaline exchange membrane fuel cells (AEMFCs).
6 Benzimidazole has been previously used as part of a ZIF precursor by Zhang et al. [40] and
7 Palaniselvam et al. for ORR, [41] as surface grafts on graphene for supercapacitors and as
8 part of an MOF precursor by Chaikittisilp et al. [42] for ORR. Herein, a direct use of
9 benzimidazole as a precursor is demonstrated for the first time using a template synthesis
10 approach to generate the ORR catalyst. We establish the novel synthesis protocol which
11 results in a unique morphology and structure of the final catalyst and further demonstrate its
12 performance using electrochemical analysis techniques.
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23 2. Experimental

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25 **2.1 Fe-N-C Catalyst Synthesis:** Benzimidazole carboxylic acid was obtained commercially
26 from Sigma Aldrich and used without further purification. Commercially obtained silica
27 powder (CAB-O-SIL[®] LM-150 fumed silica, surface area $\sim 150 \text{ m}^2 \text{ g}^{-1}$) was used as the SSM
28 template and sodium hydroxide pellets were used for the salt formation process.
29 Commercially obtained iron nitrate nonahydrate was used in the synthesis. Three catalysts
30 were synthesized using the benzimidazole carboxylic acid. They were termed as
31 benzimidazole derived catalysts (BIDC). **BIDC1:** benzimidazole carboxylic acid was mixed
32 in water with a calculated amount of NaOH only and stirred for 4 h to form the salt. The
33 water was evaporated to obtain the solid. This was further ground and mixed thoroughly with
34 the iron salt. The precursor mixture was pyrolyzed in Ar at 950°C for 45 min, the product
35 ground and washed by stirring in dilute HCl/H₂SO₄ mixture overnight. The second pyrolysis
36 for 30 min at 950°C in ammonia (10 at%, nitrogen as a balance) was carried out. **BIDC2:**
37 benzimidazole carboxylic acid was mixed with a calculated amount of silica and iron
38 followed by grinding and pyrolysis at 950 °C for 45 min. In addition to dilute HCl/H₂SO₄,
39 concentrated solution of HF was also included in the washing process for this case. A second
40 pyrolysis step was also performed in ammonia (10 at%, nitrogen as a balance) at 950°C for
41 30 min. **BIDC3:** benzimidazole carboxylic acid in water was mixed with the same calculated
42 amount of NaOH as in the case of BIDC1 and stirred for 4 h to form a salt. The water was
43 evaporated to obtain the solid. The addition of an equal amount of silica as in BIDC2 case
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1 along with iron salt was then carried out followed by grinding of the mixture. The precursor
2 mixture was pyrolyzed in Ar at 950°C for 45 min. The product was washed with dilute
3 HCl/H₂SO₄ and concentrated HF solution. A second heat treatment was then carried out in
4 ammonia (10 at%, nitrogen as a balance) at 950°C for 30 min. (Figure 1)
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8 The three catalysts were characterized physically and electrochemically. The best performing
9 case **BIDC3** was characterized in more detail as presented.
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12 **2.2 Characterization:** Scanning Electron Microscopy (SEM) images were obtained using a
13 Hitachi S-800 instrument. Transmission Electron Microscopy (TEM) imaging was carried out
14 on a JEOL 2010 instrument on a copper grid. X-ray Photoelectron Spectroscopy (XPS)
15 spectra were acquired on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer using
16 an Al K α source monochromatic source. The operating pressure was about 2×10^{-9} Torr.
17 Survey and high resolution spectra were acquired at pass energies of 80 eV and 20 eV,
18 respectively. High-resolution spectra were recorded for the C 1s, N 1s, O 1s and Fe 2p core
19 levels. A linear background subtraction was used for quantification of C 1s, O 1s, and N 1s
20 while Shirley background was applied to Fe 2p spectra. X-ray diffraction (XRD) was carried
21 out using a Scintag Pad V diffractometer (Bragg-Brentano geometry) with DataScan 4
22 software (from MDI, Inc.)
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33 Electrochemical characterization was performed using Pine Instruments analytical system.
34 Working electrodes were prepared by mixing 5 mg of BIDC with 850 μ L of DI water and
35 150 μ L of 0.5 wt% Nafion solution. The mixture was ultrasonicated, and 10 μ L was applied
36 onto a glassy carbon Rotating Ring-Disk Electrode (RRDE) three times. The loading of the
37 catalyst was calculated to be 0.6 mg cm⁻². Standard Pt/C (40wt%, JM-Alfa Aesar) was also
38 used as a reference with a loading of $\sim 30 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. The electrolyte used was O₂ saturated 0.1
39 M KOH, and Hg/HgO was used as the reference electrode. It was calibrated against the RHE,
40 and all the potentials are reported against RHE. The calibration process is described in the
41 supplementary information.
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50 A membrane electrode assembly (MEA) was fabricated by coating BIDC3 (4 mg cm⁻²) on
51 one side of the Tokuyama A201 membrane and 40 wt% Alfa Aesar Pt/C catalyst on the other
52 side of the membrane (0.3 mg cm⁻²). Cell temperature was maintained at 60 °C. O₂ and H₂
53 backpressure were set at 20 psi gauge. Ionomer AS4 (5 wt%) was used about 35 wt% of the
54 catalyst. The catalyst coated membrane (CCM) was then sandwiched between two gas
55 diffusion layers (GDL).
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3. Results and Discussion

The Brunauer–Emmett–Teller (BET) surface area of the synthesized catalysts is described in Table 1 along with their elemental atomic concentrations determined by XPS. It is evident that the B IDC3 possesses the highest surface area ($\sim 930 \text{ m}^2 \text{ g}^{-1}$) of the three cases and is a significant contributing factor towards its efficient catalytic performance. The enhanced porosity increases the access of the electrolyte to the active sites where the electrochemical O_2 reduction occurs. A significant increase in the surface area of B IDC3 as compared to the other catalysts points to a hierarchical distribution of pore size in the B IDC3 from micro-, meso- to macro-pores. This can arise because of different pore forming agents in B IDC3, the Na^+ ions and SiO_2 nanoparticles. Na^+ ions give rise to micro- and meso-porosity during pyrolysis by reacting with COO^- to yield Na_2CO_3 which is subsequently etched by acid removal while on the other hand SiO_2 particles HF etching contribute to meso and macro-porosity. [12, 34, 35] A proper pore size distribution is essential because the ORR catalytic sites generally occur in meso and micro- pores, [14, 31] whereas the macro-pores assist in electrolyte transport and accessibility. In the case of B IDC1 and B IDC2, Na^+ ions and SiO_2 contribute individually to the porosity, respectively and there is no effect in combination resulting in a reduced surface area.

XPS was performed on the B IDCs to obtain an in-depth knowledge of their elemental and chemical properties. XPS spectra of C1s and N1s in B IDC3 are shown in Figure 2. C1s spectrum demonstrates primarily the presence of sp^2 carbon species at 284.4 eV along with some sp^3 carbon (285.1 eV), C-N (at 286.1 eV) and oxygenated carbon $\text{C}_x\text{-O}_y$ at 286-289 eV. The relative content of C1s in B IDC3 is observed and calculated to be $\sim 10.4 \%$ for C-N, $\sim 4.4\%$ for C-O, $\sim 3.3\%$ for C=O and $\sim 5.8\%$ for C-OOH, the rest being C-C content. All composition has been described in at% values. The N1s spectrum of B IDC3 also indicates the presence of multiple components which mainly include imine/nitrile like N at 397.6 eV (5.7%), pyridinic N at 398.3 eV (17.6%), N bonded to Fe at 399.5 eV (16.8%), hydrogenated at 400.7 eV (24.4%), graphitic at 401.9 eV (12.2%) and cationic and N- O_x at 403.1-406.0 eV (23.4%). The detailed elemental composition of B IDC1 and B IDC2 has been described in the supplementary information. In acidic media, it has been established that pyridinic nitrogen (that occurs at the edge of the crystallite) and nitrogen coordinated to metal (eg. Co-N or Fe-N) in the carbon matrix are the atomic species that significantly contribute to the high activity

of most active PGM free electrocatalysts. [43, 44] We have demonstrated before that for alkaline media, no direct dependence of performance on the type of nitrogen present. [45] The best performing sample has smallest amount of pyridinic and Fe-N_x centers, while amount of hydrogenated (24.4 %) and protonated nitrogen (23.4 %) is the largest. The positive role of protonated nitrogen on activity in alkaline was recently demonstrated by Rauf et al [46]. Importantly, BIDC1 sample has the largest amount of defect sites in graphene network that are terminated in surface oxides which facilitated ORR in alkaline media. [45]

Catalyst	BET Surface Area (m ² g ⁻¹)	C 1s (at%)	N 1s (at%)	O 1s (at%)	Fe 2p (at%)
BIDC1	304	90.1	1.6	8.1	0.1
BIDC2	493	92.7	3.7	3.4	0.48
BIDC3	930	95.8	1.7	2.4	0.19

Table 1. Surface area and elemental composition of BIDCs

XRD pattern of the BIDC3 interestingly shows the signatures of crystalline graphite-like arrangement pointing to the presence of micro graphene crystallite morphology in the material (Figure 3a). [47] The several graphitic planes are clearly indicated in the XRD pattern. The 002 graphene peak is the major peak at 26.1 (very close to the ideal 26.6 in pure crystalline graphite). This is usually reflected as a broad peak in few-layer graphene occurring in the range of 2θ= 24-25, primarily due to lack of large stacking order in graphene or reduced forms of graphene oxide (GO). Additionally, other peaks indicative of stacked sheet morphology are 010, 101, 222 and 110 planes located at 2θ values of 42.8, 43.8, 54.5, and 77.6. The crystallinity of BIDC3 is smaller than that of commercial graphite crystal but much larger than that of chemically or thermally reduced graphene, confirming the presence of a porous microcrystalline graphene nano-stack network. A crystalline graphitic arrangement contributes to a better conductivity in the material, as is known that graphene has higher conductivity compared to activated/amorphous carbon because of less defects and a planar sheet like structure. The crystallinity of BIDC3 can thus render better electron transport for electrocatalysis as compared to porous disordered activated carbon. Furthermore, the porous network in the graphitic arrangement of BIDC3 gives rise to large number of defects, especially edge defects in graphitic sheets. This is confirmed by Raman

spectroscopy. Shen et al. recently provided a direct evidence of the higher catalytic activity of graphitic edges in comparison to the basal planes. [48] Thus the synergistic effect of higher conductivity due to graphitic crystallinity and higher catalytic activity due to the pore structure induced graphitic edge defects gives an inherent performance advantage to BDC3 catalyst over disordered activated carbon and crystalline graphite/graphene.

Raman spectrum of BDC3 (Figure 3b) reveals the typical features assigned to carbon, namely the 'G band' at 1578 cm^{-1} that arises due to the E_{2g} symmetry mode of sp^2 carbon and the 'D' Band at 1359 cm^{-1} that is a defect induced peak. The appearance of two peaks the 2D region at ~ 2700 and 2900 cm^{-1} indicates the presence of stacked graphene sheets as opposed to a single 2D peak in single/few layer of graphene. [49]

SEM images confirm the presence of a porous 3D graphene nano-stacks arranged in a flake-like morphology in the BDC. The graphite crystal like structure is observed at low resolution (Figure 4a-b) and the high surface area aspect of these crystallites is revealed at higher resolution (Figure 4c-d). TEM images further elucidate on the morphological aspects of this catalyst.

TEM images (Figure 5) offer visual insight into the microscopic graphene crystallites in the structure of the carbon catalyst obtained. As can be seen from the images, the micro-lattices have a size of about 50-100 nm and are arranged in a sequenced agglomeration to give a final flake-like morphology which was earlier seen in the SEM images.

To study the ORR catalytic properties of the BDCs, Linear Sweep Voltammetry (LSV) studies were performed on these materials using a Rotating Ring Disk Electrode (RRDE) assembly (Figure 6a). The scan rate and rotation rate used for these experiments was 5 mV s^{-1} and 1600 rpm respectively. The best catalyst BDC3 shows an impressive half wave potential ($E_{1/2}$) potential improvement of about 50 mV above the commercial Pt/C catalyst. BDC3 shows an improved $E_{1/2}$ and limiting current density as compared to the other BDCs as well. This can certainly be correlated to the increased surface area and the unique morphology obtained in the case of BDC3 since there is not much difference in the elemental surface composition as compared to the other catalysts.

Hydrogen peroxide generation by catalysts during the process of oxygen reduction is a major cause of degradation of the active catalytic sites, the fuel cell ionomer and membrane. Generation of a high percentage of H_2O_2 results in the degradation in performance of these

components. Thus, the DOE has set a target of ~2% of H₂O₂ production for an efficient system. We conducted RRDE experiments to determine the %H₂O₂ formation by the following equation:

$$\%H_2O_2 = 100 \times \frac{2I_R/N}{I_D + I_R/N} \quad \text{..... (Eq. 1)}$$

where, I_R= Ring current, I_D= Disk Current, N= Collection efficiency measured as ~37%.

Figure 6b shows the %H₂O₂ data that we obtained for B IDC3 in comparison to the standard Pt/C case. The values for B IDC3 are comparable to the standard case. The value remains around 5 % for most of the potentials, however, increases a little more at lower potentials. The B IDC thus shows a significantly low yield of H₂O₂ production. A low H₂O₂ yield indicates a direct 4e⁻ ORR mechanism which leads to intrinsically more efficient electrocatalysis. The value for %H₂O₂ production obtained for some of the best performance commercial Pt/C catalysts in other previous studies is ~4% which is comparable to the average value obtained in B IDC3. [50]

According to DOE Durability Working Group (DOE DWG) protocols, Accelerated Stress Test (AST) was performed on the B IDC3 using a Rotating Disk Electrode setup; O₂ saturated 0.1 M KOH, in the potential range of 1-0.1 V vs RHE, a scan rate of 50 mV s⁻¹ and a rotation rate of 900 rpm. A loading of 0.2 mg cm⁻² was used for these tests. [51]

500 cycles were performed on B IDC3. (Figure 7) The excellent stability is clearly demonstrated by the fact that the LSV curves almost overlap each other, and there is a negligible change in the half-wave potential of the catalyst after cycling for a long duration. This is one of the first stability test performed for PGM-free catalyst in alkaline medium utilizing the guidelines of the DOE DWG for cycling of the material over a large number of cycles.

MEA polarization test was conducted in alkaline exchange membrane fuel cell (AEMFCs) conditions (see Figure 8). The cell fabricated with B IDC3 catalyst exhibited an open circuit potential of 0.97 V. At 0.6 V the device exhibited current density value of ~25 mA cm⁻². Furthermore, the maximum power density output of the MEA is ~22 mW cm⁻². These performance values are comparable to recent literature reports on high-performance PGM-free systems in AEMFCs. [52] It has to be taken into account that the field of AEMFCs is

1 still in pre-matured stages of research and the performance is not yet comparable to PEMFC
2 literature.
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4 4. Conclusion 5 6

7 In summary, we demonstrate a novel approach towards the synthesis of a high surface area
8 Fe-N-C catalyst derived from a small organic molecule, benzimidazole carboxylic acid. The
9 sodium salt and sacrificial silica used as the templates in this process contribute to the novelty
10 of this process and render interesting properties to the material. This catalyst exhibits a
11 unique 3D porous flake-like morphology consisting of graphene nano-stacks, the synthesis of
12 which usually requires tedious protocols in the case of other methods. We conduct
13 electrochemical tests in the alkaline medium using an RRDE and MEA system to prove the
14 efficiency, stability and tolerance of this 3D catalytic system in comparison to the
15 commercially used Pt/C catalyst. This work thus offers important insights and future
16 direction to the tuning of small molecule precursors in order to obtain high surface area
17 carbon based electrocatalysts in fuel cells with specific morphologies and high performance,
18 an area that is relatively unexplored.
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Figures (with captions)

Figure 1. Schematic description of the synthesis process (a) Salt formation of the benzimidazole carboxylic acid (b) mixing with silica and iron salt (c) precursor mixture to be pyrolyzed (d) 3D porous microcrystalline graphene nano-stacks

Figure 2 (a) *C1s* XPS spectrum of BIDC3 (b) *N1s* XPS spectrum of BIDC3

Figure 3 (a) XRD pattern (b) Raman spectrum of BIDC3

Figure 4. (a-b) Low resolution SEM images of graphite-like crystallites in BIDC3 (c-d) Porous morphology visible for BIDC3

Figure 5. (a-b) TEM images of BIDC3 clearly showing the graphene nano-stacks at different scales as part of the larger carbonaceous network

Figure 6. (a) Linear Sweep Voltammetry plots of the BIDCs at a rotation rate of 1600 rpm in the RRDE and electrolyte 0.1M KOH (b) Peroxide percentage generated by BIDC3 in comparison to commercial Pt/C calculated using ring currents in RRDE

Figure 7. Accelerated stress test before and after cycling (7500 cycles at 900 rpm, scan rate: 50 mV s^{-1} , 0.1 M KOH)

Figure 8. MEA polarization test obtained using B1DC3 as the cathode and 40 wt% Pt/C- Alfa Aesar as the anode. The CCM used was the Tokuyama A201 membrane. Operating temperature: 60 °C, O_2 and H_2 backpressure: 20 psi gauge. Anode catalyst loading (0.3 mg cm^{-2}), Cathode catalyst loading (4 mg cm^{-2})