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Determining the Overpotential for a Molecular Electrocatalyst

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1. INTRODUCTION

“The additional potential (beyond the thermodynamic requirement) needed to drive a reaction at a certain rate is called the *overpotential*.”[1]

Over the past decade, there has been considerable interest in the design and testing of molecular electrocatalysts for the interconversion of renewable energy and chemical fuels.[2−7] One of the primary motivations for such research is the replacement of expensive and rare precious metal catalysts, such as platinum, with less expensive, more abundant metals.[2,8−12] To become competitive with current electrocatalytic energy conversion technologies, new catalysts must be robust, fast, and energy-efficient. This last feature, the energy-efficiency, is dependent upon the overpotential. For molecular catalysts, the determination and reporting of overpotentials can be complicated by the frequent dependence on assumptions (pK_a scales, hydrogen electrode potential, the absence of ion pairing and homoconjugation), especially when working in nonaqueous solvents.[13] As overpotentials become lower, the relative error from these assumptions will get larger. Therefore, a meaningful comparison of reported overpotentials for molecular catalysts requires improved accuracy and precision. The intended purpose of this Viewpoint is to provide a clear and concise description of overpotential and recommendations for its determination in molecular electrocatalysis.

2. DEFINITION OF OVERPOTENTIAL

Overpotential is defined as the difference between the equilibrium potential for a given reaction (also called the thermodynamic potential) and the potential at which the catalyst operates at a specific current under specific conditions. Each of these potentials can change, and there are often inconsistencies in the determination of both. When a precise and accurate overpotential is desired, it is important to avoid pitfalls associated with the determination of each potential. Regardless of the precise mechanism by which the electrocatalytic process is occurring, the calculation of overpotential remains the same. Each potential is discussed separately in this section, highlighting the assumptions necessary for the determination of these values. For simplicity, we will use the proton reduction and hydrogen oxidation reaction (the H^+/H_2 couple) to illustrate the concepts necessary for the determination of overpotential (eq 1).

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad \text{overpotential} = |E_{H^+} - E_{cat/2}| \qquad (1)$$

2.1. Definition of the Potential for Catalysis.

With respect to calculating overpotentials of molecular catalysts, there is often confusion about the relationship between overpotential and catalytic rate. In heterogeneous catalysis, overpotential and catalytic current are often related through the Tafel equation.[1] This relationship results in an exponential increase in catalytic current with increasing overpotential. For molecular catalysts, the observed relationship is often different. A catalytic response for a molecular catalyst is usually triggered by a specific redox event, thereby transitioning from “off” to “on” over a relatively small potential range (Figure 1).

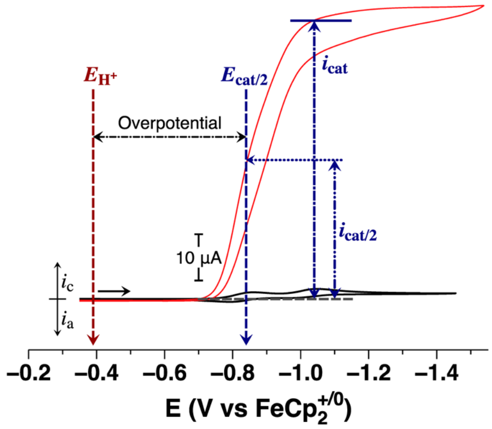

Figure 1. Experimental cyclic voltammogram illustrating determination of $E_{cat/2}$ (and overpotential) for H_2 production. Conditions: 1 mM $Ni(P^{Ph}{}_2N^{Ph}{}_2)_2(BF_4)_2$[14] in a 0.2 M NBu_4PF_6 solution in acetonitrile, 50 mV/s scan rate, 1 mm diameter glassy carbon electrode. The red trace was run in the presence of 0.26 M DMF and 0.26 M $[(DMF)H]^+$.

The potential at which a molecular catalyst operates can have numerous meanings, ranging from the onset potential (at the base of the catalytic wave) to the “peak” potential (potential at the maximum current). For an ideal molecular electrocatalyst (Figure 2), the value at half of the catalytic current used to determine the catalytic rate will result in a potential at or near the steepest point in the current vs potential trace. For this ideal catalytic wave, the choice of the catalytic current (i_{cat}) at any potential in the plateau region will result in the same i_{cat}, and therefore, the potential at half of i_{cat} will always have the same value. The determination of this point will have higher precision than the onset potential or peak potential.[13] As such, we recommend using the potential at $i_{cat/2}$ for the determination of the potential for catalysis, and we will refer to this potential as $E_{cat/2}$ (Figure 2). By using $E_{cat/2}$, the *catalytic potential* will be coupled with a specific *catalytic rate*, which is especially important for less-ideally behaved systems (Figure 3). For a nonideal catalytic wave, the use of $E_{cat/2}$ results in a smaller variance in potential for varying values of i_{cat}. An

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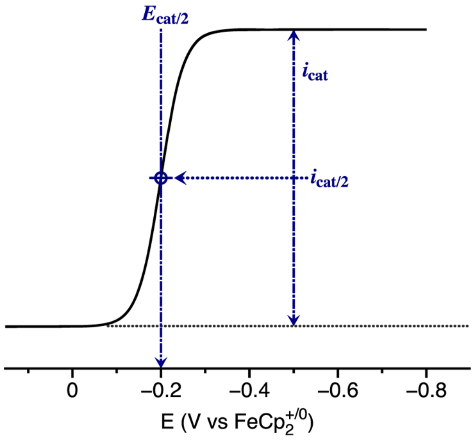

Figure 2. Simulated catalytic wave for a molecular catalyst, showing the selection of i_{cat}, $i_{cat/2}$, and $E_{cat/2}$.

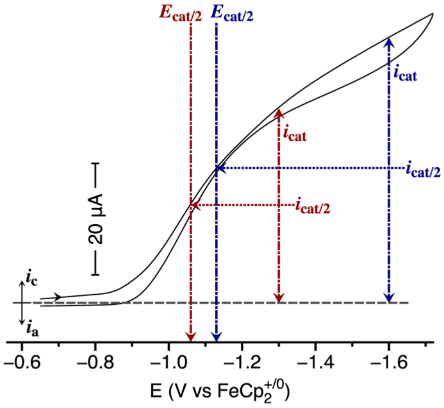

Figure 3. Experimental wave illustrating nonideal catalytic behavior,[15] showing two possible selections for i_{cat} and their corresponding $E_{cat/2}$ values.

example is illustrated in Figure 3 for two different choices of i_{cat} and the corresponding potentials. The difference in the potential at i_{cat} is 300 mV; the difference in $E_{cat/2}$ is only 70 mV.

2.2. Definition of the Equilibrium Potential.

The equilibrium potential for an electrochemical process is the thermodynamic potential at which a process occurs under specific conditions. In the case of H_2, this potential at standard conditions ($E^\circ_{H^+}$) is defined as zero for an aqueous solution with 1 M H^+ under 1 atm of H_2. For studies in which electrocatalytic production or oxidation of H_2 is carried out in aqueous solutions, the potential for the standard state hydrogen electrode can be used directly if the studies are performed under the same reaction conditions (1 M H^+ under 1 atm of H_2). As is often the case in laboratory research, the reaction conditions used to measure the performance of catalysts vary considerably from these standard state conditions. Whether operating at a different pH in an aqueous solution or in a different solvent, determining E_{H^+} under the specific operating conditions is essential for an accurate measure of the overpotential. Two methods are available for determining E_{H^+}: (1) calculating the potential based on the reaction conditions, including any needed approximations (section 2.2.1) or (2) directly measuring the equilibrium potential using an experimental method (section 2.2.2), such as an open circuit potential measurement.[16−19]

2.2.1. Calculating the Thermodynamic Potential for Proton Reduction.

When performing catalytic studies in aqueous solutions under nonsteady state conditions, the equilibrium potential for the reduction of protons (E_{H^+}) can be calculated as a function of the proton concentration and pressure of H_2 using the Nernst equation, as shown in eq 2. At 25 °C and one atmosphere of H_2, eq 2 can be simplified to eq 3, which expresses the equilibrium potential as a function of the standard state potential and the actual pH of the solution. As an example, the equilibrium potential for the reduction of protons at a pH of 7 under 1 atm of H_2 would be −0.41 mV (eq 4).

$$E_{H^+} = E^\circ_{H^+} + \frac{RT}{nF}\ln\frac{[H^+]}{P_{H_2}} \tag{2}$$

$$E_{H^+} = E^\circ_{H^+} - 0.05916\ \mathrm{V} \times \mathrm{pH} \tag{3}$$

$$E_{H^+} = 0\ \mathrm{V} - 0.05916\ \mathrm{V} \times 7.0 = -0.41\ \mathrm{V} \tag{4}$$

When working in any solvent other than water, two considerations are required: defining the equilibrium potential for the standard state H^+/H_2 couple ($E^\circ_{H^+}$) and correcting for the strength of the acid to calculate E_{H^+}, analogous to eqs 2−4. For many organic solvents, the potential for $E^\circ_{H^+}$ has not been determined. Acetonitrile is one of the few choices for which the equilibrium potential for proton reduction has been well-defined. Between 1965 and 2010, reports for this value in acetonitrile ranged between −0.034 and −0.260 V vs the ferrocenium/ferrocene couple ($FeCp_2^{+/0}$), which were determined in each case through different measurements and assumptions. Recently, Roberts and Bullock measured this value through open circuit potential measurements and determined it to be −0.028 ± 0.008 V vs $FeCp_2^{+/0}$.[19]

In addition to a reliable value for $E^\circ_{H^+}$, the correction for the strength of the acid to calculate E_{H^+} requires an established pK_a scale to adjust from $E^\circ_{H^+}$ under standard conditions (i.e., eq 2). A well-established pK_a scale exists for CH_3CN,[20,21] and, therefore, the calculation of E_{H^+} is straightforward, resulting in a more accurate potential by this method than in many other nonaqueous solvents. For example, the pK_a of protonated dimethylformamide, $[(DMF)H]^+$, in CH_3CN is known to be 6.1.[22] For a molecular H_2 production electrocatalyst using $[(DMF)H]^+$ as the proton source at 25 °C, the equilibrium potential (E_{H^+}) for the reduction of protons from a buffered 1:1 ratio of $[(DMF)H]^+$ and DMF under 1 atm of H_2 would be −0.39 mV vs $FeCp_2^{+/0}$ (eq 5), as determined on the basis of eq 3.

$$E_{H^+} = -0.028\ \mathrm{V} - 0.05916\ \mathrm{V} \times 6.1 = -0.39\ \mathrm{V} \tag{5}$$

When a reliable pK_a scale is not known or when homoconjugation of acid/base pairs is a known problem, the accuracy in the calculation of E_{H^+} is significantly decreased. As shown in Scheme 1, homoconjugation results in an increased driving force for deprotonation of an acid (and thereby effectively increased solution acidity) as a result of the depletion of the conjugate base through formation of the homoconjugated acid−base pair. As an example, trifluoroacetic acid has a relatively large homoconjugation constant ($10^{3.88}$ M^{-1})[22] in CH_3CN, and this results in an effective pK_a value of 4.4 for a 1 M solution of acid, compared with a pK_a of 12.7 for a 1:1 buffer of trifluoroacetic acid and trifluoroacetate. The difference in pK_a

Scheme 1

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

$$\mathrm{HA} + \mathrm{A^-} \rightleftharpoons [\mathrm{A{\cdots}HA}]^-$$

$$\mathrm{HA} + \mathrm{HA} \rightleftharpoons \mathrm{H^+} + [\mathrm{A{\cdots}HA}]^-$$

values in this case would produce a 490 mV difference in E_{H^+} between the acid only and buffered solutions. As a result, in organic solvents with acids where homoconjugation is known to exist, either appropriate corrections to the pK_a values must be made or the reaction must be carried out under buffered conditions to minimize the effects of homoconjugation upon the solution acidity. A recent report by Wiedner and Helm illustrates the substantial effect that homoconjugation can have upon electrocatalytic production of H_2 when using an acid that undergoes extensive homoconjugation.[23] We recommend avoiding acid/base pairs that undergo extensive homoconjugation (such as carboxylic acids and sulfonic acids along with their conjugate bases) whenever possible. Avoiding extensive homoconjugation will greatly improve the accuracy of the determined E_{H^+} when using the approach illustrated in eqs 2−4.

2.2.2. Experimentally Determining the Equilibrium Potential. In the case of H_2 production or oxidation, when either the equilibrium potential for the standard state H^+/H_2 couple ($E^\circ_{H^+}$) is not known for a particular solvent or a reliable pK_a scale is unavailable, the direct measurement of the equilibrium potential for the reduction of protons (E_{H^+}) can be accomplished through an open circuit measurement. As reported recently by Roberts and Bullock,[19] this method provides an accurate determination of the equilibrium potential for the H^+/H_2 couple under a wide range of acids and bases, as well as solvents or mixtures of solvents. For example, recent reports using this method have appeared in the literature for the determination of E_{H^+} of protic ionic liquids[24] and various acid/base pairs in both fluorobenzene[25] and acetonitrile/water mixtures.[26] The choice of solvents, acids, bases, and additives is very flexible, and values for $E^\circ_{H^+}$ and the pK_a for the relevant acid are not needed, making this a generally applicable technique.

2.3. Overpotential from E_{H^+} and $E_{cat/2}$. The accurate determination of overpotential requires an estimation of $E_{cat/2}$ and E_{H^+}, each of which can change, depending on the reaction conditions. The value for the potential for catalysis should be related to the catalytic current, and therefore, we recommend using $E_{cat/2}$. The equilibrium potential should be determined under the same conditions used for catalysis, either by calculating E_{H^+} on the basis of the $E^\circ_{H^+}$ and the pK_a value corresponding to the acid used or, if the latter two values are not known, by a direct measurement of the equilibrium potential using the open circuit potential method. An example overpotential calculation is shown in eq 6, on the basis of the conditions and data shown in Figure 1, and results in an overpotential of 0.45 V.

$$\begin{aligned}\text{overpotential} &= |E_{H^+} - E_{cat/2}| \\ &= (-0.028\text{ V} - 0.05916\text{ V} \times 6.1) - (-0.84\text{ V}) \qquad (6)\end{aligned}$$

3. PRACTICAL RECOMMENDATIONS FOR DETERMINING OVERPOTENTIAL

Rigorously determining accurate overpotentials can be a challenging and time-consuming task, but as catalysts both improve and increase in number, a reliable method for providing a meaningful comparison of catalysts is becoming increasingly important. Improving the precision of overpotential measurements between different research groups will allow for more systematic comparison of the performances for molecular electrocatalysts. To facilitate achieving this goal, we have the following recommendations for determining overpotentials.

3.1. Referencing Potentials in Nonaqueous Solvents. In addition to the specific recommendations for the determination of $E_{cat/2}$ and E_{H^+}, it is also important to recognize that in any solvent, it is essential to have a well-defined and well-behaved reference half-reaction. For nonaqueous solvents, the IUPAC standard is to use the ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) as an internal reference and to report the potentials versus this couple (defined at 0 V).[27,28] This approach avoids any errors resulting from junction potentials or assumptions about the corresponding free energies for transferring ions from one medium to another, a frequent issue when reporting the potential for nonaqueous electrochemistry versus aqueous reference electrodes such as SCE or SHE. To use eq 1, the potentials for both E_{H^+} and $E_{cat/2}$ must be known relative to the same reference half-reaction. In addition, if E_{H^+} is not known for a specific set of conditions, measuring and reporting $E_{cat/2}$ versus $FeCp_2^{+/0}$ allows the direct comparison for subsequent work without the introduction of errors and assumptions about the potential of aqueous electrodes in nonaqueous solvents.

3.2. Stabilizing Potentials through Buffering. For electrocatalytic oxidation or production of H_2, the solution composition at the electrode may vary significantly from that of the bulk solution. For example, in the electrocatalytic reduction of protons using a solution that contains only an acid, as soon as the catalyst begins to operate, its conjugate base is generated. As a result, the solution at the electrode transitions from an "infinitely unbuffered" state to a buffered state as soon as catalytic current is passed. Hence, measuring the equilibrium potential in the presence of only acid *or* only base will result in a larger error relative to using a buffered solution, as moving from these "infinitely unbuffered" conditions to the buffered conditions present under catalytic conditions will result in an appreciable difference in potential (for acid only versus a 1:1 buffered solution, the difference in E_{H^+} is ~200 mV[19] on the basis of open circuit potential measurements). When electrocatalytic studies are carried out with a buffered solution, the difference in the bulk conditions versus those present at the electrode during catalysis are minimized. To avoid this additional source of potential error, we recommend measuring catalytic performance under buffered conditions, such that a well-defined ratio of acid to base is used. By using a buffered solution, partial depletion of either species due to catalysis will result in a smaller change in the corresponding equilibrium potential. This improvement in accuracy is applicable either when using $E^\circ_{H^+}$ and the pK_a of the acid or when using a direct measurement of the equilibrium potential.

Although the simplest approach to buffering is to use a 1:1 ratio of acid to base, any ratio with a reasonable buffering capacity can be used. If the ratio is not 1:1, the equilibrium potential needs to correspond to the ratio of acid to base actually used. If the equilibrium potential is directly measured under the same conditions as those used for catalysis, then this difference will be incorporated into the measured E_{H^+} (Section 2.2.2). If the approach illustrated in Section 2.2.1 is used, eqs 2−4 would need to be modified to account for the actual ratio of acid to base used. Either approach is suitable.

3.3. Catalysis under Hydrogen. For any catalytic reaction, consideration of the influence of the products of the reaction is essential. Electrocatalytic studies for the reduction of H^+ should, in principle, be conducted in the presence of H_2; however, if the overpotential is large (>120 mV), the concentration of the product of the reaction is *unlikely* to influence catalysis. For this reason, we recommend testing catalysts for H^+ reduction in the presence of

H_2 if the overpotential is <200 mV to determine if either i_{cat} or $E_{cat/2}$ are affected. However, the direct measurement of the equilibrium potential, E_{H^+}, requires the presence of both the reactants and products. To measure E_{H^+}, the presence of H_2 is essential, and the use of a buffered solution (as discussed in SEction 3.2, above) provides the other reactants and products in a stable ratio.

4. SUMMARY AND CONCLUSIONS

An accurate and consistent determination of overpotentials for molecular electrocatalysts is important for comparing catalyst performance, both within and across catalyst families. For a meaningful comparison between different catalysts, the determination of overpotentials needs to be precise. We have attempted to provide guidance on how to accomplish this goal, especially for nonaqueous conditions. To summarize this Viewpoint:

1. Overpotential is the difference between the equilibrium potential and the catalytic potential.
2. We recommend defining the catalytic potential as being determined from the potential at half of the catalytic current, and therefore defined as $E_{cat/2}$
3. For the H^+/H_2 couple, the equiliubrium potential, E_{H^+}, can be either
   a. calculated from $E°_{H^+}$ and the pK_a of the acid, if available for the specific reaction conditions or
   b. directly measured using an open circuit potential measurement
4. To better define and stabilize E_{H^+} as well as minimize the effects of homoconjugation, a 1:1 buffer solution of acid and base is recommended
5. For H^+ reduction with overpotentials <200 mV, $E_{cat/2}$ should be measured under H_2

When these guidelines are followed, the determination of both the equilibrium potential and the potential for catalysis will yield a reasonable estimate of the overpotential for the catalytic process. Regardless of the particular method used to determine overpotential, it is essential for comparisons between different catalysts that the experimental conditions are stated and that the method for selecting points on the current versus potential trace is reported.

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Notes

The authors declare no competing financial interest.

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