Electrocatalysis of the HER in acid and alkaline media

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Abstract: Trends in the HER were studied on selected metals (M = Cu, Ag, Au, Pt, Ru, Ir and Ti) in acid and alkaline environments. It was found that with the exception of Pt, Ir and Au, due to high coverage by spectator species on non-noble metal catalysts, the experimentally established positions of Cu, Ag, Ru and Ti in the observed volcano relations are still uncertain. It was also found that while the M–H_{upd} binding energy most likely controls the activity trends in acidic solutions, the trends in activity in alkaline solutions are controlled by a delicate balance between two descriptors: the M–H_{ad} interaction and the energetics required to dissociate water molecules. The importance of the second descriptor was confirmed by introducing bifunctional catalysts such as M modified by Ni(OH); *e.g.*, while the latter serves to enhance the catalytic decomposition of water, the metal sites are required for collecting and recombining the produced hydrogen intermediates.

Keywords: volcano plot; HER; hydrogen evolution reaction; acid; alkaline.

INTRODUCTION

Electrocatalysis lies at the heart of a spectrum of chemical transformations that occur at electrochemical interfaces. In the near future, it will be the key driving force for technological innovations that are urgently needed to address the delivery of reliable, affordable, and environmentally friendly energy. There is no rigorous definition of the term "electrocatalysis", but in the broadest sense, it is the study of electrode reactions where the kinetics have a strong dependence on the nature of the electrode material.[1] Not surprisingly, virtually every electrochemical reaction in which chemical bonds are made or formed is electrocatalytic, and the kinetics varies by many orders of magnitude for different electrode materials. This is true even for the simplest electrochemical reaction in which chemical bonds are broken,[2] such as the hydrogen evolution reaction (HER), which, for decades, has served as a model reaction for probing how the

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nature of the electrode material (and/or structure of the double layer[3–6]) may affect electrochemical transformation of protons (acid electrolytes) or water (basic electrolytes) into molecular hydrogen ($2H^+$ $[2H_2O]$ + $2e^-$ ⇆ H_2 + $[2OH^-]$).[7–9] Traditionally, the mechanism of the HER is assumed to proceed by an initial formation of hydrogen intermediates (denoted hereafter as H_{ad}) which, depending on the pH of solution, are formed *via* charge-induced discharge of protons or water (H^+ $[H_2O]$ + e^- ⇆ H_{ad} [+ OH^-]). This, so-called Volmer step, is then followed either by either a Tafel chemical recombination step ($2H_{ad}$ ⇆ H_2) or by the transfer of a second electron in a Heyrovsky step (H^+ $[H_2O]$ + H_{ad} + e^- ⇆ H_2 + + [+ OH^-]).[8]

Analytical, experimental, and computation analyses of this reaction have, for the most part, been closely tied to the concept of the volcano plot. In electrocatalysis, such plots, which generally express the rate of an electrocatalytic reaction as a function of more fundamental properties of the catalyst, known as descriptors, date to the early HER rate expressions derived by Parsons[10] and Gerischer.[11] Parsons and Gerischer used of the hydrogen adsorption free energy (determined by the strength of adsorption of H_{ad} on the catalyst surface) as a descriptor for the trends in HER rates on different catalysts. This early analytical volcano was followed by experimentally derived volcanoes, developed by Trasatti[9] and extending the earlier work of Krishtalik,[12] in which the measured rates were correlated with measurements of the surface work function and the bulk heats of hydride formation. More recently, a combination of fundamental surface rate modeling, similar to the techniques employed by Parsons, with atom-specific free energy data obtained from Density Functional Theory calculations, have permitted the development of HER volcanoes in terms of descriptors (metal–hydrogen bonding) that may be rapidly calculated on both metals and metal alloys.[13–19] It should be noted that some authors, however, have identified some challenges in generating such volcano plots from experimental results, particularly when dealing with metals that are likely to form oxides or hydrides under HER conditions.[15] Given that the intrinsic activity of metal catalysts in alkaline medium are ≈2–3 orders of magnitude lower than in acid solutions, the question arises as to what type of relationships between activity in the HER and the nature of electrode material might be expect at high pH values. This has been addressed recently in several published papers[3,20,21] and will be summarized in the remaining part of this paper.

EXPERIMENTAL

The Pt, Ru, Ir, Au, Ag and Cu electrodes were prepared by radio frequency (RF) annealing at ≈800–1100 °C in a 3 % H_2–Ar gas mixture, while the Ti electrode was polished and chemically cleaned. The samples were transferred into an electrochemical cell (made from Teflon) with the surface protected with a drop of DI water and immersed under potential control at 0.05 V *vs.* the reversible hydrogen electrode (RHE) in 0.1 M KOH and 0.1 M

$HClO_4$. $Ni(OH)_2$-modified metal electrodes (*ca*. 30–40 % coverage) were prepared by chemical deposition, wherein, the pristine metal electrodes were immersed and equilibrated in 0.01–0.1 M $NiCl_2$ solutions for 2–12 h. For assessing the HER activity, a sweep rate of 50 mV s^{-1} was employed, while the rotation rate was 1600 rpm. Only the first negative going HER scan was used for activity determination, where the current densities were obtained based on the geometric surface area. Experiments were controlled using an Autolab PGSTAT 302N potentiostat with IR compensation. The used gases were of research grade (5N) Ar.

RESULTS AND DISCUSSIONS

HER activities in acid electrolytes

As in the past, Fig. 1 shows that if activities for the HER of the coinage metals (IB metals: Au, Cu, Ag), the platinum group (or PGM: Pt, Ir, Ru) metals and the valve metal (Ti) in 0.1M $HClO_4$, are plotted as a function of the M–H_{ad} binding energy (the M–H_{ad} binding energy values were taken from the literature[9]), a volcano relationship is established with Ir and Pt at the apex of the volcano curve. Further analysis of Fig. 1 reveals that the IB group elements are positioned on the ascending slope of the volcano with order in activity increasing from Au < Cu < Ag, which is different from the order predicted by DFT (Cu > > Au > Ag). The exact cause of this discrepancy is currently unknown, but considering that Cu is "less noble" than Au and Ag, it is reasonable to assume that the experimentally measured activity of Cu could be influenced by adsorbed spectator species, which may affect the availability of active sites required for adsorption of the hydrogen active intermediates. Fig. 1 also shows that the ele-
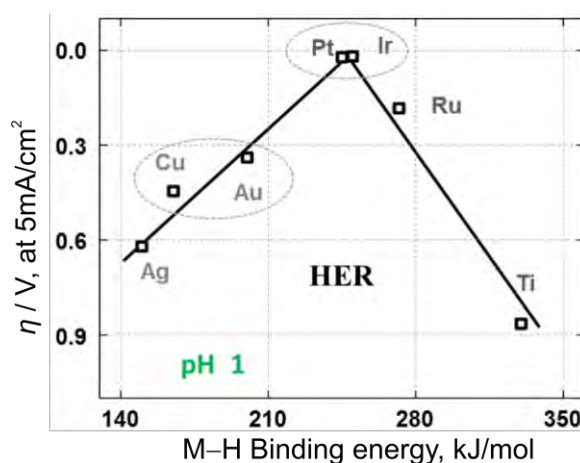

Fig. 1. A volcano plot, measured in 0.1 M $HClO_4$ (pH 1), of several metals denoting their HER activity, overpotential (η) at 5 mA cm^{-2}, as a function of their calculated M–H binding energy. At the apex of the plot are the noble metals Pt and Ir, which have nearly identical activities, while on either side are metals that either bind hydrogen too weakly (Ag) or too strongly (Ti). Note that the order of activity of the coinage metals is Au > Cu > Ag, which follows the trend in the M–H binding energies.

ments that interact strongly with H_{ad} (such as Ru and Ti) are positioned on the descending slope of the volcano, supporting previous suggestions that the M–H_{ad} binding energy can be used as a descriptor for the HER. Not in passing, given that recent analysis has demonstrated that neither Ru nor Ti are bare metals in the HER region, it is suggested that, in fact, experimentally it is very difficult (impossible) to determine unambiguously solely based on the metal–H_{ad} energetics what would be the correct position of these two elements in the observed volcano relationship. This is most likely also true for the HER in alkaline solutions, when the rates of the reaction are much slower than in acidic environments. Interestingly, with one recent exception,[20] there are no fundamental studies that have focused on deriving relationships between the nature of metals and activity of the HER at high pH values. Furthermore, there are still debates as to why the rate of the HER is 2 to 3 orders of magnitude lower at pH 13 than at pH 1 and why the reaction is sensitive to the structure of surface atoms in alkaline media but largely insensitive in acidic environments.[22–24] Finally, the question arises as to whether the HER on metal surfaces in alkaline solutions can approach the activity at low pH values. In the next two sections, focus is first directed on the differences and similarities between the volcano-type relationships in alkaline and acidic environments and, then, this knowledge is used to demonstrate that it is indeed possible to improve the activities of the HER at high pH values, simply by controlling the rates of the water dissociation step, *i.e.*, the Volmer step.

HER activities in alkaline electrolytes

Although the HER exhibits a volcano-like behavior in alkaline solutions (Fig. 2), there are three notable differences with change in pH: *i*) the activities in alkaline solutions are lower than in acid solutions (in line with previous observation that intrinsic activity of metal catalysts in alkaline medium are ≈2–3 orders of magnitude lower than in acid solutions); *ii*) significantly, in contrast to acid solutions, in alkaline solution Ir is more active than Pt (>55 mV), indicating that there might be substantial difference in the reaction mechanisms between the HER at low and high pH values; *iii*) the trend in the activity between IB group metals in alkaline solution increases from Ag < Au < Cu, an order of activity that is different from the one observed in acidic environments (Ag < Cu < Au). Clearly, these features cannot be explained solely based on the free energy of hydrogen adsorption since this descriptor should be independent of the pH of the solution. In previous reports,[3,20,21] it was argued that the main difference between the HER in acid and alkaline electrolytes lies in the source of the hydrogen; while in acid solution, active intermediates are formed from protons, in alkaline solutions an additional activation process involving the dissociation of water is required to generate the H_{ad}. It was recently shown that this is an important difference and that evolution of H_2 from H_2O in alkaline solutions requires
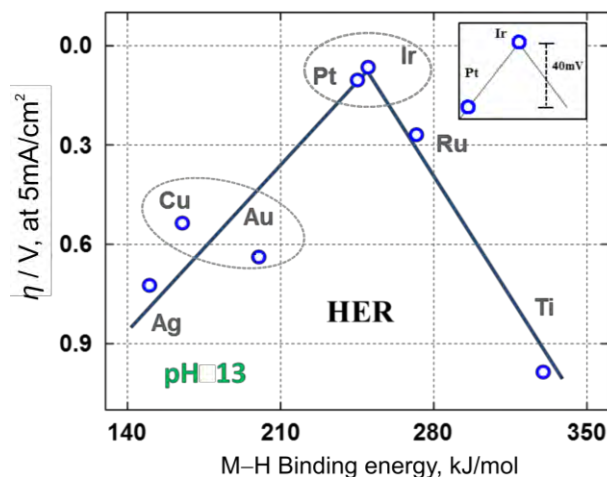
Fig. 2. A volcano plot, measured in 0.1 M KOH (pH 13), of several metals denoting their HER activity, overpotential (η) at 5 mA cm^{-2}, as a function of their calculated M–H binding energy. At the apex of the plot are noble metals Pt and Ir, while on either side are metals that either bind hydrogen too weakly (Ag) or too strongly (Ti). Note the distinctions between the volcano plot in acid electrolytes. The order of activity of the coinage metals is Cu > Au > Ag, which no longer follows the trend in their M–H binding energy and the difference in overpotential between Ir and Pt is significantly larger (≈55–60 mV) compared to acid electrolyte values (≈1–5 mV).

materials that are equally effective for water dissociation as well as H_{ad} recombination steps. In line with literature data,[20] it was concluded that Cu is more active for the HER in alkaline solution than Au because the former is a more effective water dissociation catalyst; hence, in alkaline solutions, Cu provides a higher rate for generation of hydrogen intermediates from water. The differences observed between Pt and Ir surfaces could be explained in a similar way. Considering that there is no difference in the energetics for the Tafel step on Pt and Ir (the same activities are observed in acid solutions), the higher activity of Ir compared to Pt in alkaline solution can only be due to improved dissociation of water on the Ir surface. Therefore, in order to construct the activity trends of the HER in alkaline solutions, two rather than one descriptor has to be taken into account; namely, synergy between the energy required to dissociate the water molecules (M–water energetics) and adsorption/recombination of hydrogen intermediates (M–H_{ad} energetics).

HER activities on metals modified with a "water dissociation catalyst" in alkaline electrolytes

In order to confirm the importance of both the descriptors in a complex transformation of H_2O to H_2 in alkaline solution, the metal electrodes were modi-

fied by Ni(OH)$_2$ clusters, which are known to be extremely active in the water dissociation step.[3] Thus, the activity curves in Fig. 3a and b for such modified systems were compared with the activities for the bare (unmodified) surfaces in the corresponding alkaline and acid environments. A close inspection of Fig. 3 unambiguously reveals that the activities for the Ni(OH)$_2$–M surfaces in alkaline
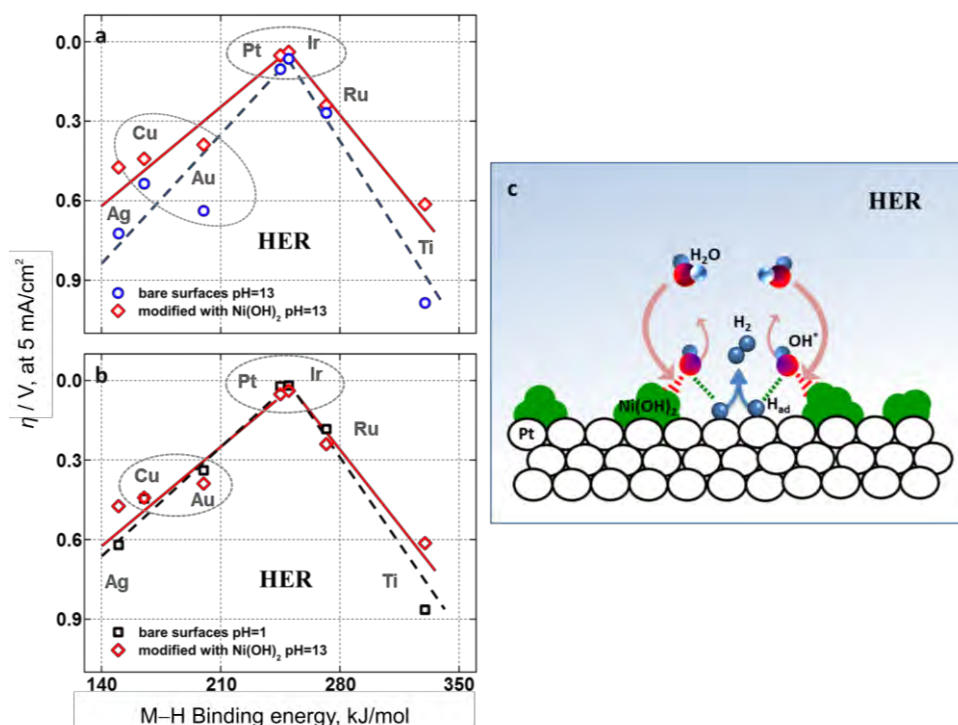

Fig. 3. a) Two volcano plots are overlaid, both measured in 0.1 M KOH (pH 13). One shows the HER activity of bare unmodified metals, while the second was measured on Ni(OH)$_2$--modified metal surfaces. Note that the HER is activated by the presence of Ni(OH)$_2$ on all of the bare metal surfaces. Furthermore, on the Ni(OH)$_2$-modified surfaces, the activities for Pt and Ir are nearly identical, and the trend of the coinage metals follows the trend in their M–H binding energies, Au > Cu > Ag. b) Two volcano plots are overlaid, in one the HER was measured in 0.1 M HClO$_4$ (pH 1) on bare metal surfaces while the other is constructed from HER activities measured in 0.1 M KOH (pH 13) on Ni(OH)$_2$-modified metal surfaces. The activities and positions of the elements are nearly identical suggesting that the elimination of the role of the water dissociation step in alkaline HER is the only way to validate the use of M–H binding energies as alkaline HER catalyst descriptors. c) A 2-D representation of the proposed model for the metal solution interface within the HER potential region of the metal surface covered by amorphous Ni(OH)$_2$ clusters. The HER is promoted by the presence of the Ni(OH)$_2$ clusters as they act as the "active" sites for water dissociation (OH* product removal and re-adsorption of H$_2$O), the resulting H$_{ad}$ species originating from the clusters recombine on metal sites to form H$_2$ (Tafel step).

solutions approach the activities in acid solution for the pure metals, *i.e.*, Pt = Ir and Au > Cu > Ag. Based on these result, it is proposed that the rate of proton production from water is significantly enhanced on the Ni(OH)–M surfaces in alkaline environments so that the rate of the overall reaction is again affected predominantly by the M–H_{ad} binding energy, as is the case for acidic solutions. It should be remembered, however, that the M–H_{ad} energies alone cannot serve as the physicochemical descriptor for the HER on metal surfaces in alkaline environments. In other words, the *sine qua non* for the HER in alkaline medium is clearly a synergy between the effectiveness of the catalyst to break water molecules (predominantly on more oxophilic sites, such as defects or hydroxyoxides) and to efficiently collect and recombine hydrogen intermediates on more noble metal sites. Based on this supposition, it is reasonable to suggest that in alkaline solutions, the more defected Pt(110) is more active than the more "perfect" Pt(111) simply because the rate of the HER is proportional to the density of surface defect sites. Along the same lines, metals covered by Ni(OH)$_2$ are more active than bare M surfaces because in a bifunctional mechanism, the edges of Ni(OH)$_2$ clusters promote the dissociation of water while the produced intermediates are adsorbed and recombined on M sites (Fig. 3).

CONCLUSIONS

It is proposed that: *i*) due to coverage by spectator species, even in the HER potential region, it is still questionable if it would be possible to establish experimentally a true relationships between M–H_{ad} energetics and catalytic activity – therefore, with the exception of Pt, Ir and Au, the experimentally established positions of the other metal catalysts in the observed volcano relations are uncertain over the entire pH range; *ii*) while in acidic solutions the M–H_{upd} binding energy controls the activity trends (supported by DFT calculations), the trends in activity in alkaline solutions are controlled by a delicate balance between two descriptors: the M–H_{ad} interaction as well as the energetics required to dissociate water molecules; *iii*) the importance of the second descriptor was confirmed by the introduction of bifunctional catalysts, such as M modified by Ni(OH); *e.g.*, while the latter serves to enhance catalytic decomposition of water, the metal sites are required for the collection and recombination of the produced hydrogen intermediates.

И З В О Д

ЕЛЕКТРОКАТАЛИЗА РЕАКЦИЈЕ ИЗДВАЈАЊА ВОДОНИКА У КИСЕЛОЈ И АЛКАЛНОЈ СРЕДИНИ

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Проучавани су трендови реакције издвајања водоника (HER) у киселој и алкалној срединини на одабраним металима (M: Cu, Ag, Au, Pt, Ru, Ir и Ti). Нађено је да су, са изузетком Pt, Ir и Au због високог степена покривености неактивним адсорбованим врстама позиције Cu, Ag, Ru и Ti на експериментално одређеним "вулканским" кривама још увек непоуздане. Такође је утврђено да су трендови активности у алкалној средини одређени осетљивим билансом два дескриптора: интеракције M–H_{ad} и енергије потребне за дисоцијацију молекула воде, док у киселој средини трендове активности највероватније одређује енергија везе M–H_{upd}. Значај енергије дисоцијације воде је потврђен уводјењем би-функционалног катализатора као што је M модификован Ni(OH). Док Ni(OH) каталитички убрзава декомпозицију воде, метал је неопходан за груписање и рекомбинацију насталих водоничних интермедијара.

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