Deciphering Reversible Homogeneous Catalysis of the Electrochemical H\textsubscript{2} Evolution and Oxidation: Role of Proton Relays and Local Concentration Effects

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Abstract: Nickel bisdiphosphine complexes bearing pendant amines form a unique series of catalysts (so-called DuBois’ catalysts) capable of bidirectional or even reversible electrocatalytic oxidation and production of dihydrogen. While this unique behaviour is directly linked to the presence of proton relays installed within the molecular structure, close to its metal center, quantitative activity descriptors are still lacking to guide the rational design of molecular catalysts with enhanced activity. We report here for the arginine derivative [Ni(P\textsubscript{2}Cy\textsubscript{N}\textsubscript{2}Arg\textsubscript{2})\textsuperscript{2+}] on a detailed kinetic treatment based on a mechanistic model that applies to the whole DuBois’ catalyst series and show that, with a unique set of parameters, it allows, for a good fit of the experimental data measured in a wide range of pH values, catalyst concentrations and partial hydrogen pressures. The bidirectionality of catalysis results from the balanced equilibrium constant of the kinetically critical hydrogen uptake and evolution chemical step and the corresponding rate constants being large enough in both directions, as well as a very fast intramolecular proton transfer, both being likely due to concentration effects resulting from the presence of proton relays at the immediate vicinity of the catalysts. In that specific case, we show that hydrogen oxidation, kinetically limited by H\textsubscript{2} insertion, has a larger turnover frequency than hydrogen evolution that is kinetically limited by H\textsubscript{2} release. The reversibility of catalysis appears also to result from a subtle balance between the characteristics of two sequential proton-coupled electron transfer square schemes and the equilibrium constants as well as the kinetic constants of both chemical steps. We illustrate experimentally that reversibility does not required that the energy landscape be flat, with in the present case redox transitions occurring at potentials ~250 mV away from the equilibrium potential. Still, large deviations from a flat energy landscape requires interfacial electron transfers to occur far from their equilibrium potential, which impacts their kinetics and the overall rate of catalysis. At that point, the rate of catalysis may be limited by the efficiency of deprotonation/reprotonation of the relays, a concern that also holds for the design of improved monodirectional electrocatalysts.
Introduction

Hydrogenases are remarkably efficient reversible natural catalysts.\textsuperscript{[1]} They have inspired a number of molecular catalysts of the electrochemical production and oxidation of dihydrogen (H\textsubscript{2}) also called HER (hydrogen evolution reaction) and HOR (hydrogen oxidation reaction).\textsuperscript{[1b, 2]} Among those, only one series of nickel bisdiphosphine complexes, called DuBois’ catalysts, exhibits bidirectionality,\textsuperscript{[3]} and to a small extent, reversibility.\textsuperscript{[4]} A remarkable breakthrough in terms of reversibility was achieved by further work from Shaw and DuBois with a series of similar complexes integrating amino-acid substituents.\textsuperscript{[5]} Recent work demonstrated that appropriate integration of these molecular catalysts into carbon nanotube-based electrodes could allow to maintain reversible HER/HOR catalysis in aqueous acidic conditions compatible with the proton-exchange membrane H\textsubscript{2} fuel-cell and electrolysis technologies with mass activities for the Ni center only one order of magnitude away from benchmark Pt electrodes.\textsuperscript{[6]}

Noteworthy is the fact that all these complexes contain pendant amine functions installed close to the metal center on the diphosphine ligands. These amine functions can act as proton relays, which can speed up catalysis\textsuperscript{[7]} thanks to a local concentration effect (which might amount to very large solution concentrations up to decamolar range) promoting the formation and increasing the reactivity of key intermediates along the cycle, namely the formation and further protonation of metal hydride species during H\textsubscript{2} evolution and activation of the Ni-bound substrate (here H\textsubscript{2}) and further deprotonation of the formed metal hydride species during H\textsubscript{2} oxidation. In addition, Savéant highlighted that these protons relays require rapid regeneration to maintain catalysis, either through reprotonation from acids in the solution during reductive processes or rapid deprotonation from bases in the solution during oxidative processes.\textsuperscript{[7]} While the above considerations allow understanding bidirectional catalysis, they fall short in providing descriptors for reversibility, which remain a unique electrochemical behavior of platinum-group metals, hydrogenases enzymes and the DuBois/Shaw catalysts for HER/HOR.\textsuperscript{[8]}

\[2H^+ + 2 e^- \rightleftharpoons H_2\]

A convenient way to investigate these systems is to observe their behavior as catalysts of the HER and HOR by means of cyclic voltammetry (CV).\textsuperscript{[9]} These effects have been analyzed in details with the simple example of a one-electron/one-proton irreversible catalytic system under canonical conditions.\textsuperscript{[10]} The treatment of the molecular catalysis of two-electron reversible reactions has been recently provided considering general reaction schemes without specific description of the nature of the steps involving the proton relays as above stated.\textsuperscript{[11]} Building on such work, the purpose of the present work is to provide the first thorough kinetic analysis of a two-electron reversible system supported by formal kinetics of reversible two electron catalytic systems. This analysis emphasizes the critical role of proton relays taking the example of the arginine derivative, [Ni(P\textsubscript{2}CyN\textsubscript{2}Arg\textsubscript{2})\textsubscript{3}\textsuperscript{6+} (Figure 1),\textsuperscript{[5c, 5d]} which was selected for its
remarkable reversibility properties and because of its solubility in water. The latter property indeed simplifies the pH-dependency investigation, an essential basis of the mechanism and kinetics discussion.

Figure 1. Structure of [Ni(P2CyN2Arg)2]6+, each R-N moieties stands for a protonated arginine residue similar to that highlighted in blue.

We will first summarize the catalytic properties measured with this complex under different experimental conditions. Then we will show how Pourbaix diagrams can be constructed and identify the above-mentioned fast deprotonation and reprotonation processes required for closing the catalytic loop. We will then propose a comprehensive reaction scheme relevant to this remarkable molecular system and develop a thorough analysis for extracting all the kinetic constants and reveal the key features allowing bidirectionality and reversibility.

Results and Discussion

Raw catalytic CV data. All experiments were carried out in buffered aqueous solutions. Based on previously reported data,[5c, 5d] a temperature of 40°C was selected to measure catalytic currents that are both sizeable at low scan rates (down to 0.05 V/s) and low enough to be overcome at fast scan rate (5 V/s and upwards). CV catalytic currents are indeed decreasing functions of the dimensionless parameter $k_0/(F\nu/RT)$ where $\nu$ is the scan rate, $k_0$ the first order or pseudo-first order rate constant of the catalytic reaction, $T$ the temperature, $R$ the gas constant and $F$ the Faraday constant.[8b]

The CVs are recorded at a glassy carbon electrode (surface area $S = 0.02 \text{ cm}^2$) in 0.05 M 2-(N-morpholino)ethanolsulfonate (MES) buffer added with 0.05 M Na₂SO₄ (unless stated otherwise) or in 0.1 M sulfuric acid solutions, at a series of pHs varying from 1 to 9 in the absence of H₂ or in the presence of 1 atm. H₂. The moderately low water solubility of the catalyst, and hence the small concentration used (50 or 100 µM), results in CV responses showing a substantial double layer capacitive charging current on top of which appears the faradaic responses of interest. Raw data had thus to be corrected from the
double layer charging current before going to the kinetic analysis via subtraction of a blank CV recorded in the absence of catalyst (examples are given in Figure S1). Another consequence of the poor water solubility of the catalyst is its facile adsorption onto the electrode surface, which had to be carefully polished before each run.\textsuperscript{[12]} Typical background corrected CV responses obtained at low scan rate are shown in Figure 2, showing archetypal steady-state S-shaped responses characteristic of canonical kinetic conditions in which diffusion and chemical steps combine within a thin reaction-diffusion layer through which the substrate concentration remains constant.\textsuperscript{[9b]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure2.png}
\caption{Background corrected catalytic responses measured at a glassy carbon electrode at 40°C and 0.1 V/s in a) the absence of H\textsubscript{2} and b) under 1 atm. H\textsubscript{2} at various pH values: 1 (black), 2 (red), 3 (blue), 4 (green), 5 (magenta), 6 (orange), 7 (cyan), 8 (light green), 9 (navy). Catalyst concentration: 100 µM in 0.05 M MES buffer (+0.05 M Na\textsubscript{2}SO\textsubscript{4}) or 0.1 M sulfuric acid solutions.}
\end{figure}

Catalysis being revealed by the S-shape of the CV response and the height of the plateau current, the experiments under H\textsubscript{2} indicate in the first place that catalysis is bidirectional: the same catalyst is indeed able to catalyze the oxidation of H\textsubscript{2} and the reduction of proton from the solution. Within this framework, it is observed that, in the presence of saturated H\textsubscript{2} atmosphere (Figure 2b), H\textsubscript{2} oxidation catalysis is much more pronounced than H\textsubscript{2} evolution catalysis. In the latter case, significant catalysis only appears at the lowest pH values, both in the absence and presence of H\textsubscript{2}. Conversely, the catalytic plateau currents for H\textsubscript{2} oxidation increase with pH at low to intermediate pH values.

It is also remarkable that the potentials at which the CV responses stand are practically the same for H\textsubscript{2} oxidation and evolution, which reflects reversible catalytic behavior. The equilibrium potentials experimentally measured from CVs (Figure 2b) at \(i = 0\) at various pH values data (theoretically corresponding to 0 V vs. RHE) are plotted in figure S2 and overlaid with the theoretical curve. It is seen that the agreement is fair but a substantial deviation is observed at pH above 7 indicating that the equilibrium is maybe more difficult to reach. This resonates with the fact that both reductive and oxidative
catalytic currents decrease at pH values above 7 concomitantly with a flattening of the catalytic response. We nonetheless observe at pH < 6 a slight anodic shift (of ca. 10-35 mV depending on the pH value) of the experimental value compared to the theoretical value (Figure S2). We do not have a definite explanation for this shift that might be due to some junction potential. This shift was added in simulations described below to get a match with the experimental data.

Finally, the HER currents observed in the absence of H₂ (Figure 2a) are significantly higher (with a two-fold factor at pH 1) than when H₂ is present (Figure 2b), a typical behavior for product-hindered catalytic kinetics that has been already reported for such reversible catalysts[5, 6c] and hydrogenase enzymes.[1d]

**Thermodynamics characteristic of the Ni⁺/Ni²⁺ system.** Pourbaix diagrams can be very useful to understand the catalytic properties of such bidirectional systems, as exemplified by Muckerman and coll. a decade ago.[13] To establish such a diagram, we first recorded a set of CV responses over the whole pH range at 40°C and at a scan rate high enough to overcome catalysis.[9b, 9c] Reversible signals could be measured at all pH values and are shown in Figure 3a.

![Figure 3](image.png)

**Figure 3.** a) Background corrected CV responses at 40°C and 50 µM catalyst concentration in the absence of H₂ at a scan rate of 5 V/s at various pH values: from right to left: 1 (black), 1.5 (violet), 2 (red), 3 (blue), 4 (green), 5 (magenta), 6 (orange), 7 (cyan), 8.2 (light green), 9.2 (navy). b) Electron stoichiometry of the CV responses (see text). Electrolyte: 0.1 M MES, pH adjusted with H₂SO₄ or NaOH.

Figure 3b compares the peak current of CVs, recorded at 5 V/s after correction from the capacitive current, to the classical Randles-Sevcik relationship for a one electron stoichiometry:[14]

\[
    i_p = 0.446 F S C_0 \sqrt{D \sqrt{F v / R T}}
\]

relating, in the case of a fast, diffusion controlled electron transfer, the peak current, \(i_p\), to the surface area \(S\) (0.02 cm²), the catalyst concentration \(C_0\) (50µM), the scan rate \(v\), the temperature \(T\) (313.16 K) and the diffusion coefficient \(D\) (in cm²/s). For the latter we used 2.8 10⁻⁶ cm²/s, a value previously determined by Shaw and coworkers using NMR pulsed field gradient methods.[5d][15] From these data, we can conclude
that the electron stoichiometry is 1.

The Pourbaix diagram (Figure 4a) positioning the Ni(II) and Ni(I) species of the system in their different protonation states can then be obtained by relating the pH value and the apparent standard potential derived from the midpoint between the anodic and cathodic one-electron peaks (Figure 3a). It is worth noting that the slope of the central descending straight-line (62 mV per pH unit) in Figure 4a corresponds to the value expected for a one-electron/one-proton process at the operating temperature (40°C). The ensuing zones of thermodynamic stability of the various reactants are as shown in Figure 4b. In the following, we will represent by the subscript letter “r” a properly positioned amine acting as proton relay, “+Hr” representing a protonated form of the relay.

**Figure 4.** a) Black dots: Apparent standard potential vs. pH (Pourbaix diagram) in the same conditions as in Figure 3. The dashed straight line shows the apparent standard potential of the H⁺/H₂ couple at this temperature. The black full line corresponds to the fitted apparent standard potential vs. pH according to equation (2) (see text). The red full line corresponds to the Pourbaix diagram of square scheme 2 in figure 5, according to equation 14 (see text). b) Domains of thermodynamic stability of the Pourbaix diagram of the square scheme 1 in figure 5. c) Domains of thermodynamic stability of the Pourbaix diagram of the square scheme 2 in figure 5.

This set of experiments allowed evaluating four thermodynamics values corresponding to a proton-
coupled electron transfer square scheme shown in Figure 5 (square scheme 1) via a fitting of the experimental data with:

\[
E^0_{\text{red}} = E^0_{\text{ox}} + \frac{RT}{F} \ln \left( \frac{[\text{H}^+] + K_{\text{H}}^{1/2}}{[\text{H}^+] + K_{\text{H}}^{1/2}} \right) = E^0_{\text{ox}} + \frac{RT}{F} \ln \left( \frac{K_{\text{H}}^{1/2} [\text{H}^+] + K_{\text{H}}^{1/2}}{K_{\text{H}}^{1/2} [\text{H}^+] + K_{\text{H}}^{1/2}} \right)
\]

(2).

We obtain:

\[
pK_{\text{H}}^{\text{II}} = 1.0, \quad pK_{\text{H}}^{\text{I}} = 7.2
\]

and

\[
E^0_{\text{1/He}} = 0.015 \text{ V vs. SHE}, \quad E^0_{\text{1/He}} = -0.370 \text{ V vs. SHE}.
\]

The Pourbaix diagram (Figure 4) confirms that \( \text{Ni}^{\text{II}} \) gets protonated at low \( pH \) values, as previously demonstrated by NMR measurements,\(^{[5a, 5d]} \) and in line with previous determination of \( pK_a \) values for pendant amines of the same complex (\( pK_a = 0.64 \) in water for the \( \text{Ni}^{\text{II}}/\text{H}_{\text{r}}\text{Ni}^{\text{II}} \)).\(^{[17]} \) The \( pK_a \) value at which the Ni(I) species is protonated is significantly higher, around 7, in line with the increased basicity of a complex with a reduced overall charge following reduction of the Ni center.

**Insights into the nickel-hydride species and overall mechanistic scheme.** As highlighted by Muckerman and coll.,\(^{[13]} \) getting a comprehensive understanding of the catalytic system requires gaining data for the redox couples involving metal-hydride intermediates. To that aim, we recognize that, under 1 atm. H\(_2\), \( \text{Ni}^{\text{II}} \) is fully converted into the doubly protonated /doubly reduced species \( \text{H}_{\text{r}}\text{Ni}^{\text{II}}\text{H}^- \) as previously demonstrated by UV–visible spectroscopy\(^{[18]} \) and \( ^{31}\text{P} \) NMR measurements.\(^{[5a, 5d, 19]} \)

In an attempt to get the thermodynamic values characterizing a second square scheme involving such metal-hydride species, CVs were recorded at 5 V/s under 1 atm. H\(_2\) (Figure S3). At such high scan rate, we were expecting to characterize solely the one-electron oxidation of Ni(II)-H into Ni(III)-H species. Unfortunately, we observe that, at all \( pH \) values, the oxidation wave is bielectronic and that the return reduction wave is smaller, likely monoelectronic. This indicates that, starting from \( \text{H}_{\text{r}}\text{Ni}^{\text{II}}\text{H}^- \) (or \( \text{Ni}^{\text{II}}\text{H}^- \) at \( pH \) values > ~7), it is not possible to isolate the lower square scheme 2, shown in Figure 5, only involving Ni(II)-H and Ni(III)-H species. In other words, the Ni(III)-H species react fast in a way allowing their further oxidation. This resonates with the key property of this family of catalysts\(^{[20]} \) and with the expected role of a proton relay,\(^{[3c, 7, 21]} \) allowing for fast intramolecular proton transfer generating \( \text{H}_{\text{r}}\text{Ni}^{\text{II}} \) from \( \text{Ni}^{\text{II}}\text{H}^- \) via the concentration effect discussed in the introduction.\(^{[7]} \) Hence, the bielectronic oxidation wave observed at 5 V/s starting from \( \text{H}_{\text{r}}\text{Ni}^{\text{II}}\text{H}^- \) (or \( \text{Ni}^{\text{II}}\text{H}^- \) at \( pH \) values > ~7)\(^{[17]} \) captures its proton-coupled oxidation to \( \text{Ni}^{\text{II}}\text{H}^- \), intramolecular deprotonation of the hydride species by the pendant base generating the \( \text{H}_{\text{r}}\text{Ni}^{\text{II}} \) species.
(characterized by the $k_1$ constant in Figure 5) and oxidation of the former into a Ni(II) species. Consistently with the measurements shown in Figure 3, the return reduction wave is monoelectronic and corresponds to the formation of a Ni(I) species. Here the protonation of the Ni(I) to form the Ni(III)-H species actually involved in catalysis (characterized by the $k_1$ rate constant in Figure 5 and thus observed at lower scan rate) is too slow to be observed at 5 V/s.

Figure 5 gathers all the mechanistic elements assembled so far with the two square schemes (only the upper one, i.e. square scheme 1 is fully characterized at the moment) connected on the right by the previously reported hydrogenation equilibrium (hereafter named C_2 with the $K_2=k_2/k_{-2}$ thermodynamic constant)\cite{5a, 19} and on the left by the intramolecular proton transfer step (hereafter named C_1 with a $K_1=k_1/k_{-1}$ thermodynamic constant) discussed just above.

In the H_2 evolution process, fast proton-coupled reduction of the $^\cdot$Ni^{II} species generates $^\cdot$H$\cdot$Ni^{I} (square scheme 1). Then intramolecular proton transfer converts $^\cdot$H$\cdot$Ni^{I} into $^\cdot$Ni^{III}H$^-$; this step is characterized by the equilibrium constant $K_1$, and, although it is fast in the H_2 oxidation direction (see above), it may be rate determining for H_2 evolution. $^\cdot$Ni^{III}H$^-$ is in equilibrium via proton coupled electron transfer (PCET) with $^\cdot$H$\cdot$Ni^{III}H$^-$ (square scheme 2). From this species, dihydrogen can evolve through a second potentially rate-determining chemical step, characterized by the equilibrium constant $K_2$, closing the loop between both one electron/one proton square schemes and enabling catalysis. H_2 oxidation can proceed through the reverse pathway thanks to activation of H_2 by the frustrated Lewis pair formed between the pendant proton relay and the Ni^{II} ion, to generate $^\cdot$H$\cdot$Ni^{II}H$^-$. Here again fast PCET generates $^\cdot$Ni^{II}H$^-$ (square scheme 2), which undergoes rapid intramolecular hydride deprotonation by the pendant base to reach the upper square scheme 1.

Although introducing a new doubly-branched structure, the mechanistic scheme shown in Figure 5 actually captures most of the catalytic sequences proposed so far,\cite{3c, 5a, 5c, 5d, 17} with the exclusion of those initially proposed and involving a non-protonated Ni^{0} intermediate, that we know from the Pourbaix diagram that it is not accessible under the experimental conditions used here. The introduction of the two square schemes in the model allows including pathways avoiding high energy intermediates over the whole range of pH values. Importantly, this scheme allows to differentiate between the intermolecular proton transfer steps (within the two square schemes) that are diffusion-controlled and vital to regenerate the catalytic species and maintain catalysis\cite{7} and the intramolecular proton transfer steps, involving the formation or the cleavage of metal-hydride and H-H bonds positioned vertically on the left and right sides. These chemical steps, C_1 and C_2, involving changes in the formal oxidation state and coordination sphere of the central nickel ion, are likely to be rate determining in one or the other direction.
Figure 5. Catalytic reaction scheme. The Ni catalyst structure has been simplified to only show one diphosphine ligand with one properly positioned amine as proton relay. In the notation indicated in green, proton relays are represented by the subscript letter r under their deprotonated forms and $^+$Hr under their protonated forms.

**Thermodynamics of the chemical steps.** The intramolecular proton transfer between Ni$^{III}$ and $^+$H$^+$Ni likely remains at equilibrium under catalytic conditions where CV responses have S-shaped canonical forms as represented in figure 2b. Obviously, this equilibrium is strongly displaced with $k_1 \gg k_1$ and thus $K_1 = k_1/k_{-1} < 1$ but no direct evaluation of $K_1$ is possible at this stage. Still, as shown later on, it will be possible to extract kinetic information from the data gathered at 5 V/s under H$_2$ atmosphere once the thermodynamics of the intramolecular proton transfer has been indirectly evaluated from the analysis of the catalytic response at pH > 7.
The hydrogenation equilibrium involving $^{1}\text{H}_{r}\text{Ni}^{II}\text{H}^{-}$ and $^{1}\text{Ni}^{II}$ can be characterized by UV-visible spectroscopy, similarly to other DuBois/Shaw catalysts.[18] Measurements carried out under various partial pressures of $\text{H}_2$ allowed the evaluation of $K_2 = 20$ (see SI for details, Figure S4) when $p_{\text{H}_2} = 1 \text{ atm}$. In other words, $K_2 = K_{2,0}^{\text{p}\text{H}_2} / p^{\text{p}\text{H}_2}$ with $K_{2,0} = 20$ and $p^0 = 1 \text{ atm}$. Stable spectra are obtained within seconds after mixing and the observation of an isosbestic point is a strong indication that the equilibrium conditions were met, although this value certainly captures reversible isomerization of $^{1}\text{H}_{r}\text{Ni}^{II}\text{H}^{-}$ into other doubly protonated $\text{Ni}^{0}$ species.[5c]

Then, simple thermodynamic relationships corresponding to the scheme shown in figure 5 lead to:

$$E^{0}_{\text{H}^{+}/\text{H}_2} = \frac{E^{0}_{2,\text{Hr}^{1,\text{He}}} + E^{0}_{1,\text{He}}}{2} + \frac{RT}{2F} \ln \left( \frac{K_1}{K_{2,0}} \right) - \frac{RT}{2F} \ln \left( K_{\text{H}^{1,\text{II}}} \right)$$

and

$$E^{0}_{\text{H}^{+}/\text{H}_2} = \frac{E^{0}_{2,\text{Hr}^{1,\text{He}}} + E^{0}_{1,\text{He}}}{2} + \frac{RT}{2F} \ln \left( \frac{K_1}{K_{2,0}} \right) - \frac{RT}{2F} \ln \left( K_{\text{H}^{1,\text{II}}} \right)$$

with $E^{0}_{\text{H}^{+}/\text{H}_2} = 0 \text{ V vs. SHE}$.

Because the pendant amine is not electronically linked to the nickel active site, we can make the assumption that its $pK_a$ is only sensitive to electrostatic effects from the active site. Hence we make the assumption that complexes with the same overall charge, i.e. $^{1}\text{H}_{r}\text{Ni}^{II}\text{H}^{-}$ and $^{1}\text{H}_{r}\text{Ni}^{I}$ on the one side and $^{1}\text{H}_{r}\text{Ni}^{III}\text{H}^{-}$ and $^{1}\text{H}_{r}\text{Ni}^{II}$ on the other side have similar $pK_a$'s, which leads to $pK_{\text{H}^{1,\text{II}}} = 1.0$ and $pK_{\text{H}^{1,\text{II}}} = 7.2$. This hypothesis is further supported by previous estimation of the $pK_{\text{H}^{1,\text{II}}}$ value between 6.8 and 7.9.[17]

Thus, we obtain:

$$E^{0}_{\text{2,He}} + \frac{RT}{F} \ln (K_1); \quad -0.06 \text{ V vs. SHE} \quad (3)$$

and

$$E^{0}_{\text{2,He}} + \frac{RT}{F} \ln (K_1); \quad -0.445 \text{ V vs. SHE} \quad (4)$$

As already mentioned, the determination of $K_1$ is not possible at this stage. Nonetheless, with the
thermodynamic parameters obtained so far, we can first attempt to interpret the catalytic CV responses shown in Figure 3b considering, as a first approach, that the two squares schemes in Figure 5 are at equilibrium, i.e., assuming fast protonation/deprotonation of the pendant amine over a large range of pH from acid/base couples in the solution, either MES or sulfate-based buffer or water acid/base couples.

**Simplified reformulation of the reaction mechanism and analytical treatment.** Building on previous analysis of two electron reversible catalytic systems,[11] we demonstrate in the SI that instead of considering the time and space variations of the concentrations of the whole set of eight forms of the catalyst, one may consider the four two-by-two sums of the species that have been assumed to be under unconditional proton transfer equilibria, i.e., successively,

\[
[A] = [\text{Ni}^{II}] + [\text{H}^+ \text{Ni}^{II}], \quad [B] = [\text{Ni}^{II}] + [\text{H}^+ \text{Ni}^{III}],
\]

\[
[C] = [\text{Ni}^{III} \text{H}^+], \quad [D] = [\text{Ni}^{III} \text{H}^+] + [\text{H}^+ \text{Ni}^{III} \text{H}^+].
\]

The first square scheme may thus be represented by the two first sums as if they were two redox reactants giving rise to a single Nernst law, after taking into account the various PCET equilibria. The same applies to the second square scheme, introducing C and D. We consider the case where the solution is buffered so as to maintain proton concentration, [H⁺], constant. In total, the whole reaction scheme in figure 5 may be replaced by the simpler equivalent ECᵢECᵢ mechanism shown in figure 6. \(k_2^*\) (and \(k_2\)) is a pseudo first-order rate constant (in s⁻¹) including the concentration of H₂; hence we can write: \(k_2^* = k_2 \frac{p_{H_2}}{p^0}\), where \(p_{H_2}\) is the partial pressure of H₂ and \(p^0\) is 1 atm (similarly, we will define \(k_2 = k_{2,0} \frac{p_{H_2}}{p^0}\)). At equilibrium (i.e. at current nil), we have:

\[
E_{eq} = \frac{E_{eq,1} + E_{eq,2}}{2} = \frac{RT}{2F} \ln \left( \frac{k_1^*}{k_2^*} \right)
\]

(5)
Figure 6. Simplifying reformulation of the reaction mechanism of figure 5.

The corresponding kinetics relationships are (see SI):

\[ k_1^+ = \frac{k_1^+}{k_{-1}^+}, \quad k_2^+ = \frac{k_2^+}{k_{-2}^+} \]

(6)

\[ k_2^+ = \frac{k_2^+}{k_{-2}^+}, \quad k_3^+ = \frac{k_3^+}{k_{-3}^+} \]

(7)

The analytical expression of the CV corresponding to this equivalent EC\textsubscript{r} mechanism is given in the SI and is equivalent to the equations previously reported by Fourmond and Léger.\cite{footnote11} The limit corresponding to a fast and equilibrated intramolecular proton transfer corresponding to the conversion between \( ^+ \text{H}_x\text{Ni}^{II} \) and the nickel hydride \( ^+ \text{Ni}^{III}\text{H} \) is simply obtained by considering \( k_1^+ \rightarrow \infty \) and \( k_{-1}^+ \rightarrow \infty \) in the general expression thus leading to:

\[
\begin{aligned}
2FSC^0 \sqrt{\frac{k_2^+}{k_2^+ + k_{-2}^+}} \left[ -1 + \exp \left( \frac{2F}{RT} (E - E_{eq}) \right) \right] \\
= \frac{\exp \left( \frac{2F}{RT} (E - E_{eq}) \right)}{1 + \frac{1 + K_2^+}{K_2^+} \exp \left( \frac{F}{RT} (E_{eq} - E) \right) \exp \left( \frac{F}{RT} (E - E_{eq}) \right)}
\end{aligned}
\]

(8)
A first outcome of the above analysis is the determination of the rate constants for the H$_2$ addition/evolution steps. As seen from equation (8), both apparent rate constants $k'_2$ and $k''_2$ can be easily obtained from a combination of the plateau currents:

$$k'_2 = \left( \frac{i_{anodic, pl}}{2FSC_Dk^2} \right)^2 \left( 1 + \frac{1}{k'_2} \right)$$

(9)

and

$$k''_2 = \left( \frac{i_{cathodic, pl}}{2FSC_Dk^2} \right)^2 \left( k'_2 + 1 \right)$$

(10)

Considering the plateau currents obtained from experiments performed with 50 µM of catalyst with 100%, 50%, 25% and 12.5% H$_2$ at pH 1 (Figure 7) and $k'_2 = k_1^{II} \left[ H^+ \right] + k_1^{III} \left[ H^+ \right] + k_1^{IV}$ knowing that $k'_2 = 20$, application of
equation (9) and (10) gives $k_2^+$ and $k_2^-$. Then, by application of equation (7), we obtain the averaged values:

$$k_2 = k_{2,0} \frac{p_{H_2}}{p^0}$$

with $k_{2,0} = 10 \text{ s}^{-1}$ and $k_{-2} = 0.5 \text{ s}^{-1}$. 
Analysis of the catalytic data for pH=1. In principle, simulations of the CVs according to the analytical expression (equation 8) could provide an evaluation of $\kappa_1^*$ and hence of $\kappa_1$ because it is the only unknown parameter. However, simulations show that any value corresponding to $\kappa_1^* < 0.1$ leads to satisfactory fitting (see figure S5). Using equation 5, only an upper value of $\kappa_1$ can thus be obtained from this set of data: $\kappa_1 < 0.2$. Simulations considering $\kappa_1^* \to 0$ and taking into account the experimental deviation of $E_{\text{eq}}$ (Figure S2) are shown in Figure 7 together with the experimental data. Excepted for one experimental condition (upper right panel) where the anodic current is clearly off,[22] a fair agreement is obtained between experiments and simulations showing the consistency of the analysis as the shape of CVs in between the two plateaus is correctly reproduced. Remarkably, a single set of determined parameters allows reproducing the decrease of the anodic plateau current and the increase of the cathodic plateau current as H$_2$ partial pressure is decreased. This is a strong validation of the proposed model and its analytical expressions when taking into account the explicit linear dependence of $\kappa_2^*$ with $p_{H_2}$.

Analysis of the catalytic data for 1<pH<6. With all required parameters in hand, we can now calculate the plateau currents at different pH values (taking into account the pH dependence of $\kappa_2^*$, $\kappa_3^*$ and $\kappa_4^*$). As shown in figure 8, the model predicts that the anodic plateau current increases as pH is increased and it is indeed observed experimentally. The reason for this increase is that the relay on $^*\text{H}_2\text{Ni}^{\text{iii}}$ gets fully deprotonated at pH > 2 therefore increasing the amount of $\text{Ni}^{\text{iii}}$ available in solution for H$_2$ uptake. Consequently, the observed increase of the anodic plateau current from pH =1 to pH = 4 is a confirmation that the $pK_a$ of $^*\text{H}_2\text{Ni}^{\text{iii}}$ ($pK_a^{\text{ni}}$) is indeed close to 1 as previously determined[17] and guessed from the Pourbaix diagram where the inflexion of the apparent standard potential is barely seen (Figure 4a).
Figure 8. Absolute values of plateau currents (anodic in black and cathodic in red) as function of pH for 100 µM [Ni(P₂Cy₂Arg)₂]⁶⁺ under 1 atm H₂ at 50 mV/s and 40°C. Dots correspond to experimental values taken from data presented in Figure 2, lines to simulations.

Analysis of catalytic data measured at pH > 7 and determination of remaining thermodynamic data. At pH > 7, we observe two striking features calling for a thorough review of the assumptions corresponding to the framework allowing the satisfactory analysis at acidic pH (figure 2b): (i) CVs are distorted: the experimental anodic current is much more sluggish than predicted by the analytic expression and (ii) plateau currents are smaller than predicted considering that H₂ addition is the only rate-determining step. Given the pKₐ's of the pendant amine acting as a proton relay, we first recall that the dominant sequence at pH > 7 is, in the H₂ oxidation direction:

\[ \text{rNi}^{II} + \text{H}_2 \overset{c}{\longrightarrow} \text{H}^+ \text{rNi}^{III} \overset{PT}{\longrightarrow} \text{rNi}^{II} \text{H}^- \overset{C_1}{\longrightarrow} \text{rNi}^{III} \overset{C_2}{\longrightarrow} \text{rNi}^{II} \overset{H}{\longrightarrow} \text{PT}\]

Here deprotonations (PT) of \( \text{H}^+ \text{rNi}^{III} \) and \( \text{H}^+ \text{rNi}^{II} \) have the same moderate driving force because the pKₐ of \( \text{H}^+ \text{rNi}^{III} \) and \( \text{H}^+ \text{rNi}^{II} \) are close to 7 while the pKₐ of the buffer base (MES) is 6.15. Plateau currents being related to the characteristics of the chemical steps (PT, C₁ and C₂) and C₁ and C₂ being pH independent, the observed deviation of the plateau current from predictions given by equation (8) necessarily implies that at least one proton transfer step should not be considered at equilibrium, the effect being larger for the PT step not following or preceding the slow C₂ chemical step. In other words, the simple equivalent EC₇EC₇ mechanism shown in figure 6 has now to be replaced by another simple four elements scheme corresponding to an EP,EC₇ sequence with the thermodynamic and kinetic parameters defined in figure 9 together with:

\[ E^{0}_\text{ap} = E^{0}_2 - \frac{RT}{F} \ln \left( 1 + \frac{1}{K_1} \right) + \frac{RT}{F} \ln \left( 1 + \frac{[\text{H}^+]^{1/3}}{K_H^{1/3}} \right) \]

(11)

and

\[ i_{\text{anodic,pl}} = \frac{2FSC^0 \sqrt{D}}{\sqrt{k_p \frac{[A^-]}{[\text{H}^+]} + k \frac{[AH]}{k_1}}} + \sqrt{k_2 + k_3} \]

(12)

taking into account that \( K_1 \ll 1 \) and with \( k_p \frac{[AH]}{k \frac{[A^-]}{[\text{H}^+]}^{1/3}} = \frac{[\text{H}^+]}{K_H^{1/3}} \) (see SI for details).
Figure 9. Catalytic reaction scheme at $pH > 7$; $A^-$ and $AH$ correspond to base and acids in solution, i.e. $OH^-$, $H_3O^+$ and constituents of the MES buffer.

Application of equation (12) to the experimental anodic plateau currents at $pH 8$ we obtain $k_p[AH] = 10 s^{-1}$ and $k_p[A^-] = 63 s^{-1}$ for rate-determining protonation and deprotonation steps. These pseudo-first order protonation/deprotonation rate constants can be rationalized as follows. Protonation can arise from $AH = H_3O^+$ with a rate constant equal to $10^9 M^{-1}s^{-1}$, i.e. close to diffusion limit in line with a reaction with a large driving force. Alternatively the buffer (MES) acid form can be the source of proton with a second order rate constant being only $1.4 \times 10^4 M^{-1}s^{-1}$ as a consequence of the small driving force unable to compensate the fact that the pendant amine is buried into the ligand sphere. Regarding deprotonation, if hydroxide ion is considered as proton acceptor, the deprotonation rate constant is $6 \times 10^7 M^{-1}s^{-1}$ whereas it would be only $1.25 \times 10^3 M^{-1}s^{-1}$ with the buffer base. Again these values are in agreement with the corresponding
driving forces and accessibility of the solution base to the proton relay.

We now analyze the shape of the CVs at pH > 7. As already mentioned, the variation of the current between the two plateaus is more sluggish than predicted by the analytic expression resulting from replacement of the reaction pathway by a simpler equivalent EP,EC, scheme in which true and apparent electron transfer are assumed to be fast. We thus infer that the observed sluggishness is due to interference of electron transfer kinetics. At pHs 5-7, we note that the peak separation (78 mV) of the reversible wave under N₂ at 5 V/s (Figure 3) is larger than the canonical Nernstian value (62 mV at 40°C) although this pH range corresponds to the buffering capacity of MES buffer. From the 78 mV anodic- to-cathodic peak separation at 5 V/s under N₂ at pH > 7 and 40°C, it is possible to evaluate the standard rate constant $k_{1,r}^{1,r} = 0.05$ cm/s corresponding to the redox couple \( \text{Ni}^{III}/\text{Ni}^{II} \). Fitting the CV at pH = 8 considering the simplified reaction scheme depicted in figure 9 and the already evaluated thermodynamic and kinetic parameters \( E_{0,r}^{0,\text{H}^{-}}, k_{1}, k_{2,1}[\text{AH}], k_{p}[\text{A}^{-}], \) and \( k_{1,r}^{1,r} \) gives the adjusted parameter $k_{2,ap}^{2,\text{ap}} = 2 \times 10^{-4}$ cm/s (see figure S6 and details for simulations in the SI). As shown in the SI, assuming a Butler-Volmer type kinetic law for the \( \text{Ni}^{III}/\text{H}^{-}/\text{Ni}^{II}/\text{H}^{-} \) couple with a transfer coefficient equal to 0.5, the apparent standard rate constant is:

$$ k_{2,ap}^{2,\text{ap}} = \frac{k_{2,r}^{2,r}}{\sqrt{\frac{1}{k_{1}^{1}} + \frac{1}{K_{H}^{\text{III}}} + \frac{1}{K_{H}^{\text{H}^{-}}}}} $$

If we assume that both redox couples \( \text{Ni}^{III}/\text{Ni}^{II} \) and \( \text{Ni}^{III}/\text{H}^{-}/\text{Ni}^{II}/\text{H}^{-} \) have similar reorganization energy associated to electron transfer, then $k_{1}^{1,2} = k_{2}^{1,2}$ and therefore $k_{2,ap}^{2,\text{ap}}$ allows evaluating $k_{1} = 2 \times 10^{-5}$ via equation (13). As a consequence, from the relationships previously derived linking $E_{0,r}^{0}$, $E_{0,\text{H}^{-}}^{0}$, and $k_{1}$ (equations (3) and (4)) we obtain $E_{0,r}^{0} : \ -0.15 \ V \ vs. \ SHE$ and $E_{0,\text{H}^{-}}^{0} : \ 0.24 \ V \ vs. \ SHE$, thus providing a complete thermodynamic characterization of the reaction scheme shown in figure 5.

Such a positive positioning of the standard potential of the Ni^{III}/Ni^{II}H/Ni^{III}H couples (in both protonation states of the relay) compared to the Ni^{II}/Ni^{III} couple is in full agreement with previous calculation on cobalt-based H₂ evolution catalysts: the standard potentials of the Co^{III}/H/Co^{II}H couples of cobaloximes[24] and cobalt diimine-dioxime complexes[25] were also found positive by 100 and 130 mV to the respective Co^{III}/Co^{II} couples.

Hence the Pourbaix diagram corresponding to square scheme 2 can be drawn according to equation (14) (red line in figure 4a and figure 4c).
We can now come back to the data gathered at 5 V/s. under 1 atm. H₂ (Figure S3) to evaluate the kinetics of the fast, energetically unbalanced, intramolecular proton transfer step C₁. The scheme to be considered is an ECE process corresponding to the D/C/B/A sequence in figure 6 as if there were no chemical connection between A and D because hydrogen uptake/evolution is too slow to be efficient at 5 V/s. Simulations of the CV taking into account values of $E^0_{a1}, E^0_{aq2}$ and $k_1^{-1}$ shows that the position of the anodic peak requires that $k_1^{-1}$ is in the order of $5 \times 10^9$ s⁻¹ (Figure S7) and thus $k_1 \approx 10^5$ s⁻¹. This is in line with a very fast intramolecular proton transfer in both direction and remaining at equilibrium in catalytic conditions. Still, according to the theoretical investigation of the ECE process,[26] the contribution of the second electron transfer remains small provided $\kappa_1^{-1}/(Fv/RT)$ is small, typically smaller than 0.1. At 5 V/s and considering the evaluated values of $\kappa_1$ and $k_1^{-1}$, this condition is achieved for $pH > 1$, in line with the observation of the monoelectronic waves described earlier (Figure 3a).

All parameters corresponding to the reaction scheme in figure 5, and their compacted version in figure 6 (valid at $pH < 7$) and in figure 9 (valid at $pH > 7$) have now been evaluated. Simulation of the whole CVs with the analytical expression (equation (8)) are shown in figure 10b for $pH = 1$ to 6. For $pH = 7$ to 9, numerical simulations were performed (see SI for details) according to the reaction scheme in figure 10. As shown in Figures 10 and S6, this single set of parameters allow to obtain a good agreement of the proposed model with the experiments performed over the whole range of $pH$ values. This is also true when catalysts concentrations and partial pressures of H₂ are varied as previously shown in figure 7. Importantly the data at $pH > 7$ illustrate the critical role of equilibrated proton transfers to exogenous acid/base couples to maintain efficient catalysis. The HOR turnover frequency is indeed partially limited by proton transfer in basic conditions.[27]
**Figure 10.** HER and HOR at 1 (black), 2 (red), 3 (blue), 4 (green), 5 (magenta), 6 (orange), 7 (cyan), 8 (light green), 9 (navy). \( \nu = 0.1 \text{ V/s}, [\text{Ni(P}_2\text{CyN}_2\text{Arg})_2]^{6+} 100\mu\text{M}, \text{under 1 atm H}_2. \) Comparison a) experiments and b) simulations. See text for details on simulations.

**Turnover frequencies, catalytic bias and reversibility.** We have shown that, at \( p\text{H} < 7 \), the critical chemical step for both HER and HOR is \( \text{H}_2 \) uptake and evolution. Chemical step \( \text{C}_2 \) is thus the one to be optimized to get a better catalyst. Indeed, the proton relay is responsible for the high local concentration allowing a very fast intramolecular proton transfer in chemical step \( \text{C}_1 \).

It also appears that the catalyst is catalytically biased,\textsuperscript{[28]} being much more efficient for HOR than HER at all \( p\text{H} \) values. The bidirectionality of the catalyst is made possible because the slowest process in both directions, \( \text{H}_2 \) uptake and evolution, is fast enough (respectively 10 s\textsuperscript{-1} at 1 atm \( \text{H}_2 \) and 0.5 s\textsuperscript{-1}) for a substantial current to flow at moderate scan rate. This study confirms that the presence of the proton relay installed inside the catalyst molecule close to its metallic active site, thus forming a frustrated Lewis pair to capture and activate \( \text{H}_2 \) during HOR and allowing for optimal hydride proton coupling during HER, is key for bidirectionality.

However, \( \text{H}_2 \) uptake and evolution steps are convoluted with proton transfers equilibrium constants between the proton relay and exogeneous acid or base that affect the solution concentration of the species able to react with or evolve \( \text{H}_2 \), as expressed by \( k_2^\ast \) and \( k_2^\ast \) (equation 7). Hence the \( p\text{H} \) variation of the apparent rate constants (figure 11) shows the effect of relays protonation/deprotonation on the kinetic of both HER and HOR catalysis. Because the intramolecular proton transfer is fast, the maximal turnover frequencies correspond to \( k_2^\ast \) and \( k_2^\ast \), as shown in reference \textsuperscript{[29]}:

\[
\text{TOF}_{\text{max}} \text{HER} = \frac{1}{1/k_1^\ast + 1/k_2^\ast} = k_2^\ast \tag{15}
\]

and

\[
\text{TOF}_{\text{max}} \text{HOR} = \frac{1}{1/k_1^\ast + 1/k_2^\ast} = k_2^\ast \tag{16}
\]
Figure 11. Apparent chemical rate constants and maximum turnover frequencies (log scale) as function of pH under 1 atm. H\textsubscript{2}: \(k^*_2\) (HOR, black), \(k^*-2\) (HER, red).

At low pH, H\textsubscript{2} uptake competes with the protonation of the relay in \(\text{Ni}^{\text{III}}\) leading to a small decrease of the catalytic HOR current. The same applies at high pH, but at the expense of catalytic HER current which is almost shut-down due to an unfavorable protonation of the relay preceding H\textsubscript{2} evolution. We note here that the pH variation of maximal turnover frequencies (Figure 11) and of plateau currents (Figure 8) are not identical because the plateau currents are also related to the size of the diffusion reaction layer that are pH dependent.\(^{29}\) Nonetheless, from equations 15 and 16 (or 9 and 10), the catalytic bias seems to be controlled by, and only by, the \(K_2\) value convoluted with protonation equilibria, which favors, in the present case, H\textsubscript{2} uptake over evolution. This is at variance with previous models, that were relating the catalytic bias to the positioning of the \(H^+/H_2\) equilibrium with the Pourbaix diagram of the catalytic system.\(^{30}\)

Besides bidirectionality, one remarkable feature of the present system is its reversibility. As discussed by Fourmond et al.,\(^{11}\) there is no need for every chemical step to be thermoneutral (equilibrium constant close to unity) to achieve reversibility. It is indeed illustrated experimentally by the present example (Figure 12). Despite the mismatch between the \(pK_a\) of the proton relay functionality (\(pK^H_{\text{II}} = 7.2\)) and the \(pK_a\) of the active site hydride (\(pK_{\text{H}, \text{Ni}} = 2.5\)) estimated from the value of \(pK_1 = 4.7\), the system is reversible over a large range of pH. Actually, this unbalanced equilibrium (\(\kappa_1 << 1\)) is compensated by the Pourbaix diagram corresponding to the second square scheme in figure 5 being ca. 250 mV more positive than that of the first square scheme (Figure 4), so that Eq. 5 is fulfilled with \(E_{\text{eq}} = 0\) V vs RHE. Such a positioning of the two Pourbaix diagrams correspond to the inverted configuration making the second PCET step always easier.
than the first one whatever the direction (HER or HOR) of catalysis. This configuration is the only one that allows for reversibility, with the limit being a superposition of the two Pourbaix diagrams. Noteworthy, this condition applies to the apparent $E^0_{\text{eq}}$ potentials values, taking into account the various protonation equilibria. Note that it is even not required for the two Pourbaix diagrams of the catalyst to overlap the Pourbaix diagram of the catalyzed reaction.

**Figure 12.** Energy landscape (in eV) at the equilibrium potential at a) pH = 0 b) and pH = 8. The free enthalpy barriers (dotted lines) were evaluated from the rate constants using as pre-exponential factor $k_B T / h = 6 \times 10^{12} \text{ s}^{-1}$).

An important finding is that large deviations from a flat energy landscape may still be detrimental to the rate of catalysis as observed here for $pH > 6$. The unbalanced energetics of chemical step $C_1$ compensates the large deviation of the second Pourbaix diagram from the equilibrium potential of the $H^+/H_2$ reaction (and vice-versa) (Figure 12b) but this has consequences on the reversibility of the system. Indeed, for catalysis to take place at small overpotential (i.e. with substantial current at potentials close to the equilibrium potential), an electron transfer must occur far away from its standard potential. This is illustrated in figure 12b where the driving force for the electron transfer $\text{Ni}^{II}/\text{Ni}^{III}$ has a driving force as large as 0.33 eV at $pH = 8$ (Note that the driving force is only 0.24 eV at $pH = 0$). This results in an apparent slowness of the electron transfer when this electron transfer is directly coupled to the energetically
unbalanced intramolecular proton transfer as it is the case in the dominant pathway at $pH > 7$. This effect does not modify the bidirectionality or the catalytic bias, i.e. the turnover frequencies, but it slows down the apparent reversibility corresponding to a sluggish increase of the current around the equilibrium potential.

**Conclusion**

We show here that a model based on elements from the first and second coordination spheres suffice to explain the reactivity of the system, with the outer sphere obviously playing a role to tune the properties of these elements so as to fulfill the conditions required to reach reversibility and maybe also preventing the system to follow other routes towards inactivation. The kinetic treatment developed here allows a satisfactory fit of the experimental data for reversible catalysis of the oxidation and production of dihydrogen to and from acids over a large range of $pH$ values, partial H$_2$ pressure and catalyst concentration.

The reversibility of catalysis appears from (i) unbalanced chemical steps thermodynamically compensating the deviation of the redox potentials of the catalyst from the equilibrium potential of the catalyzed reaction, (ii) fast intramolecular proton transfers due to concentration effects inherent to the presence of the installed amine group, acting here as proton relay and (iii) the relative efficiency of the reversible H$_2$ insertion step enabled by the frustrated Lewis pair formed by the pendant amine and the Ni center. The catalytic bias measuring the bidirectionality is directly impacted by local concentration effects allowed by the presence of proton relays integrated within the catalyst molecule close to its metal center and allowing for the capture and heterolytic splitting of H$_2$ and the effective and reversible formation and deprotonation of a nickel-hydride species. Importantly, we confirm here that reversibility does not required a flat energy landscape as previously advocated following the Sabatier principle. Nevertheless, our study shows that large deviations from a flat energy landscape requires interfacial electron transfers to occur far from their equilibrium potential, which impacts their kinetics and the overall rate of catalysis. At that point, the rate of catalysis may be limited by the efficiency of deprotonation/reprotonation of the relays, a concern that also holds for the design of improved monodirectional electrocatalysts.

The success of the described treatment in predicting correctly the experimental data is an encouraging benchmarking test of the general methodology consisting in identification of the key kinetically limiting processes. Indeed, the possibility of mastering such a profuse reaction mechanism rests on the distinction between the (generally) diffusion-controlled chemistry of the proton-coupled electron transfers that are involved the reaction and the “slower” chemistry involving the central metal and its coordination sphere, here hydrogen insertion and evolution.
We hope that the methodology developed here can inspire the study of other reversible molecular catalysts, for example in the context of water oxidation or CO$_2$ valorization.

**Experimental Section**

Experimental section is detailed in the Supporting Information together with additional cyclic voltammetry, UV-visible absorption data and numerical simulations.

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**Keywords:** Molecular Catalysis • Hydrogen evolution • Hydrogen oxidation • Electrochemical Reversibility • Proton relay

**References**


[12] Rinse test indicate that around 6 \(10^{-12}\) mol cm\(^{-2}\) remain chemisorbed at the surface of the electrode immediately after rinsing. In addition, their CV signal fully disappears within 10 min after soaking into the solution, indicating complete redissolution of the chemisorbed species.


[15] According to the Stokes-Einstein law the diffusion coefficient at 313 K is only 1.047 times larger than at 298 K.

[16] By “apparent standard potential” we means the thermodynamic potential in which all reactants are taken in standard state with the exception of the proton, whose state is defined by the value of the pH rather than be considered to be in its standard state.


[22] We cannot exclude here a contribution from the low amount of chemisorbed catalyst.
[27] Few remarks can be made. At pH = 7, simulations are not sensitive to the value of kp provided it is large enough, hence indicating that the proton transfer with the buffer is at equilibrium, in line with buffering capacity of MES at this pH. At pH 5 and 6, the simulated CV is steeper than the experiments (see figure S9). This may be attributed to some interference of the electron transfer kinetics of the square schemes not considered in equation 7.