

# Electrocatalytic O<sub>2</sub> Reduction by [Fe-Fe]-Hydrogenase Active Site Models

Subal Dey,<sup>†</sup> Atanu Rana,<sup>†</sup> Danielle Crouthers,<sup>‡</sup> Biswajit Mondal,<sup>†</sup> Pradip Kumar Das,<sup>†</sup> Marcetta Y. Darensbourg,<sup>\*,‡</sup> and Abhishek Dey<sup>\*,†</sup>

<sup>†</sup>Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata, India 700032

<sup>‡</sup>Department of Chemistry, Texas A & M University, College Station, Texas TX-77843, United States

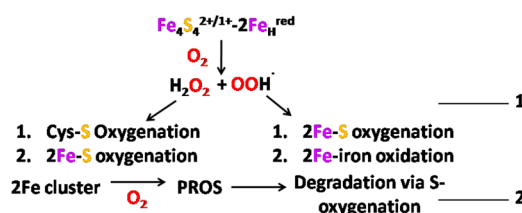
## Supporting Information

**ABSTRACT:** The instability of [Fe-Fe]-hydrogenase and its synthetic models under aerobic conditions is an inherent challenge in their development as practical H<sub>2</sub> producing electrodes. The electrochemical oxygen reduction reaction of a series of synthetic model complexes of the [Fe-Fe] hydrogenase is investigated, and a dominant role of the bridgehead nitrogen in reducing the amount of partially reduced oxygen species (PROS), which is detrimental to the stability of these complexes, is discovered.

The natural [Fe-Fe]- and [Ni-Fe]-hydrogenases (H<sub>2</sub>ases) as well as a hybrid construct composed of the apo-[Fe-Fe]-H<sub>2</sub>ase outfitted with a synthetic 2Fe subsite can efficiently catalyze the conversion of H<sup>+</sup> to H<sub>2</sub> under optimal physiological conditions.<sup>1–4</sup> H<sub>2</sub>ases are potential electrocatalysts for H<sub>2</sub>/O<sub>2</sub> fuel cells due to their low overpotentials, high catalytic rates, and high turnover numbers.<sup>5,6</sup> However, their sensitivity to O<sub>2</sub> has limited practical applications as electrode materials for H<sub>2</sub>/O<sub>2</sub> fuel cells, an area of great contemporary importance.<sup>7–9</sup> The low-valent reduced [Fe-Fe]-H<sub>2</sub>ase active site reduces O<sub>2</sub> to produce partially reduced oxygen species (PROS) such as O<sub>2</sub><sup>•-</sup> and H<sub>2</sub>O<sub>2</sub> which can rupture the nearby Fe-S clusters involved in delivering the electrons necessary to reduce H<sup>+</sup> to H<sub>2</sub> and/or stay bound to the cluster after electron transfer from the 2Fe2S cluster.<sup>10</sup> Computational investigations have suggested that the thermodynamics of O<sub>2</sub> binding to the cluster is indeed favorable, and there are gas channels available for O<sub>2</sub> to access the active site.<sup>11,12</sup> Investigations of intermediates formed during reaction of O<sub>2</sub> with the active site suggest formation of O<sub>2</sub> bound intermediates at the 2Fe subsite which lead to formation of PROS which degrades the Fe<sub>4</sub>S<sub>4</sub> cluster.<sup>12</sup> The reduction of O<sub>2</sub> to O<sub>2</sub><sup>•-</sup> as well as H<sub>2</sub>O<sub>2</sub> at the 2Fe site has been computationally predicted.<sup>11</sup> Scheme 1 displays these hypothesis that have driven the design of biomimetic research, oriented toward understanding the potential for oxygen damage of the 2Fe subsite of the H-cluster, i.e., the [Fe-Fe]-H<sub>2</sub>ase active site. Direct electrochemical reduction of O<sub>2</sub> in an aqueous medium by synthetic analogues of H<sub>2</sub>ases has, to our knowledge, not yet been investigated.

Over the last two decades numerous synthetic analogues of 2Fe subsite of the [Fe-Fe]-H<sub>2</sub>ase active site have been reported.<sup>13</sup> Recently, some of these have been proven to be efficient catalysts for proton reduction under acidic aqueous conditions.<sup>14–17</sup> The catalytic abilities of these models, in both aqueous and organic

**Scheme 1. PROS Generation by [Fe-Fe]H<sub>2</sub>ases and Its Possible Reactivities**

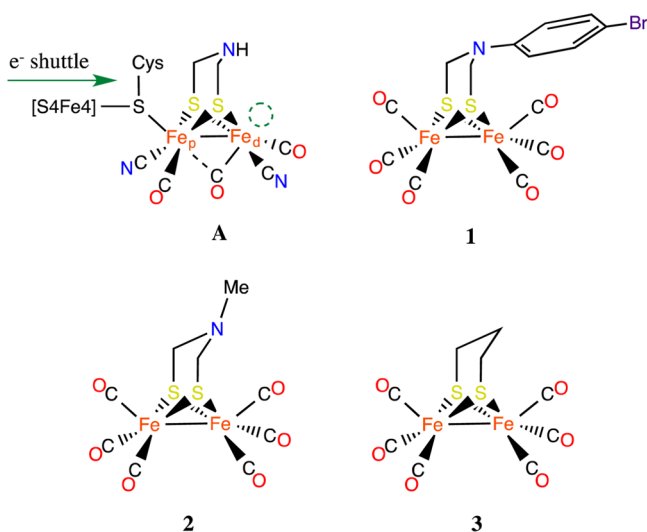


mediums, are limited to strictly anoxic conditions as the low-valent iron as well as the bridging thiolate ligands, for an alkane dithiolato ligand, were found to be prone to oxygenation.<sup>18</sup> We posit that investigation of the ORR activity of a synthetic analogue of the [Fe-Fe]-H<sub>2</sub>ase active site, that is a proven efficient hydrogen evolution reaction (HER) catalyst in aqueous medium, may provide valuable insight aiding design of better oxygen-tolerant H<sub>2</sub> evolving catalysts. Here, we describe the O<sub>2</sub> reduction reaction catalyzed by three [Fe-Fe]-H<sub>2</sub>ase active site models with different bridgehead substituents in the S to S linker (Figure 1). The first two models (1 and 2) bear dimethylazadithiolate (ADT), and the model 3 contains the propane-dithiolate (PDT) bridging ligand. The results demonstrate a major role played by the bridgehead nitrogen in lowering the amount of H<sub>2</sub>O<sub>2</sub> produced during O<sub>2</sub> reduction, offering longer HER catalyst lifetime under ambient aerobic conditions.

Complex 1 has been recently demonstrated to effect facile H<sub>2</sub> production under anoxic acidic aqueous solutions with a turnover frequency as high as 6000 s<sup>-1</sup>, turnover numbers as high as 10<sup>8</sup>, and faradaic efficiencies >95%.<sup>15</sup> Under aerobic conditions the same catalyst shows significantly lower electrolytic current (Figure S1, green) and a faradaic efficiency of only 65%. The decay of electrocatalytic current indicates decay of the catalyst under oxic conditions, and the lower faradaic yield suggests the presence of competitive electrocatalytic O<sub>2</sub> reduction. Under anoxic conditions the cyclic voltammogram (CV) of 1 physisorbed on a pyrolytic edge-plane graphite electrode (EPG) shows two consecutive quasi-reversible redox couples (E<sub>1/2</sub>) at -0.24 and -0.37 V vs NHE at pH 7 that correspond to the [1]<sup>-</sup> and [1]<sup>2-</sup> states, respectively.<sup>15</sup> Under oxic environments a clear mass transport-limited current response to the added O<sub>2</sub> occurs at -0.26 V, indicating that 1

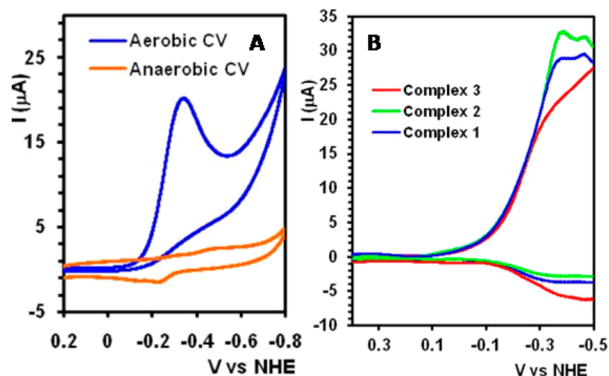
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**Figure 1.** Active site structure of the [Fe-Fe]-H<sub>2</sub>ase enzyme (A). Dinuclear iron models with Fe<sub>2</sub>S<sub>2</sub>(CO)<sub>6</sub> core bearing ADT (1 and 2), when an aromatic group is attached to the N in 1 and an alkyl group in 2. Complex 3 contains PDT bridging moiety.

in the Fe<sup>I</sup>-Fe<sup>0</sup> state can catalyze oxygen reduction reaction (ORR) (Figure 2A). The catalytic current increases linearly with O<sub>2</sub> concentration indicating a pseudo-first-order kinetics of ORR (Figure S2).

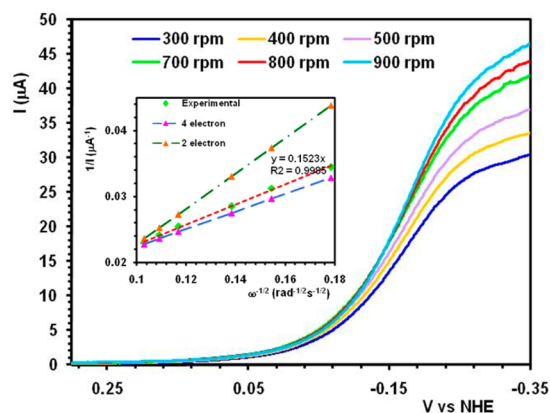


**Figure 2.** (A) CV of 1 under anaerobic (100 mV/s) and aerobic (50 mV/s) environment at pH 7. (B) RRDE of complexes 1–3 in 0.5 M H<sub>2</sub>SO<sub>4</sub> (50 mV/s).

Rotating ring disk electrochemistry (RRDE) is an analytical technique that is used to quantitatively estimate H<sub>2</sub>O<sub>2</sub> produced during ORR.<sup>19,20</sup> In a RRDE set up a Pt ring electrode encircles the working EPG electrode where any H<sub>2</sub>O<sub>2</sub> formed, due to the incomplete reduction of O<sub>2</sub> by 1, and is reoxidized to O<sub>2</sub> generating an oxidation current (Figure 2B, red). For model complexes 1–3, the Pt ring shows an oxidation current which profiles similarly to the ORR current with the applied potential (Figure 2B). The amount of H<sub>2</sub>O<sub>2</sub> produced during O<sub>2</sub> reduction by 1 is determined to be 57%. Similarly the amount of the PROS is estimated to be 62% for 3 and 49% for 2 at pH 7. Release of reactive H<sub>2</sub>O<sub>2</sub> in significant quantities can degrade the catalyst and account for the decrease of HER activity with time during bulk electrolysis experiments, performed in aerobic solution. FTIR data on the electrode before and after ORR clearly show decrease in the carbonyl peak intensities (Figure S3A) and increase in peak intensities at 800 and 1020 cm<sup>-1</sup> (S-O stretches

of RSO<sub>2</sub><sup>-</sup> and RSO<sub>3</sub><sup>-</sup> groups, Figure S3B)<sup>18</sup> suggesting degradation of the catalyst via thiolate oxidation by the H<sub>2</sub>O<sub>2</sub> produced during ORR. XPS data obtained after ORR show S 2p<sub>3/2</sub> ionizations at 168–170 eV characteristic of RSO<sub>2</sub><sup>-</sup> and RSO<sub>3</sub><sup>-</sup> groups in addition to the thiolate peak at 162.5 eV (Figure S3C).<sup>15,18e</sup> In the presence of 25 μM catalase, a heme enzyme responsible for dismutating H<sub>2</sub>O<sub>2</sub> to O<sub>2</sub> and H<sub>2</sub>O at very high rates, the ORR current of 1 is sustained over a longer period (Figure S4) directly implicating the role of H<sub>2</sub>O<sub>2</sub> produced in cluster degradation.

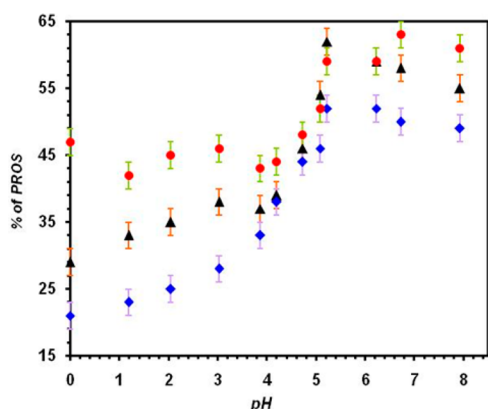
The linear sweep voltammetry data collected at various pH's show minimal variation in the onset potential for O<sub>2</sub> reduction (Figures S5–S7). The reduction of these complexes from their native Fe(I)Fe(I) redox level to the reactive Fe(I)Fe(0) step does not involve a proton and may be the pH-independent potential-determining step involved in ORR. Alternatively, the amount of PROS is lowered significantly as the pH of the solution is lowered and reaches a limiting value around pH 2–3 (Figure 3). The amount of H<sub>2</sub>O<sub>2</sub> for 2 (the complex bearing an



**Figure 3.** RDE for the complex 1 on EPG electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a different rotation speed in aerobic environments. Inset: K-L plot (1/I vs ω<sup>-1/2</sup>).

alkylamine bridge) is lowered to 21% in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution relative to 49% at pH 7. The amount of H<sub>2</sub>O<sub>2</sub> produced by 1 is lowered to 29% from 57% as the pH is lowered from 7 to 0. Similarly for 3 the amount of H<sub>2</sub>O<sub>2</sub> is lowered to 45% at pH = 0 relative to 62% at pH 7. Note that the decrease in H<sub>2</sub>O<sub>2</sub> with pH 5 to pH 4 is observed for a carbon-bridged (3), an alkylamine-bridged (2), and an aromatic amine-bridged (1) complex. However, the magnitude of decrease is minimum for the carbon-bridged (3) and maximum for the alkylamine-bridged (2) complex. These data suggest that the decrease of PROS observed between pH 5.5–4.5 may not originate from the bridgehead atom; however, the gradual decrease below pH 4 arguably does.

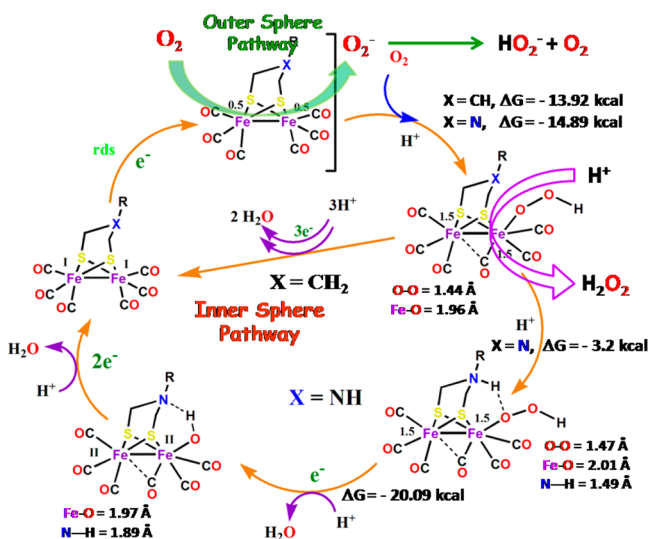
Koutecky–Levich (K-L) analysis of the electrochemical reduction of O<sub>2</sub> by 1 in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Figure 4) indicates that the number of electrons transferred to the substrate O<sub>2</sub> is 3.5 ± 0.1.<sup>19</sup> The partial reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> is responsible for lowering the number of electrons delivered to O<sub>2</sub> from its ideal value of 4. A value of 3.5 implies 75% 4e/4H<sup>+</sup> reduction of O<sub>2</sub> to H<sub>2</sub>O, i.e., 25% reduction to H<sub>2</sub>O<sub>2</sub>. This is in good agreement with the observation of 29% PROS observed for the same complex in the RRDE experiments at the same pH. Unfortunately, the number of electrons delivered to the substrate, O<sub>2</sub>, could not be exactly determined using K-L analysis, because at higher pHs the H<sub>2</sub>O<sub>2</sub> generated (~50%)



**Figure 4.** Amount of  $\text{H}_2\text{O}_2$  produced at  $-0.4$  V vs NHE at various pHs with **1** (black  $\blacktriangle$ ), **2** (blue  $\blacklozenge$ ) and **3** (red  $\bullet$ ).

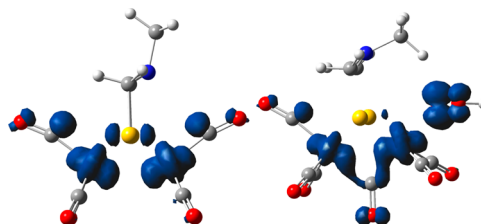
degrades these complexes before a K-L analysis can be performed. Nevertheless, the RRDE result suggests that under neutral conditions  $\sim 50\%$  of the  $\text{O}_2$  is directly converted to water, a  $4e^-$  reduction process ( $\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$ ), and the rest contributes to the PROS formation ( $\sim 50\%$ ). Note that while a  $4e^-/4\text{H}^+$  reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$  entails an inner-sphere mechanism, the reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  does not. Unlike **3**, where the  $\text{H}_2\text{O}_2$  produced sharply decreases from  $60\%$  in pH 5.1 to  $43\%$  at pH 4 and then stays constant at lower pHs, the  $\text{H}_2\text{O}_2$  produced by **1** and **2** gradually reduces with lowering of the pH after the initial sharp decrease between pH 5 and 4. The  $\text{H}_2\text{O}_2$  produced for **2**, with an alkylamine (higher  $\text{pK}_a$ ) bridge, is lower relative to **1** which has an aromatic amine bridge (lower  $\text{pK}_a$ ). These sets of data imply that the sharp drop in  $\text{H}_2\text{O}_2$  between pH 5 and 4 is inherent to the 2Fe cluster, but the gradual drop from pH 4 to pH 0 is due the amine bridge. Note that release of less  $\text{H}_2\text{O}_2$  (inner-/outer-sphere) implies a greater extent of  $4e^-/4\text{H}^+$  reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$ .

These experimental data can be rationalized by considering the terminal binding of  $\text{O}_2$  to singly reduced diiron complex, as reported previously,<sup>10</sup> and formation of  $\text{Fe}^{\text{I}}-\text{O}_2^-$  type adducts as intermediates (Figure 5) in the ORR. DFT calculations (BP86/



**Figure 5.** Proposed mechanistic scheme for  $\text{O}_2$  reduction by ADT-bridged Fe-Fe hydrogenase mimics ( $e^-$  are obtained from the electrode and  $\text{H}^+$  are obtained from solution).

$6-311\text{g}^*$  in Gaussian 03)<sup>22–24</sup> of the reduced  $\text{Fe}(\text{I})-\text{Fe}(\text{0})$  state indicate that it is best described as a  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  system as the unpaired electron is added to an unoccupied Fe-Fe  $\sigma^*$  orbital of the resting  $\text{Fe}(\text{1})-\text{Fe}(\text{1})$  state. Thus, the spin density resulting from the reduction is evenly delocalized on both the Fe centers (Figure 6, left). This leads to decrease in bond order of the Fe-Fe



**Figure 6.** Spin density on the reduced  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  cluster (left) and  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})-\text{OOH}$  species (right).

bond from 1 in the  $\text{Fe}(\text{1})\text{Fe}(\text{1})$  state to 0.5 in the  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  state.<sup>24</sup> The Fe-Fe distances increase from  $2.55$  Å in the  $\text{Fe}(\text{1})\text{Fe}(\text{1})$  state to  $2.71$  Å  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  state consistent with the above proposal. These calculations indicate that  $\text{O}_2$  binding is only possible if it is associated with a protonation (Figure 5). The energy for this proton-assisted  $\text{O}_2$  binding varies little with the nature of the bridgehead atom ( $-13.92$  kcal/mol for  $\text{CH}_2$  and  $-14.89$  kcal/mol for NMe, Figure 5). Judging by the O-O bond ( $1.44$  Å, Table S1) and the lack of significant spin density on the  $\text{O}_2$  unit (Figure 6, right), the resultant species is best described as a peroxide, i.e.,  $\text{O}_2$  is reduced by two electrons.<sup>11</sup> The calculated spin density (Figure 6, left) is delocalized uniformly on both the Fe centers such that it is best described as  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})-\text{OOH}$ . The Fe-Fe bond length in the  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})$  species is  $2.71$  Å, similar to that of the  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$ . This is because as the  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  state is oxidized by two electrons to a  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})$  state by  $\text{O}_2$ , one electron is removed from the singly occupied Fe-Fe  $\sigma^*$  orbital and the other from the doubly occupied Fe-Fe  $\sigma$  orbital. The Fe-Fe bond order is thus 0.5 for both  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  and  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})$  states resulting in  $0.2$  Å longer Fe-Fe distances relative to the  $\text{Fe}(\text{1})\text{Fe}(\text{1})$  state.

The initial drop in  $\text{H}_2\text{O}_2$  production between pH 5.5 and 4.5, independent of the bridgehead atom, likely represents the  $\text{H}^+$ -assisted oxidation of the  $\text{Fe}(\text{0.5})\text{Fe}(\text{0.5})$  state to form the  $\text{Fe}(\text{1.5})\text{Fe}(\text{1.5})-\text{OOH}$  species (Figure 5). The computations indicate that binding of  $\text{O}_2$  shifts one of the terminal CO ligands to a bridging position in this intermediate (Figure 6, right). This is the first intermediate of the inner-sphere  $4e^-/4\text{H}^+$  ORR mechanism which leads to lowering of  $\text{H}_2\text{O}_2$  production. Hydrogen bonding between the -OOH and the bridgehead nitrogen may explain lower  $\text{H}_2\text{O}_2$  production by **1** and **2** relative to **3** at pH 7. Further protonation of the NMe group is exothermic and activates the Fe-OOH unit for cleavage via hydrogen bonding as indicated by elongation of the O-O bond to  $1.47$  Å (Table S1). Interestingly this effect is analogous to a terminal hydride intermediates involved in proton reduction.<sup>13c</sup> Further reduction of these species to cleave the O-O bond, resulting in  $4e^-/4\text{H}^+$  reduction of  $\text{O}_2$ , will require both electrons and protons. The fact that the PDT-bridged species does not show any decrease in  $\text{H}_2\text{O}_2$  production below pH 4 (i.e., no increase in the extent of  $4e^-/4\text{H}^+$  reduction of  $\text{O}_2$ ) and that the ADT-bridged complexes do is consistent with the observed role of the hydrogen bonding from the protonated bridgehead nitrogen in aiding O-O bond cleavage. The weakening of the O-O bond will promote O-O bond cleavage favoring  $4e^-/4\text{H}^+$

reduction of O<sub>2</sub>, thus producing less H<sub>2</sub>O<sub>2</sub> as observed experimentally. This stabilization via H-bonding is not available for the PDT-bridged complex 3. Hence, no further reduction of the amount of H<sub>2</sub>O<sub>2</sub> is observed below pH 5. The stabilization of the terminal hydroperoxide (-OOH) species by H-bonding is further supported by the fact that the alkylamine-bridged 2, with a greater availability of the nitrogen lone pair, exhibits greater 4e/4H<sup>+</sup> reduction of O<sub>2</sub> and less H<sub>2</sub>O<sub>2</sub> than the aromatic amine-bridged complex 1. An ~20% H<sub>2</sub>O<sub>2</sub> production implies that the proton-assisted hydrolysis of the Fe(1.5)Fe(1.5)-OOH intermediate competes with O-O bond cleavage under acidic conditions. The H<sub>2</sub>O<sub>2</sub> production step shows a solvent isotope effect of 2.08 ± 0.02 (Figure S8) consistent with the above proposal. The O-O bond cleavage requires two electrons, derived either from the cluster or from the electrode (Figure S9) and a proton. These calculations indicate that the most energetically favored path involves extraction of one electron from the cluster (resulting in a Fe(2)Fe(2) state and another from the electrode).

In summary, the electrocatalytic O<sub>2</sub> reduction by synthetic models of the [Fe-Fe]-H<sub>2</sub>ase, one of these complexes, 1, is known to produce H<sub>2</sub> under anoxic acidic conditions over 12 h without appreciable decay, are investigated. The results show that these complexes, irrespective of the nature of the bridge, reduce O<sub>2</sub> in their Fe(0.5)Fe(0.5) state producing >50% H<sub>2</sub>O<sub>2</sub> above pH 5 leading to catalyst decay during HER under aerobic conditions. Although these clusters do not react with H<sub>2</sub>O<sub>2</sub> in their oxidized Fe(I)Fe(I) state (Figure S10), they degrade via Fe<sub>2</sub>S<sub>2</sub> oxidation (Scheme 1) by H<sub>2</sub>O<sub>2</sub> generation during the reaction of O<sub>2</sub> with the reduced cluster. The presence of an antioxidant, catalase, also increased the longevity of the catalyst in an oxic environment. The extent of H<sub>2</sub>O<sub>2</sub> production is significantly lowered at acidic pH's and attenuated by the nature of the bridging ligand; vis-a-vis a N-alkyl ADT bridge produces the lowest amount of H<sub>2</sub>O<sub>2</sub> under acidic conditions. The reduction in H<sub>2</sub>O<sub>2</sub> production during O<sub>2</sub> reduction at low pHs, facilitated by the hydrogen bonding from the protonated bridgehead nitrogen atom, observed in these synthetic complexes demonstrates that the bridgehead nitrogen atom may protect the natural active site as well, i.e., a protonated ADT ligand may be an intrinsic mechanism for protection of the H-cluster from oxidative damage by H<sub>2</sub>O<sub>2</sub> produced from competitive O<sub>2</sub> reduction.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Detailed materials and methods and full ref 21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Authors

icad@iacs.res.in

marcetta@chem.tamu.edu

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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