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Enhancing the Alkaline Hydrogen Evolution Reaction Activity through the Bifunctionality of $Ni(OH)_2$/Metal Catalysts**

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The hydrogen evolution reaction (HER) plays a key role in a number of technologically important areas such as water and chlor-alkali electrolysis,[1] metal deposition,[2] corrosion,[3] and fuel production from CO_2 reduction.[4] The HER is also of fundamental importance, serving for decades as a model reaction for exploration of the relationship between the electrode material and the kinetic rates of electrochemical transformation of protons (acid) or water (alkaline) into molecular hydrogen ($2H^+[2H_2O] + 2e^- \rightleftarrows H_2 + [2OH^-]$).[5] Traditionally, the mechanism of the HER is usually assumed to proceed by an initial formation of hydrogen intermediates (denoted hereafter as H_{ad}) which, depending on the pH value of solutions, is formed by an electron-transfer step through the discharge of protons or water ($H^+[H_2O] + e^- \rightleftarrows H_{ad}$-$[+OH^-]$). This, so-called Volmer step, is then followed either by the Tafel chemical recombination step ($2H_{ad} \rightleftarrows H_2$) or by a second electron transfer through the Heyrovsky step ($H^+[H_2O] + H_{ad} + e^- \rightleftarrows H_2[+OH^-]$). Although the reaction pathways are similar because of the activated water dissociation step the HER activities for most catalysts in alkaline medium are usually about two to three orders of magnitude lower than in acid solutions.[5b,6] This recognition initiated development of the $Ni(OH)_2$/Pt catalysts for which, in a bifunctional mode of action, the edges of $Ni(OH)_2$ promote the dissociation of water and the production of hydrogen intermediates that then adsorb on nearby Pt sites and recombine into molecular hydrogen.[15] However, one key question still remains open; can this method be successfully applied to design active, cost-effective catalysts for the HER in alkaline solutions. So far, the conventional alkaline water electrolyzers use high-surface-area Raney Ni and Ni alloys,[5e,7] materials that are cheaper but not active enough, thus providing a significant scope for improving the reaction kinetics at the cathode.

Here, we demonstrate that the HER on a Ni electrode modified by $Ni(OH)_2$ nanoclusters is about four times higher than on bare Ni surfaces, thereby providing a means to enhance the activity of cost-effective catalysts for alkaline electrolyzers. To emphasize the importance of the bifunctional mechanism, we also report the results for the HER on IB group (Group 11) metals (M = Cu, Ag, Au) as well for the Pt group (Group 10) metals (M = Ru, Ir, Pt) and transition metals (3d TMs = Ni, V, Ti) modified by $Ni(OH)_2$. Rather than attempting to present the data in a volcano-like fashion for this multifaceted (and often esoteric) area, the overall emphasis here is on providing a straightforward analysis of the underlying physical concepts and the experimental insights on the activity trends along the periodic table for the alkaline HER. These will be further supported by drawing comparisons with the corresponding acid HER activities.

For decades, practical design of metal catalysts for the HER in acidic media has been based on the well-known concept of volcano plots,[8] which is generally used to express the relationship between the rate of the HER and some of the physicochemical properties (descriptors) of metals such as, for example, the hydrogen adsorption energies,[9] bulk heats of metal-hydride formation,[10] and the metal work function.[11] With rare exceptions,[11b] a classical volcano-shaped correlation is found from both experimental results[11a] as well as computational approaches[9b,c,12] with metals that adsorb hydrogen neither strongly nor weakly (the Pt group metals) occupying the apex of the volcano curve. While the metals that adsorb hydrogen strongly (Ru and 3d elements) are positioned on the descending part of the volcano plot, the IB group metals which exhibit a weak M–H_{ad} interaction are found on the ascending part. In contrast to the computationally derived volcano plots on "ideal" metal surfaces, however, one might anticipate that either because of metal-hydride formation during the HER (e.g., Pd, 3d TMs) and/or the presence of hydroxides/oxides on many metals even in the HER potential region (e.g., Ru, 3d TMs) it is very difficult (if not impossible) to establish, solely based on experimental results, the true relationship between rates of the HER and the metal surfaces. In fact, only Pt, Ir, and Au (and to some extent Cu and Ag) may be considered as metals in the HER potential region. Consequently, experimentally derived volcano plots could easily be "contaminated" with adsorption of "spectators"[13] such as, for example, anions and oxygenated species. Furthermore, because the rates of the HER on Pt and Ir in acidic environments are facile, it is plausible that the HER activities measured in this case are dominated by the concentration overpotential instead of kinetics. In the following, therefore, analysis of the experimental results for the

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HER in acid and alkaline solutions will not be tied to the concept of the volcano plot (notice, the results when plotted using the conventional approach form "volcano trends", as shown in the Supporting Information). As summarized in Figure 1, variations of HER activities in acid and alkaline environments will simply be expressed as the measured overpotential (η) at a constant current density (I). For clarity, results will be clustered into three groups; IB group metals, Pt group metals, and 3d TMs (for more details see the Method Section in the Supporting Information and the figure captions). We will also avoid any rigorous kinetic analysis of the HER in acid and alkaline solutions in the present discussion. Tafel slopes provided in the Supporting Information are merely for comparison purposes.

In acid environments (Figure 1), three distinct relationships are noteworthy: 1) while there is no difference in the activities between Pt and Ir (presumably because of similar metal-H_{ad} energetics), Ru is the least active either because of a strong Ru-H_{ad} interaction and/or the presence of oxygenated species even in the HER potential region;[14] 2) for the IB group elements, the activity trends increase in the order Au > Ag > Cu, signaling that the HER activities may increase in the same order as the hydrogen adsorption energy on the IB group metals;[9b,c,12] 3) considering that in electrochemical environments all of the 3d TM elements are covered by oxides/hydroxides (with unknown stoichiometries) in varying degrees, the observed trends (Ni > V > Ti) may or may not correspond to the M-H_{ad} energetics. For the latter systems, given that there are no available in situ methods capable of resolving the exact nature of the surface atoms of 3d TM elements in the HER potential regions (e.g. as pointed out in the Supporting Information, the Ni surface is at least partially covered with oxide species), at this moment it is not possible to propose any correlation between the rate of the HER and the M–H bonding, thereby validating why we refrain from using the traditional volcano-type plots here.

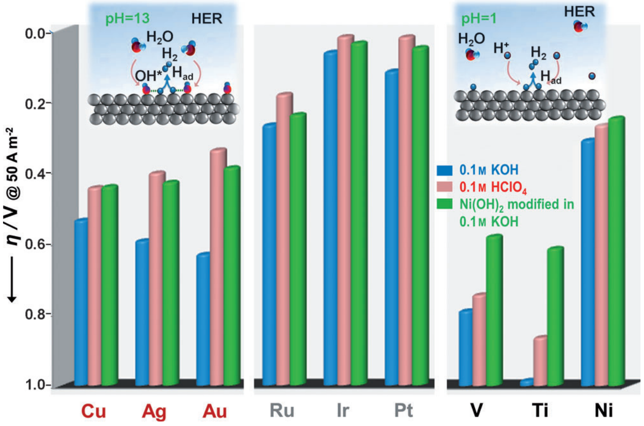

Figure 1. a) Comparison between activities for the HER, expressed as overpotential (η) required for a 5 mA cm^{-2} current density, in 0.1 M $HClO_4$ and 0.1 M KOH for both bare metal surfaces and $Ni(OH)_2$-modified surfaces. Metals are grouped into three distinct groups, the IB group (Cu, Ag, Au), the Pt group (Pt, Ir, Ru), and the 3d transition elements (V, Ti, Ni). We refrain from using the volcano plot form because of the ambiguity related to the exact nature of the "metal" surface, especially for the non-noble metals. As inset, 2D representations of the mechanism for the transformation of protons (pH 1) and water (pH 13) into H_2. The IB group exhibits opposite trends in acid versus alkaline solutions. Pt group metals show no discernible differences in acid solution between Ir and Pt, but a much larger potential difference in alkaline solution. These differences are found to disappear when we compare the trends between acid and $Ni(OH)_2$/M surfaces in alkaline solution, confirming the role of the water dissociation step. No clear understanding is possible for 3d transition metals because of the poorly defined surface properties of such materials, which are often covered with "oxide" species. However, given that the HER activity is enhanced for all these metals with the introduction of $Ni(OH)_2$, it is clear that the oxide species are important for the water dissociation step and relevant for the HER.

As pointed out earlier,[15] catalytic activity of the HER at high pH values can be simultaneously controlled by the M-H_{ad} bond strength as well as by the energy required to dissociate water into H and OH^-. From Figure 1 we conclude that: 1) the activities in alkaline solutions are significantly lower than in acid solutions, consistent with the observed inferior activities of the HER in alkaline solution; 2) unlike in acidic media, in alkaline solutions the activity increases in the order Ir > Pt > Ru (see also the polarization curves in the Supporting Information), suggesting that for a similar energy of hydrogen adsorption on Pt and Ir, the rate of the Volmer step is enhanced on more oxophilic Ir; 3) also, the activity trend for the IB metals is inverse to that found in acids (Cu > Ag > Au), signaling that the rate of reaction may be controlled by the dissociation energy of water rather than by the adsorption energy of hydrogen; and 4) the order of activity of the 3d elements is the same as in acidic environments, confirming that the nature as well as the coverage by surface oxides may be more important than the energy required for the water dissociation step. Based on these observations and keeping in mind that the M-H_{ad} binding energy should be pH independent,[13,16] we suggest that the rate of the water dissociation step must provide an important contribution to the observed pH variations in activity trends. Consequently, then, for the catalysts with comparable M-H_{ad} energetics, improving the water dissociation step can improve the alkaline HER activities.

Recently, the electrocatalytic trend for the HER has been established on 3d $TM(OH)_2$/Pt pseudo monofunctional catalysts[15a] with $Ni(OH)_2$/Pt having the highest activity. Here, we aim to transform the bifunctionality of $Ni(OH)_2$/3d TM to a pseudo monofunctional type of catalysts, which is dependent on the substrate–H_{ad} interaction, akin to the acid HER. As shown in Figure 1, the $Ni(OH)_2$/M surfaces are always more active (about 3–5 fold) than on the corresponding bare substrates. In turn, this suggests that, the edges of $Ni(OH)_2$ clusters do promote the dissociation of water and the generated hydrogen is "collected" and recombined on the substrate sites at a rate similar to that in acid solutions. On the basis of this, one should expect that reactivity trends on $Ni(OH)_2$/M catalysts should be very similar to those observed in acidic solutions. Indeed, the trends for the HER on IB metals established in acid solution are re-established in alkaline solutions on surfaces modified by $Ni(OH)_2$ (Au > Cu > Ag), implying that the rates are controlled again by the M-H_{ad} energetics. Furthermore, there is no discernible difference in activity between $Ni(OH)_2$/Pt and $Ni(OH)_2$/Ir, indicating that, as in acid solution, the HER is almost completely controlled by a similar hydrogen adsorption energy on these two surfaces. Although the relative coverages of the $Ni(OH)_2$ clusters is expected to be different between the elements within the same group (depending on, e.g., oxophilicity and metal sites available), our objective here is to show the phenomenological changes brought about by the introduction of such clusters (very little dependence on the coverage expected at sufficient low current densities) and not to quantify activities for the corresponding HER. Finally, the overpotentials for the HER on $Ni(OH)_2$/3d TMs are significantly smaller, depending on the nature of 3d TM elements, ranging from 0.2 to 0.5 V. Given that the nature of 3d TM elements during the HER is unknown (see above), it is not straightforward to propose a model that explains the improved activity on the $Ni(OH)_2$/3d TM surfaces. At this point, however, it is reasonable to propose that $Ni(OH)_2$ serves to enhance the water dissociation step (it does this on IB group metals and Pt group metals) and its ability is superior to that of the native oxide species present on the 3d TM surfaces. The presence of $Ni(OH)_2$ on these 3d TM systems was confirmed by analyzing X-ray absorption spectra (XAS) for the $Ni(OH)_2$/V system (for details see Figure S9). To determine the presence of the oxide species on the Ni electrode, ex situ X-ray photoelectron spectroscopy (XPS) analysis was performed. These results reveal two chemical states; the metallic state at 852 eV ($2p^{3/2}$) and 869 eV ($2p^{1/2}$) and the oxide state characterized by the binding energy of 855 eV ($2p^{3/2}$) (see the Supporting Information for more details). Although XPS methods are not surface sensitive they show that on the Ni electrode there are some metal sites that, in turn, may serve to "collect" and recombine the hydrogen atoms produced from the water dissociation step on $Ni(OH)_2$ through a similar bifunctional mechanism.

Finally, to emphasize the importance of tailoring the active sites for the HER in alkaline solutions, we present the results for $Ni(OH)_2$/M (M = Cu, Ag, and Ni); all three metals are low-cost alternatives to Pt-group metals. Ag and Cu have unique advantages because of the relatively low affinity towards formation of hydrides over long-term operations, whereas Ni offers the highest activity. Importantly, the results for the HER on Ag, Cu, and Ni modified by $Ni(OH)_2$ (Figure 2) reveal that the activities of these surfaces nearly match those in acid solutions on unmodified electrodes. Furthermore, the activity of $Ni(OH)_2$/Ni is enhanced by a factor of four versus the $Ni(OH)_2$-free Ni surfaces, confirming that the nature of the oxide species on the surface is critical. To our knowledge, this is the first report displaying that for some hydroxide-modified "metal" surfaces the HER can be made even more active in alkaline solutions than in acid environments. This is particularly relevant for Ni, Ni alloys, and Raney Ni, which are used as commercial catalysts in alkaline environments. We believe that extending our bifunctional approach to such systems will, in turn, help further towards bridging the gap between noble and non-noble HER "metal" catalysts, especially with the possibility of using a higher loading of non-noble materials. We conclude, therefore, the indispensable condition for the HER in alkaline medium is a synergy between the effectiveness of the catalyst to break water molecules and to efficiently form hydrogen that subsequently can be adsorbed and associated on metal surfaces.

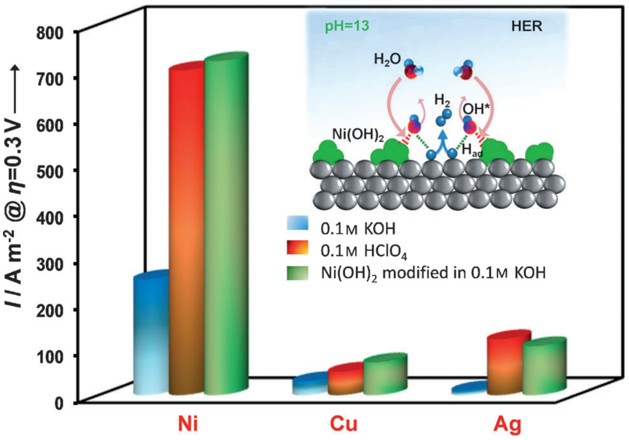

Figure 2. Activity enhancement achieved by the introduction of bifunctionality through $Ni(OH)_2$ addition to the surface of metal M. Ni, Ag, and Cu are shown here for comparison. Ni for being the most active, whereas Ag and Cu offer the unique advantage of low costs and low affinities towards the formation of hydrides, which have been known to decrease the activities for the HER. Activities were measured from the first polarization scan, and the current densities at $\eta = 0.3$ V are plotted.

Experimental Section

Chemicals: Alkaline solutions were prepared from respective alkali salts (Multipharm, Sigma Aldrich, JT Baker, and Alfa Aesar), perchloric acid from concentrated $HClO_4$ (Sigma Aldrich), and Milli-Q deionized (DI) water. Pt, Ru, Ir, Au, Ag, Cu, and Ti metal electrodes were of 4N purity and had a diameter of 6 mm.

Pristine electrode preparation: The electrodes were prepared by radiofrequency (RF) annealing at about 1100 °C (Pt, Ru, Ir), about 800 °C (Au, Ag, Cu), in a 3 % H_2–Ar gas mixture for 7 minutes. Ti was polished and de-oxidized in strong acid prior to testing. The samples were transferred into the electrochemical cell with the surface protected with a drop of DI water and immersed under potential control at 0.05 V versus the reversible hydrogen electrode (RHE).

Oxide-modified electrodes: $Ni(OH)_2$-modified electrodes were prepared by chemical deposition, whereby the pristine electrode samples were immersed and equilibrated in 0.01–0.1 M $NiCl_2$ (Sigma Aldrich) solutions for 4–12 h, and washed thoroughly before being introduced into the electrolyte. The procedure, which was found to provide the desired oxide coverage, was used for all the materials. The time for the final oxide coverage was achieved by observing no change in both the HER activities (and in some cases the voltammetries, see the Supporting Information). Determination of the exact coverage of the oxides is very difficult for most of the systems considered here. For Pt, and to some extent Ir, it can be determined from the suppression of the under potentially deposited hydrogen (H_{upd}) as shown in the Supporting Information. As we move to more oxophilic systems, for example, Ru, such determinations are extremely difficult because of the relatively large pseudo capacitance exhibited by the metal substrates as well as the lack of clearly defined regions for hydrogen or OH adsorption. Typical coverages of 30–40 % were obtained based on the H_{upd} of the modified surface of Pt and Ir compared with that of the bare surfaces. Coverages on the surface of other elements are hard to detect electrochemically. Preliminary XPS measurements reveal coverages ranging between 30–50%. No attempt was made to control the coverages because of the lack of well-defined geometry or surface "chemistry". It is important to note that in this work, our main focus was to demonstrate the applicability of bifunctionality to enhance the HER activity of the material considered by introducing $Ni(OH)_2$. Therefore, we have not performed any optimizations of the catalyst design here nor did we perform any comparison of the activity trends across the different groups of metals.

Electrochemical measurements: A typical three-electrode Fluoroethylene polymer (FEP) cell was used to avoid contamination from glass components, for the ring disc electrode (RDE) measurements. An Ag/AgCl reference (−0.96 V vs. RHE) was used for electrochemical measurements. The counter electrodes used were Au (Au, Ag and Ti), Cu (for Cu), and Pt (Pt, Ru, Ir). The sweep rates used in the cyclic voltammetry (CV) experiments were $50\,mV\,s^{-1}$, whereas the rotation rate was 1600 rpm. For the hydrogen oxidation reaction (HOR) and HER experiments the potential was swept in the cathodic direction from the hold potential. The data presented is taken from first sweep curves. Ohmic compensations were applied for all the data reported here. Experiments were controlled using an Autolab PGSTAT 302N potentiostat. The gases used were research grade (5N) Ar and H_2. The HER measurements were also performed at different scan rates ($50\,mV\,s^{-1}$, $20\,mV\,s^{-1}$, and $5\,mV\,s^{-1}$) with little change in the activity values reported. Also, rotating ring disc electrode (RRDE) measurements were performed for various systems to quantify the HER currents. For the ring electrode, with a collection efficiency of 21%, the currents from the ring and disc electrodes confirmed that all the currents measured were mainly from the hydrogen evolution reaction and the contributions from other side reactions were negligible.

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[1] a) J. Moorhouse, *Modern Chlor-Alkali Technology*, *Vol. 8*, Wiley-Blackwell, Oxford, **2001**; b) K. Zeng, D. Zhang, *Prog. Energy Combust. Sci.* **2010**, *36*, 307–326.

[2] S. S. Djokic, *Electrodeposition: Theory and Practice*, Springer, **2010**.

[3] R. W. Revie, *Uhlig's corrosion handbook*, *Vol. 57*, Wiley, Hoboken, **2011**.

[4] H. Gasteiger, A. Lamm, W. Vielstich, *Handbook of Fuel Cells: Fundamentals, Technology, Applications. Fuel Cell Technology and Application*, *Part 7*, Wiley, Chichester, **2003**.

[5] a) W. Sheng, H. A. Gasteiger, Y. Shao-Horn, *J. Electrochem. Soc.* **2010**, *157*, B1529–B1529; b) T. J. Schmidt, P. N. Ross, *J. Electroanal. Chem.* **2002**, *524*, 252–260; c) D. Miousse, A. Lasia, *J. New Mater. Electrochem. Syst.* **1999**, *2*, 71–78; d) N. M. Marković, S. T. Sarraf, H. A. Gasteiger, P. N. Ross, *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3719–3725; e) P. Los, A. Rami, A. Lasia, *J. Appl. Electrochem.* **1993**, *23*, 135–140; f) Q. Han, K. Liu, J. Chen, X. Wei, *Int. J. Hydrogen Energy* **2003**, *28*, 1345–1352.

[6] a) N. M. Marković, B. N. Grgur, P. N. Ross, *J. Phys. Chem. B* **1997**, *101*, 5405–5413; b) B. E. Conway, B. V. Tilak, *Electrochim. Acta* **2002**, *47*, 3571–3594; c) B. E. Conway, J. Barber, S. Morin, *Electrochim. Acta* **1998**, *44*, 1109–1125.

[7] a) A. Lasia, *Handbook of fuel cells: Fundamentals, technology and applications*, *Vol. 2*, Wiley, Chichester, **2003**, pp. 416–416; b) L. Birry, A. Lasia, *J. Appl. Electrochem.* **2004**, *34*, 735–749.

[8] A. A. Balandin, *Adv. Catal.* **1969**, *19*, 1–210.

[9] a) R. Parsons, *Trans. Faraday Soc.* **1958**, *54*, 1053–1063; b) J. Greeley, J. K. Nørskov, L. A. Kibler, A. M. El Aziz, D. M. Kolb, *ChemPhysChem* **2006**, *7*, 1032–1035; c) W. Schmickler, E. Santos, *Interfacial Electrochemistry*, Springer, Berlin, **2010**, pp. 163–175.

[10] L. I. Krishtalik, *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *130*, 9–21.

[11] a) S. Trasatti, *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *39*, 163–184; b) O. A. Petrii, G. A. Tsirlina, *Electrochim. Acta* **1994**, *39*, 1739–1747.

[12] a) J. Greeley, J. K. Nørskov, L. A. Kibler, A. M. El-Aziz, D. M. Kolb, *ChemPhysChem* **2006**, *7*, 1032–1035; b) E. Santos, P. Hindelang, P. Quaino, E. N. Schulz, G. Soldano, W. Schmickler, *ChemPhysChem* **2011**, *12*, 2274–2279; c) E. Santos, A. Lundin, K. Pötting, P. Quaino, W. Schmickler, *Phys. Rev. B* **2009**, *79*, 235436–235436.

[13] N. M. Marković, P. N. Ross, Jr., *Surf. Sci. Rep.* **2002**, *45*, 117–229.

[14] J. X. Wang, N. S. Marinković, H. Zajonz, B. M. Ocko, R. R. Adžić, *J. Phys. Chem. B* **2001**, *105*, 2809–2814.

[15] a) R. Subbaraman, D. Tripkovic, K. C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan, J. P. Greeley, V. R. Stamenkovic, N. M. Markovic, *Nat. Mater.* **2012**, *11*, 550–557; b) R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic, N. M. Markovic, *Science* **2011**, *334*, 1256–1260.

[16] N. M. Marković, T. J. Schmidt, B. N. Grgur, H. A. Gasteiger, R. J. Behm, P. N. Ross, *J. Phys. Chem. B* **1999**, *103*, 8568–8577.