Synthesis of nitrogen-doped onion-like carbon and its use in carbon-based CoFe binary non-precious-metal catalysts for oxygen-reduction

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ABSTRACT
Nitrogen-doped onion-like carbon-rich materials were synthesized by heat treatment of a "hybrid" containing hexamethylene diamine complex in the presence of Co and Fe species while preparing non-precious metal electrocatalyst for oxygen-reduction. As demonstrated by electrochemical rotating disk electrode and fuel cell tests, the binary CoFe-based catalyst containing graphitized onion-like carbon nanostructures provides for improved performance relative to the single Fe-based catalyst in which no such carbon structure was observed. In the binary catalysts, variation of the ratios of Co to Fe and the total metal loading during the synthesis leads to a markedly different activity and four-electron selectivity for oxygen reduction. The optimized binary catalyst was studied in fuel cell lifetime tests using both constant current and voltage models, showing a good combination of activity and durability. Possible reasons for the improved performance of the CoFe-based binary catalyst are discussed. The graphitized onion-like carbon structure exclusively derived from Co in this work may be providing a robust matrix to host non-precious metal active sites, which would prevent water flooding of them, and increase the resistance to oxidative attack in the oxygen cathode, thereby leading to an improvement in performance durability.

1. Introduction
Onion-like carbon (OLC) structures have been envisioned to be quasi-spherical nanoparticles consisting of fullerene-like carbon layers enclosed by concentric graphitic shells, but their \( \pi \) and \( \sigma \) electronic structures are different from those of graphene [1,2]. This novel carbon nanostructure was observed and described for the first time by Iijima [3]. The many subsequent efforts in exploration of diverse synthesis methods and their formation mechanisms make this observation more important [1–10]. Intensive electron beam irradiation was found first to result in the curling and closure of graphitic networks of carbon soot assembling into OLC particles [1,10]. Later, through annealing nanodiamonds, Kuznetsov et al. developed an inexpensive process for generating large amounts of OLC (several grams) with sizes in the range 2–20 nm [8]. An alternative generation mechanism without irradiation and annealing (but most probably also far from equilibrium) has been described by Cabioc'h et al. [6] who implanted carbon ions into metal substrates. In an arc-discharge method developed by Sano et al. [9], foreign materials such as metal crystals have been encapsulated by polyhedral
graphitic cages, when the metals were evaporated together with carbon. Recently, via the heat treatment of hydrocarbon polymer [11] and acetylene black [12] in the presence of metal catalysts, hollow and metal encapsulated nanometric carbon onions also were synthesized.

In an ideal case, OLC could be considered as multishell giant fullerenes, but real particles have discontinuous and defective shells [13]. The carbon onions offer a moderate specific surface area (~500 m²/g) compared to that of carbon blacks and activated carbons, but this surface is fully accessible to ion adsorption due to an almost perfect graphite network with a high degree of curvature [13]. As a result, the closed and spherical carbon shells can provide interesting catalytic properties, which have been demonstrated with a high selectivity and catalytic activity in the oxidative dehydrogenation of ethyl benzene to styrene [14,15]. Just as importantly, the highly graphitized onion-like carbon structure would provide desirable features as a supporting material in electrocatalyst [16,17], where it can provide enhanced corrosion-resistance and high electron conductivity. As an advanced electrode material for electrochemical energy storage, Pech et al. recently reported a novel application of nanostructured carbon onions in supercapacitors, enabling the generation of an increased energy density and discharge rates when compared to traditional activated carbon [13,18].

In our recent efforts to develop a non-platinum group metal (non-PGM) catalyst for the oxygen reduction reaction (ORR), it is of note that an OLC nanostructure was formed through the heat-treatment of a carbon–nitrogen precursor in the presence of transition metals (Co and Fe). As a consequence, it is important to further explore the role of such carbon nanostructures in ORR activity of non-PGM catalysts, of which currently is a major challenge for development of high-power fuel cell applications at a sustainable cost [19,20].

The state-of-the-art cathode ORR catalyst in polymer electrolyte fuel cells (PEFCs) is based on platinum (Pt), and its high price and relative scarcity account for a significant fraction of the overall projected cost of the technology. Greatly reducing or eliminating the required Pt content is a necessary step before fuel cells can become a significant part of the world’s energy portfolio. Although ideally Pt should be replaced at both fuel cell electrodes, its substitution at the cathode with a non-PGM catalyst would have comparatively greater impact, because the slow ORR there requires much more Pt than the non-PGM catalysts, thereby resulting in better performance.

### 2. Experimental section

#### 2.1. Materials synthesis

Hexamethylene diamine, HDA (H₂N(CH₂)₆NH₂), was employed as a nitrogen-carbon precursor to complex with transition metals (Fe and Co). In a typical approach, 5.0 g carbon black support, typically commercial Ketjenblack EC 300J (Akzo Nobel) was treated in 500 ml 6.0 M HCl solution for 24 h to remove the possible metal impurities. The BET surface area measured of the HCl-treated carbon black is ~780 m² g⁻¹. A mixture of two transition metal salts [Co(NO₃)₂·6H₂O and FeCl₃·6H₂O] in a total amount of 0.1 mol with various Co:Fe atomic ratios (Co alone, 3:1, 1:1, 1:3, and Fe alone) were first added into 0.1 M HDA ethanol solution. While the transition metals were mixed with HDA at room temperature, a dark-yellow suspension gradually appeared, suggesting the formation of an interlinked HDA–M (M:Fe and Co) complex. Subsequently, 0.40 g HCl-treated carbon black supports was mixed with the above suspension. The optimized ratio by mass between the carbon supports to HDA is around 1:10. After constant stirring for 24 h to allow the complex to fully impregnate into the porous carbon black, the mixture was vacuum-dried and then heat treated at 900 °C using a tube furnace in flowing nitrogen gas for one hour. Then these heat-treated samples were chemically leached in 0.5 M H₂SO₄ solution at 80 °C for 8 h to remove unstable and inactive species from the catalysts with an aim to meet the stability requirement in the acidic Nafion-based fuel cell environment. Finally, the samples were
thoroughly washed with de-ionized water, and dried in vacuum oven overnight at 80 °C. The final products are denoted here as M-N-C.

### 2.2. Physical characterization

The surface areas of these carbon based catalysts were measured by nitrogen adsorption at 77 K using BET method on a Micromeritics ASAP 2010C instrument. Each sample was degassed by heating at 150 °C under vacuum prior to measuring the surface area. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Mettler TGA/SDTA 851 under a flowing dry air atmosphere. The temperature was ramped at 5 °C min⁻¹ to 1000 °C and held until mass change was less than 0.05% min⁻¹, then ramped down to 25 °C at 30 °C min⁻¹. The residual powder was determined to be Fe₂O₃ and Co₃O₄ by XRD. After correcting the nitrogen and oxygen content based on XPS, carbon content in catalyst bulk can be approximately estimated. High-resolution transmission electron microscopy (HR-TEM) images were taken on a JEOL JEM-2100F microscope with a resolution of 0.102 nm operating at 200 kV. The crystallinity of the samples was determined by X-ray diffraction (XRD) performed on an automated Rigaku diffractometer equipped with a Cu Kα radiation source and a graphite monochromator operating at 45 kV and 40 mA. The diffraction patterns were scanned at a rate of 1.2° min⁻¹ with a step of 0.02°. These samples also were characterized by X-ray photoelectron spectroscopy (XPS) using an ESCA 210 and MICROLAB 310D spectrometer for elemental quantification and species analysis. For recording the spectra, Mg Kα irradiation was employed as the X-ray source. High resolution spectra were acquired at 20 eV pass energy. The area of analysis was 700 × 300 μm in size, and each sample was analyzed at 90° take-off angle with a depth of 3–4 nm.

### 2.3. Electrochemical characterization

Activity and four-electron selectivity for ORR were electrochemically evaluated by rotating disk (RDE) and ring disk electrodes (RRDE), respectively. The RDE and RRDE tests were carried out using a CHI Electrochemical Station (Model 750b) in a conventional three-electrode cell at a rotating disk speed of 900 rpm, and at room temperature. The catalyst loading was controlled at 0.6 mg cm⁻². For recording the ORR polarization plots, the potential was set to 1.2 V, and a potential step of 0.03 V was applied to the ring electrode held at 1.0 V. The disk potential was swept from 1.0 to 0 V with a potential step of 0.03 V and a period of 5 s. The collection efficiency was obtained from the ring-to-disk current ratio: \( N = -\frac{I_D}{I_R} \). The determined collection efficiency was 36% that is very close to the value (37%) provided by the manufacturer based on the geometry of the electrodes.

These non-PGM catalysts were further tested as cathodes in a real PEFC environment to evaluate their activity and durability. The catalyst “ink” was prepared by ultrasonically mixing the catalyst powder with Nafion suspension for 4 h. The obtained “ink” was successively applied to the gas diffusion layer (GDL), ELAT LT 1400 W, E-TEK) using an air spray gun until the cathode catalyst loading reached to designed ones. The Nafion content in the cathode layers was maintained at 35 wt.% close to its volume content due to the similar density value of carbon and Nafion. Commercial Pt-catalyzed carbon cloth GDE (E-TEK, 0.25 mgPt cm⁻²) was used at the anode. The geometric MEA area was 5.0 cm². Fuel cell testing was carried out with a single cell with serpentine flow channels. Pure hydrogen and oxygen, humidified at 85 °C, were supplied to the anode and cathode at a flow rate of 200 and 300 mL min⁻¹, respectively. Fuel cell polarization and life test plots were recorded using fuel cell test stations (Fuel Cell Technologies Inc.).

### 3. Results and discussion

#### 3.1. HR-TEM images

The nanostructures of the Fe–N–C and optimized binary CoFe–N–C catalysts were studied using HR-TEM images as shown in Fig. 1. While the onion-like graphitic carbon nanostructure cannot be found easily in the Fe–N–C sample (Fig. 1a), they are dominant in the binary CoFe–N–C catalyst (Fig. 1b–f). Low magnification images for overall morphology of CoFe–N–C catalyst also are shown in Fig 1b and c. Notably, in the binary metal catalyst, both hollow (Fig. 1d and f) and metal-encapsulated (Fig. 1e) onion-like carbon nanostructures consisting of concentric spherical graphitic shells can be clearly observed. Incomplete spheroidal shells also were found in Fig. 1c and d, indicating that the onion-like structure obtained from carbonization of hydrocarbon compound in this work is not as well-ordered as ones obtained through annealing nanodiamond or under electron-beam irradiation [2,8,10,18].

As a rule, amorphous carbon can transform into graphite at temperatures of 2500–3500 °C. However, in the presence of such catalysts as Fe, Co, and Ni, the graphitization process substantially accelerates, and takes place at a much lower temperature (600–900 °C) [30]. The formation mechanism of such metal-encapsulating onion-like carbon in this work could be explained based on the topochemical reactions of
carbon containing species decomposition in presence of iron group metal compounds [5,11,30–34]. In this work, during heat treatment under an inert atmosphere, transition metals in the interlinked HDA–M complex, which is a molecular-scale continuous phase initially, are reduced to metallic clusters before the temperature reaches 200 °C. Then these segregated particles are thus surrounded and encapsulated by the interlinked complex, leading to the formation of an “island” structure [11]. With increasing temperatures, the carbonization results in a high carbon content and a closely enlaced structure. At the same time, the metallic nanoparticles are gradually embedded by carbon and nitrogen species, and oppositely these small species are dissolved into these metallic nanoparticles. In particular, based on the cobalt-carbon phase diagram, during the heat treatment, these cobalt nanoparticles are thought to be melting, and become nanodroplets due to the diffusion of carbon into cobalt with a carbon content up to 12 at.% [5]. In fact, Krivoruchko and co-workers once reported that liquid metal–carbon particles can be formed at a temperature far below the liquidus in the phase diagram [32,34]. With the diffusion of carbon into the liquid metals, the resolved carbon and nitrogen species can be separated out as curved graphite layers, when supersaturation is reached to overcome the size of critical carbon nucleus, namely up to a dissolution–precipitation dynamic equilibrium [30]. These metal–carbon–nitrogen species can

Fig. 1 – High-resolution TEM images for (a) Fe–N–C catalyst and CoFe(1:3)–N–C catalyst at various magnifications and areas: (b and c) overall morphology, (d) representative onion-like carbon structures, (e) typical metal-encapsulated onion-like carbon, and (f) hollow onion-like carbon nanostructures.
also interact with amorphous carbon particles leading to the rearrangement of their surface [12]. Also, the energy minimization principle could explain why the carbon species were rearranged into closed concentric graphitic shells [32]. Usually, when onion-like carbon nanoparticles were catalytically formed, the temperature dropped gradually to room temperature. While some metallic nanoparticles did not have enough time to agglomerate and were encapsulated into carbon shells (Fig. 1c), most of the catalytic particles left the shells (Fig. 1c, d, and f) and accumulate in large spherical aggregates outside [11,30]. As a result of these processes, carbon shells replicated the shapes of the metal particle surface. During their formation process, the onion-like carbon nanoparticles underwent a long period of condensation, dissolution, precipitation and rearrangement of mobile carbon species, which is essential for the formation of a new carbon nanostructure through condensation [11]. It is worth noting that small graphitic layers coalesced from the dangling bonds at the edges of carbon fragments are not definitely concentric to each other, thereby usually forming discontinuous graphitic layers such as dislocations and irregular curvature. Moreover, the intrusion of nitrogen atoms suppresses surface diffusion of carbon atoms during graphitization, leading to more disorder and compact structures in these graphite sheets [35].

Although some aspects of the formation mechanism of onion-like carbon require further investigation, the significant morphological differences between the Fe–N–C and CoFe–N–C catalysts imply a strong effect of transition metal precursor selection on the structures of catalysts during the heat-treatment of carbon–nitrogen complex precursors. It seems that Co was a more effective catalyst for the decomposition of interlinked HDA–M, then these carbon and nitrogen species would re-arrange and coalesce together, forming highly graphitic onion-like carbon structures during carbonization. In a different way, perhaps the complex was broken into smaller species or moieties under the catalysis of Fe. Although Co species facilitate to form such highly graphitized carbon structures that would be beneficial for electrocatalysis [36], the Co-based catalyst is less active for ORR than the Fe-based one. This probably is due to the difference in the nature of the ORR active sites that are derived from different transition metals. A binary catalyst involving Co and Fe simultaneously will benefit from both catalytic properties. This will be addressed below in the electrochemical characterization.

### 3.2. XRD patterns

The XRD patterns for the M–N–C non-PGM catalysts and a metal-free N–C control were compared in Fig. 2. In these carbon-based samples, the strongest peak around 2θ = 24.5–25.5° corresponds to the (0 0 2) basal plane diffraction in the graphitic structure. The broad (0 0 2) peaks can be attributed to two separate forms of carbon referred to as turbostratic carbon (amorphous carbon) and graphene carbon (graphitic carbon) [37,38]. When compared to the metal-free N–C sample, all metal-involved catalysts (Fe–N–C, Co–N–C and CoFe–N–C) display a slightly positive shift in the (0 0 2) peak. This is partially attributed to a better graphitic crystalline structure possibly related to graphitization catalyzed by these transition metals. Notably, the positive shift of the (0 0 2) peak in XRD patterns possibly is also resulted from a significant nitrogen doping, leading to a more compact graphitic structure with a decrease in d-spacing of (0 0 2) crystal planes [35,39]. Relative to Fe alone catalyst, the Co based catalysts seem to exhibit a much sharper carbon (0 0 2) peak, indicative of a higher degree of graphitization possibly resulting from the formation of onion-like carbon structures. These structural changes may correlate with the enhanced ORR performance of CoFe(1:3)–N–C catalyst when compared to Fe–N–C, as attested by electrochemical characterization below.

It should be noted that, according to the XRD data, Fe and Co species look segregated from each other, and no reflexes attributed to Fe–Co alloy are obvious. This suggests that the binary HDA–FeCo complexes tend to form Fe-rich and Co-rich particles during pyrolysis. A possible explanation is due to the difference in stability of HDA-complexes with Co or Fe. The pH of precipitation of iron hydroxide is near 4, while cobalt hydroxide precipitates at pH higher than 6.5. At the same time, Co forms complexes with amines much more easily than with Fe, so the Co complexes are much more stable than those with Fe [40]. As a result, the more stable HDA–Co complexes lead to an efficient catalysis process to form OLC structure in pyrolysis, when compared to the Fe, which is in a good agreement with the TEM data.

### 3.3. XPS analysis

Quantitative elemental analysis using XPS for these samples synthesized from various transition metals is shown in Table 1. The carbon content in the catalyst surface layer is more than 90 at.%, but is a function of the transition metals used. The highest carbon content is observed with Co–N–C catalyst (95%), when compared to Fe alone and CoFe binary catalysts, suggesting a higher degree of carbonizing the HDA–Co complex to a graphitized carbon structure, most likely the onion-like carbon. Also, it should be noticed that the carbon content in the surface layer determined by XPS is also dependent on the amount of carbon black support used in synthesis. The change of carbon black-to-HDA ratio by mass from 0.025 to 0.2 led to a significant variation of ~30% in carbon content in surface layer. The ratio used in this work has been
optimized in terms of the catalyst activities. However, the influence on total carbon content is not significant, and less than 10% change in carbon content being determined by TGA. Nitrogen content on the catalysts rises from 1.9 at.% for Co–N–C to 5.5 at.% for Fe–N–C, and the binary CoFe(1:3)–N–C has the highest nitrogen content of 6.0 at.%.

The content of transition metals on the CoFe(1:3)–N–C catalyst that was subjected to a thorough acid treatment was found to be around 0.81 at.% for Fe and below the detection threshold for Co. XRD proved that metallic Co or Fe aggregates were formed in the catalyst as shown in Fig. 2. However, during acid treatment, while the metal species on the surface layers are nearly leached out, that which is encapsulated can remain under the onion-like carbon structure.

As nitrogen doping into the carbon structure is likely to play an important role inducing ORR activity for such type of non-PGM catalyst [41], N 1s spectra for these samples are compared in Fig. 3. Two dominant nitrogen peaks at 401.1 eV and 398.5 eV are observed with these catalysts. According to previous work [42–44], as for pyrolyzed nitrogen-containing carbon materials (above 700 °C), the nitrogen atoms can incorporate into the graphene layers to replace carbon atoms at different sites, and in doing so they show various binding energies in the XPS spectra: pyridinic N (398.6 ± 0.3 eV), pyrrolic N (400.5 ± 0.3 eV), and quaternary N (401.3 ± 0.3 eV). The pyridinic form is the nitrogen atoms doped at the edges of the graphitic carbon layers, and the quaternary nitrogen is defined as doping inside the graphitic carbon plane. Pyrrolic form is often assigned to nitrogen atoms in a pentagon structure, but is considered indistinguishable from pyridone (pyridinic-N next to an OH group) [42]. However, both of these pyrrolic nitrogen and pyridone species have been shown to decompose at temperatures above 600 °C to pyridinic-N and quaternary-N [42]. Importantly, more than one specific nitrogen functionalities could be attributed to the quaternary nitrogen so far, due to insufficient evidences to distinguish them. Quaternary nitrogen could include protonated pyridine or the "graphitic" nitrogen in which nitrogen is within a graphite plane and bonded to three carbon atoms. Also, the assignments to the high-binding energy (402–405 eV) in the N 1s region may be related to the interaction of graphitic nitrogen with other nitrogen atoms, or to the differences in the binding energy of graphitic nitrogen depending on its position in the graphite plane [42,43]. Therefore, the two dominant peaks observed with these M–N–C samples at 398.5 and 401.1 eV in Fig. 3 can be assigned to pyridinic and quaternary nitrogen, respectively, suggesting that the N atoms were successfully incorporated into the carbon structures to replace the carbon atoms which were located at the edges and inside of the graphitic carbon layers. In comparison to the Co–N–C sample, the Fe–N–C sample has relatively higher peak intensity for quaternary nitrogen, indicating that nitrogen atoms favor doping at the interior rather than the edges of the graphene layer in the presence of Fe. Generally, during the pyrolysis of carbon containing nitrogen groups, the ratio of pyridinic and quaternary nitrogen would reach equilibrium [45,46]. The comparison of N 1s spectra implies that the addition of Fe is able to shift the equilibrium towards quaternary nitrogen. In these studies, taking the undetectability of Co species on the catalyst together with the similarity of electrochemical properties (ORR onset potential) to metal-free catalysts [17], it may suggest that the Co-derived ORR active sites are related to the pyridinic type C–N structures without a participation of metal. On the other hand, the presence of Fe species lead to more nitrogen atoms.

<table>
<thead>
<tr>
<th>Catalyst samples</th>
<th>Atomic concentration, %</th>
<th>C 1s</th>
<th>O 1s</th>
<th>N 1s</th>
<th>Co 2p</th>
<th>Fe 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–N–C</td>
<td></td>
<td>95.1</td>
<td>1.9</td>
<td>1.9</td>
<td>1.1</td>
<td>–</td>
</tr>
<tr>
<td>Fe–N–C</td>
<td></td>
<td>88.8</td>
<td>4.9</td>
<td>5.5</td>
<td>–</td>
<td>0.8</td>
</tr>
<tr>
<td>CoFe(1:3)–N–C</td>
<td></td>
<td>89.6</td>
<td>3.8</td>
<td>6.0</td>
<td>0</td>
<td>0.6</td>
</tr>
</tbody>
</table>
doping into the interior of graphitized carbon plane, and generate more intrinsically active ORR sites (see below electrochemical characterization), so the active sites may be more complex, simultaneously comprising Fe species and C–N\textsubscript{x} structures. Although the pyridinic nitrogen has been believed to facilitate oxygen reduction [43], these data may indicate that the quaternary, and the optimal C–N\textsubscript{x} structure reflected by the ratio between quaternary and pyridinic nitrogen also are important to the oxygen reduction mechanism. Further investigate is required to clearly address this issue.

### 3.4 BET surface area analysis

Table 2 shows the BET surface areas for these synthesized M–N–C catalysts, as well as the carbon black baseline materials. Even though the surface area of the HCl-treated Ketjenblack supports is as high as 780 m\textsuperscript{2} g\textsuperscript{-1}, after mixing with HDA–M complex, the pore structures of the carbon support were nearly filled in. A significantly decreased surface area of \(\sim 50\) m\textsuperscript{2} g\textsuperscript{-1} was measured with the un- pyrolyzed carbon supported HDA–M sample. However, after a heat treatment at 900 °C, and a subsequent acid leaching treatment, the porous characteristic of catalysts is mostly retrieved. Just as importantly, generated surface area for Co–N–C is around 560 m\textsuperscript{2} g\textsuperscript{-1} that is much higher than that of Fe–N–C catalyst (300 m\textsuperscript{2} g\textsuperscript{-1}). The value of surface area for the mixed binary metal catalyst CoFe(1:3)–N–C (370 m\textsuperscript{2} g\textsuperscript{-1}) is located between that of Co– and Fe-based catalysts, but closer to that of Fe catalyst. Discussion on the correlation between the surface areas of catalyst and catalytic activities is detailed in the electrochemical characterization section below.

### 3.5 RDE and RRDE tests for oxygen reduction

The ORR catalytic activities for these binary CoFe–N–C catalysts synthesized from various nominal Co:Fe atomic ratios were studied using RDE and RRDE tests. As shown in Fig. 4a, relative to the Co–N–C catalyst, a significant improvement in activity is observed with the Fe–N–C sample, as evidenced by 80 and 50 mV positive shifts in onset (from 0.82 to 0.90 V) and half-wave, \(E_{1/2}\) (from 0.70 to 0.75 V) potentials, respectively. However, the binary catalyst CoFe(1:3)–N–C synthesized with a Co:Fe ratio of 1:3 was found to yield the highest activity, i.e. the most positive onset and \(E_{1/2}\) potentials. As for the four-electron selectivity of ORR, the hydrogen peroxide yield of these catalysts determined using a RRDE generally correlates well with their activity, as shown in Fig. 4b. While Co–N–C catalyst generates relatively high \(\text{H}_2\text{O}_2\) around 10%, the lowest \(\text{H}_2\text{O}_2\) yield measured with the Fe–N–C catalyst is below 2% across all potentials, followed by the best RDE active CoFe(1:3)–N–C catalyst with 2–3%. The significantly low peroxide yield attests to high selectivity of \(\text{O}_2\) reduction to \(\text{H}_2\text{O}\) through a four-electron route rather than to \(\text{H}_2\text{O}_2\) in a much less efficient, two-electron reaction.

As transition metals are necessary for the creation of highly active ORR catalysts, the RDE activities and four-electron selectivity were studied as a function of total metal loadings of Co and Fe varied from 0 to 10 wt.% in the initial reaction mixture used for CoFe(1:3)–N–C catalyst synthesis. The activity initially increases with the metal content from 0.5 to 3 wt.%, but the addition of more metal to 10 wt.% results in no statistically significant changes to the catalyst activity (Fig. 5a) and four-electron selectivity (Fig. 5b). Compared to some previous reports [19,47], the amount of Fe required to generate the maximum activity for catalysts synthesized through reaction of ammonia gas is as low as 0.2 wt.% Fe [47], which the activity probably can be ascribed to the formation of high density Fe–N\textsubscript{x} catalytic sites hosted in micropores provided by high surface-area carbon supports through a four-electron route rather than to \(\text{H}_2\text{O}_2\) in a much less efficient, two-electron reaction.

### Table 2 – BET surface areas for employed carbon support and synthesized M–N–C catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>HCl treated carbon black</th>
<th>Un-pyrolyzed HDA–CoFe(1:3)–C</th>
<th>Co–N–C</th>
<th>CoFe(1:3)–N–C</th>
<th>Fe–N–C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET, m\textsuperscript{2} g\textsuperscript{-1}</td>
<td>780</td>
<td>60</td>
<td>560</td>
<td>370</td>
<td>300</td>
</tr>
</tbody>
</table>
However, the role of the metals in catalysts studied in this work appears to be not only associated with directly populating the active sites, but also with forming the onion-like carbon structures from the carbonization of interlinked HDA-M complexes as shown in the above HR-TEM images. This observation is consistent with the widespread use of transition-metal catalysts to generate carbon structures [48]. As a consequence, the need for a higher metal content in this case as opposed to other catalyst types can thus be readily rationalized. A factor other than the metal species supply is very likely to limit the further increase in the density of active sites on catalyst, with the most likely limiting factors being morphology and nanostructures of the graphitized carbon. Further investigation to address these issues is required.

Tafel slope \( (b) \) was determined to evaluate the ORR kinetic character for these non-PGM catalysts. Kinetic current densities, extracted from the steady-state polarization plots according to the Koutecky–Levich equation, were used to plot these Tafel curves as shown in Fig. 6. Using linear fitting, the values of the Tafel slopes are found to be ca. 59 and 84 mV dec\(^{-1}\) for Co–N–C and Fe–N–C catalysts, respectively. As the Fe–N–C catalyst is more active and exhibits a more than 80 mV positive shift in ORR onset potential relative to Co–N–C catalyst, this significant difference in Tafel slope between both catalysts implies that the nature of their active sites is likely to be different. The Tafel slope of the hybrid CoFe(1:3)–N–C (81 mV dec\(^{-1}\)) is more close to that of the Fe–N–C, suggesting that the Fe-based active sites are important to the overall catalyst activity. Theoretically, a Tafel slope of 120 mV dec\(^{-1}\) is due to the rate-determining step associated with the first-electron transfer, while a Tafel slope of 60 mV dec\(^{-1}\) has been explained by the migration rate of adsorbed oxygen intermediates with a Temkin isotherm [49]. Hence, a Tafel slope of 59 mV dec\(^{-1}\) observed with the Co–N–C catalyst suggests that the ORR rate is primarily determined by the migration of adsorbed oxygen intermediates. In the case of the Fe–N–C catalysts, Tafel slope between 80 and 90 mV dec\(^{-1}\) is indicative of a more complicated ORR mechanism. The rate-determining step most likely simultaneously involves both intermediate migration and charge transfer [50,51].

### 3.6. Fuel cell tests for oxygen reduction

Fuel cell polarization plots recorded on the Co–N–C, Fe–N–C and optimized binary CoFe (1:3)–N–C catalysts are compared in Fig. 7. In good agreement with the RDE results, the open-cell voltage (OCV) value measured with Co–N–C is around 0.82 V. This is significantly lower than that of Fe–N–C catalyst (~0.90 V). The OCV of the CoFe(1:3)–N–C is comparable to that of Fe–N–C catalyst. Importantly, the binary CoFe-based hybrid catalyst performs noticeably better than Fe-based one, especially when the voltage is lower than 0.80 V, confirming the promotional role of Co in the binary catalyst to ORR performance. Under these experimental conditions, the best performing catalyst can generate a current density of 0.05 A cm\(^{-2}\) at 0.8 V, and the power density is as high as 0.42 W cm\(^{-2}\). Performance comparison of fuel cells operating with a state-of-the-art Pt/C catalyst (using air rather than oxygen) at a catalyst loading of 0.2 mgPt cm\(^{-2}\) also has been included in Fig. 7 (dashed line). At 100 mA cm\(^{-2}\), the best non-PGM cathode catalyst trails the Pt reference by ca. 80 mV, a value indicative of possible significant mass transport and IR losses.

Viewing the above mentioned BET surface area data collectively, it can be seen that no direct proportional correlation could be established between the surface areas measured...

![Fig. 5](image1.png)  
Fig. 5 – Effect of total metal loadings in synthesis of optimized binary CoFe(1:3)–N–C catalysts on RDE activity (a), and \( \text{H}_2\text{O}_2 \) yield (b) in oxygen reduction in 0.5 M \( \text{H}_2\text{SO}_4 \) at 25 °C and 900 rpm.

![Fig. 6](image2.png)  
Fig. 6 – Tafel plots of ORR on Co–N–C, Fe–N–C and CoFe(1:3)–N–C catalysts.
with catalysts and their catalytic activities. Although the surface area is reduced for CoFe(1:3)–N–C catalyst (370 m² g⁻¹) compared to Co–N–C (560 m² g⁻¹), much improved ORR activity is demonstrated by RDE and fuel cell tests. The re-plotted fuel cell polarization curves based on the BET surface area of the cathode catalyst is shown in Fig. 7b. Much higher activity, even in mass transportation voltage range, was observed with the Fe involved catalysts (Fe–N–C and CoFe(1:3)–N–C) when compared to Co-based catalysts. This may suggest that a higher active-site density on the smaller surface area in the CoFe binary catalyst exists, which could explain its higher activity. Also the observed positive shifts in ORR onset potential of RDE and OCV of fuel cell tests may imply a different nature of active site derived from Fe in the CoFe(1:3)–N–C mixed-metal catalyst with higher intrinsic activity. As a matter of fact, such-synthesized catalyst is a mixed system, including both the carbon black supports and HDA-derived graphitized onion-like carbon. Therefore, it is very difficult to identify how much surface area is attributed to newly formed onion-like carbon that might be more important to ORR activity, relative to the pristine carbon black supports. Ongoing work with support-less catalysts will help clarify the relationship between catalyst surface area and activity.

Besides the requirement for high activity, non-PGM catalysts must also demonstrate sufficient durability to be useful in a practical device. This has been a major challenge to non-PGM catalysts for decades. In previous efforts in the development of non-PGM catalysts for PEFC, high activity has often been coupled with a fast degradation rate [19]. In this work, the performance durability of onion-like carbon-based M–N–C catalyst in fuel cell environment was studied using both constant current and voltage models, as shown in Fig. 8a and b, respectively. In the constant current model, the tests were carried out at various current densities ranged from 0.10 to 0.40 A cm⁻² using H₂ and air with relatively low, but more practical backpressures 1.0 bar for both sides. To minimize the effect of water flooding in cathode layers, a low catalyst loading of 2.0 mg cm⁻², rather than traditional 4.0 mg cm⁻², was used for the long-term life test. Note that only ~11% performance loss (ca.100 μV h⁻¹) was observed for 400-h operation at a current density of 0.40 A cm⁻². In the meantime, a 200-h fuel-cell performance test at a constant cell voltage of 0.40 V reveals very promising performance stability for the CoFe(1:3)–N–C catalyst at the fuel cell cathode. The cell current density in a lifetime test remains nearly constant at ca. 0.30 A cm⁻². The current density declines by only 6%, from the average value of 0.316 A cm⁻² in the first 24 h to 0.298 A cm⁻² in the last 24 h of the test with an average current loss of 90 l Ah⁻¹. It is worth noting that...
Fe–N–C catalyst is less stable than CoFe(1:3)–N–C, incurring performance loss of ca. 170 μA h⁻¹. Also when compared to CoFe(1:3)–N–C catalyst, the lower current density generated from Fe–N–C catalyst is in line with the RDE and initial fuel cell polarization plots.

So far, there is no complete explanation of the promotional role of Co in the improvement of the durability of the binary CoFe(1:3)–N–C catalyst. However, it is very likely that the highly graphitized onion-like carbon structure exclusively derived from the Co may prevent water flooding of active sites or increase the resistance of active sites to oxidative attack, thereby leading to an improvement in durability. The possibility of direct (improvement of electron conductivity, corrosion resistance, and water management) and indirect (catalytic properties) effects of such onion-like carbon structures on the performance of non-PGM catalyst will be the focus of future work.

4. Conclusion

A nitrogen-doped onion-like carbon-based non-PGM ORR catalyst was synthesized by heat treatments of nitrogen-carbon containing hexamethylene diamine in the presence of Co and Fe. The optimal binary CoFe-based catalyst, synthesized from an initial Co:Fe ratio of 1:3 and a total metal loading of 10 wt.% in reacting solution, exhibits an improved activity and durability for oxygen reduction when compared to Fe- and Co-alone catalysts. The promotional role of Co may be attributable to the formation of onion-like carbon structures in the binary catalyst due to the exclusive catalytic properties of Co in this work. The graphitized nitrogen-doped onion carbon appears to be a robust matrix in hosting ORR active sites, and ensuring the enhanced stability of catalysts. Although no direct correlation between BET surface area and catalyst activity could be identified, the marked changes in the carbon structure that correspond to large performance differences point to the importance of the metal-catalyzed transformation of the precursors into new carbon forms in such non-PGM catalysts. Future work should focus on a more precise control of the metal/carbon-nitrogen precursor interaction during the heat treatments. The effects of supporting materials including different carbon blacks, carbon nanotubes, or non-carbon oxides on catalyst morphology and performance will be an interesting topic in Non-PGM catalyst development.

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References

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