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Hydrogen Production

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Electrochemical Hydrogen Production: Bridging Homogeneous and Heterogeneous Catalysis

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The hydrogen evolution reaction (HER), $2\,H^+ + 2\,e^- \rightarrow H_2$, is one of the most intensively studied and prototypical electrochemical reactions. Detailed discussions on the kinetics of the HER and its reverse reaction, the hydrogen oxidation reaction (HOR), have a long history.[1] With the increased interest in finding new and cheaper materials for the catalytic production of fuels, for which hydrogen is a prominent future candidate, the HER has regained the attention of the chemistry community. Although with platinum an excellent catalyst for both HER and HOR is available, the cost and scarcity of this material is believed to potentially hamper large-scale (photo-)electrochemical production of hydrogen. Inspired by the efficacy of naturally occurring enzymes, that is, hydrogenases, that catalyze both the HER and HOR with an activity comparable to platinum, inorganic chemists have put considerable effort in recent years into the development of coordination complexes that are molecularly similar to the active sites of Fe-Fe and Fe-Ni hydrogenases and into the study of these compounds' catalytic activity in the HER, mostly in non-aqueous solutions.[2] Simultaneous but largely independent efforts in heterogeneous electrocatalysis have recently also led to new metallic catalysts as well as to a better understanding of the origin of the overpotential in the HER/HOR.[3]

In a recent study, Le Goff et al.[4] report on a nickel phosphane compound that, when grafted onto carbon nanotubes, shows an unprecedented activity for the HER in acetonitrile, and most significantly, also in water. Inspired by the active sites of the hydrogenases, initial research efforts for new HER catalysts have been focused on FeFe and NiFe compounds. Whereas numerous NiFe complexes have been synthesized, their activities in HER/HOR have either not been investigated, or they proved to be unstable or unreactive.[2c] The use of FeFe complexes was more successful, and the first example of HER catalyzed by a dinuclear iron compound was reported by Rauchfuss and co-workers in 2001.[5] Since then, advances on the first model were achieved by substitution of the ligands. Especially the introduction of proton-accepting basic sites resulted in major improvements. Other approaches deviating from the actual hydrogenase modeling proved to result in more-successful HER catalysts, the two most interesting examples being the nickel phosphane compound **1**[2a] and a cobalt glyoxime system (**2**)[2b] (Figure 1 a). Intriguingly, both of these systems have now been shown to be highly efficient in HER as immobilized electrocatalysts. Adsorption of the cobalt system onto a glassy carbon electrode also yields an active electrocatalyst for HER in aqueous solution requiring only low overpotentials.[6] Both the cobalt and the nickel compound yield immobilized electrocatalysts showing high Faradaic yields (80–95 %), comparable current densities (1–2 mA cm^{-2}), and high stabilities with turnover numbers of (2–8) × 10^4 per hour. However,

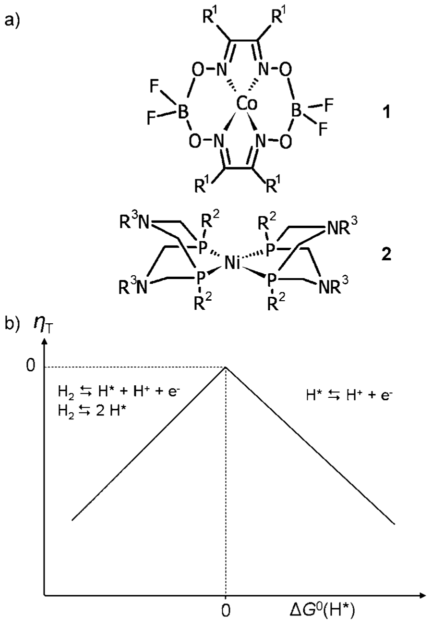

Figure 1. a) Structures of the hydrogen-producing electrocatalysts discussed herein. R^1 = Me; R^2 = Ph; R^3 = *p*-$C_6H_4CH_2C(O)O$-phthalimide. b) Plot of the thermodynamic overpotential versus the binding energy of H*. The potential-determining steps differ on either side of the apex of the optimal catalyst.

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a fully meaningful comparison between different catalysts in non-aqueous solvents and Pt in the HER in aqueous solution remains problematic as long as there appears to be no agreement in the literature on the correct conversion factors involved in the reference potential (for a discussion, see Ref. [7]). Moreover, estimating the overpotential for the HER in a non-aqueous solvent by using the NHE (aqueous) potential scale ignores the role of the solvent in the equilibrium potential of the HER/HOR in non-aqueous solvents.

It is interesting to discuss these results in terms of the recent progress made in the understanding of the origin of the overpotential in the HER. The essential principle of this theory was derived by Parsons in 1958[8] and follows from an older principle formulated by Sabatier.[9] The two-electron-transfer nature of the HER/HOR implies that the reaction should take place in at least two steps. In a first step, a proton reacts with an electron to form a catalyst-bound hydrogen intermediate H* [Eq. (1)]. On metal surfaces, H* is considered to be essentially uncharged, but for coordination complexes H* is often considered a hydride (H^-), in which case two electrons would have been transferred in the reaction in Equation (1), one of them derived from the metal ion, at least formally. In a next step, either two H* recombine to form H_2 ("homolytic bond making"), or another proton reacts with H* ("heterolytic bond making"), as shown in the reaction in Equation (2). If H* is a hydride, this step would be a heterolytic recombination reaction without (formal) electron transfer.

$$H^+ + e^- \rightleftharpoons H^* \qquad (1)$$

$$H^+ + H^* + e^- \rightleftharpoons H_2 \qquad (2)$$

Let us assume a mechanism consisting of the reactions in Equations (1) and (2); the conclusions to be derived below may be generalized to any two-step mechanism. The standard equilibrium potential E^0 for the overall HER/HOR is 0 V, by convention. From the binding energy of H* to the catalyst ($\Delta G(\mathrm{H}^*)$), the standard equilibrium potentials for the elementary steps in Equations (1) and (2) may be calculated [Eqs. (3) and (4); e_0: elemental charge].[10]

$$E^0{}_1 = -\Delta G(\mathrm{H}^*)/e_0 \qquad (3)$$

$$E^0{}_2 = \Delta G(\mathrm{H}^*)/e_0 \qquad (4)$$

Note that these expressions satisfy the thermodynamic constraint $(E^0{}_1 + E^0{}_2)/2 = E^0$. These equations illustrate the simple concept that if we develop a catalyst that binds H* more strongly, that is, one that makes the reaction in Equation (1) more thermodynamically favorable, we automatically pay the price by thermodynamically disfavoring the reaction in Equation (2). If, to a first-order approximation, we disregard the influence of the activation energy, then in this two-step mechanism the overpotential is determined by the step that is least thermodynamically favorable, that is, the one with the most negative standard equilibrium potential.[8] We refer to this overpotential as the thermodynamic overpotential and to this step as the potential-determining step. A plot of the thermodynamic overpotential versus $\Delta G(\mathrm{H}^*)$ (Figure 1 b) gives a "volcano plot", thus illustrating that a situation of zero thermodynamic overpotential can be achieved by having a catalyst with $\Delta G(\mathrm{H}^*) = 0$. This simple concept is an example of the Sabatier principle,[9] which states that the best catalyst binds the intermediate neither too strongly nor too weakly. The statement can be generalized to other multistep mechanisms of the HER/HOR by defining the best catalyst as the one that ensures that each step is thermodynamically neutral at the overall standard equilibrium potential, that is, that produces an energy landscape without a thermodynamic sink.

At first glance, ignoring the role of the activation barrier in multistep reactions appears as a crude approximation. However, if various catalysts are compared in the same solvent, the solvent contribution to the activation barriers is likely to be more or less constant. Moreover, changes in the activation barrier are often directly related to a change in the thermodynamic driving force of an elementary step (i.e., the H* binding energy) through the Brønsted–Evans–Polanyi (BEP) relationship between activation energy and reaction energy.[10b] The idea that $\Delta G(\mathrm{H}^*) = 0$ for a good catalyst has been demonstrated experimentally for solid bimetallic catalysts in the work of Kibler et al.[11] and Greeley et al.[3a]

The groups of Dubois[2a] and Gray[2b] have recently pointed out the importance of the thermodynamics of H binding to the active site for the HER by molecular complexes, thus suggesting that the simple concept outlined in Figure 1 b should also work for molecular catalysts, even if they have an inherently more varied and complex chemical environment than solid surfaces. In simple terms, the best catalyst is the one that binds H* just as strongly as hydrogen is bonded in the H_2 molecule. It has been shown recently that if the DFT-calculated interaction energies for H binding to a model Fe-Ni hydrogenase are properly rescaled, the resulting $\Delta G(\mathrm{H}^*)$ is close to zero,[10c] as it should be for a good HER catalyst. Therefore, it would be expected that the Ni-based catalyst reported by Le Goff et al.[4] conforms to this rule. The rather significant effect of the solvent, which is more or less a side result in the paper by Le Goff et al., therefore stands out as an interesting fundamental puzzle that has received attention in the coordination chemistry community but has been largely ignored by the electrocatalysis community.

The idea that the best catalyst for a multistep reaction is the one that produces an energy landscape without a thermodynamic sink can be generalized to reactions that involve more than two steps and more than one intermediate. There is a caveat here, however. As soon as more than one intermediate needs to be optimized energetically, finding the optimal catalyst with zero thermodynamic overpotential becomes significantly less trivial, as binding energies of related intermediates can usually not be varied independently.[10b,c] This issue appears to be the fundamental reason why catalyzing the four-electron transfer reaction between water and oxygen, that is, water splitting and oxygen reduction, is a significantly harder nut to crack than catalyzing the HER/HOR. This important catalytic challenge will require the combined and concerted efforts of the homogeneous and heterogeneous catalysis communities. We hope that the concepts and developments briefly outlined in this Highlight, but discussed in detail in the cited literature, may help to bridge these two primary fields of catalysis.

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