Hydrogen Production from Water Catalyzed by an Air-stable Di-iron Complex with a Bio-relevant $Fe_2(\mu\text{-}S)_2$ Core

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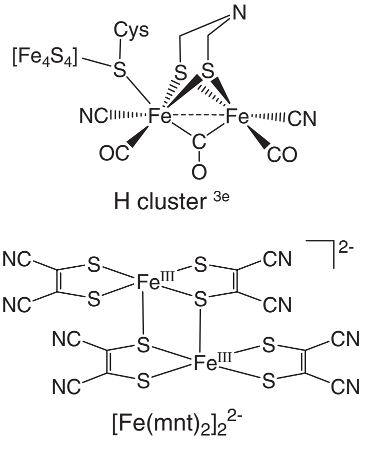
An air-stable dinuclear iron–dithiolene complex with an $Fe_2(\mu\text{-}S)_2$ core, $[Fe^{III}(mnt)_2]_2^{2-}$ (mnt = maleonitriledithiolate), has been found to serve as an electrode catalyst toward the reduction of water into molecular hydrogen with an overpotential of 560 mV. The acid form of a buffer reagent, such as CH_3CO_2H, has been found to serve as a major proton mediator during the electrocatalytic hydrogen evolution.

In order to realize a hydrogen-based economy, extensive studies have been carried out to develop H_2-evolving (HE) catalysts in various fields of chemistry.[1] Although platinum is highly active in lowering the activation barrier for HE,[2] alternative catalysts with much lower costs must be pursued to ensure their widespread use in society. On the other hand, iron is known as one of the most abundant and cheapest metals on the earth's crust and exhibits much lower HE activity.[2] Nevertheless, an $Fe_2(\mu\text{-}S)_2$ cluster (H-cluster, shown in Scheme 1) in Fe-only hydrogenase (FeHase) exhibits extremely high HE activity.[3] A large variety of structural and functional models of FeHase have been developed, and their HE activities have been evaluated.[4] Up to now, only two water-soluble models of FeHase have been reported to show HE activity in aqueous media, even though their HE activities are quite low.[5] On the other hand, an iron–dithiolene complex, $[Fe^{II}(1,2\text{-benzenedithiolato-}S,S)_2]^{2-}$, considered as a biorelevant model, was previously reported to exhibit HE activity in tetrahydrofuran in the presence of HCl.[6] In order to develop more highly effective models of FeHase, our recent interests concentrate on such iron–dithiolene complexes which are stable in both air and water. In this study, the HE activity of $[Fe^{III}(mnt)_2]_2^{2-}$ (mnt = maleonitriledithiolate) in aqueous media (pH 4–7) has been investigated by means of electrochemical methods, in which a water-soluble salt of the complex, $[Fe^{II}(15\text{-crown-}5)(OH_2)_2][Fe^{III}(mnt)_2]_2 \cdot 2(15\text{-crown-}5)$ (**1**),[7] together with a water-insoluble salt of the complex, $[(n\text{-}Bu)_4N]_2[Fe^{III}(mnt)_2]_2$ (**2**),[8] has been employed.



Scheme 1.

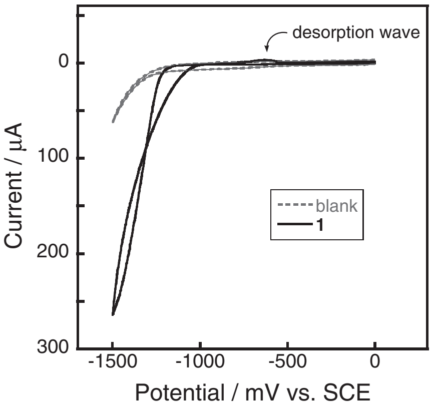


Figure 1. The cyclic voltammogram of **1** (0.025 mM) in an aqueous acetate buffer solution (pH 5; 0.03 M CH_3CO_2H, 0.07 M CH_3CO_2Na, and 0.1 M $NaClO_4$) at 20 °C under Ar atmosphere, recorded at a sweep rate of 50 mV/s. The working, counter, and reference electrodes were a glassy carbon disk, a Pt wire, and a saturated calomel electrode, respectively.

The cyclic voltammogram of **1** in an aqueous acetate buffer solution (pH 5) is shown in Figure 1. In the presence of **1**, a large catalytic current corresponding to HE is observed at −1100 mV (all potentials reported in this paper will be given in volts vs. SCE). The amount of H_2 evolved during controlled potential electrolysis at −1200 mV was analyzed by an automatic H_2-analyzing system developed in our group.[9] The current efficiency and the turnover number (TON) were respectively determined as 98% and 158 times over 5 h (Figure 2). Note that this TON is an apparent estimate, supposing that all the catalyst molecules involved in the bulk have an equal contribution to the HE process.

Importantly, repeated voltammetric sweeps in the potential range from −800 to −1300 mV resulted in a gradual increase in the cathodic current corresponding to the electrocatalytic HE process (Figure S1).[10] This clearly indicates that the active species for the catalysis is gradually deposited over the surface of the glassy carbon (GC) electrode. This was further ascertained by the fact that a quite similar catalytic current was observed for thus treated electrode even after replacing the electrolysis solution with a solution free of catalyst. The oxidation state of the active species is now assumed as an Fe^{I}_2 species (Figure S2).[10] Probably, the anodic wave observed at −600 mV in Figure 1 corresponds to a desorption wave of the active species adsorbed over the surface of the GC electrode.

In order to ascertain the validity of the above assumption, a GC electrode modified with $[(n\text{-}Bu)_4N]_2[Fe^{III}(mnt)_2]_2$ (**2**),

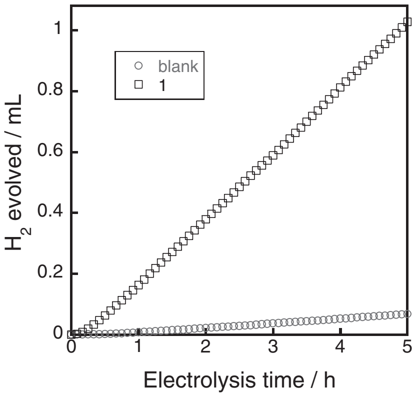


Figure 2. Hydrogen evolution profiles observed during the controlled potential electrolysis at −1200 mV vs. SCE of a solution (10 mL) containing 0.03 M CH_3CO_2H and 0.07 M CH_3CO_2Na (pH 5), at room temperature, under Ar atmosphere, in the absence (○) and the presence (□) of catalyst **1** (0.025 mM), where the surface area of the electrode was 0.07 cm^2.

which was reported to possess a dinuclear structure illustrated in Scheme 1,[8] was prepared by dropping an acetonitrile solution of **2** onto the electrode surface followed by evaporation of the solvent. The powder X-ray diffraction (XRD) pattern of the **2**-modified electrode prepared in this way was confirmed to be identical to that of a microcrystalline sample of **2** (Figure S3).[10] The cathodic sweep using the **2**-modified electrode in an aqueous acetate buffer solution (pH 5) results in a large catalytic current based on the HE process (Figure S4),[10] which is quite similar to that observed for a solution of **1** under the same experimental conditions (Figure 1). Moreover, the quantitative analysis of H_2 evolved during the controlled potential electrolysis at −1200 mV revealed that the current efficiency for the electrocatalytic HE process is 99% and the TON after 5 h is determined as 3900 (Figure S5).[10] This value is much higher than that of **1**, clearly due to the fact that all the catalyst molecules are adsorbed over the electrode surface in the experiment using **2**. In addition, the IR spectra of the **2**-modified ITO electrode measured before and after the controlled potential electrolysis reveal that **2** is fundamentally stable during the electrocatalytic HE process (Figure S6).[10]

The electrochemical HE reaction catalyzed by **2** was also investigated by varying the pH and also by changing both the concentration and the kind of buffer reagent. As a result, the catalytic current was found to increase as the pH decreases (Figure S7).[10] On the other hand, the catalytic current resulting from HE drastically decreases as the total acetate buffer concentration decreases in spite of the constant pH maintained at 5.0 (Figure S8).[10] Since the UV–vis absorption spectrum of **1** in aqueous media is nearly identical to that in a 0.1 M acetate buffer solution at pH 5.0 (Figure S9),[10] it is not very likely that the ligand substitution reaction of **1** by acetate takes place under the present experimental conditions. Indeed, complexation between **1** and acetate does not take place in water/methanol (1:1, v/v), which was confirmed by ESI-TOF mass spectrometry (Figure S10).[10] In addition to these results, quite similar dependences of the catalytic current on the concentration of a buffer reagent were observed even when other buffer reagents, such as phosphate, methoxyacetate, and 2-bromoacetate, were employed instead of acetate (Figure S11).[10] Judging from these results, the acid form of each buffer reagent, such as CH_3CO_2H, rather than H_2O has a major contribution to the catalytic reduction of protons into molecular hydrogen. Such examples have been reported in the literature.[11]

In summary, a di-iron complex with a bio-relevant $Fe_2(\mu\text{-}S)_2$ core, $[Fe^{III}(mnt)_2]_2^{2-}$, has been found to exhibit catalytic activity toward electrochemical HE in aqueous media, in which acid forms of buffer reagents behave as proton mediators. Although the overpotential for the HE process in the present system (560 mV) is still large in comparison with that of platinum electrodes (100 mV),[12] this is a very important example demonstrating that such an air-stable $Fe_2(\mu\text{-}S)_2$ core can serve as a catalyst toward HE. It is also noteworthy that the smallest overpotential of HE reported so far for structural mimics of FeHase has been 1000 mV in aqueous media,[5] which is by far larger than the value of 560 mV observed in this study. Thus, the development of highly active HE catalysts with the use of inexpensive transition metals is still a great challenge for the fabrication of solar energy conversion systems based on water-splitting processes. Efforts to better understand the mechanism of H_2 formation and to develop more highly effective iron-based molecular catalysts are now in progress in our laboratory.

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