

Macromolecular Engineering of the Outer Coordination Sphere of [2Fe-2S] Metallopolymers to Enhance Catalytic Activity for H₂ Production

William P. Brezinski,^a Metin Karayilan,^a Kayla E. Clary,^a Keelee C. McCleary-Petersen,^a Liye Fu,^b Krzysztof Matyjaszewski,^b Dennis H. Evans,^c Dennis L. Lichtenberger,^{*a} Richard S. Glass,^{*a} and Jeffrey Pyun^{*a,d}

^a Department of Chemistry and Biochemistry, The University of Arizona, 1306 E. University Blvd., Tucson, Arizona 85721, United States

^b Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh 151213, United States

^c Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907, United States

^d Department of Chemical and Biological Engineering, Program for Chemical Convergence for Energy & Environment & the Center for Intelligent Hybrids, Seoul National University, Seoul 151-744, Korea

KEYWORDS: *Metallopolymers, ATRP, hydrogen evolution, electrocatalysis*

ABSTRACT: Small molecule catalysts inspired by the active sites of [FeFe]-hydrogenase enzymes have long struggled to achieve fast rates of hydrogen evolution, long term stability, water solubility, and oxygen compatibility. We profoundly improved on these deficiencies by grafting polymers from a metalloinitiator containing a [2Fe-2S] moiety to form water soluble poly(2-dimethylamino)ethyl methacrylate) metallopolymers (**PDMAEMA-*g*-[2Fe-2S]**) using atom transfer radical polymerization (ATRP). This study illustrates the critical role of the polymer composition on enhancing hydrogen evolution and aerobic stability by comparing the catalytic activity of **PDMAEMA-*g*-[2Fe-2S]** with a non-ionic water soluble metallopolymer based on poly(oligo(ethylene glycol) methacrylate) prepared via ATRP (**POEGMA-*g*-[2Fe-2S]**) with the same [2Fe-2S] metalloinitiator. Additionally, the tunability of catalyst activity is demonstrated by the synthesis of metallocopolymers incorporating the 2-(dimethylamino)ethyl methacrylate (DMAEMA) and oligo(ethylene glycol) methacrylate (OEGMA) monomers. Electrochemical investigations into these metallo(co)polymers show that **PDMAEMA-*g*-[2Fe-2S]** retains complete aerobic stability with catalytic current densities in excess of 20 mA·cm⁻², while **POEGMA-*g*-[2Fe-2S]** fails to reach 1 mA·cm⁻² current density even with the application of high overpotentials ($\eta > 0.8$ V) and loses all activity in the presence of oxygen. Random copolymers of the two monomers polymerized with the same [2Fe-2S] initiator showed intermediate activity in terms of current density, overpotential, and aerobic stability.

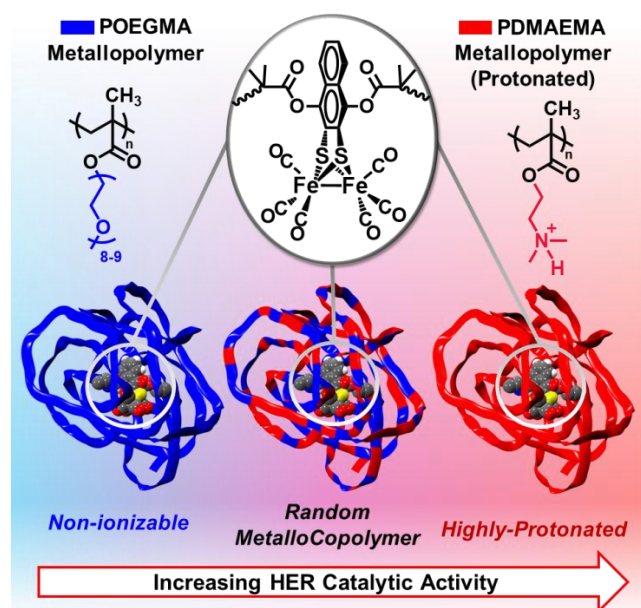
The increase in renewable generation of electricity, via wind and solar radiation, demands efficient methods for storing excess energy to mediate the intermittent nature of these generation methods. The electrochemical generation of molecular hydrogen (H₂) offers a chemical storage method which produces an energy dense fuel with carbon-free emissions.¹ Current aqueous electrolysis cells generally use platinum (Pt) as a catalyst for the hydrogen evolution reaction (HER). However, due to the high cost and low-Earth abundance of noble metals, there have been extensive efforts on the development of HER electrocatalyst systems composed of inexpensive, heterogeneous carbon electrodes in conjunction with high activity catalysts of various types.²⁻⁴ [FeFe]-hydrogenase (H₂ase) enzymes have long been known to efficiently catalyze the conversion of protons and electrons to H₂ in nature and to be highly active HER electrocatalysts.^{5,6} The preparation of synthetic

organometallic HER catalysts mimicking the [FeFe]-hydrogenase active site based on [2Fe-2S]-complexes has been widely explored as a route to developing improved HER electrocatalysts.⁷ Despite extensive work on small molecule HER electrocatalysts, there remain several important challenges to address namely: (1) *modular modification of the outer coordination sphere to tune activity in water*, (2) *improving catalyst stability and increasing turnover number*, (3) *catalyst site isolation against associative deactivation*, (4) *increasing turnover frequency*, (5) *decreasing overpotential* and (6) *improving air stability*.

The synthesis of functional ligands and [2Fe-2S] complexes has been explored to modify the outer coordination sphere of these homogeneous HER catalysts and impart water solubility. Structural analysis of the enzyme and seminal small molecule catalyst systems by

Dubois and Bullock has demonstrated the crucial role of flexible amines as proton relays in the outer coordination sphere for [FeFe]-hydrogenase enzymes and the fast small molecule HER catalysts they have inspired.⁸⁻¹⁴ Polymer supported [2Fe-2S] systems have been particularly effective in photocatalytic systems where Fréchet-type dendrimers, poly(acrylic acid) and polyethylenimine (PEI)

Scheme 1. Representation of PDMAEMA-*g*-[2Fe-2S] and P(OEGMA-*g*-[2Fe-2S] Metallopolymers and P(DMAEMA-*r*-OEGMA)-*g*-[2Fe-2S] Metalloco-polymer



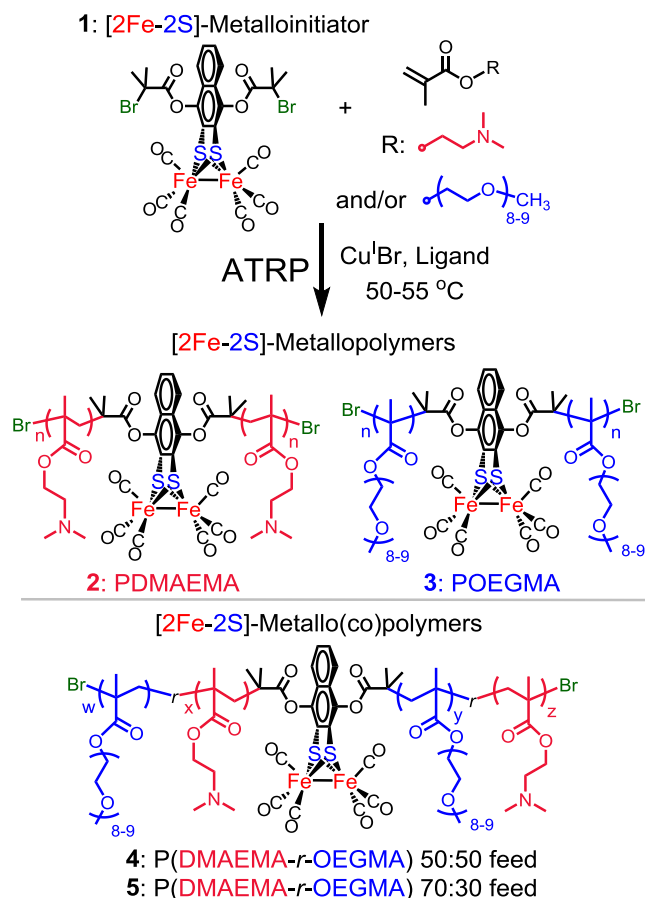
grafted [2Fe-2S] systems have demonstrated improved turnover numbers (TON, on the order of 10^4)¹⁵⁻¹⁸ and a significant improvement over an analogous water soluble small molecule which was observed to exhibit much lower TON (5×10^2).¹⁹ Metallopolymers which were synthesized by incorporating [2Fe-2S]-complexes along the main chain,²⁰⁻²² side chain²³⁻²⁵ or as single chain nanoparticles as demonstrated by Berda *et al.*²⁶ in the polymer support have shown better site isolation and improved stability.

The effect of macromolecular scaffolds on electrocatalytic systems is less well studied, but membrane electrodes fabricated with [2Fe-2S]-metallopolymers have demonstrated reasonable catalytic currents in aqueous media.^{21,27} Notably, a pendant carboxylate group was demonstrated to improve the current density of membrane electrodes in water with added acetic acid²¹ but so far all functionalized electrode systems suffered from decomposition of the [2Fe-2S] system upon extended electrocatalysis. Schubert and Weigand *et al.* also elegantly demonstrated the use of the reversible addition-fragmentation chain transfer (RAFT) polymerization to incorporate [2Fe-2S] units as side chains into metallopolymers.²⁸ While all of these systems point to the benefits of conjugation of [2Fe-2S] HER catalysts into metallopolymer systems, there remain important challenges to develop versatile and facile synthetic methods to create HER metallopolymers with

improved activity, aerobic stability and extended catalytic lifetime in neutral aqueous media.

We recently demonstrated using atom transfer radical polymerization (ATRP)^{29,30} the synthesis of well-defined, water soluble poly(2-dimethylamino)ethyl methacrylate functional [2Fe-2S] metallopolymers (PDMAEMA-*g*-[2Fe-2S]) with profoundly improved HER electrocatalytic activity in neutral water.³¹ This solution-phase metallopolymer electrocatalyst was found to exhibit greatly enhanced aerobic stability in neutral water and extremely fast rates for HER at low overpotentials (an order of magnitude faster than [FeFe]-hydrogenases and

Scheme 2. Synthesis of [2Fe-2S]-grafted metal-lo(co)polymers via ATRP of methacrylic monomers initiated with [2Fe-2S]-metalloinitiator 1



current densities comparable to platinum) while operating at 1-2 ppm catalyst loadings. This remarkable improvement of HER catalytic activity in water was attributed to both enhanced chemical stability of the [2Fe-2S] due to site isolation in the metallopolymer and the presence of protonated ammonium groups (PDMAEMA ~ 90% protonated in pH 7.0 ± 0.1 aqueous and buffered medium). While this initial demonstration pointed to the benefits of this metallopolymer approach to improve catalytic performance, there remain numerous questions on whether the presence of amine groups is critical to improved H_2 generation. Hence, the preparation of new

functional metallopolymer affords the possibility of further improving HER electrocatalytic activity. In particular, the versatility of ATRP allows for a wide range of functional monomers to be incorporated into metallopolymer.

Herein, we report on the first comparative HER catalytic study on the effects of homo- and copolymer compositions in well-defined [2Fe-2S] metallopolymer derived from ATRP (Scheme 1). In this study, a new, non-ionic, water soluble metallopolymer based on poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) was synthesized via ATRP from a [2Fe-2S] metalloinitiator and directly compared with the activity of charged PDMAEMA-*g*-[2Fe-2S] metallopolymer to interrogate if ammonium, proton donating side chain groups on the metallopolymer are essential for enhanced HER activity. Furthermore, we prepare for the first time random metallocopolymers of poly(DMAEMA-*r*-OEGMA) to demonstrate tuning of the outer coordination sphere as means to modulate HER catalytic activity. With access to a range of these model metallopolymer with systematic variation of composition in the outer coordination sphere, we are able to create structure-activity correlations for these systems for HER overpotential, turnover frequency (rate) and aerobic stability.

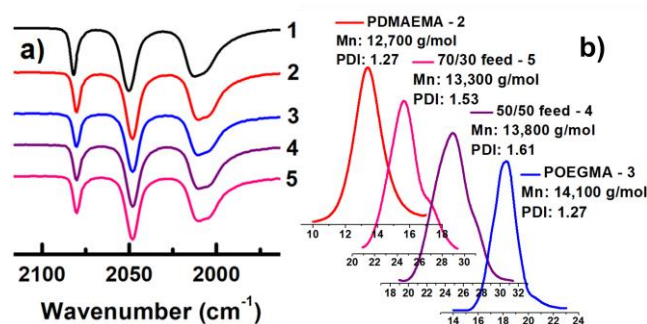


Figure 1. a) IR spectra of the Fe-CO region for metalloinitiator 1, homopolymers 2 and 3 and random copolymers 4 and 5. b) SEC traces for 2-5 (x-axis is retention time in minutes, see SI for details).

The general synthetic approach to prepare these HER electrocatalysts started with the synthesis of a difunctional [2Fe-2S] metalloinitiator complex bearing two α -haloesters³¹ for polymer conjugation via ATRP of various commercially available methacrylate monomers. The key advantage of this approach is the ability to ensure covalent tethering of polymers to a single [2Fe-2S] site per metallopolymer in a single step while also enabling facile modification of metallopolymer composition using controlled radical polymerization methods. For the synthesis of metallo(co)polymers for this study, difunctional metalloinitiator 1 was prepared as previously described for the ATRP of DMAEMA to prepare PDMAEMA-*g*-[2Fe-2S] metallopolymer 2 (Scheme 2).³¹ The ATRP of an OEGMA macromonomer ($M_n = 475$ g/mol) from metalloinitiator 1 was performed to prepare

the desired, non-ionic POEGMA-*g*-[2Fe-2S] metallopolymer 3 (Scheme 2). Similar ATRP conditions were employed to prepare poly(DMAEMA-*r*-OEGMA)-*g*-[2Fe-2S] metallocopolymers (4 and 5) of varying copolymer composition (Scheme 2).

Metallo(co)polymers 2-5 (Scheme 2) were prepared possessing molar masses in the range of 10,000-15,000 g/mol, where structural characterization of the targeted materials was confirmed using a combination of SEC, NMR and IR spectroscopies (see Supporting Information). The covalent incorporation of the [2Fe-2S] system was confirmed by SEC of PDMAEMA-*g*-[2Fe-2S] 2 and POEGMA-*g*-[2Fe-2S] 3 with UV-Vis detection at a wavelength characteristic of the [2Fe-2S] system. Both metallopolymer 2 and 3 were found to have M_n of approximately 10-15 kg/mol (Figure 1b). Further, IR spectroscopy confirmed structural retention of Fe-CO stretching frequencies characteristic of the [2Fe-2S] catalytic core (Figure 1a). Similar findings were confirmed in the synthesis of metallocopolymers 4 and 5 (see Supporting Information). Copolymer compositions of metallocopolymers were determined via ¹H NMR spectroscopy of these materials; the DMAEMA/OEGMA ratios were found to be 56-mol%/44-mol% for 4 (50/50 feed) and 72-mol%/28-mol% for 5 (70/30 feed), respectively (see Supporting Information for synthetic details).

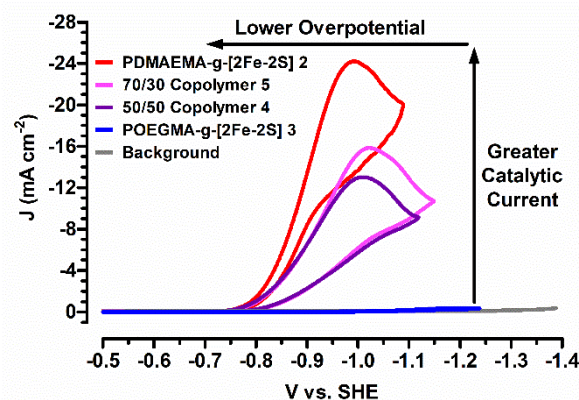


Figure 2. Comparison of cyclic voltammograms of 2-5 (100 μ M based on [2Fe-2S] concentration) in an aqueous solution (pH 7.0 \pm 0.1) buffered with sodium phosphate (0.75 M). Scans were performed at a sweep rate of 50 mV/s using a gold amalgam working electrode.

Metallo(co)polymers 2-5 were investigated electrochemically to observe the effect of polymer composition on HER catalysis. Electrochemical experiments were conducted in pH 7.0 \pm 0.1 water using 0.75 M sodium phosphate as the buffering agent with polymer loadings of 100 μ M based on [2Fe-2S] concentration by IR. Although sodium phosphate is not the optimal buffering agent for metallopolymer 2 due to the lower concentration of proton substrate species relative to the tris(hydroxymethyl)aminomethane (TRIS) buffer used previously,³¹ it was chosen for this study to eliminate the contribution of protonated amines from the

buffering medium. Additionally, a gold amalgam working electrode was used to mitigate complex adsorption effects seen on glassy carbon electrode surfaces and to reduce the current of direct reduction compared to a glassy carbon electrode.³¹

The initial comparative investigation between the electrocatalytic behaviors of metallo(co)polymers 2-5 was done using cyclic voltammetry (CV). The CV data in Figure 2 show that **PDMAEMA-*g*-[2Fe-2S] 2** homopolymer and the two random metallocopolymers 4 and 5 exhibit electrocatalytic hydrogen evolution in neutral water. **PDMAEMA-*g*-[2Fe-2S] 2** achieves the highest current density and lowest overpotential, while **POEGMA-*g*-[2Fe-2S] 3** only exhibits weak electrocatalysis that is negligible on the scale of Figure 2. The random copolymers 4 and 5 have intermediate current densities directly as a consequence of reduced DMAEMA content in the metallocopolymers. Further, we would like to emphasize that the substantial difference in activity seen in the voltammograms between 2 and 3 occurs under these conditions with no structural change to the [2Fe-2S] catalytic core.

In Figure 3, we report the performance of metallo(co)polymer systems 2-5 versus a Pt disk electrode as a standard for HER activity using Tafel analysis. Compared to CV analysis, Tafel analysis offers a more direct measure of catalytic current density as a function of overpotential requirement in practical electrolysis conditions. As shown in Figure 3, the difference of overpotentials between **PDMAEMA-*g*-[2Fe-2S] 2** and Pt surface is approximately 360 mV at a current density of 1 mA/cm². Accentuated by plotting the current density on a log scale, the catalytic current onset of **PDMAEMA-*g*-[2Fe-2S] 2**, metallocopolymers 4 (50/50 feed), and 5 (70/30 feed), occur at a similar overpotential requirement of approximately 360 mV.

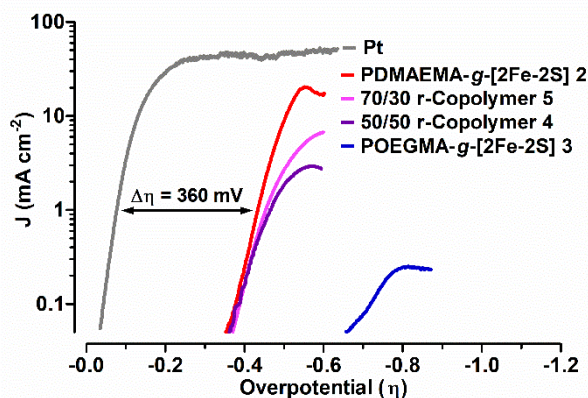


Figure 3. Tafel comparison between 2-5 and a Pt disk electrode from linear sweep voltammetry of a rapidly stirred solution. Solution and catalyst conditions are the same as Figure 2. The $\Delta\eta$ is the difference in overpotential between Pt and 2.

Additionally, at current densities below 0.3 mA/cm², 2, 4 and 5 show comparable Tafel slopes of 55 mV/dec, 69 mV/dec, and 58 mV/dec, respectively. As the current

density increases above 0.3 mA/cm², the Tafel slope of the random copolymers decreases with the copolymer 4 diminishing more rapidly than the copolymer 5. The **POEGMA-*g*-[2Fe-2S] 3** has a significant overpotential of 722 mV at 0.1 mA/cm² and a Tafel slope of 155 mV/dec, which dramatically manifested the reduced activity of this non-ionic metallopolymer catalyst.

The hydrogenase enzyme and small molecule mimics of the [2Fe-2S] active site suffer from lack of oxygen stability; however, in our previous study, we demonstrated that **PDMAEMA-*g*-[2Fe-2S] 2** is oxygen stable under catalytic operating conditions.³¹ To determine if the polymer composition directly affected oxygen stability, linear sweep voltammetry (LSV) experiments were performed to examine the catalytic current response in the absence and presence of oxygen for metallo(co)polymer systems 2-5 (Figure 4). The LSV data mirror the activity trend of the cyclic voltammograms. **POEGMA-*g*-[2Fe-2S] 3** in an anaerobic environment shows the weakest response and is barely catalytic in the potential window. Under aerobic conditions, **POEGMA-*g*-[2Fe-2S] 3** does not achieve a catalytic current that is above the increased background current of the aerated solution (see inset in Figure 4). In contrast, the copolymer 4 retained approximately 60% of its peak catalytic current under aerobic conditions and the copolymer 5 improves to 82% retention of catalytic current under aerobic conditions. **PDMAEMA-*g*-[2Fe-2S] 2** was again found to retain essentially all of its catalytic activity under aerobic conditions, consistent with our previous report.³¹

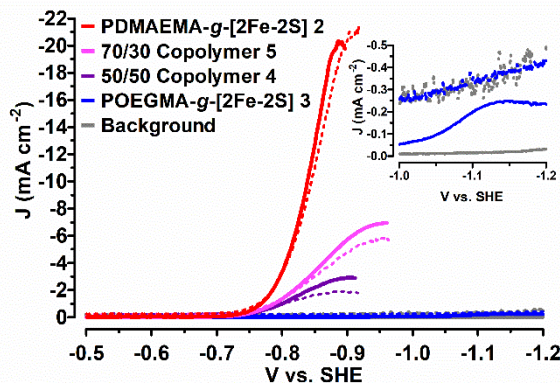


Figure 4. Linear sweep voltammetry of the four metallo(co)polymer systems 2-5 under aerobic (dashed lines) and anaerobic (solid lines) conditions in pH 7.0 \pm 0.1 sodium phosphate buffer (0.75 M) with rapid stirring and a sweep rate of 5 mV/s. The inset shows a zoomed-in region to show the current response of **POEGMA-*g*-[2Fe-2S] 3**.

The electrochemical results of metallo(co)polymers 2-5 show that increasing the DMAEMA/OEGMA molar ratios in the metallocopolymers has three beneficial effects on catalysis; (1) achieving higher current densities, which is correlated to faster rates of hydrogen generation, (2) lower overpotentials, increasing the efficiency of the

catalytic reaction by reducing the energy required to run the reaction and (3) providing aerobic stability to a class of catalysts which are typically irreversibly deactivated by the presence of even small amounts of oxygen. The most significant chemical difference between the polymers is the presence of the protonated amines in the DMAEMA monomers, but the different 3-dimensional structures, charges, and dynamics of the polymers may also play a role. Further studies are underway on the role of the protonated amines. In any event, this work demonstrates an exciting new application for atom transfer radical polymerization techniques in which the polymer functions not only as a support to modulate the physical properties of the catalyst (i.e., solubility, processability, etc.), but also provides a modular synthetic handle which allows for tuning of catalyst activity by simply varying the choice of monomer, including many commercially available options. We have shown that by varying the identity and modulating the polymer composition, we can drastically improve the activity and stability of a small molecule organometallic catalyst.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>. Experimental details, synthesis and characterization of metaloinitiator and metallopolymers, electrochemical analysis

AUTHOR INFORMATION

Corresponding Authors

* E-mail: jpyun@email.arizona.edu

* E-mail: rglass@email.arizona.edu

* E-mail: dlichten@email.arizona.edu

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

DLL, RSG, and JP gratefully acknowledge support of this work by NSF (CHE-1664745). KM acknowledges support of this work by NSF (DMR 1501324).

ABBREVIATIONS

ATRP, atom transfer radical polymerization; HER, hydrogen evolution reaction; PDMAEMA, poly(2-dimethylamino)ethyl methacrylate; POEGMA, poly(oligo(ethyleneglycol) methacrylate); TON, turnover number; TOF, turnover frequency

SYMBOLS

η , overpotential

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