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Electrode initiated proton-coupled electron transfer to promote degradation of a nickel(II) coordination complex†

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A Ni(II) bisphosphine dithiolate compound degrades into an electrode-adsorbed film that can evolve hydrogen under reducing and protic conditions. An electrochemical study suggests that the degradation mechanism involves an initial concerted proton–electron transfer. The potential susceptibility of Ni–S bonds in molecular hydrogen evolution catalysts to degradation *via* C–S bond cleavage is discussed.

Introduction

The decomposition of molecular catalysts can limit the lifetime of their activity and hinder mechanistic study.^{1,2} Given the tremendous effort applied to developing new catalysts for areas of societal importance, including sunlight-to-fuel schemes,^{3,4} identifying *when* catalysts are decomposing,⁵ understanding the mechanisms by which catalysts decompose, and recognizing what structural factors predispose a catalyst towards degradation is of importance. To date, most work has focused on identifying only if a molecular complex degrades into a catalytically competent heterogeneous species, a non-trivial task.^{1,5}

Electrocatalysis is an attractive means of converting electrical energy into chemical fuels like hydrogen.^{3,4,6} Several wireless device structures have been proposed which integrate catalysts with light absorbing molecules and materials to drive fuel production from sunlight.^{6–13} Many molecular electrocatalysts have been prepared which convert protons into hydrogen at excellent efficiencies in both aqueous and non-aqueous solutions.^{3,4,14,15} While a few reports have discussed the general instability of electrocatalysts,^{5,16,17} work in the last few years has begun explicitly investigating the instability of certain molecular electrochemical catalysts under reducing and protic conditions.^{2,18–24} In each of these cases degradation resulted in a heterogeneous material *still active for hydrogen evolution*.

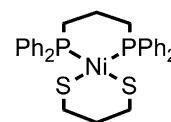
Studies of catalyst stability have largely focused on reporting which molecular compounds degrade electrochemically

and characterizing the catalytically active material they form, though some effort has been directed towards determining the mechanisms by which these processes occur. Degradation pathways have been proposed to occur through initial ligand modification,^{19–22,24,25} such as hydrogenation of C=N bonds, for some complexes. Interpreting the reaction pathways for catalyst modification under electrocatalytic conditions is particularly challenging, as the species of interest transforms from a molecular complex to a heterogeneous species, such as nanoparticles or an amorphous film, during the course of the reaction. Equally challenging, reactivity under reducing and protic conditions typically involves proton-coupled electron transfer (PCET) processes, which can occur *via* stepwise or concerted pathways and can be difficult to distinguish. Understanding the details of PCET processes in molecular electrocatalysis—whether it leads to productive fuel production or it prompts catalyst degradation—is essential for interpreting the free-energy landscape of these systems.^{26–31} Herein we examine the reactivity of a nickel(II) compound (**1**, Scheme 1), which has several structural motifs of interest for molecular hydrogen evolving catalyst design, including a bisphosphine backbone and a dithiolate ligand. Upon identifying that **1** degrades under electrocatalytic conditions, intriguing features were observed in the voltammograms, prompting us to examine the pathway of degradation. In this study, we reveal unique PCET reactivity that is promoted under electrocatalytic conditions and ultimately leads to degradation and formation of a heterogeneous active species.

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Scheme 1



Results and discussion

Characterization of **1**

Compound **1** was prepared in 15% yield *via* a related approach to a previously reported derivative of **1** with a methyl amine group at the bridgehead of the phosphine (see ESI† for details).³² One- and two-dimensional NMR confirmed the structure of **1** shown in Scheme 1 (Fig. S1–S5†). A reversible, one-electron wave assigned to the Ni^{II/I} couple is observed *via* cyclic voltammetry (CV) with an $E_{1/2}$ of -1.92 V as well as an irreversible oxidation attributed to the Ni^{III/II} couple with $E_{p,a} = -0.34$ V (Fig. 1). The redox properties of **1** are very similar to the previously reported methyl amine derivative.³²

Scan rate studies of the Ni^{II/I} couple reveal that **1** is under diffusion control (Fig. S8†), as expected for a homogeneous species, with a diffusion coefficient of 1×10^{-5} cm² s⁻¹ (Fig. S9†). The Nicholson method³³ was used to estimate a value of 0.1 cm s⁻¹ for the heterogeneous electron transfer rate constant (k^0) of the Ni^{II/I} couple (see ESI for details†).

Electrochemistry of **1** in the presence of acid

Addition of 10 mM [Et₃NH][BF₄] ($pK_a = 18.82$ in CH₃CN³⁴) to a solution of **1** results in loss of the reversible Ni^{II/I} wave and the appearance of two irreversible waves, both positive of the direct electrode reduction of [Et₃NH][BF₄] as shown in Fig. 2A. The large current of the second wave suggests proton reduction catalysis. The onset of the first wave occurs hundreds of millivolts positive of the Ni^{II/I} reduction. Prewaves preceding apparent catalytic waves have been observed previously for nickel and cobalt complexes and in these cases assigned to either ligand hydrogenation or decomposition of the initial molecular species into a heterogeneous, electrode adsorbed material.^{19,20,22,23} **1** was also found to transform into an electrode-bound active species *via* a rinse test: in a solution of **1** and 10 mM [Et₃NH][BF₄], an electrode was scanned through the prewave and second wave, rinsed with acetonitrile and transferred to a solution of only 10 mM [Et₃NH][BF₄]. In this acid-only solution, the catalytic response was maintained (Fig. 2B). Dipping an electrode in a solution of **1** and 10 mM [Et₃NH][BF₄] without applied bias did not produce the same result.



Fig. 1 Cyclic voltammogram of 0.4 mM **1** at 100 mV s⁻¹ in 0.25 M [Bu₄N][PF₆] acetonitrile solution. The Ni^{II/I} couple has an $E_{1/2}$ of -1.92 V and the irreversible Ni^{III/II} couple has an $E_{p,a}$ of -0.34 V.



Fig. 2 (A) Cyclic voltammograms of [Et₃NH][BF₄], **1**, and **1** plus [Et₃NH][BF₄] at 100 mV s⁻¹ in 0.25 M [Bu₄N][PF₆]. (B) Cyclic voltammograms using an electrode treated at -1.78 V for 60 s with 0.4 mM **1** and 10 mM [Et₃NH][BF₄], rinsed, and then scanned in a solution of 0.25 M [Bu₄N][PF₆] (black line) and in a solution of 10 mM [Et₃NH][BF₄] + 0.25 M [Bu₄N][PF₆] (pink) at 100 mV s⁻¹.

Characterization of modified electrodes

X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to characterize the electrode surface after treatment with **1** and [Et₃NH][BF₄]. SEM of glassy carbon plate electrodes electrolyzed in solutions of **1** and [Et₃NH][BF₄] revealed the presence of a smooth film with no evidence for discrete particles (Fig. S10 and S11†), contrasting similar studies where nanoparticle deposition was observed.^{19,20,22,24}

XPS analysis of a bare glassy carbon plate revealed the presence of only carbon and oxygen (Fig. 3A), as expected for glassy carbon which normally has surface oxygen moieties.³⁵ Plates electrolyzed with **1** and [Et₃NH][BF₄], however, were found to have additional elements (Fig. 3B) including Ni, F, S, and P. For comparison, XPS spectra were obtained for dropcast samples of **1**, [Bu₄N][PF₆], [Et₃NH][BF₄], and bis(diphenylphosphino)propane (see ESI†). The relative atomic ratios of Ni : S : P in the dropcast spectrum of **1** were 1 : 1.8 : 2 (Fig. S14 and Table S5†), as expected for a species with two sulfur and two phosphorus atoms per nickel atom. In contrast, the relative atomic ratios of Ni : S : P in the electrolyzed sample were 1 : 1.23 : 0.34 indicating that the deposited material has substantially different atomic stoichiometry than **1**. While the XPS binding energy positions for the Ni 2p and S 2p peaks in the high resolution spectra of electrolyzed **1** (Fig. S16 and S17†) did not permit unambiguous assignment of the species, nickel metal – with a binding energy of 852.6 eV³⁶ – can be ruled out, at least within the XPS sampling depth (~ 10 nm). The Ni 2p peak at 853.9 eV may possibly represent the presence





Fig. 3 (A) XPS spectra of a bare glassy carbon plate and (B) a glassy carbon plate electrolyzed at -1.74 V for 30 minutes with 0.3 mM **1** and 10 mM $[\text{Et}_3\text{NH}][\text{BF}_4]$. The presence of sodium is due to an unknown impurity which was also observed as a very minor component in the dropcast **1** data.

of nickel sulfide; NiS was recently suggested to be the electrodecomposition product of $[\text{Ni}(\text{bdt})_2][\text{Bu}_4\text{N}]$ under protic and reducing conditions.²³

To assess the hydrogen evolution ability of the deposited material, a glassy carbon plate was held at -1.7 V for 10 minutes in a solution of 0.4 mM **1** and 10 mM $[\text{Et}_3\text{NH}][\text{BF}_4]$. After rinsing the electrode, the plate was held at -1.7 V vs. Fc/Fc^+ in a bulk electrolysis cell containing 25 mM $[\text{Et}_3\text{NH}][\text{BF}_4]$ for 15 minutes. Sampling of the headspace by gas chromatography confirmed the production of hydrogen with a Faradaic efficiency of approximately 100% (see ESI† for experimental details).

Proton-coupled electron transfer pathways

Understanding the mechanism by which a catalyst degrades can help inform strategies to protect against degradation in future systems. Consequently, mechanistic details of the initial electrochemically-initiated steps leading to decomposition of **1** were probed. Specifically, we sought to examine the PCET process that initiates structural modification of **1**. How many protons and electrons are initially transferred to the molecular species? Do the electron transfer (ET) and proton transfer (PT) steps occur sequentially or through a concerted process?³⁷ While some mechanistic insight to PCET processes in molecular hydrogen-evolving electrocatalysts have been provided through both theoretical^{29–31,37,38} and electrochemical^{27,28,39} studies, examining PCET in our system is complicated by the fact that these steps are part of a degradation mechanism which ultimately produces an ill-defined heterogeneous material. To minimize complications, we examined the PCET reactivity at stoichiometric and sub-stoichiometric acid-catalyst ratios (up to one equivalent of acid), allowing us to determine how PCET modification proceeds *when only one equivalent of protons is present*. Even under these limiting conditions, caution was necessary when interpreting results: the larger diffusion coefficient of $[\text{Et}_3\text{NH}^+]$ relative to **1** (see below) means that even for

solutions prepared with 1 : 1 ratios of **1** : $[\text{Et}_3\text{NH}^+]$ more than one equivalent of $[\text{Et}_3\text{NH}^+]$ per molecule of **1** can arrive at the electrode on the CV time scale.

To approximate a 1 : 1 ratio of **1** : $[\text{Et}_3\text{NH}^+]$, a solution of $[\text{Et}_3\text{NH}^+]$ was titrated into a solution of **1** and the reversible $\text{Ni}^{\text{II/I}}$ wave of **1** monitored by CV until reversibility was lost. Assuming that acid at the electrode preferentially reacts irreversibly with unreacted **1**, complete loss of the reversible wave of **1** should indicate an approximate 1 : 1 ratio of **1** : $[\text{Et}_3\text{NH}^+]$.

With one equivalent of $[\text{Et}_3\text{NH}][\text{BF}_4]$ the resulting irreversible prewave (Fig. 4) corresponds to the transfer of about two electrons, as determined *via* current integration. As might be expected for a system undergoing degradation, it was difficult to reliably measure exactly two electrons each time this experiment was repeated; however, the number of electrons passed was consistently found to be between 1.5 and 2. A scan rate study of this new irreversible wave found that the peak current varied linearly with the square root of the scan rate (Fig. S18†), as expected for a freely diffusing species, indicating that the 2-electron/1-proton electrochemistry occurs in solution and not on the electrode surface.⁴⁰ We suggest that this proton–electron reactivity forms a hydride species, a putative intermediate in many catalytic cycles for the Ni-mediated formation of H_2 .^{41–43}

Notably, the peak of this irreversible prewave appears *ca.* 0.28 V positive of the cathodic peak position of the reversible wave of **1** observed in the absence of $[\text{Et}_3\text{NH}][\text{BF}_4]$. In order to explain this large positive shift for the two-electron irreversible wave with one equivalent of acid present, we recognized that the coupled one proton and two electron transfers that give rise to this prewave can occur through stepwise (sequential) mechanisms or involve concerted proton–electron transfer (CPET). Specifically, we considered a stepwise PT–ET–ET mechanism (an electrochemical CEE mechanism), a stepwise ET–PT–ET mechanism (an electrochemical ECE mechanism), and a CPET–ET process (here denoted $(\text{EC})_{\text{concertedE}}$) (Fig. 5).

A CEE mechanism which produces a new intermediate $\mathbf{1-H}^+$ would be expected to be more easily reduced than **1** by virtue of the positive charge and so account for the 0.28 V potential shift.

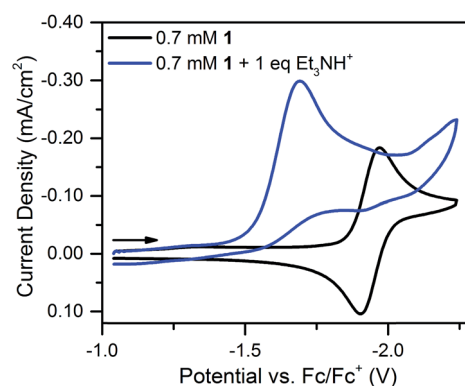


Fig. 4 Cyclic voltammograms of 0.7 mM **1** and 0.7 mM **1** plus one equivalent of $[\text{Et}_3\text{NH}][\text{BF}_4]$. Recorded at 100 mV s^{-1} in 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$.





Fig. 5 Square scheme depicting possible mechanisms for addition of two electrons and one proton to compound **1**. Relevant constants are indicated.

A variation of this mechanism is transient formation of a hydrogen-bonded complex. Intramolecular hydrogen bonding has been used to explain the positive peak shifts of the electrochemistry of organic molecules⁴⁴ and inorganic compounds (e.g., the “hangman effect”).²⁹ Neither UV-vis or ¹H NMR found any evidence of interaction between **1** and over 100 molar equivalents of [Et₃NH][BF₄] (see ESI†). This lack of evidence does not rule out transient interactions producing an undetectable population of **1-H⁺** or hydrogen-bonded **1**, but no evidence supporting a CEE mechanism was found.

An EC-type pathway could also explain the positive shift of the reduction wave in the presence of protons.^{28,29} For a E_rC_i mechanism (reversible electron transfer followed by irreversible chemical reaction)



the magnitude of the rate constant k can have a dramatic effect on the CV peak position and shape. In the absence of reactant A, electron transfer, if reversible and Nernstian, results in predictable relative concentrations of P and Q at the electrode surface based on the reduction potential.^{40,45} Even at potentials sufficiently positive of the formal reduction potential, small concentrations of the reduced species Q will still exist, as predicted by the Nernst equation. If Q reacts with substrate A to irreversibly form species QA, more Q will be produced near the electrode to maintain equilibrium. For large rate constants this results in a shift of the peak to potentials more positive than the formal reduction potential, as shown by simulation in Fig. 6A for an $E_rC_iE_i$ process. The peak shift magnitude is dependent on both the heterogeneous electron transfer rate constant k^0 (cm s⁻¹) for the P/Q couple and the second order forward rate constant k (M⁻¹ s⁻¹). For the simpler E_rC_i mechanism the new peak position E_p is given by^{29,46}

$$E_p = E^{0'} - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \left(\frac{RTk_{obs}}{Fv} \right)$$

where k is the rate of the chemical step (e.g., protonation, $k_{obs} = k[A]$). As the mechanism here involves a second electron transfer, digital simulations were performed to model the peak shift.



Fig. 6 (A) Simulated CVs for an $E_rC_iE_i$ reaction. (B) Prewave potential shift (relative to the cathodic peak of the original reversible wave) versus the rate of protonation. The horizontal green line indicates the experimentally observed peak shift while the vertical blue line indicates the estimated diffusion limited rate for **1** and [Et₃NH][BF₄], see text for details. Simulated with *DigiElch*: $\alpha = 0.5$ for (A) and 0.3, 0.5, or 0.7 as indicated for (B); $k^0 = 0.1 \text{ cm s}^{-1}$ for both E steps; $[P] = [A] = 0.005 \text{ M}$; surface area of electrode = 0.071 cm^2 ; $\alpha = 0.5$ used for E of second electron transfer where E_2 was 0.5 V more positive than the E for the first step (see ESI† for details).

Prior to simulation, several constants were estimated experimentally. As described above, k^0 for **1** was estimated by the Nicholson method to be 0.1 cm s^{-1} . The rate constant k is unknown; however, the upper limit for k is expected to be the diffusion limited rate k_{diff} , which is the maximum rate two reactants can diffuse to one another in solution. The value k_{diff} was estimated using the Debye–Smoluchowski relation⁴⁷

$$k_{diff} = 4\pi N_A(D_1 + D_2)\beta$$

where D_1 and D_2 are the diffusion coefficients of the two reacting species (here **1** and Et₃NH⁺) and β is the effective reaction radius, taken as the sum of the radii for **1** and Et₃NH⁺ and estimated to be 8.5 \AA . As both reactants **1⁻** and Et₃NH⁺ are charged, β was further modified to reflect electrostatic interactions (see ESI† for full calculations).⁴⁷ The diffusion coefficient of **1⁻** was assumed to be equal to that of **1** which was found electrochemically to be $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (see above) while the diffusion coefficient of Et₃NH⁺ was estimated by ¹H DOSY NMR to be $2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (see ESI†). The maximum diffusion limited rate was then estimated as $4.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Fig. 6B plots the prewave peak shift versus the forward rate constant. Around $10^3 \text{ M}^{-1} \text{ s}^{-1}$ the peak shift actually becomes



more negative, as predicted theoretically for an ECE mechanism.⁴⁶ The peak shift experimentally observed is in excess of the simulated peak shifts for an ECE mechanism. Even allowing the transfer coefficient α to vary away from the assumed value of 0.5 to 0.3 and 0.7 (0.3 to 0.7 is the general range of observed α values⁴⁰) does not reproduce the large observed peak shift.

With an ECE mechanism found theoretically implausible by digital simulations and with no evidence of a CEE mechanism, a concerted (EC)_{concerted}E mechanism was considered. For concerted pathways not involving heavy atom bond cleavage⁴⁸ electrochemical kinetic isotope effects have been used as a diagnostic for CPET.^{49–54} Therefore, cyclic voltammograms were obtained of **1** in the presence of sub-stoichiometric amounts of [Et₃NH][Cl] (to permit observation of the position of **1**'s reversible wave) and either 0.24 M H₂O or 0.24 M D₂O. These solutions were allowed to equilibrate for *ca.* 5 minutes after addition of H₂O/D₂O. The chloride salt rather than the BF₄[−] salt of Et₃NH⁺ was utilized to avoid the possibility of BF₄[−] hydrolysis.⁵⁵ A clear kinetic isotope effect is observed with a difference in prewave peak positions of *ca.* 20 mV (Fig. 7). This is consistent with a concerted pathway where simultaneous transfer of a proton with the electron reduces the magnitude of the applied potential necessary for reduction by decreasing buildup of negative charge on **1** in the transition state. This data consequently supports a CPET to **1** followed by a second reduction as the initial mechanism of degradation.

Structural features impacting stability

The decomposition of hydrogen-evolving catalysts into surface-adsorbed catalytically active species has only recently received dedicated attention. A summary of complexes reported to electrochemically decompose into electrode adsorbed materials active for hydrogen evolution in acetonitrile is presented in Table 1. Although at present the dataset is small, clear structural similarities have emerged that may bias a complex towards decomposition. Specifically, complexes with C=N or N=O bonds, which are reported to be susceptible to hydrogenation and hydrogenolysis, respectively, make up the majority of the reports.



Fig. 7 Cyclic voltammograms of equimolar solutions of **1** with sub-stoichiometric [Et₃NH][Cl] and either 0.24 M H₂O or D₂O.

The last two literature examples in Table 1 show cases without C=N or N=O bonds and this work adds a third example of a complex lacking C=N or N=O bonds that also degrades. Notably, these three complexes all have Ni–S bonds, indicating that Ni–S bonds may render a complex susceptible to degradation under reducing and protic conditions. CV data featuring catalytic pre-waves exists for other Ni–S species proposed to be molecular electrocatalysts,^{57,58} suggesting that these compounds may also decompose, possibly into heterogeneous species also active for hydrogen evolution.

The formation of Ni/S containing material upon degradation of **1** suggests degradation of the organosulfur ligands. While no literature was found explicitly for electrochemical C–S cleavage by nickel, numerous examples of Ni-catalyzed desulfurization of C–S bonds have been reported. Ni compounds have been found to insert into C–S bonds, occasionally releasing the alkyl group if a hydride equivalent is available, including the example presented in Scheme 2.^{59–63}

While nickel hydrides are not necessary for desulfurization,^{60,61} they are implicated in some cases of Ni-mediated C–S cleavage.⁵⁹ In the case of compound **1**, it is plausible that initial formation of a nickel hydride then initiates C–S cleavage in the 1,3-propanedithiolate ligand. Scheme 3 presents two possible pathways by which 1-propanethiol or propane fragments would be released. Formation of short-lived Ni=S bonds, followed by dimerization, has been proposed for Ni desulfurization.⁶²

One caveat is that C–S insertion by nickel does not always proceed to a single product. C–S bond cleavage of dibenzothiophene by a nickel compound was found by ³¹P NMR to slowly form a variety of Ni containing products.⁶¹ We attempted to probe the degradation of **1** through a series of experiments. Attempts to isolate the nickel hydride 1–H[−] *via* reaction of **1** with NaBH₄ and LiEt₃BH were unsuccessful (no reactivity was seen with either hydride source). Several experiments were done to try identifying decomposition fragments directly from bulk electrolysis experiments. A solution of 1.8 mM **1** and 50 mM [Et₃NH][BF₄] was electrolyzed at −1.97 V using a 1 × 2 × 0.2 cm glassy carbon plate (about 1 × 1 cm was immersed) in an air-tight cell for 15 minutes. No detectable byproducts (such as propane) were observed upon sampling of the headspace by GC. ³¹P{¹H} NMR of the solution revealed unreacted **1**, free phosphine ligand, and four unidentified peaks (Fig. S21[†]). The appearance of free phosphine helps explain the decrease in phosphorus content of **1** upon degradation, as observed by XPS, and suggests the loss of free phosphine during decomposition. Two of the unidentified peaks were located near that of **1**, suggesting a similar structure; however, the other two were located further downfield. This multitude of P-containing species is in line with literature precedent for S–C bond cleavage resulting in a multitude of Ni species.⁶¹

In an attempt to isolate any volatile fragments (such as 1-propanethiol), the electrolysis solution was vacuum distilled at room temperature into a Schlenk flask immersed in liquid nitrogen. No P-containing species were detected in the distillate by ³¹P{¹H} NMR. GC/MS of the distillate found only





Scheme 3 Proposed decomposition mechanisms of 1.

Conclusions

1 was found to electrochemically degrade in the presence of $[\text{Et}_3\text{NH}][\text{BF}_4]$ to form an electrode adsorbed film containing Ni and S. These films are electrocatalytically active for the evolution of hydrogen from acetonitrile solutions of $[\text{Et}_3\text{NH}][\text{BF}_4]$. Importantly, the initial degradation mechanism of **1** appears to involve a CPET step rather than stepwise electron and proton transfers. Additionally, comparison of the structure of **1** with that of other molecules reported to electrochemically degrade suggests the vulnerability of species containing Ni-S bonds. This vulnerability may stem from Ni-mediated S-C bond cleavage followed by further decomposition. More generally, this work underscores the susceptibility of molecular electrocatalysts to degradation.

This work outlines an approach to electrochemically studying CPET using metal complexes. Further questions remain, foremost being: (1) what are the products of proton and electron addition? and (2) can PCET be tuned between stepwise and concerted pathways? Compound **1** is not ideal for answering these questions due to the meager synthetic yield, poor solubility, mismatched diffusion coefficient relative to the acid source, and ultimate loss of homogeneity. Resolution of these concerns has motivated us to begin exploring similar electrochemistry using a related family of metal compounds.

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