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ELECTROCATALYSTS FOR HER

Water-Soluble and Air-Stable [2Fe-2S]-Metallopolymers: A New Class of Electrocatalysts for H_2 Production via Water Splitting

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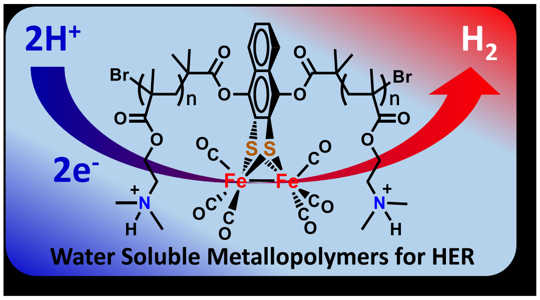
ABSTRACT *[2Fe-2S] organometallic complexes are effective electrocatalysts for the reduction of weak acids in acetonitrile to generate molecular hydrogen (H_2) (hydrogen evolution reaction, HER). Incorporation of such a [2Fe-2S] catalytic site into metallopolymers has been achieved using atom transfer radical polymerization (ATRP). These well-defined polymers have been structurally characterized by SEC, ^1H NMR and IR spectroscopy. These metallopolymers catalyze the electrochemical reduction of acetic acid in acetonitrile. In addition, [2Fe-2S] metallopolymers appended with amino groups were shown to be water-soluble and potent electrocatalysts for H_2 production at pH 7. In addition to the exceptional activity of these [2Fe-2S] metallopolymers in water, these catalysts maintain catalytic activity in air unlike comparable molecular catalysts.*

GRAPHICAL ABSTRACT



KEYWORDS Energy storage, metallopolymers, hydrogen evolution reaction, [FeFe]-hydrogenase

INTRODUCTION

The creation of clean and abundant energy from renewable resources is a major challenge in addressing the supply for global energy needs. The enormous energy requirements are growing rapidly due to the dramatic economic growth in China and India. Renewable energy sources generated from a variety of methods and feedstocks, such as solar photovoltaic systems, are very promising due to materials and device advances. In one hour, enough solar energy reaches the Earth to meet the world's energy requirements for a year. Furthermore, much

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progress has been made with increasing the efficiency and decreasing the cost of solar photovoltaic cells which convert solar light into electricity. However, the problem with solar photovoltaic cells is that solar light energy is unavailable at night or on rainy or cloudy days. In addition, electricity storage can be a solution to mitigate intermittent windows for solar electrical generation. Consequently, we and others have been interested in converting electrical energy into storable chemical energy such as in the H-H bond in molecular hydrogen. This stored energy can be recovered as desired directly by combustion or indirectly by a fuel cell. The ΔH_f for such an oxidation is -285 kJ/mol and the product is water. If the H_2 is made by splitting water then this process is recyclable and no CO_2 is produced. It might be noted that this process has some analogy to fossil fuels. That is, in photosynthesis solar light energy is converted into storable C-H and C-C chemical bond energies from CO_2 and water initially as carbohydrates. The C-C and C-H compounds are converted over geological time into fossil fuels which on burning release the stored energy and reform CO_2 and water. Notably, our proposed use of H_2 avoids CO_2 formation. It might be noted that the energy stored in H_2 by weight exceeds the energy stored in fossil fuels (although it is less by volume). Thus the challenge is to devise a catalyst that efficiently converts electrical energy into H_2 from protons available in water. While the use of noble metal electrocatalysts (i.e., platinum, Pt) have been demonstrated, platinum supplies are limited and there remains a serious need for less expensive, earth abundant catalysts for the generation of H_2. Designing such a catalyst de novo is challenging, however, Nature provides useful insight into designing such systems, notably in the form of certain anaerobic bacteria that utilize hydrogenase enzymes to produce and metabolize molecular hydrogen. A number of these enzymes have been isolated and structurally characterized via X-ray crystallography. These hydrogenase enzymes have been classified on the basis of their active sites for H_2 production, namely: (1) [Fe], (2) [FeFe] and (3) [NiFe].[1] It is noteworthy these active sites incorporate inexpensive and abundant metals. This contribution outlines our research inspired by these enzymes to develop readily available and inexpensive organometallic catalysts for HER.

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We have been most interested in the [FeFe]-hydrogenases because of the highly active nature of these systems for producing H_2, i.e. 6,000-10,000 molecules of H_2 are produced per second per active site[1] – incredible rates. We are not interested in discerning the biochemical mechanism by which the enzymes operate but rather use them to inspire simple organometallic compounds that are cheap, easily made, and efficient electrocatalysts. A view of the enzyme active site which is buried in the protein is shown in Fig. 1.[2]

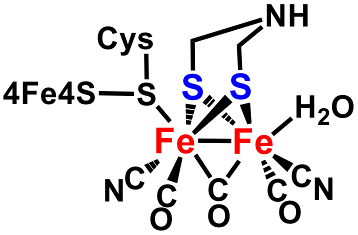
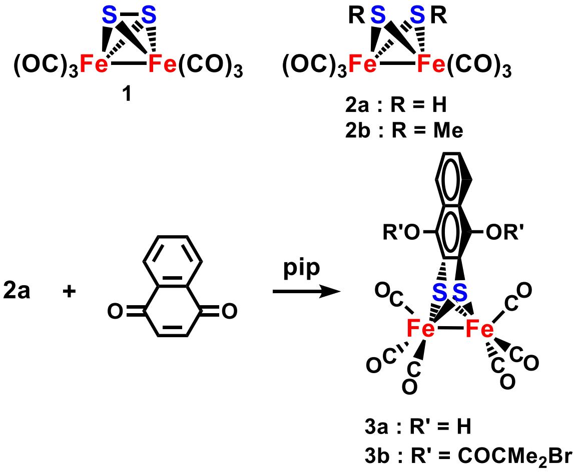


Figure 1. [FeFe]-Hydrogenase active site

Electrons are transported to the active site via [4Fe4S] clusters incorporated into the enzyme. A notable limitation of this enzyme is that it is very oxygen sensitive. This is not a concern in anaerobic environments but is an issue for water splitting in aerobic environments. The active site is inspirational because it is relatively simple and analogous to well-known organoiron complexes with CO and CN ligands. Another feature of the active site core is the amino group in the bridge which functions as a proton relay.[3] The synthesis of the basic core of the diiron disulfur moiety, that is, $Fe_2S_2(CO)_6$ (**1**) is readily achieved by reaction of $Fe(CO)_5$, elemental sulfur and base.[4] Seyferth and co-workers[5] reported the reduction of the S-S bond in this complex to give the corresponding dithiolate followed by protonation to dithiol **2a**, alkylation or conjugate addition. An example of conjugate addition[6] forming **3a** is shown below in Scheme 1:



Scheme 1. Synthesis of 2Fe-2S complexes

Nucleophilic addition of organolithium or Grignard reagents to disulfide **1** followed by alkylation was also reported.[7] All of these reactions are analogous to those of organic disulfides and, consequently, **1** was dubbed an "inorganic disulfide." In addition, dithiols

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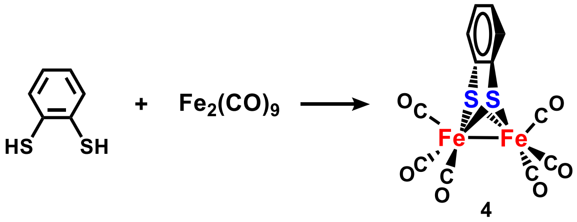
react with $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ to yield analogous complexes[8] as illustrated below in Scheme 2 in the synthesis of **4**.[9]



Scheme 2. Synthesis of **4**

This species can also be made by the reaction of the dithiolate obtained from **1** with 1,2-diiodobenzene.[10]

RESULTS AND DISCUSSION

Complex 4 as an Electrocatalyst for H_2 Production

Complex **4** was studied as a potential catalyst for the electrochemical reduction of weak acids in acetonitrile as solvent.[11] By itself **4** undergoes reversible $2e^-$ reduction in acetonitrile with a reduction peak potential of -1.32 V *vs.* Fc/Fc^+ as studied by cyclic voltammetry. It is surprising that a *reversible* $2e^-$ reduction is observed. This means that addition of the second electron occurs at a *less negative* potential than the first, i.e. there is potential inversion. One expects that addition of $1e^-$ to a neutral species to give an anion would occur at a less negative potential for electrostatic reasons. Addition of acetic acid (which is a weak acid in acetonitrile, $pK_a = 22.3$) to a solution of **4** in acetonitrile results in a new irreversible peak at *ca.* -2.1 V. Increasing the concentration of acetic acid results in increasing current and even bubbles form at the cathode. GC analysis of the gas produced shows that it is H_2. The calculated thermodynamic potential for reducing protons from acetic acid in acetonitrile as solvent is -1.48 V.[12] Thus the overpotential for the production of H_2 in this system is approximately 0.6 V. To improve the catalyst (e.g. lower the overpotential) it was deemed necessary to determine the mechanism for H_2 production.

DFT Calculated Mechanism for H_2 Generation

DFT functionals were validated and then used to calculate the mechanism.[11] The calculated mechanism is shown in Scheme 3. Note that addition of $1e^-$ to **4** results in dramatic molecular reorganization, i.e. lengthening of an Fe-S bond, rotation about an $Fe(CO)_3$ moiety and movement of a CO toward a bridging position to form anion $\mathbf{4}^-$. These changes result in an anion whose LUMO is lower in energy than that in **4** accounting for the potential inversion. The

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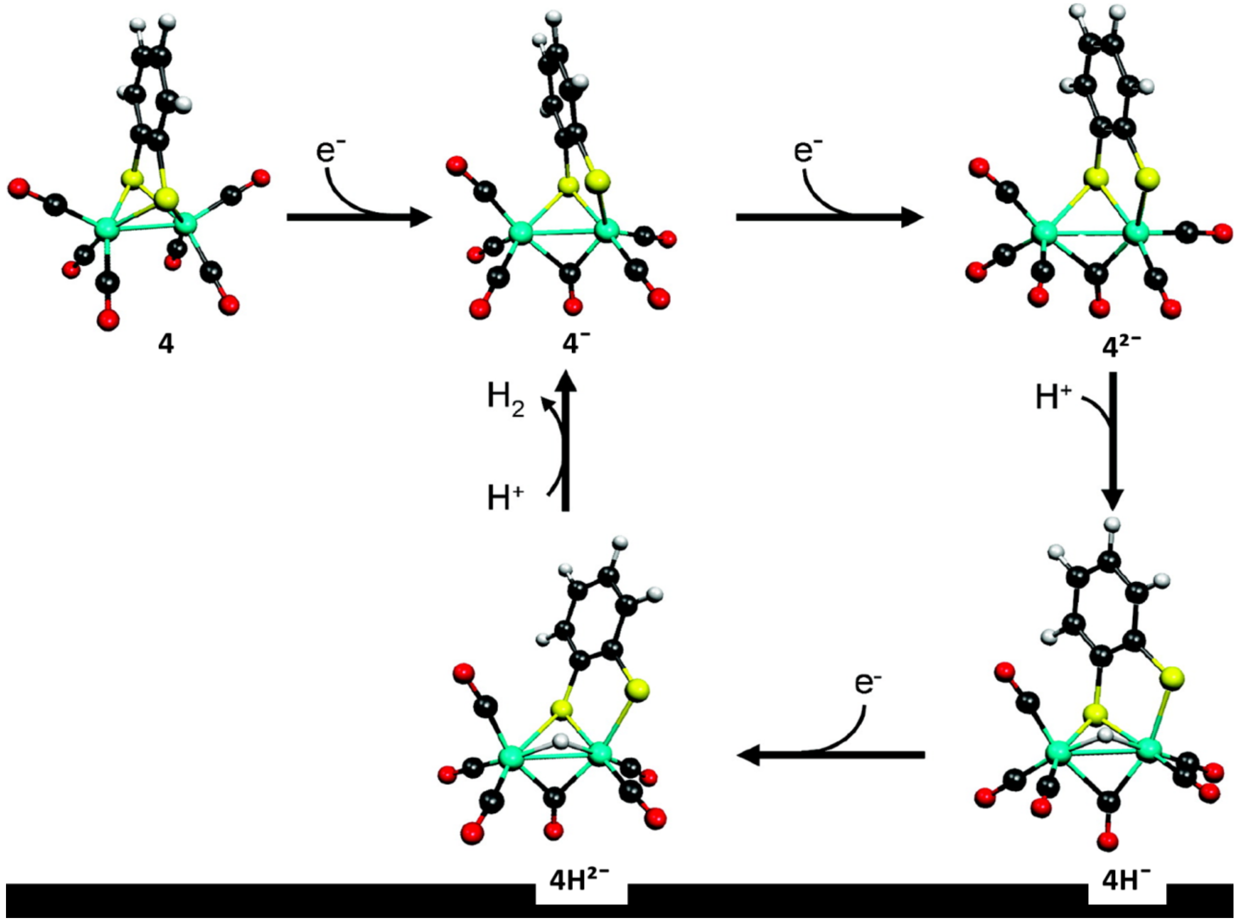
dianion **4**$^{2-}$, in which the Fe-S bond is broken and there is a bridging CO, is then protonated to give H-bridged hydride anion **4**H^{-}. Simulation of the CV data suggests that this protonation is the rate determining step.

The hydride thus formed is insufficiently hydridic to react with acetic acid to produce H_2.



Scheme 3. Calculated mechanism for HER with 4

Consequently, another electron must be added at rather negative potentials (accounting for the overpotential) to generate **4**H^{2-} which is sufficiently hydridic to react with acetic acid in an energetically downhill process to produce H_2 and regenerate anion **4**$^{-}$. Thus **4** is the pre-catalyst and the catalytic cycle begins with anion **4**$^{-}$. Dianion **4**$^{2-}$ has been isolated and its X-ray crystal structure is in accord with the calculated structure proposed in this mechanism.[13] This showed that small, simple [2Fe-2S] complexes inspired by the active site of [FeFe]-hydrogenase could

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function as electrocatalysts for H_2 production from weak acids in an organic solvent.[14]

Another related system which provided some insight into why the active site of [FeFe]-hydrogenase is buried in the protein matrix of the enzyme was obtained on studies with complexes **2b**. Cyclic voltammetric studies with **2b** in acetonitrile showed an irreversible $2e^-$ reduction at *ca.* -1.6 V *vs.* Fc^+/Fc and a number of oxidation peaks following reduction on reversing the direction of scan. It was initially surmised that the corresponding dianion decomposed into a mixture of oxidizable species. However, careful studies revealed that reoxidation of these species regenerated **2b** as shown by recovery of the current due to reduction of **2b**. This suggested that reduction of **2b** led to the corresponding dianion which homoassociates reversibly with neutral **2b**. Consequently, oxidation regenerates **2b**. Controlled potential coulometry results support the homoassociation of the dianion with neutral **2b** because the total integrated charge passed was $1e^-$ per molecule. Thus burying the active site of [FeFe]-hydrogenase into the protein matrix sterically shields it from homodimerization on reduction.

[2Fe-2S]-Metallopolymers

With these results and that of others in mind, we decided to design a metallopolymer containing a [2Fe-2S] catalytic site for electrochemical generation of H_2. The polymer would be engineered so as to be soluble in water as well as organic solvents, would site isolate the catalytic core, and would promote proton transfer. The polymerization method chosen to achieve these goals was atom transfer radical polymerization (ATRP).[16] To check the feasibility of this methodology, previously synthesized **3a**, was converted to dibromoester **3b**, which was characterized spectroscopically and by an X-ray crystallographic structure determination.[17] Under the initial conditions selected for this reaction dibromoester **3b** was treated with Cu(I) bromide, an amino ligand and methyl methacrylate (MMA). The idea is that the ligated Cu(I) homolytically cleaves the C-Br bond generating a Cu(II) species. The corresponding carbon radicals are formed in a controlled fashion which add to the methacrylate monomers and initiate the controlled radical polymerization. Note that the polymerization occurs on both sides of the [2Fe-2S] moiety.

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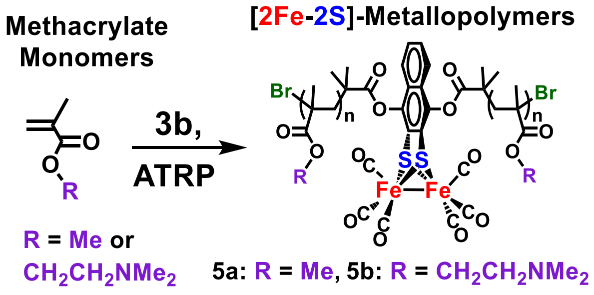

Scheme 4. [2Fe-2S] metallopolymers via ATRP method

The polymers **5a** and **5b** obtained in this way were analyzed by size exclusion chromatography (SEC) and the results shown in Figure 2. To determine whether [2Fe-2S] moiety survived the ATRP intact the IR spectrum of the polymer was measured in the metal carbonyl region (1900 – 2100 cm^{-1}). Three peaks were observed with the same stretching frequencies and intensities as those in **3a** and its derivative dibromoester **3b** demonstrating that the crucial [2Fe-2S] system survived the polymerization intact. Polymer **5a** is not water-soluble but is soluble in acetonitrile. In acetonitrile solution electrochemical reduction of this polymer in the presence of acetic acid generates H_2.

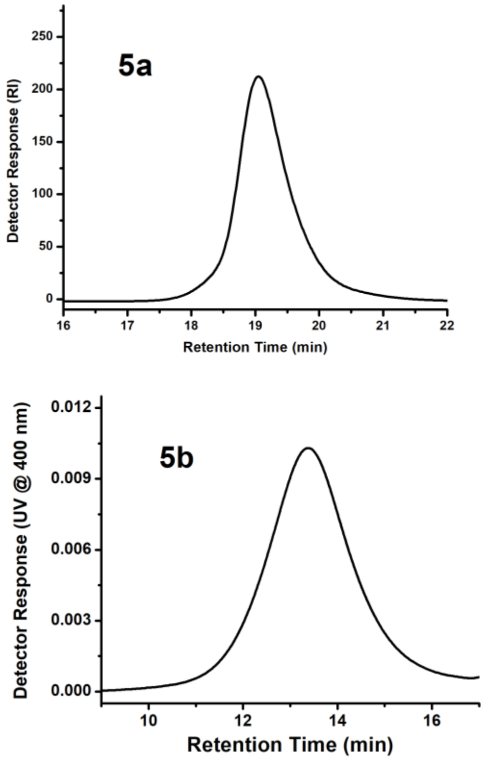

Figure 2. GPC data for **5a**, (top); GPC data for **5b**, (bottom)

To obtain a water-soluble polymer, ATRP was carried out as above but with 2-(N,N-dimethylamino)ethyl methacrylate in place of methyl methacrylate. Analysis of the new polymer **5b** obtained via ATRP by size exclusion chromatography showed M_n = 12,700 g/mol and M_w/M_n = 1.27. Again IR spectroscopic analysis showed three peaks in the metal carbonyl stretching frequency region analogous to those found in **5a**. This new polymer **5b** was soluble in acetonitrile and in the presence of acetic acid catalyzed its electrochemical reduction to H_2. In addition, this polymer **5b**, unlike **5a**, is soluble in water. Polymer **5b** (25 µM) dissolved in buffered pH 7 water rapidly and produced molecular hydrogen (H_2)

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electrochemically in essentially quantitative Faradaic yield. Comparison of the performance of this catalyst (75µM) in pH 7 tris buffer using a glassy carbon electrode with standard planar platinum is shown in the Tafel plots (log of current density *vs.* overpotential) in Fig. 3. Not only is the Tafel slope with the polymer comparable to that of platinum but the overpotential is less than 0.2 V greater than that with platinum. Furthermore, the turnover frequency of the metallopolymer (10 µM concentration) is estimated to be 250,000 s^{-1} – an order of magnitude faster than the enzyme.

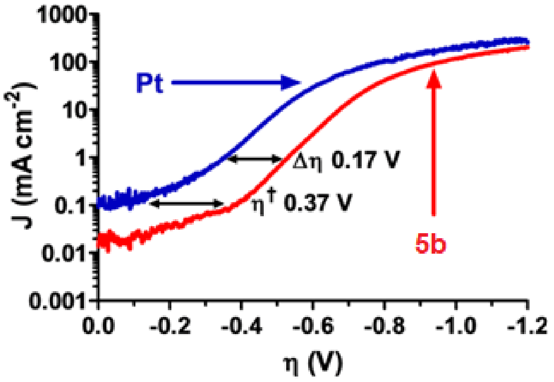

Figure 3. Tafel plot of Pt disk electrode and **5b** (75 µM) in aqueous pH 7 1.0 M tris buffer and glassy carbon disk electrode

In addition, in contrast to the enzyme, this catalyst is unaffected by air during catalysis. Indeed the turnover number determined by controlled potential electrolysis (CPE) is 4 (±2) × 10^4 molecules of H_2 per catalytic site under inert gas or air.

Homogeneous vs Heterogeneous Catalysis

To determine whether the catalysis by **5b** is best described as homogeneous given the water solubility of the polymeric catalyst or heterogeneous, in which the catalyst or a decomposition product is adsorbed on the electrode, the following study was done. After catalysis using a carbon electrode the surface was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). No adsorbed iron was detected on the electrode after a couple of hours of controlled potential electrolysis (CPE). This result suggested homogeneous catalysis. However, varying the catalyst concentration and monitoring the current concurred with a Langmuir adsorption isotherm as shown in Figure 4. This concurs with a monolayer cover of the electrode but this monolayer is in dynamic equilibrium with the solution and easily washed off. Complete monolayer formation occurs at 10µM catalyst but the current profile continues to rise rather than level off due to additional contributions beyond formation of the complete monolayer. Thus a novel mode

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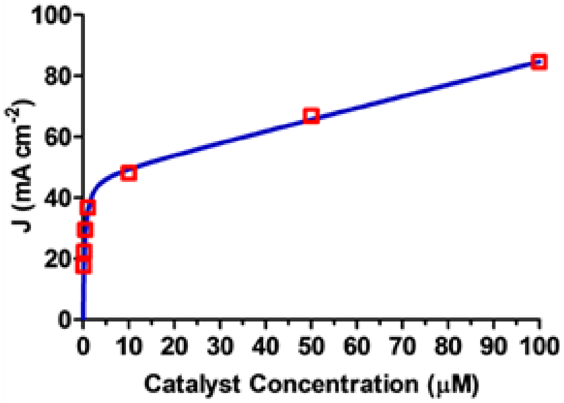

Figure 4. Peak current density from CV of **5b** fitted with a Langmuir type adsorption isotherm and additional contributions above 10μM catalyst

of catalysis appears to occur perhaps due to electrostatic interaction of the polycationic nature of the metallopolymer and negatively charged electrode.

CONCLUSIONS

Incorporation of an amino group in the [2Fe-2S] metallopolymer not only enables electrocatalysis of H_2 production in water at pH 7 but results in rates over an order of magnitude faster than [FeFe]-hydrogenase at low overpotentials in air or under inert gas. Also, ATRP, can be used to synthesize many other [2Fe-2S] metallopolymers from vinylic monomers with useful properties, and perhaps provide some insight into the role of secondary coordination spheres on the catalytic site.

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