

# **Characterizing Complex Gas-Solid Interfaces with in Situ Spectroscopy: Oxygen Adsorption Behavior on Fe-N-C Catalysts**

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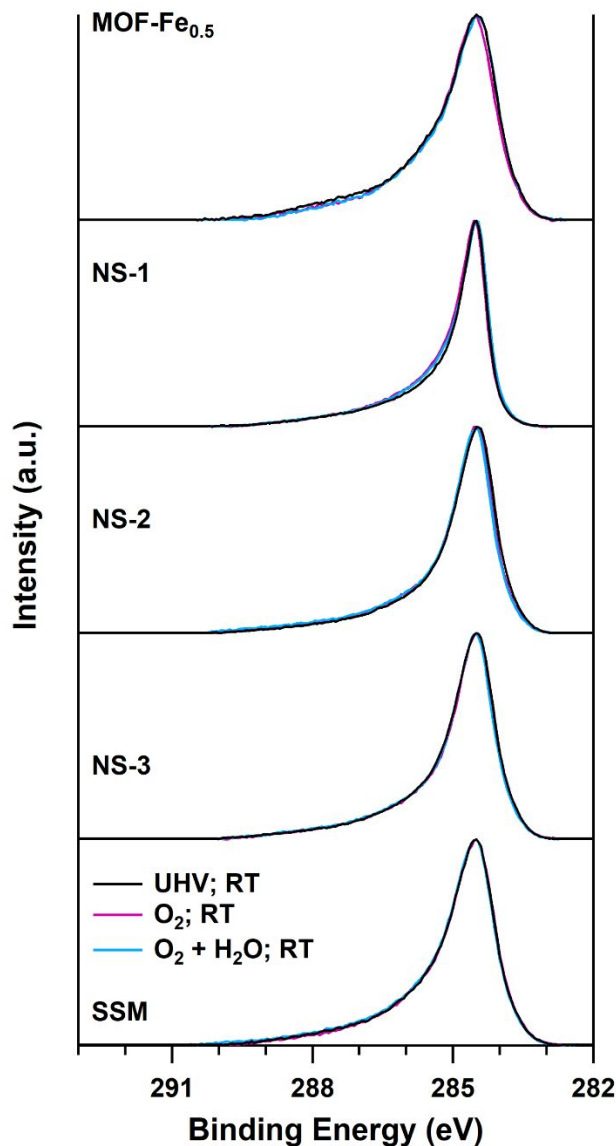
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## Supporting Information

Figure S1:

The C 1s of each sample measured at all three conditions is displayed with the background subtracted and the data normalized to the peak-maximum value, in order to best display any possible changes in the spectral features of the C 1s. While some slight variation from sample to sample is present, essentially no change in the C 1s is seen for any given sample from one measurement condition to the next. This validates that the energy scale calibration is consistent when changing measurement conditions, and that the C 1s has no appreciable interaction with O<sub>2</sub> or H<sub>2</sub>O, or change due to increased temperature detectable within this dataset.



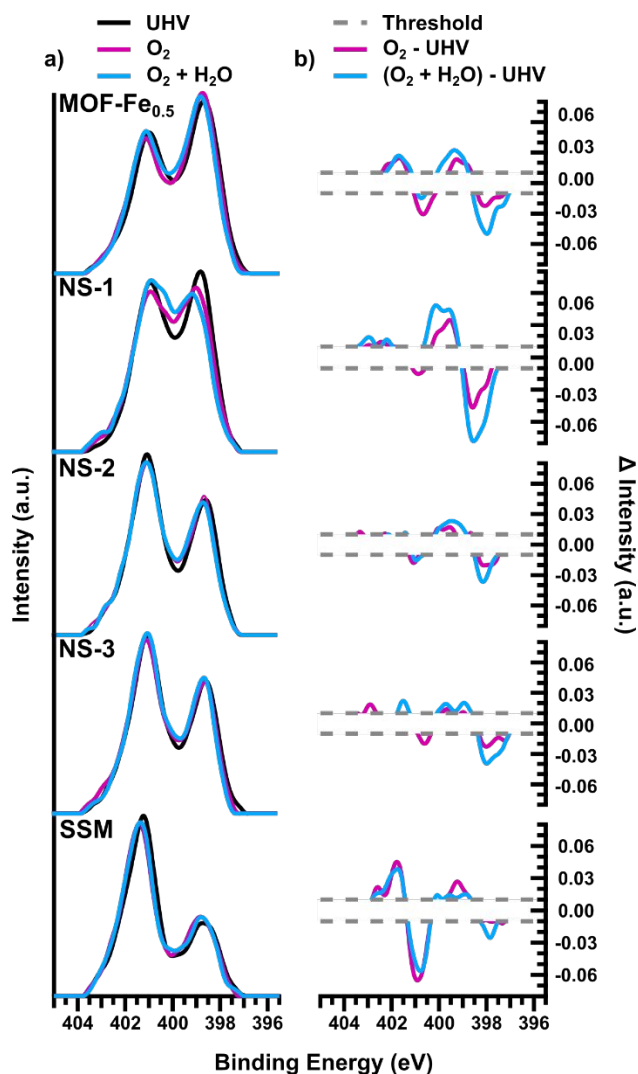
**Figure S1:** Background subtracted normalized C 1s data is shown for all samples at all measurement conditions.

Table S1:

Table S1. Room temperature hyperfine parameters obtained from the fitting of the  $^{57}\text{Fe}$  Mössbauer spectra. IS, QS and LW are isomer shift, the quadrupole splitting and the line width respectively. All IS-values are given with respect to  $\alpha$ -Fe iron standard at room temperature.

Sample	Component	IS ( $\text{mm}\cdot\text{s}^{-1}$ )	QS ( $\text{mm}\cdot\text{s}^{-1}$ )	LW ( $\text{mm}\cdot\text{s}^{-1}$ )	H (Tesla)	Assignment	Rel. Abs. area (%)
<b>MOF- Fe<sub>0.5</sub></b>	D1	0.36	0.98	0.69	-	Fe(III)N <sub>x</sub> HS	58.0
	D2	0.40	2.59	1.32	-	Fe(II)N <sub>x</sub> LS or MS	42.0
<b>NS-1</b>	D1	0.36	0.98	0.69	-	Fe(III)N <sub>x</sub> HS	70.7
	D4	0.82	2.61	1.04	-	Fe(II) in tetrahedral coordination	23.0
		0.14	-	0.29	20.5	Fe <sub>3</sub> C	6.3
<b>NS-2</b>		-0.05	-	0.38	33.1	$\alpha$ -Fe	28.5
		0.18	-	0.35	20.4	Fe <sub>3</sub> C	14.4
		-0.13	-	0.32	-	$\gamma$ -Fe	10.2
		0.35	-	8.2	-	Magnetic relaxation	23.0
<b>NS-3</b>		-0.02	-	0.31	33.1	$\alpha$ -Fe	18.0
		0.15	-	0.32	21.1	Fe <sub>3</sub> C	38.7
		0.14	-	0.32	20.3	Fe <sub>3</sub> C	39.4
		0.14	0.93	0.42	-	Fe <sub>2+x</sub> N	3.9
<b>SSM</b>		-0.06	-	0.39	-	$\gamma$ -Fe	1.1
	D1	0.40	1.07	0.87	-	Fe(III)N <sub>x</sub> HS	39.8
	D2	0.54	2.05	1.23	-	Fe(II)N <sub>x</sub> LS or MS	45.7
	D3	0.37	3.54	0.98	-	Fe(II)N <sub>x</sub> MS	12.9

Figure S2:

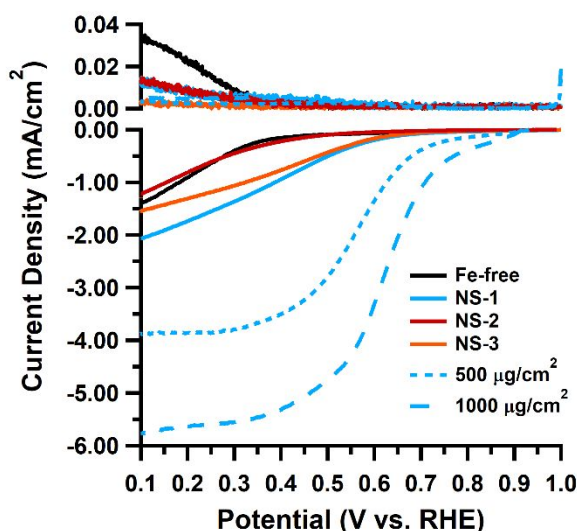


**Figure S2:** Overlaid, background subtracted N 1s spectra normalized to the total region area are displayed for both UHV, RT 100 mTorr O<sub>2</sub>, 80 °C, and 100 mTorr O<sub>2</sub> + 100 mTorr H<sub>2</sub>O environments for all samples (a), alongside the resulting difference spectra (b). A dashed vertical line is included at ~398.6 eV to draw attention to the shift in adsorption peak position unique to NS-1. Note that the UHV and O<sub>2</sub> only data is the same as in Figure 6 of the manuscript, and was included here for comparison to the O<sub>2</sub> + H<sub>2</sub>O data.

Figure S3:

RRDE testing was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte using an RHE reference electrode, Pt-mesh counter electrode, and catalyst film deposited on the glassy carbon tip of a Pine RRDE. To prepare the catalyst film, the NS sample was added to an aliquot of ethanol along with an aliquot of 5 wt.% Nafion in water solution such that a Nafion loading of 10  $\mu\text{L}/\text{mg}$  was used. The ink was then sonicated in an ice bath for 30 minutes before a volume of ink was deposited on a polished and cleaned RRDE glassy carbon surface such that the desired catalyst loading (50, 500, or 1000  $\mu\text{g}/\text{cm}^2$ ) was achieved. The ink was then allowed to dry under ambient pressure and temperature. Prior to RRDE measurements, a break in procedure was performed in N<sub>2</sub> saturated electrolyte by sweeping a potential range of 1.0 V – 0.4 V at 500 mV/s while rotating at 1600 rpm until no change in the data was observed. RRDE measurements were performed by scanning from 1.0 V to 0.1 V in O<sub>2</sub> saturated electrolyte at 20 mV/s and 1600 rpm while the Pt ring potential was held at a constant value of 1.0 V. All measurements were performed with a BioLogic SP-300 potentiostat. Prior to any measurement, glassware was cleaned by boiling in pure deionized water for several hours.

RRDE measurements of both the MOF-Fe<sub>0.5</sub> sample<sup>33</sup> and the SSM sample<sup>10,61</sup> have been previously reported. RRDE measurements performed on the three NS samples, as well as an Fe-free NC analogue, are reported in Figure S2. Initial screening of the three NS samples was done using a very low loading of the catalyst (50  $\mu\text{g}/\text{cm}^2$ ) to preserve the thin film nature of the measurement such that accurate ring current values could be attained. NS-2, which is primarily Fe-NPs and contains no FeN<sub>x</sub>C<sub>y</sub> active sites, shows essentially no improvement in activity over the base Fe-free material, indicating that if the ORR is occurring to any extent, it is most likely due to



**Figure S3:** RRDE measurements of NS-1, NS-2, NS-3 and an Fe-free NS reference material are shown above. Each material was measured at a catalyst loading of 50  $\mu\text{g}/\text{cm}^2$ , and NS-1 was also measured at catalyst loadings of 500 and 1,000  $\mu\text{g}/\text{cm}^2$ .

N defects also present in the Fe-free reference material. NS-3 and NS-1 show modest improvements in activity over the Fe-free baseline while still appearing largely inactive at this catalyst loading. While NS-1 has  $\text{FeN}_x\text{C}_y$  sites in its Mössbauer spectrum, NS-3 mainly has carbide species. Since the overall N 1s features as shown by XPS in Figure 3 of NS-3 and NS-2 are nearly identical, it is most likely the difference comes from the presence of iron carbide, which has been shown, in certain cases, to be active, although likely less active on a per site basis than highly active  $\text{FeN}_x\text{C}_y$  sites.<sup>74</sup> NS-1 was also evaluated at higher catalyst loadings of 500  $\mu\text{g}/\text{cm}^2$  and 1000  $\mu\text{g}/\text{cm}^2$  in order to attempt to draw comparison with literature examples, and prior published results on MOF- $\text{Fe}_{0.5}$  and SSM. The  $E_{1/2}$  of NS-1 at 500  $\mu\text{g}/\text{cm}^2$  is  $\sim 0.57$  V, while an  $E_{1/2}$  of  $\sim 0.64$  V is observed at 1000  $\mu\text{g}/\text{cm}^2$ . In prior work, SSM had an  $E_{1/2}$  of  $\sim 0.8$  V,<sup>10</sup> while MOF- $\text{Fe}_{0.5}$  was  $\sim 0.78$  V.<sup>33</sup> While this is in no way meant to be a robust, systematic study of the 5 materials, it is still clear from the initial screening that the lower temperature NS-1 sample does not exhibit a similar level of activity as that of the SSM and MOF- $\text{Fe}_{0.5}$  samples. In fact, the ORR behavior of NS-1 is not unsimilar to lower-temperature materials presented in the literature like that of the 400 °C sample presented in a study on the temperature dependent formation of  $\text{FeN}_4$  bonding.<sup>68</sup> It is likely that further optimization of both ink properties and processing, as well as electrochemical testing parameters will result in an improvement in performance for the NS-1 sample, however it is unlikely that this would result in the level of performance seen for the other two active catalysts. Further optimization of the performance of this material were not warranted due to the more fundamental nature of this study and motivation to develop reliable analysis tools that help understand adsorption behavior of complex catalysts.