

Directing the Reactivity of $[\text{HFe}_4\text{N}(\text{CO})_{12}]^-$ toward H^+ or CO_2 Reduction by Understanding the Electrocatalytic Mechanism

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Supporting Information

ABSTRACT: Selective reactivity of an electrocatalytically generated catalyst–hydride intermediate toward the hydrogen evolution reaction (HER) or reduction of CO_2 is key for a CO_2 reduction electrocatalyst. Under appropriate conditions, $\text{Et}_4\text{N}[\text{Fe}_4\text{N}(\text{CO})_{12}]$ ($\text{Et}_4\text{N-1}$) is a catalyst for the HER or for CO_2 conversion at -1.25 V vs SCE using a glassy carbon electrode.

Storage of energy from solar flux for use during periods of insufficient available radiation could be achieved with high energy density by electrocatalytic conversion of CO_2 into a fuel such as formic acid or MeOH. Although high-efficiency photovoltaic (PV) cells are available, current methods for storing electrons generated by PV warrant improvement.¹ Several challenges for effectively facilitating electrocatalytic small-molecule conversions remain. In particular, both the reduction of CO_2 to reduced products such as formic acid or MeOH and the reduction of protons to H_2 can proceed via catalyst–hydride intermediates.² Thus, the two reactions can compete, and the mechanistically simpler hydrogen evolution reaction (HER) must be controlled to obtain an effective catalyst for reduction of CO_2 . Selective formate production has been accomplished in rare cases.³ However, the majority of electrocatalysts that effect CO_2 reduction promote CO formation as the major product.⁴

Metal carbonyl clusters (MCCs) containing interstitial anionic atoms have redox properties that make them amenable to study for electrocatalytic CO_2 reduction by multielectron pathways.⁵ Furthermore, monometallic metal carbonyl–hydride complexes have been shown to interact with CO_2 .⁶ Herein we demonstrate that $\text{Et}_4\text{N}[\text{Fe}_4\text{N}(\text{CO})_{12}]$ ($\text{Et}_4\text{N-1}$) operates as a reduction catalyst at -1.23 V vs SCE, a potential which permits the use of a glassy carbon working electrode. We present a mechanism for the rate of formation and subsequent reaction of $[\text{HFe}_4\text{N}(\text{CO})_{12}]^-$ (H-1^-) and use this understanding to optimize the reaction conditions to favor reduction of CO_2 over reduction of protons to hydrogen.³

The synthesis of the butterfly-shaped cluster **1** [Figure 1a and Table S1 and Figure S1 in the Supporting Information (SI)] was achieved following a procedure modified from Muetterties and co-workers (see the SI for details).⁷ To confirm our hypothesis that $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ (**1**⁻) can catalyze the reduction of protons to hydrogen, electrochemical measurements were performed on a 0.34 mM solution of $\text{Et}_4\text{N-1}$ in MeCN containing 0.1 M Bu_4NClO_4 . Cyclic voltammograms (CVs) revealed a reversible $\text{1}^{-/2-}$ couple at -1.23 V vs SCE and a $\text{1}^{2-/3-}$ couple at -1.6 V vs SCE, each of which represents a one-electron process

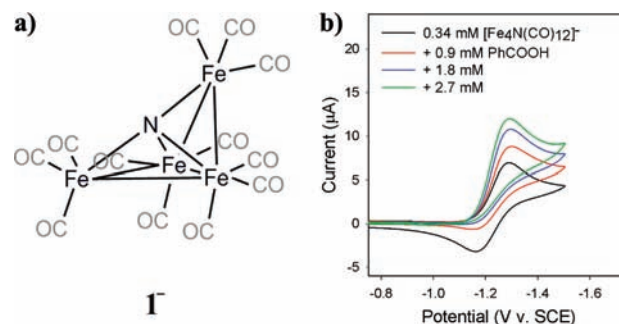


Figure 1. (a) Line drawing of the monoanion **1**⁻. (b) CVs of 0.34 mM solutions of $\text{Et}_4\text{N-1}$ in CH_3CN containing 0.1 M Bu_4NClO_4 and added benzoic acid (0.91, 1.8, and 2.7 mM). Glassy carbon working electrode, scan rate = 100 mV s^{-1} .

(Figures S2 and S3).⁸ In the presence of organic acids such as benzoic acid, electrocatalytic hydrogen evolution was observed at a potential corresponding to the $\text{1}^{-/2-}$ couple (Figure 1b). Controlled-potential electrolysis (CPE) experiments confirmed that hydrogen is evolved in 80% yield ($\eta = 280$ mV),⁹ as determined by GC analysis of the headspace gas (see the SI). Catalyst $\text{Et}_4\text{N-1}$ is stable in MeCN solution for at least 72 h in the presence of excess benzoic acid and under ambient air (Figure S4).¹⁰

The reaction of **1**⁻ with strong acids is known to produce H-1 ,⁷ but the formation of H-1 or $(\text{H-1})^-$ is not understood under electrochemical conditions. To provide a better understanding of the formation and stability of a potential $(\text{H-1})^-$ intermediate and the HER, the kinetics of H_2 evolution were investigated with organic acids with a range of pK_a values (Table 1). At a very low $[\text{H}^+]/[\text{1}^-]$ ratio, the rate of the reaction [which is proportional to $(i_c)^2$]¹⁴ is second-order with respect to $[\text{H}^+]$ and first-order with respect to $[\text{1}^-]$ (Figure S6). When $[\text{H}^+]/[\text{1}^-]$ is greater than $\sim 8:1$, catalysis occurs independently of acid diffusion (Figure S7), and the rate of the reaction is pseudo-zeroth-order in $[\text{H}^+]$ and first-order in $[\text{1}^-]$ and does not increase as more acid is added. At intermediate values of $[\text{H}^+]/[\text{1}^-]$, the reaction appears to be first-order in $[\text{H}^+]$ and remains first-order in $[\text{1}^-]$ (Figures S8 and S9). In this intermediate region, for each acid (Table 1, Figure 2a, and Figure S10), the scan-rate independence of i_c between 2 and 20 mV s^{-1} indicates that the reaction can be modeled according to the equation $i_c = nFSC_p^\circ (DkC_s^\circ)^{1/2}$,¹⁵ from which the rate constants k for the formation of hydrogen were obtained (Table 1). As expected, the rate of reaction decreases as the overpotential for the reaction falls from 990 to

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Table 1. Rate Constants for H₂ Evolution with Different Acids

acid	$E_{1/2}(\text{H}^+/\text{H}_2)^{a,b}$	η (mV) ^c	k (M ⁻¹ s ⁻¹) ^d
TsOH·H ₂ O	-0.24	990	29.5
chloroacetic acid	-0.65	580	22.4
benzoic acid	-0.95	280	17.4
butanoic acid	-1.04	190	10.1

^aIn units of V vs SCE and corrected for homoconjugation effects as necessary.¹¹ ^bCalculated from pK_a in MeCN.¹² ^cOverpotential with respect to -1.23 V vs SCE. ^dUsing the equation $i_c = nFSC_p(DkC_s)^{1/2}$,¹⁵ with $n = 2$, $S = 0.07$ cm², and $D = 1.6 \times 10^{-5}$ cm² s⁻¹.¹³

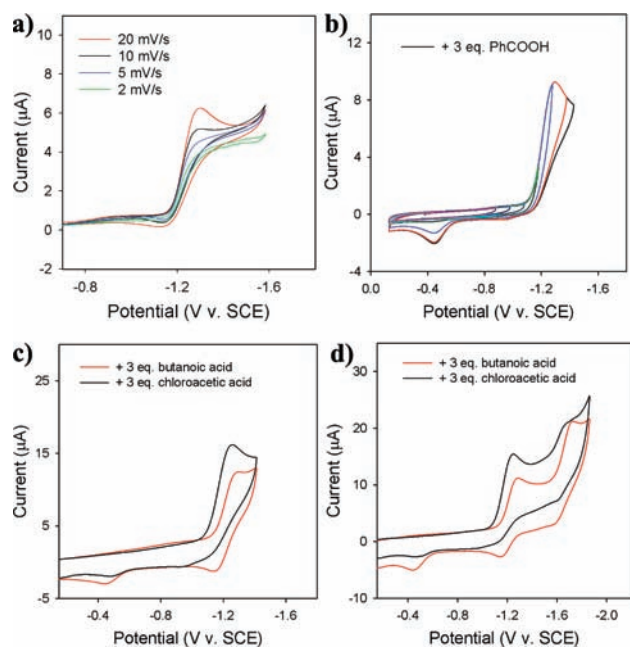
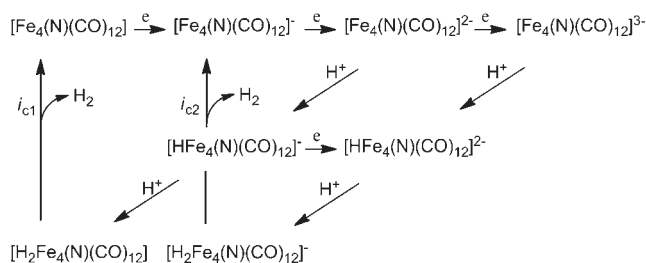


Figure 2. CVs of 0.1 M Bu₄NClO₄ MeCN solutions of Et₄N-1 (a) 0.24 mM **1** + 7.1 mM PhCOOH, (b–d) 0.34 mM **1**, scan rates 100 mV/s. The scans were reversed at (b) various voltages, (c) -1.4 V, and (d) -1.8 V.

190 mV (Figure S11). As an example, for benzoic acid ($\eta = 280$ mV), the turnover frequency (TOF), expressed as mol of H₂ evolved (mol of catalyst)⁻¹ s⁻¹, can be obtained from the rate equation $\text{rate} = k[\text{H}^+][\text{I}^-]$, which gives a TOF of 1.0 s⁻¹ for $[\text{I}^-] = 0.34$ mM and $[\text{H}^+] = 50$ mM.¹⁶

With knowledge of the rate of hydrogen evolution in hand, we wished to gain a better understanding of the mechanism of the HER and to control the rates of formation and disappearance of presumed (H-1)⁻ intermediate species and their reactivity toward H⁺ or CO₂. Mechanistic insight into the HER was obtained by comparing CVs recorded with **1**⁻ and small amounts of acids of various strengths (Figure 2b–d). As expected, stronger acids give a greater rise in the peak current for the **1**^{-/2-} couple (*i*_{c1}). The observed acid dependence elicits the question of which elementary step in the reaction mechanism is rate-determining. On the basis of a mechanism that is unimolecular in **1**⁻ (Scheme 1), either protonation of the electroreduced catalyst or protonation of the intermediate hydride (H-1)⁻ could be rate-limiting.

Electrochemical evidence supports the mechanism in which protonation of (H-1)⁻ is rate-limiting in the *i*_{c1} catalytic cycle.

Scheme 1

A scan in the presence of benzoic acid in the anodic direction, after the *i*_{c1} event, displayed an oxidation wave at -0.45 V that was absent when the scan was reversed at -0.8 V (Figure S13). This corresponds to oxidation of unreacted (H-1)⁻ (Figure 2b)¹⁷ and implies that (H-1)⁻ is formed at the electrode more quickly than it is protonated. By inference, protonation of (H-1)⁻ is rate-limiting. With a stronger acid, chloroacetic acid, only a small oxidation wave at -0.45 V was observed because more (H-1)⁻ was protonated, and with a weaker acid, butanoic acid, the peak current at -0.45 V increased because protonation of (H-1)⁻ had slowed (Figure 2c). These observations are consistent with protonation of (H-1)⁻ as the rate-limiting step in an ECCE- or ECCEC-type mechanism for the HER.¹⁸ The same acid-strength dependence was observed when the scan was extended past the second reduction event for **1**⁻ (*i*_{c2}) before scanning in the anodic direction (Figure 2d). With the stronger chloroacetic acid, a very minor oxidation event was observed on the return anodic scan at -0.45 V. When the weaker butanoic acid was employed, the oxidation event at -0.45 V was more apparent.¹⁹ Taken together, these observations indicate that acid strength is a key factor in the rate of reaction of (H-1)⁻ with H⁺.^{3a}

We have not yet considered a bimolecular mechanism, which has two possible rate-determining steps: formation of (H-1)⁻ and bimolecular elimination of H₂ from two molecules of (H-1)⁻. As discussed previously, formation of (H-1)⁻ is not rate-limiting. We also established that the HER is first-order in **1**⁻ (see below). Therefore, a bimolecular reaction mechanism is unlikely.

These insights gained from mechanistic investigations could indeed be used to favor CO₂ reduction over H⁺ reduction by (H-1)⁻. Electrochemical measurements in the presence of CO₂ were investigated using an acid that reacted slowly enough with (H-1)⁻ that we could observe its presence on the return anodic scan. Accordingly, with benzoic acid ($\eta = 280$ mV), we observed CO₂ reduction by (H-1)⁻. This was apparent from the loss of reversibility in the **1**^{-/2-} couple and a decrease in current of the -0.45 V feature upon sparging with CO₂ (Figure 3a). With the stronger acid tosic acid ($\eta = 990$ mV), only H₂ evolution was observed even in the presence of CO₂ (Figure 3b). Hence, the thermodynamic potential of the acid employed determines relative rates of reduction of protons or CO₂. Reduction of CO₂ was confirmed by CPE experiments performed on a 0.34 mM solution of **1**⁻ in MeCN containing 0.1 M Bu₄NClO₄ along with benzoic acid and CO₂. After 16 h at -1.25 V, formic acid was identified as a major C1 product by ¹³C NMR spectroscopy (Figure S14). CPE experiments performed with tosic acid and CO₂ yielded only hydrogen.

A limited number of previous reports of formic acid production by molecular catalysts exist. The second-row transition metal ruthenium affects catalysis at -1.3 V,^{3a} and examples of nickel and cobalt molecular catalysts effective for trace formic

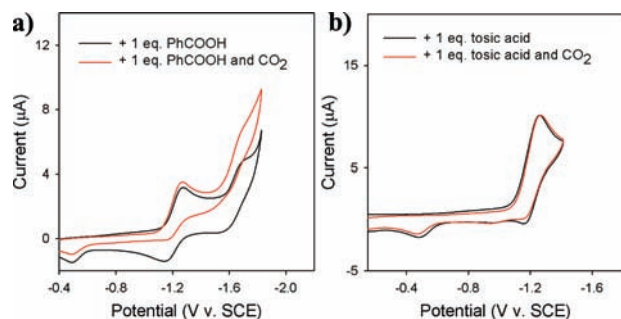


Figure 3. CVs of 0.34 mM solutions of **1** in MeCN containing 0.1 M Bu₄NClO₄, CH₃CN. Glassy carbon electrode, 100 mV/s. (a) PhCOOH, black; with CO₂, red. (b) tosic acid, black; with CO₂, red.

acid production operate at -1.25 V via ligand-based reduction events.^{3c} We speculate that the ability of **1**[−] to effect proton and CO₂ reduction at -1.25 V arises from the favorable interaction between H⁺ and the 2[−] charge on the reduced complex **1**^{2−}; the majority of known HER catalysts have neutral or positive charges.²⁰ The presence of the 12 strongly electron-withdrawing carbonyl groups prevents prohibitively high reduction potentials for negatively charged **1**[−]. In a similar manner, we could speculate that the 2[−] charge on catalytically active **1**^{2−} contributes to the higher reaction rate for formation of (H-**1**)[−] than for protonation of (H-**1**)[−].

In summary, we have demonstrated that the operating potential of a low-valent iron electrocatalyst can be relatively positive as a result of multiple carbonyl ligands and the delocalization afforded by the metal–metal-bonded structure of **1**[−]. We have proposed that that anionic charge on the catalyst facilitates reduction of protons at low overpotentials (190 mV). Understanding of the relative rates of formation and subsequent reaction of the (H-**1**)[−] intermediate allowed the reduction ability of (H-**1**)[−] to be directed toward CO₂ or H⁺. Future work will build on these principles of molecular electrocatalyst design to probe electrocatalytic reactions of small molecules in organic and aqueous media.

■ ASSOCIATED CONTENT

S **Supporting Information.** Synthesis and characterization of **1** and electrochemical and NMR measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) η is the overpotential.

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- (14) i_c is the catalytic plateau current.

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- (16) **1** is stable in the presence of 50 mM PhCOOH.

- (17) The event at -0.45 V vs SCE was identified as the (H-**1**)^{0/−} couple by comparison with an authentic sample of H-**1** (Figure S11).⁷

- (18) ECCE denotes successive electrochemical, chemical, chemical, and electrochemical elementary steps for the reaction mechanism. ECEC denotes a mechanism with successive electrochemical, chemical, electrochemical, and chemical steps.

- (19) No (H-**1**)^{2−/−} event was observed. We speculate that oxidation of (H-**1**)^{2−} overlaps with oxidation of **1**^{2−}.

- (20) For example, see: ref 3a, ref 4a, and Beley, M.; Collin, J.-P.; Rupert, R.; Suavage, J.-P. *J. Am. Chem. Soc.* **1986**, *108*, 7461.