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# Hydrogen-evolution-reaction kinetics pH dependence: Is it covered?

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**Writing in *Joule*, Surendranath and coworkers report intrinsic hydrogen-evolution-reaction activity and kinetic parameters for Pt and Au electrodes using "innocent" buffers that don't substantially affect electrode kinetics. A pH- and potential-dependent coverage of metal-H species is proposed to modulate apparent activity, findings that are important for a range of electrochemical technologies.**

The hydrogen evolution reaction (HER), i.e., the reduction of water or protons to H<sub>2</sub>, occurs at the cathode during key electrolytic processes that convert molecules like H<sub>2</sub>O, CO<sub>2</sub>, and N<sub>2</sub> to fuels, fertilizer, and organic building blocks. These technologies operate over a range of pH values. Water electrolyzers produce green H<sub>2</sub>, allowing for storage of intermittent renewable electricity that can be used as an energy-dense and stable chemical fuel to replace fossil fuels in transport and aviation and for long-duration energy storage.<sup>1</sup> Water electrolyzers operate in acidic or alkaline environments. Although HER is fast on noble metals like Pt in acid, it is much slower in alkaline media.<sup>2</sup> For emerging CO<sub>2</sub>- and N<sub>2</sub>-reduction technologies, the HER occurs at similar potentials and thus represents a parasitic loss of faradic efficiency.<sup>3</sup> Optimizing or mitigating HER activity is inhibited by an incomplete understanding of the experimentally observed pH dependence of the HER.

There are multiple explanations for the pH-dependent activity of the HER. It is often argued that the HER activity is controlled by the hydrogen binding energy (HBE). The peak potential associated with desorption of underpotentially deposited hydrogen (H<sub>UPD</sub>) shifts positively with increasing pH on Pt-

group metals,<sup>4</sup> which has been interpreted as an increase in HBE with pH and thus decreased activity. Despite the intuitive appeal of the HBE descriptor, it was not clear fundamentally why HBE would be pH dependent or even that it is itself an appropriate activity descriptor. Further, the HBE fails to explain observations such as the apparent changes in H<sub>UPD</sub> potential with pH to Pt(110) and Pt(100) but not Pt(111), even though all show the decreases in HER activity with pH.<sup>5</sup> Koper proposed a descriptor related to the solvent structure near the electrode during HER and argued that the activity of HER on metals like Pt is pH dependent due to pH-dependent surface charge. When the Pt potential is close to its point of zero formal charge (pzfc), as in acidic conditions, the structure of interfacial water is fluid and unstructured, but in alkaline conditions, far from the metal's pzfc, interfacial water is less fluid and strongly oriented. Consequently, there is a larger solvent reorganization penalty for charge transfer across the structured water layer in alkaline conditions.<sup>5</sup>

Peterson further challenged HBE as a sole descriptor for HER kinetics based on computation of kinetic barrier heights.<sup>6</sup> Koper also found a volcano-type relation between alkaline HER ac-

tivity and hydroxide-adsorption energy for adatom-decorated Pt. The right branch of the volcano consisted of catalysts with hydroxide binding energy that was too weak, and activity was therefore limited by the rate of formation of adsorbed hydrogen via water dissociation, whereas the those on the left branch were limited by slow hydroxide desorption.<sup>7</sup> Koper also reported that adsorbed cations can accelerate the rate-determining Volmer step by favorably interacting with the dissociating water molecule (\*H-OH<sup>δ-</sup>-cat<sup>+</sup>).<sup>8</sup> These studies are consistent with related work from Markovic<sup>9</sup> showing how bifunctional catalysts consisting of metal surfaces and metal oxide or hydroxide absorbates, that have been shown to active for water dissociation in bipolar membranes,<sup>10</sup> can speed the alkaline HER. Although these studies are compelling for qualitatively explaining how HER can be accelerated by facilitating water dissociation, they don't provide a clean mechanistic description that explains the full range of pH-dependent activity.

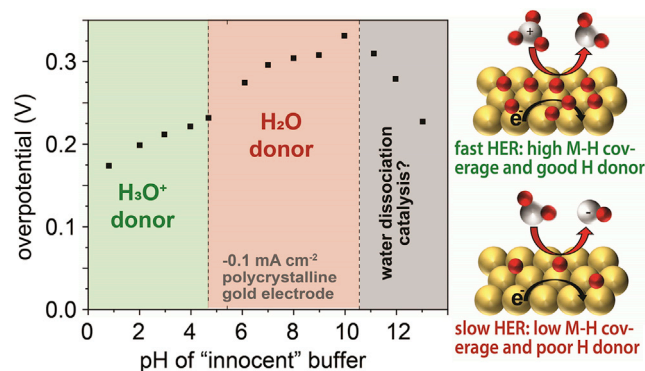
One challenge in understanding the pH dependence of the HER is the inability to use a single electrolyte across the entire pH range. If unbuffered electrolytes are used, pH gradients develop and convolute measurements. If buffers are used, the buffer species can interact with the surface in ways not easy to account for. These complications can obscure actual reaction pathways. Now writing in *Joule*, Jung et al. report clean, intrinsic (i.e., purely activation-controlled) HER activity as a function of pH on Pt and Au substrates.<sup>11</sup> This is achieved by identifying "HER-innocent" buffers that do not significantly affect the HER rate as demonstrated

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**Figure 1. pH dependence of the HER in innocent buffers that prevent transport-related pH gradients but don't substantially affect HER kinetics**

The trend is largely explained by two factors, the facility of the hydronium versus water as a proton donor, and the variable metal hydride (M-H) coverage with pH/potential. The increasing activity in strong base might be due to additional species, like cations or unintentional deposits, catalyzing water dissociation.

through reaction-order studies and by ensuring fast mass transport. They discover fractional reaction orders in hydronium for Pt and Au across a wide pH range. This experimental result could be explained in microkinetic models only by relaxing the typical assumption of extremely low or high coverage of metal hydride (M-H) on the electrode surface. The model is also consistent with the qualitative notion that HER activity is inhibited in alkaline conditions by the slow kinetics of proton donation from water as opposed to hydronium.

Specifically, the authors found that the measured overpotential required to pass a constant current increases in a non-trivial manner with pH (Figure 1). On Au, at  $-0.1 \text{ mA cm}^{-2}$ , the overpotential increases by  $\sim 10\text{--}15 \text{ mV/pH-unit}$  between pH  $\sim 1\text{--}4$  and between  $\sim 6\text{--}11$ . Between pH 4 and 6 there is larger jump of  $\sim 20\text{--}30 \text{ mV/pH-unit}$ . Between pH 10 and 13 the trend reverses, and the overpotential goes down by  $\sim 30 \text{ mV/pH-unit}$ . Although not discussed substantially in this report, this is perhaps due to cations or other adsorbed metal species accelerating the Volmer (water dissociation) step. The data on Pt is similar, except there is less improvement in overpotential at high pH.

Mechanistic models of HER typically consist of three possible steps: Volmer (absorption of H onto the M surface), Heyrovsky (reaction of proton donor in solution with M-H to form  $\text{H}_2$ ), and Tafel (the reaction of two M-H to form  $\text{H}_2$ ). Usually, it is thought that one of these steps is rate determining, which is equivalent to the assumption that the coverage of H on the catalyst surface is either very low (if the Volmer step is rate determining) or very high (if the Heyrovsky or Tafel step is rate determining). However, none of these models can fit the experimental data that show a fractional reaction order of  $[\text{H}_3\text{O}^+]$  in the rate law (0.3 and 1) depending on pH range. Therefore, the authors proposed intermediate M-H coverage  $\theta$  during HER. When  $\theta$  changes substantially with pH and potential as a function of the measured current, fractional reaction orders emerge, consistent with the experimental data. The Tafel slope also varies with the coverage term  $\theta$ , which suggests that a "Tafel-only" analysis of HER mechanism can be misleading, mechanistically.

The new results here are of fundamental importance: mechanistic insights aid in an improved understanding of the basic elements of electrode kinetics and enable the development of design rules for improving technology. Many elec-

trochemical processes require M-H species as intermediates, including for reduction of  $\text{CO}_2$  and  $\text{N}_2$  and other electrochemical processes. Controlling the surface coverage in such applications is critical; too much M-H, and the faradic efficiency will decrease as the M-H recombine to make  $\text{H}_2$  instead of the desired product. Too little M-H, and the desired reduced product production rate, for example methanol from  $\text{CO}_2$ , will be slowed. In this way, it is quite useful to have a core understanding of the coverage dependence of M-H on different metals and for different pH and electrolyte conditions.

The authors' new results also generally align with the findings of others; the decrease in HER activity as pH increases appears largely due to slower proton-coupled electron transfer from  $\text{H}_2\text{O}$  versus  $\text{H}_3\text{O}^+$ , with the new insight of how the M-H coverage can also be pH and potential dependent and thus lead to unexpected fractional reaction orders in  $\text{H}_3\text{O}^+$ . Broadly, these ideas illustrate the importance of electrolyte design for electrocatalytic fuels synthesis through controlling the ability of water to act as a proton donor (e.g., using water dissociation catalysts or even perhaps "suppressors"<sup>9,10</sup> in neutral-to-basic pH while also modulating the M-H coverage based on the buffering species used.

In the context of the fundamental electrode kinetics, one limitation of the author's model is that it only considers coverage of "kinetically competent" adsorbed M-H. Other literature has pointed to the prominent role for adsorbed hydroxide and the hydroxide binding strength.<sup>7</sup> Further experimental, microkinetic modeling, and computational work would be needed to parse the number of sites populated by hydroxide and hydrogen atoms at relevant pH and how these populations change among different metals. The complexity of even the simplest electrochemical reaction, the HER,

illustrates the depth of the challenge in developing truly predictive and mechanistically rigorous electrochemical models for interfacial coupled electron-ion transfer that underly technologically important devices.

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### DECLARATION OF INTERESTS

The authors declare no competing interests.

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## Magnetic-field-promoted photocatalytic overall water-splitting systems

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**In the current issue of *Energy and Environmental Science*, Wu et al. reported a superparamagnetic photocatalytic overall water splitting (POWS) system promoted by local magnetic field. An unprecedented solar-to-hydrogen (STH) conversion efficiency of 11.9% ± 0.5% is achieved, exceeding the 10% goal proposed by the United States Department of Energy.**

Photocatalytic overall water splitting (POWS) into H<sub>2</sub> and O<sub>2</sub> is expected to be able to produce green energy for future sustainable development.<sup>1-3</sup> Although great efforts have been made, the solar-to-hydrogen (STH) conversion efficiency is still hindered due to fast recombination of photogenerated carriers. As we all know, compared with the intrinsic driving force of the photocatalyst itself, the one generated by external field can inject more energy into photocatalytic reaction and greatly

promote the separation of photogenerated carriers.<sup>4</sup> Magnetic field has attracted much attention, because even if the Zeeman energy caused by the magnetic field is several orders of magnitude lower than the band gap of semiconductors, it is still beneficial for promoting photocatalysis via other pathways.<sup>5</sup>

In a recent issue of *Energy and Environmental Science*, Wu and coworkers reported an Au-supported Fe<sub>3</sub>O<sub>4</sub>/

N-TiO<sub>2</sub> POWS system promoted by local magnetic field effects.<sup>6</sup> In detail, placing N-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) in proximity to superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles under an external magnetic field, a strong local magnetic flux can be induced, leading to an extremely high H<sub>2</sub> evolution rate (21.2 mmol g<sup>-1</sup> h<sup>-1</sup>), quantum efficiency (88.7% at 437 nm), and STH efficiency (11.9% ± 0.5%). The considerably enhanced POWS activity can be mainly attributed to the magnetically induced Lorentz

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