Deconvolution of Utilization, Site Density, and Turnover Frequency of Fe–Nitrogen–Carbon Oxygen Reduction Reaction Catalysts Prepared with Secondary N-Precursors

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Supporting Information

ABSTRACT: Metal–nitrogen–carbon (MNC) catalysts represent a potential means of reducing cathode catalyst costs in low temperature fuel cell cathodes. Knowledge-based improvements have been hampered by the difficulty to deconvolute active site density and intrinsic turnover frequency. In the present work, MNC catalysts with a variety of secondary nitrogen precursors are addressed. CO chemisorption in combination with Mössbauer spectroscopy are utilized in order to unravel previously inaccessible relations between active site density, turnover frequency, and active site utilization. This analysis provides a more fundamental description and understanding of the origin of the catalytic reactivity; it also provides guidelines for further improvements. Secondary nitrogen precursors impact quantity, quality, dispersion, and utilization of active sites in distinct ways. Secondary nitrogen precursors with high nitrogen content and micropore etching capabilities are most effective in improving catalysts performance.

KEYWORDS: oxygen reduction reaction, nonprecious metal catalysts, fuel cells, Mössbauer spectroscopy, electrocatalysis

INTRODUCTION

A significant impediment of commercialization of proton exchange membrane fuel cells (PEMFCs) is the cost of catalysts. Most of the cost is at the cathode, where the sluggish oxygen reduction reaction (ORR) is usually catalyzed with the use of precious metals.1–3 One of the research directions to solve this problem is the search for suitable nonprecious metal alternatives. The most promising alternatives are in a broad class of catalysts called metal–nitrogen–carbon (MNC) catalysts. Specifically, a promising nonprecious metal alternative has been synthesized by pyrolysis of polyaniline with a metal salt on a carbon support (PANI). Effectually, aniline is polymerized around the metal and carbon precursors during a wet-impregnation procedure. Following this mixing step, pyrolysis in nitrogen atmosphere at 900 °C incorporates the nitrogen and metal precursors into the carbon matrix.4,5

Building on this PANI process, other works have shown that adding a secondary nitrogen precursor to a MNC catalyst synthesis process improves performance.7,8 Similarly, Lefèvre et al. and others also used two nitrogen precursors for a different MNC synthesis process.9–11 For example, in the work of Lefèvre et al. an initial heat treatment with iron acetate, phenanthroline, and a carbon black was followed by a second heat treatment under an ammonia atmosphere.9 For both of these works, the hypothesis was that one of the roles of the secondary precursor, cyanamide/ammonia, was etching the primary nitrogen precursor, PANI/phenanthroline. This etching process is believed to create the pores that might host additional active sites. In the current work we tested this hypothesis by varying the secondary nitrogen precursor.

One counter argument to this hypothesis is that highly active MNC catalysts have been synthesized without a second nitrogen precursor or even highly volatile precursors. For example, catalysts obtained by the sacrificial support method (SSM) or by oxalate-supported pyrolysis have been synthesized with nitrogen precursors such as aminoantipyrine, nicarbazin, or porphyrins.12–14 For these catalysts, the important factor has been mesoporosity, even when a volatile precursor was also used.14 Similarly, a closed pyrolysis method also showed a correlation between mesoporosity and activity despite having a more volatile nitrogen precursor, melamine.15 For these catalysts, one of the challenges to synthesizing high performance MNC catalysts has been incorporation of nitrogen species into the carbon matrix. Although it has been shown that high nitrogen content is important for high activity,8 the ambiguity of the active site has prevented quantification of the
relationship between metal and nitrogen content and active site quantity. Ultimately, the question remains as to the role of secondary precursors in MNC catalysts. Specifically, to what extent does the secondary nitrogen precursor etch pores for active sites, and how do they participate in the reactions associated with active site formation or later the performance of active sites in the oxygen reduction reaction. This is especially an aspect of crucial interest for such synthesis protocols where iron is not directly coordinated by a sufficient number of nitrogen ligands, as is the case for PANI-based FeNC.

In the present study we use carbon monoxide adsorption to quantify potential active sites. These numbers are correlated with chemical information to allow for quantitative observation of changing surface chemistry as the nitrogen content is tuned by varying the precursors. Furthermore, these catalysts are analyzed with nitrogen physisorption to measure microporosity. Ultimately, the data will allow a comparison of the roles of secondary nitrogen precursors on porosity and active site creation while keeping the primary nitrogen precursor and carbon substrate constant.

### EXPERIMENTAL METHODS

#### Materials. Catalysts were synthesized similarly to other processes in the literature. Ketjen 600 EJ was pretreated by with 0.5 M HCl for 24 h. After vacuum filtration, the resulting powder was mixed into HNO₃ at 90 °C under reflux for 7 h. After a second vacuum filtration, the resulting powder is considered pretreated carbon.

For the catalysts synthesis, iron(III) chloride (5 g), aniline (3 mL), and ammonium peroxodisulfate (5 g) were mixed in 1 M HCl. Optionally 0.333 mol of nitrogen were added in the form of a secondary nitrogen precursor, based on a optimization of cyanamide. These were selected from common MNC catalyst nitrogen precursors: cyanamide (PANI-CM), melamine (PANI-Mel), urea (PANI-Urea), and nicarbazin (PANI-NCB). Labels of the resulting catalysts are in the parentheses; the catalyst synthesized without secondary nitrogen precursors is labeled PANI. After 4 h of mixing, the pretreated carbon is added, and the mixture is stirred for 48 h. After this stirring period, the mixture is dried at 110 °C. The dried powder is ball-milled and pyrolized for 1 h at 900 °C. After the first heat treatment, the catalyst is washed with 2 M HNO₃ for 16 h at 90 °C under reflux. Then the catalyst is vacuum filtered and dried. After drying the catalyst undergoes a second heat treatment at 900 °C. A second acid wash and third heat treatment are performed. At this point XRD data is used to assess whether a third acid wash is necessary. After each acid wash and heat treatment, XRD is used to assess whether inorganic iron species have been adequately removed. Often times the catalysts are clean after two acid washes, but if inorganic iron species can still be observed via XRD, a third acid wash and fourth heat treatment were performed. This additional cycle was necessary for the control catalyst (PANI) as well as the nicarbazin based catalyst (PANI-NCB). The final XRD signature for each catalyst is included in Figure S1 in the Supporting Information. Multiple batches were made of all catalysts except the NCB, and the RDE activity was found to be reproducible. For the remaining characterization techniques, a single batch was chosen.

#### Physical Characterization. Nitrogen physisorption data acquired on an Autosorb-1 (Quantachrome Instruments) were used to determine the surface area. Pore size distributions were calculated from a nonlocal density functional theorem (NLDFT) pore model on carbon pores with both slit and cylindrical geometries. Bulk iron content was measured by ICP and elemental analysis was used for bulk nitrogen and sulfur contents. The thermal decomposition of the catalyst precursors were investigated by a thermal gravimetric analyzer (PerkinElmer, STA 8000) under N₂ atm (10 mL/min). The samples were kept at 30 °C for 1 h to clean the atmosphere and, then, heated at 30 °C/min ramp from 30 to 900 °C, holding for 1 h.

#### Mössbauer Spectroscopy. The Mössbauer measurements were performed in transmission mode with a Mössbauer spectrometer "MS96" from RCPMT with a 100 mCi ⁵⁷Co/Rh source. Calibration of the velocity scale was made using the sextet lines of alpha-iron. Measurements were performed at room temperature with a scintillation detector in a velocity range of ±8 mm/s. PTFE sample holders were filled with the required catalyst mass and closed with TESA tape. Spectra were analyzed using the program Recoil.

For determining the amount of iron assigned to the different iron species, the Lamb–Mössbauer factors as determined by Sougrati et al. were used.

#### X-ray Induced Photoelectron Spectroscopy. X-ray photoelectron spectra (XPS) were measured with a Specs Phoibos 150 hemispherical analyzer and a Specs XR50 M Al Kα X-ray source. The system was calibrated with a silver reference sample. For the measurements catalyst powder was pressed on an indium foil and transferred into the high-vacuum system. Spectra were analyzed using CasaXPS. Peaks were fitted using a Shirley background and mixed Gauss/Lorentz peaks.

On the basis of the different elemental regions for Fe 2p, S 2p, N 1s, O 1s, and C 1s the elemental composition was determined. Measurements were performed for the four catalysts prepared under addition of a secondary N-precursor.

#### Electrochemical Characterization. Catalysts were electrochemically characterized with rotating-disk electrodes (RDE). Initially an ink was prepared by sonicating a mixture of 7.85 mg catalysts in 760 μL of deionized water, 190 μL isopropanol, and 50 μL of 5 wt % Nafion solution. After sonicating for 15 min 10 μL were drop cast on a 5 mm diameter glassy carbon disk. After drying for at least 10 min, electrodes were ready for use.

Catalysts deposited RDEs were inserted in oxygen saturated 0.1 M HClO₄ electrolyte. Initially electrodes were conditioned by cycling ten times between 1 and 0.2 V vs RHE with a scan rate of 100 mV/s. After this conditioning, a 5 mV/s cycle was collected between 1.05 and 0 V vs RHE. Following the characterization cycle, the electrolyte was bubbled with nitrogen for 15 min, and a capacitive scan was collected. Oxygen polarization curves were corrected for capacitive current using the nitrogen data, and the iR-corrected based on high frequency resistance as measured by galvano-controlled ELS at 0 A vs RHE.

#### CO Chemisorption. CO pulse chemisorption experiments and temperature programmed desorption (TPD) were performed using a Thermo scientific TPD/R/O 1110 instrument under a 20 mL min⁻¹ helium flow. Each chemisorption experiment required 100–150 mg catalyst and consisted of three steps. The first step was a cleaning pretreatment in inert helium gas. The sample powder was heated up to 600 °C with a ramp of 10 °C min⁻¹ followed by a hold of 15 min and subsequent cooling down to room temperature. The second step is CO pulse chemisorption carried out at ~−80 °C using a bath of dry ice and acetone. Six consecutive 0.338 mL CO
pulses at 25 min intervals were passed over the samples, and CO uptake per mole was monitored and quantified using a TCD detector. The last step was TPD after CO was adsorbed on catalysts by ramping the temperature from −80 °C to 600°C (10 °C min⁻¹).

**RESULTS AND DISCUSSION**

**Role of Secondary N-Precursor on Microporosity.** A number of catalysts were made using a single primary nitrogen precursor and four different secondary nitrogen precursors as shown in Table 1: cyanamide, melamine, urea, and nicarbazin. An overview of the physical and chemical characteristics of these catalysts are provided in the Supporting Information (Table S1).

The catalysts that were synthesized using these precursors were characterized using nitrogen physisorption to better understand porosity and to check the literature theories about porosity created by secondary nitrogen precursors. The pore size distributions shown in Figure 1 are relatively similar for the different catalysts. Comparison of the catalysts to the support (black line) indicates a loss in mesoporosity and gain in microporosity. The exception is the PANI-NCB sample, which appears to lose both micro- and mesoporosity. The exceptionally low porosity of the PANI-NCB catalyst is not surprising considering that NCB has the highest carbon content of the secondary nitrogen precursors. It is likely that this excess carbon material remains after the pyrolysis and blocks pores. This is consistent with the work of Nallathambi et al. in which precursors with lower N/C ratios produced catalysts with lower porosity and performance. Thermogravimetric data shown in the Supporting Information Figure S5 also support the idea of pore blockage by excess carbon material. It is evident that the NCB does not decompose to a similar mass as the other catalysts. This indicates a large amount of the secondary nitrogen precursor is left behind. The large mass left behind may also be due to the large amount of NCB that was required in the synthesis process to attain a similar amount of added nitrogen as with the other secondary precursors. It is also possible that the fourth heat treatment used for the PANI and PANI-NCB plays a role in their lower porosity.

The catalysts were electrochemically characterized via rotating disk electrode, as shown in Figure 2. The samples show varying catalytic performance as indicated by their behavior in the kinetic regime of the polarization curves, with PANI-CM and PANI-Mel showing the highest performance and PANI and PANI-NCB showing the lowest performance. At lower potentials, most of the catalysts exhibit a similar mass transport limiting plateau.

To account for the mass transport effects, the kinetic current was calculated with the Koutecky–Levich expression:

\[
\frac{1}{i_k} = \frac{1}{i} - \frac{1}{i_l}
\]

Where \(i_l\), the kinetic current can be calculated from the measured current, \(i\), and the mass transport limited current, \(i_l\). The resulting kinetic curves are shown in the Tafel plot (Figure 3). The initial slopes are similar suggesting similar reaction kinetics. Again the exception is the PANI-NCB which has a

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**Table 1. List of Secondary Nitrogen Precursors Used**

<table>
<thead>
<tr>
<th>Nitrogen Precursor</th>
<th>Formula</th>
<th>MW/(g/mol)</th>
<th>N/C</th>
<th>Precursor Mass Added</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyanamide</td>
<td>CH₂N₂</td>
<td>42</td>
<td>2/1</td>
<td>7 g</td>
</tr>
<tr>
<td>melamine</td>
<td>C₃H₆N₆</td>
<td>126</td>
<td>6/3</td>
<td>7 g</td>
</tr>
<tr>
<td>urea</td>
<td>CH₄N₂O</td>
<td>60</td>
<td>2/1</td>
<td>10 g</td>
</tr>
<tr>
<td>nicarbazin</td>
<td>C₅H₉N₅O₆</td>
<td>426</td>
<td>6/19</td>
<td>23.7 g</td>
</tr>
</tbody>
</table>

**Figure 1.** Pore size distribution of support and catalysts.

**Figure 2.** Polarization curves from rotating disk electrode studies of various catalysts. Conditions: 0.1 M HClO₄, O₂ saturated, room temperature, 1500 rpm, loading 0.4 mg/cm².

**Figure 3.** Kinetic current as calculated from rotating disk electrode data. Conditions: 0.1 M HClO₄, O₂ saturated, room temperature, 1500 rpm, loading 0.4 mg/cm².
higher Tafel slope. This higher Tafel slope could indicate a change in the mechanism.

The impact of secondary nitrogen precursors on pore etching and consequently on electrochemical performance can be probed by comparison of Figure 2 with the pore size distribution in Figure 1. One can see from Figure 4 that all the catalysts exhibit higher microporosities than the carbon support, which supports the theory that secondary nitrogen precursors are involved in etching of the catalyst surface. On the other hand, the poor correlation between microporosity and current indicates that this etching process is only part of the story concerning how secondary nitrogen precursor impact performance.

In order to explore the relationship between secondary nitrogen precursors and performance, this work will discuss three different aspects of the catalysts: number of active sites, number of exposed active sites, and quality of active sites. The relation of surface exposed active sites toward the total number of active sites is defined as catalyst utilization.

Effect of Secondary N-Precursor on Quantity of Active Sites. Mössbauer spectroscopy was used to measure total number of active sites. That means the sum of surface accessible sites and those hidden in the bulk.\(^6\) The Mössbauer spectra of the two most active catalysts are shown in Figure 5, and the associated results are shown in Table 2. All other Mössbauer spectra are provided in the Supporting Information, Figure S2.

It is found that the relative content of FeN\(_4\) sites in relation to the overall iron-signature of the catalysts is relatively high, especially when compared to other PANI-based catalysts.\(^23,24\)

It is particularly striking that similar to the work of Kramm et al.\(^24\) and Zitolo et al.\(^25\) we managed to produce a catalyst with exclusive presence of FeN\(_4\) sites as found for PANI-Urea. The D\(_2\) related FeN\(_4\) site is attributed to a structure similar to FePc with ferrous iron in the midspin state.\(^14,23\) Beside this, some catalysts indicate the presence of iron carbide (Sext1),\(^26\) troilitite (Sext2),\(^27\) and most probably very small iron nitride particles\(^28,29\) (Sext3 in PANI-CM). The high level of troilitile in the PANI-NCB is corroborated by the XRD data and the high sulfur content. This is indicative of the poor iron utilization in the PANI-NCB catalyst.

A bulk mass-based site density (MSD) was calculated from Mössbauer results assigned to the D\(_1\) doublet (Fe\(_{\text{D1}}\)) that was previously identified as ORR active site.\(^21,22,24,39\) The following equation was used for determination:

\[
\text{MSD}_{\text{bulk}} = \frac{\text{Fe}_{\text{D1}} \text{[wt %]}}{100} \times \frac{M_{\text{Fe}} \text{[g mol}^{-1}\text{]} \times N_A}{M_{\text{cat}}}.
\]

where \(M_{\text{Fe}}\) represents the molecular mass of iron and \(N_A\) is Avogadro’s number. This is similar to previous work by Sahraie et al., in which CO-adsorption data were used to quantify adsorption sites on the catalyst surface (surface exposed active sites).\(^6\) For reasons of comparison also mass-based site densities related to FeN\(_4\) sites assigned to doublet D\(_2\) as well as to the overall number of FeN\(_4\) sites were calculated and the related comparison to CO sorption data are given in the Supporting Information, Figure S3 (MSD\(_{\text{D1}}\) replotted for comparison reasons). We will come back to this later.

In the present work it is assumed that CO-adsorption sites are indicative of O\(_2\) adsorption sites. End-on O\(_2\) binding is assumed based on modeling results.\(^30\) With end-binding, as opposed to side-on binding, a single CO-adsorption site will correspond to one oxygen adsorption site due to the similar orientation of the CO and O\(_2\) molecule. Additional concerns that should be addressed are that it is possible that some CO-binding sites are not suitable for ORR, and some ORR sites do not bind CO. The first concern is difficult to control for, and requires the reader to understand that our TOF should be thought of as an average TOF for all possible ORR sites. This is with the assumption that CO-binding sites can be considered to be at least a possible ORR site. The authors feel this a good assumption considering the success with which CO-adsorption...
has been used as sensor in precious-metal catalysis. The second concern mentioned, i.e. that it is possible that some ORR sites do not bind CO, is addressed by referring readers to the body of literature that has indicated time and time again the importance of metal content for ORR activity in acidic media.\textsuperscript{32,34} This observation is important because CO binds strongly to metals. Although it is true that nonmetallic catalysts can contain some ORR activity, their performance is generally limited to potentials below 0.7 V vs RHE. Considering that our potential of interest is 0.8 V, these active sites should not impact our calculations of TOF.\textsuperscript{35} As further evidence of CO as a successful indicator of ORR sites, we see that ORR activity increases with increasing CO-adsorption as shown in Figure 6. Representative adsorption traces for the various catalysts are shown in the Supporting Information, Figure S4. Assuming that each active site adsorbs one CO molecule a mass-based site density (MSD) can be calculated from CO adsorption data \((n_{\text{CO}})\) by the following equation:

\[
\text{MSD [sites per g]} = n_{\text{CO}} \text{[nmol/mg]} N_A \times 10^{-6}
\]

The MSD values as calculated for Mössbauer and CO adsorption are shown in Figure 7, in which the Mössbauer represents a bulk quantification of active sites and the CO-adsorption represents a surface sensitive quantification.

Due to this relationship the ratio of MSD/MSD\textsubscript{bulk} represents the catalysts utilization factor. As would be expected, this utilization is a strong function of porosity as shown in Figure 8. Effectively, increasing porosity controls access to the catalysts surface. In this way the porosity induced by the secondary nitrogen precursor plays a large role in catalyst utilization. Similar plots for the utilization of FeN\textsubscript{4} centers assigned to D2 or the sum D1 + D2 versus the BET surface area are shown in Supporting Information, Figure S3d and f. It becomes evident from the comparison of all three possibilities that the FeN\textsubscript{4} centers assigned to D1 give by far the best correlation. This is the case for both a linear correlation with the y-intercept, \(y_0\) free to change, but also for the correlation

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**Table 2. Mössbauer Parameters for Iron Sites As Found in the Five Catalysts**\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>(\delta) / mms(^{-1})</th>
<th>(\Delta E_q) / mms(^{3})</th>
<th>(H_0) / T</th>
<th>(\text{fwhm}) / mms(^{1})</th>
<th>Rel. Area / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>0.41</td>
<td>1.06</td>
<td>0.66</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>0.51</td>
<td>2.35</td>
<td>2 (fixed)</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Sext1</td>
<td>0.16</td>
<td>-0.09</td>
<td>20.7</td>
<td>0.20</td>
<td>2.9</td>
</tr>
<tr>
<td>Sext2</td>
<td>0.51</td>
<td>-</td>
<td>31.1</td>
<td>0.34</td>
<td>7.9</td>
</tr>
<tr>
<td>PANI-NCB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>0.38</td>
<td>0.98</td>
<td>0.56</td>
<td>25.5</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>0.48</td>
<td>2.10</td>
<td>1.44</td>
<td>39.6</td>
<td></td>
</tr>
<tr>
<td>Sext1</td>
<td>0.16</td>
<td>0.03</td>
<td>20.8</td>
<td>0.26</td>
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</tr>
<tr>
<td>Sext2</td>
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<td>-0.09</td>
<td>31.2</td>
<td>0.36</td>
<td>27.8</td>
</tr>
<tr>
<td>PANI-Urea</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>0.38</td>
<td>0.98</td>
<td>0.58</td>
<td>36.3</td>
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</tr>
<tr>
<td>D2</td>
<td>0.49</td>
<td>2.09</td>
<td>1.48</td>
<td>64.0</td>
<td></td>
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<tr>
<td>PANI-Mel</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>D1</td>
<td>0.38</td>
<td>1.05</td>
<td>0.62</td>
<td>33.4</td>
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<tr>
<td>D2</td>
<td>0.49</td>
<td>2.10</td>
<td>1.38</td>
<td>50.5</td>
<td></td>
</tr>
<tr>
<td>Sext1</td>
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<td>0.00</td>
<td>20.8</td>
<td>0.26</td>
<td>16.2</td>
</tr>
<tr>
<td>PANI-CM</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>0.40</td>
<td>1.08</td>
<td>0.60</td>
<td>57.4</td>
<td></td>
</tr>
<tr>
<td>D2</td>
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<td>2.55</td>
<td>1.06</td>
<td>36.8</td>
<td></td>
</tr>
<tr>
<td>Sext 3</td>
<td>0.27</td>
<td>0.07</td>
<td>13.1</td>
<td>0.26</td>
<td>5.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The catalysts are ordered with increasing ORR activity.

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**Figure 6.** Kinetic current density at 0.8 V vs RHE varying with adsorbed CO (adsorbed at 193 K via CO pulses).

**Figure 7.** Mass based site density of catalysts as measured by CO-adsorption and Mössbauer spectroscopy. Catalysts ranked by bulk site density as measured by Mössbauer spectroscopy.

**Figure 8.** Variation of catalyst utilization with porosity as measured by BET surface area.
with the constraint $y_0 = 0$. However, the correlations with free $y_0$ is significantly better. Note that the fact that negative $y$-intercepts, $y_0 < 0$, suggest that a minimum in surface area is required to get any finite utilization. This is another indication, that it is (mainly) the D1-related FeN$_4$ site that is probed by CO sorption. This is understandable, taking into account that the Mössbauer parameters of the D2 related FeN$_4$ site are similar to iron phthalocyanine where a pseudo-6-fold coordination leads to the quadrupole splitting. Hence, it can be assumed that also for our D2 site the axial positions might not be available for gas adsorption.

Although porosity plays a significant role in utilization, there are other important factors to performance. For example, from Figure 8, we can see that a good catalyst (PANI-CM) has low utilization, whereas a mediocre catalyst (PANI-Urea) has high utilization. Part of the answer to this question is the role of the secondary nitrogen precursor in creating active sites.

**Role of Secondary N-Precursor on the Quality of Active Sites.** Some secondary nitrogen precursors result in high quantities of active sites such as PANI-Mel, PANI-NCB, and PANI-CM as shown by the Mössbauer data in Figure 7 by the MSD$_{bulk}$ parameters.

PANI-Mel and PANI-CM likely create a lot of active sites due to their high nitrogen contents. NCB may create a lot of active sites for a number of reasons. One hypothesis is that the low porosity of the material traps reactive gases during the heat treatment. The smaller release of gaseous products is also visible in the thermogravimetric analysis shown in the Supporting Information, Figure S5. The trapped reactive gases build up, creating high partial pressures which have been shown to improve ORR activity. But ultimately, these active sites are useless in RDE conditions due to the extremely low utilization. Nonetheless, it is evident from these catalysts that the secondary nitrogen precursors play a role in both active site synthesis as well as active site utilization as it was discussed earlier.

Now that active site synthesis and utilization have been discussed, turnover frequencies will be calculated to gain further understanding of how the secondary nitrogen precursors influence the intrinsic performance of active sites. A plot of kinetic current density from Figure 3 vs CO adsorption data indicates the relative intrinsic activity of these catalysts (Figure 6). Specifically, the slope of a line from the origin to any of the data points represents a measure for the mean turnover frequency (TOF) of the CO adsorption sites for ORR. The lines in Figure 6 represent the range of TOF that is evident in this work. For example, it is observed that PANI-CM has the highest TOF due to the slope of the line drawn in Figure 6 through the PANI-CM data point. Additionally, it is clear that the other catalysts have a similar, but lower TOF. The high TOF of PANI-CM is calculated due to a high ORR activity but low MSD (from CO sorption).

Although it is difficult to ascertain why the TOF of the PANI-CM is significantly higher than the other catalysts, the answer can be obtained partially from nitrogen content. A plot of TOF vs bulk nitrogen (Figure 9) allows comparison of the intrinsic activity of the active sites to catalyst nitrogen contents. TOF at 0.8 V vs RHE were calculated from the adsorbed CO and kinetic current ($i_k$) by the following equation:

$$\text{TOF} = i_k F^{-1} n_{CO}^{-1}$$

where $n$ are the moles of chemisorbed CO molecules and $F$ is Faraday’s constant. It is evident that the PANI-CM is significantly different than the other catalysts not only in TOF but also in bulk nitrogen content. In fact, the best explanation for the high TOF of the cyanamide catalyst is its high nitrogen content with respect to the other catalysts. Multiple works have indicated that nitrogen species in the vicinity of the active site may play an important role in iron center electronics. Hence, nitrogen may play a subtle role in active site electronics as suggested by Kramm et al. and Ramaswamy et al. To further evaluate this, X-ray induced photoelectron spectroscopy was performed for the PANI catalysts prepared with secondary N-precursor. The convoluted N 1s spectra are shown in the Supporting Information, Figure S6. In Figure 10 the reference catalyst PANI is compared in terms of intensity with the four catalysts prepared with a secondary N-precursor.

In this graph also the energetic positions for the observation of the different nitrogen functionalities are indicated. While the nitrogen content related to graphitic and oxidic nitrogen remains the same for all catalysts, major changes are visible in the lower binding energy region, related to N$_{pyridinic}$ N$_{Me-N}$ and N$_{pyrid}$. It is interesting to note that the PANI

**Figure 9.** Turnover frequency varying with bulk nitrogen content as measured from elemental analysis.

**Figure 10.** N 1s finescans of the four catalysts prepared with a secondary N-precursor in comparison to the PANI reference catalyst. Please note, XPS data on PANI were already reported in ref 6 but measured with another spectrometer. For comparison, the count rate per unit nitrogen was therefore changed accordingly to enable a direct comparison to the other samples (therefore the count rate is given as cps$^{-1}$).

$$\text{TOF} = i_k F^{-1} n_{CO}^{-1}$$
The other three samples lead to the incorporation of significantly larger fractions of \( N_{\text{pyrid}} \), \( N_{\text{mes}} \), and \( N_{\text{pyr}} \). While all three of them can— to some extent— be attributed to different types of FeN\(_x\) sites, particularly pyridinic nitrogen is discussed to promote the ORR by an assisted proton transfer.\(^{41,42}\) Indeed, the intensity in the \( N_{\text{pyr}} \) region is one of the highest for PANI-CM, but on the basis of the overall data set it can hardly be at the origin of the significant improved TOF. Further work will be required to get a better understanding of the origin of improved TOF for using cyanamide as secondary N-precursor. In anyway, its very different behavior in comparison to the other four catalysts also becomes apparent from the comparison of bulk and “surface-related” (XPS) nitrogen contents, as shown in the Supporting Information, Figure S7. Due to the use of a carbon support (free or almost free of nitrogen) the nitrogen content is higher on the surface (XPS) compared to the bulk. However, while the slope is similar for the four catalysts, in the case of PANI-CM, a different relation is observed. This indicates that the carbon burnoff (related to the support) was larger in comparison to the other samples. As TGA (Figure S5) indicates, the same overall mass loss in comparison to PANI-Urea, one has to conclude that the thermal induced reactions appearing for PANI-Urea (rather then the carbon in this sample) must have been more pronounced compared to catalyst PANI-CM. Maybe the changed ratio of N contents had a positive effect on the electronic interaction of active sites with the carbon. If so, however, one would not expect the correlation of TOF with the bulk nitrogen content. Further work will be required to identify the origin of improved TOF for PANI-CM.

**CONCLUSIONS**

Four different secondary nitrogen precursors were used to explore and deconvolute the complex relations between active site density, active site utilization, and active site turnover frequency of iron-based Fe–N–C ORR fuel cell electrolytes. Using Mössbauer spectroscopy, X-ray induced photoelectron spectroscopy, and CO and \( N_2 \) sorption studies, we demonstrated how close to perfect utilization (active site dispersion) is offset by intrinsically less active catalytic surface sites (TOF values) and vice versa. We also demonstrated that the total nitrogen content not only increases the number of FeN\(_x\) sites, but in addition modulates their intrinsic activity (TOF) in agreement with previous studies. Furthermore a few basic chemical mechanisms were uncovered in which such secondary precursors enhance the catalytic activity. One such mechanism consisted in significant etching of micropores (urea and melamine). Others work by creating a high density of active sites (melamine and cyanamide). Finally, it was discovered that one secondary nitrogen precursor (cyanamide) also incorporates significantly more nitrogen into the bulk catalyst framework, leading to higher TOF values, which explains the high values obtained for PANI-CM catalyst. Our study clarifies how secondary nitrogen precursors serve as a flexible means of improving MNC catalyst performance by a number of different phenomena.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b02897.

Additional physical characterization, CO-adsorption data, thermogravimetric data, and the remaining Mössbauer data (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to acknowledge Dr.-Ing. Ralph Krähnert, Dr. Denis Bernsmeier, and Huan Wang, for their help with the nitrogen physisorption experiments. U.I.K. and S.W. acknowledge financial support by the BMBF via contract 05K16RD1 and by the Graduate School of Excellence Energy Science and Engineering (GRC1070). P.S. acknowledges support by the European Commission and the Horizon2020 framework funding under the FCH JU 2 program via the “CRECENDO” project.

**REFERENCES**


