

INORGANIC ADDITIVES for HER INHIBITION IN AQUEOUS BATTERIES

Tyler Farnsworth, PhD
Head of Technical and Product Development

1. What is HER?

The Hydrogen Evolution Reaction, or HER, describes the generation of hydrogen gas when water is reduced during a process known as electrochemical splitting, or *electrolysis*. The oxygen evolution reaction (OER) is a parallel process at higher potentials that oxidizes water to create oxygen gas. The HER mechanism is perhaps best known for its role in the production of hydrogen fuel via “water splitting” for zero-emission fuel cells.

2. Challenges of HER for Aqueous Batteries

The electrolysis of water presents a natural limit to the effective output voltage of aqueous batteries, with a stable voltage window spanning 1.23 V, outside of which the water will decompose into its hydrogen and oxygen components. This stability window is pH-dependent (see Figure 1), with HER occurring at more negative, or reducing, potentials (voltages) and OER occurring at the more positive, or oxidizing, potentials. The value of 1.23 V is thermodynamically derived and represents a rather narrow electrochemical window within which the battery’s anodic (oxidation) and cathodic (reduction) chemical processes can occur.

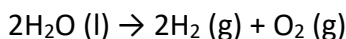
Aqueous batteries are plagued by HER during the charging cycle. Because water is reduced at a (relatively) small reducing potential (-0.828 V), hydrogen evolution is a direct competitor to the metal reduction (or plating) occurring at the battery anode. This competition reduces the available active sites on the electrode, limiting the efficiency of e^- transfer to adsorbed cations and thereby hindering the reduction process that reforms metal at the electrode surface.

Going beyond the efficiency challenges, the generation of flammable hydrogen gas from HER at the anode presents a serious safety concern in a closed battery cell. Mechanical methods of removing (venting) or adsorbing hydrogen gas are possible, but do not address the key challenge of HER: **the Hydrogen Evolution Reaction fundamentally limits the output voltage of water-based batteries**. Mitigating HER would extend the stability window of water to deeper reducing potentials, effectively widening water’s narrow voltage window and unlocking higher output voltages for aqueous-based batteries. Greater output voltages would position aqueous electrolytes as a viable alternative to lithium-ion batteries, presenting a non-flammable, lower cost solution for both home- and grid-scale energy storage.

MERGE Chemistry offers specialized additives, known as **HER Inhibitors**, to mitigate hydrogen generation and extend the stability window of water. Combined with the full electrolyte, additive, and stabilizer (EAS) package, MERGE’s HER Inhibitors unleash the full potential of water-based energy storage systems to achieve higher voltages, improved efficiencies, and increased safety.

3. Water electrolysis & H₂ evolution

At the core of hydrogen evolution is the breakdown, or splitting, of water under an applied voltage, known as **electrolysis**. It is important to first understand the mechanistic chemistry behind the water splitting and formation of hydrogen gas molecules in order to create methods to counteract it. Water electrolysis occurs when water is adsorbed to an electrode surface and undergoes an e⁻ transfer (reduction process) to form a chemical intermediate (H⁺, OH⁻, etc.). The intermediate then undergoes subsequent reaction(s) to generate hydrogen or oxygen gas. The simple reaction to describe the electrolysis is:



Focusing on HER, hydrogen gas generation is described by a one-intermediate, 2-electron reaction mechanism. At a potential of 0 V vs. SHE (standard hydrogen electrode), water is reduced and “split” to form hydrogen atoms, which can then combine to form hydrogen gas. The reaction mechanism is pH-dependent, as described below.

In an **acidic environment**, the first step of hydrogen evolution follows the Volmer mechanism:



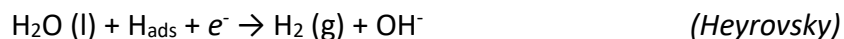
where a free hydrogen from the acid matrix (H⁺) interacts with an electron provided by the electrode and is adsorbed onto the surface. The adsorbed hydrogen (H_{ads}) then either reacts with another H_{ads} (Tafel mechanism) or with a free hydrogen from the acid matrix (Heyrovsky mechanism) to generate H₂ gas:



or



In an **alkaline environment**, the water is the reactant for both the Volmer (first step) and Heyrovsky (second step) mechanisms:



These mechanism(s) of hydrogen evolution can be used to develop methods and materials to prevent the formation of hydrogen-forming intermediates that otherwise would lead to hydrogen gas generation.

4. MERGE HER Inhibitors

Aqueous battery electrolytes are complex, and there is, unfortunately, no one-size-fits-all approach to selecting an additive(s) to prevent hydrogen gas generation. MERGE Chemistry works with our customers to supply HER Inhibitors that are individually tailored to the electrolyte matrix. The additives act as kinetic disruptors of hydrogen evolution by taking up active sites on the metal electrode and interrupting the formation of hydrogen intermediates.

Table 1 showcases a sampling of HER Inhibitors that are offered by MERGE Chemistry. While higher -log*i*₀ values tend to be more powerful HER Inhibitors, the practical effectiveness is dependent on several factors, to include pH of the electrolyte matrix, electrode/electrolyte

chemical composition and structure, and concentration of additive(s) package. Our dedicated team works with our clients to design an HER Inhibitor package that is stable in their proprietary electrolyte matrix under the most strenuous environments, whether acidic, neutral, or alkaline.

Table 1. MERGE inorganic additives listed by Exchange Current Density ($-\log i_0$). The best HER inhibitors are characterized by higher “ $-\log i_0$ ” values. The “MERGE concentration” is representative of a standard, stable acid matrix and can be adjusted based on customer need.

HER Inhibitor	Exchange current density, $-\log i_0$, [acid] ⁷	MERGE Concentration [acid matrix]	
		ppm	g/L
Hg	12.30	20,000	20
Cd	11.60	40,000	40
Pb	11.40	30,000	30
Mn	10.90	70,000	70
Zn	10.50	50,000	50
Tl	9.60	20,000	20
In	9.50	60,000	60
Ga	8.40	27,000	27
Nb	8.40	20,000	20
Ti	8.30	27,000	27
Ag	7.90	25,000	25
Bi	7.80	40,000	40
Cu	7.80	95,000	95
Sn	7.80	50,000	50
Mo	7.30	25,000	25

5. How is HER prevented?

5.1. Thermodynamics

It is well-understood that the hydrogen bonding strength between water molecules has a direct impact on the internal H–O bond strength within a water molecule (H–O–H). The stronger the H–O bond strength, the less likely the water molecule will lose a hydrogen atom to H₂ gas production. The strength, or reactivity, of water is classified as *activity*. If the activity of water is lowered, the molecules will be less likely to undergo e^- transfer to form the hydrogen intermediate. Aqueous electrolytes with low activity will therefore be less affected by HER. Organic additives are commonly used to disrupt the hydrogen bonding network, lower the activity of water, and suppress H₂ evolution.

A secondary method to reduce water activity is through the use of Alkali metals (K⁺, Na⁺, etc.). Alkali metal ions in an aqueous solution disrupt the solvation shell around the primary cation of the electrolyte (example, Zn²⁺). If the alkali ion penetrates the solvation shell of Zn²⁺, it will kick out a water molecule and occupy the vacancy. The more alkali ions in the solvation shell, the fewer water molecules available for direct e^- transfer with Zn²⁺ and the fewer hydrogen intermediates that can be formed. Thus, H₂ evolution is suppressed.

5.2. Kinetics

5.2.1. HER Overpotentials

As discussed above, water exhibits an **electrochemical stability window** (voltage window) of 1.23 V. The pH-dependence of this window is shown in Figure 1 as the difference between the red and blue solid lines. The onset voltage (or potential) at which hydrogen gas is generated is represented by the blue line. The OER onset voltage is shown by the red line and occurs at a more positive potential where water is oxidized in a multi-step, 4-electron mechanism to release oxygen gas.

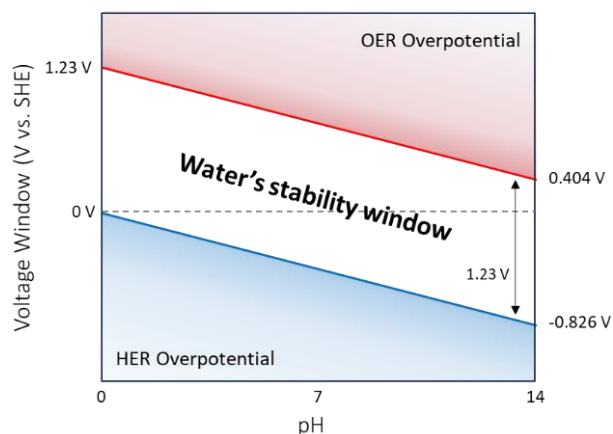


Figure 1. Electrochemical stability window of water

If the reducing voltage exceeds the blue line (negative potentials) or the oxidizing voltage exceeds the red line (positive potentials), water molecules will split into their hydrogen or oxygen constituents, respectively. For a real solution, the experimentally realized voltage for the onset of hydrogen/oxygen gas is at more negative/positive potentials than represented by the blue/red line. This difference is called overvoltage, or overpotential. The overall overpotential is a summation of overpotentials including activation overpotential, ohmic (intrinsic resistance) overpotential, and concentration overpotential.

The **HER Overpotential** is a type of activation overpotential that quantifies the voltage required to produce a specified current, resulting in H₂ gas generation. It can be directly correlated with the interaction strength of the adsorbed hydrogen ions (H_{ads}) on the surface of a metal electrode and is dependent on factors including electrolyte matrix/pH, electrode composition, temperature, and interaction of chemical additives. Materials with high HER overpotential extend the operating window of water-based electrolytes well beyond the thermodynamic stability window of 1.23 V. For example, mercury is known for its weak binding with hydrogen and exhibits an HER overpotential of ~1 V (see red row in Table 2). The large overpotential significantly widens the stability window of water before spontaneous decomposition of water occurs.

Table 2. Overpotentials (V) of metal electrodes as a function of current density⁵ (mA/cm²) in 2N H₂SO₄

Electrode	Current Density @25°C (mA/cm ²)			
	1	10	100	1000
Ag	0.475	0.762	0.875	1.089
Al	0.565	0.826	0.996	1.286
Au	0.241	0.39	0.588	0.798
Bi	0.78	1.05	1.14	1.23
Cd	0.981	1.134	1.216	1.254
Cu	0.479	0.584	0.801	1.254
Fe	0.404	0.557	0.818	1.292
Graphite	0.599	0.779	0.977	1.22
Hg	0.9	1	1.1	1.1
Ni	0.563	0.747	1.048	1.241
Pb	0.52	1.09	1.179	1.262
Pd	0.1	0.3	0.7	1
Pt (Platinized)	0.015	0.03	0.041	0.048
Pt (Smooth)	0.024	0.068	0.288	0.676
Sn	0.856	1.077	1.223	1.231
Te	0.3	0.4	0.5	0.6
Zn	0.716	0.746	1.064	1.229

Platinum, by comparison, has an HER overpotential of 0.02 – 0.05 V (blue row, Table 2), requiring nearly two orders of magnitude less voltage to facilitate the electrolysis of water and generate hydrogen gas. Platinum, iridium, and rhodium all exhibit low overpotentials and are regularly used as electrocatalysts for hydrogen gas generation in the green hydrogen industry.

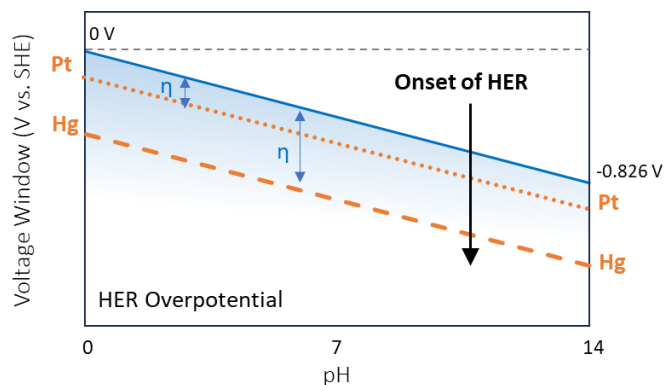


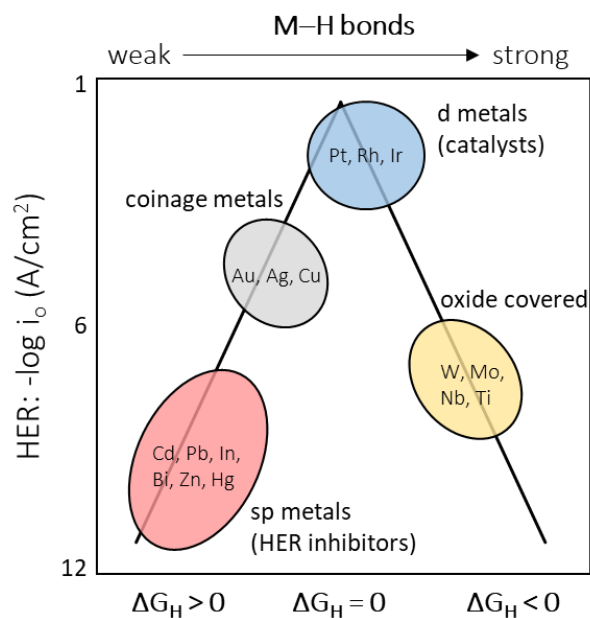
Figure 2. Onset voltage of HER for Pt (orange dotted line) and Hg (orange dashed line) electrodes compared to water alone (blue solid line). HER overpotential (η) shown as double arrows.

In Figure 2, the electrochemical stability window of water has been replotted to illustrate the HER Overpotential for Pt and Hg electrodes. The onset voltage of HER in water as a function of pH is still displayed as a solid blue line. Platinum (Pt) has a low HER Overpotential (η), with an onset voltage (orange dotted line) close to the solid blue line. By comparison, the large HER Overpotential of Hg (orange dashed line) pushes the onset voltage to deeper reducing potentials.

To summarize, metals with high HER overpotential require higher voltages to generate H₂ gas, resulting in a wider water stability window and less H₂ outgassing. By comparison, metals with low HER overpotential require less energy to generate H₂, resulting in H₂ gas generation at lower voltages and a narrower water stability window.

5.2.2. Hydrogen Exchange Current Density

The strength of the metal-hydrogen bond plays a significant role in the Hydrogen Evolution Reaction. The stability of this bond dictates the rate of formation of hydrogen intermediates that can lead to outgassing. The strength of the metal-hydrogen bond varies by element. The **volcano plot** (Figure 3) is one of the more widely recognized visuals to describe the selection of “good” vs. “bad” metals for electrocatalysis. Good electrocatalysts are defined as having a near-zero ΔG_H (Gibb’s Free Energy of metal-hydrogen interaction). These metals, namely platinum, iridium, rhodium, and palladium, significantly *reduce* the HER overpotential and create an easier pathway for hydrogen evolution.



The metals on the left side of the volcano plot exhibit weaker metal-hydrogen interactions, or a $\Delta G_H > 0$. The weaker bond strength means that the hydrogen ion is less likely to be adsorbed to the metal surface and undergo e^- transfer to

Figure 3. Volcano plot of $-\log i_0$ (hydrogen exchange current density) against strength of metal-hydrogen interaction

generate intermediates that can form H₂ gas. These metals can be exploited as HER Inhibitors for aqueous battery electrolytes.

Lead (Pb) is an example of a metal with $\Delta G_H > 0$, or a weak metal-hydrogen interaction (high HER Overpotential) and therefore less hydrogen evolution. This is a primary reason for the longtime success of lead-acid batteries! The intrinsically high HER overpotential of Pb enables higher voltage output than allowed by the thermodynamic window of the water electrolyte.

The ΔG_H values of the metal-hydrogen interaction can be further understood from a molecular orbital perspective. The strength of the metal-hydrogen interaction is directly related to the filling of the bonding and antibonding molecular orbitals. The energy value of the metal's d-band center (ϵ_D) is particularly relevant, as a deeper ϵ_D implies that the metal's d-band orbitals are not able to interact as strongly with the H 1s bonding orbitals. The lack of overlap of the bonding orbitals results in greater occupation of the anti-bonding orbitals in the metal-hydrogen bond structure, destabilizing the interaction. Example metals include Pb, Bi, Tl, and In. These elements are classified as "sp metals" and have low d orbitals and therefore a weak hydrogen interaction.

This interaction is quantified using the **hydrogen exchange current density (i_o)**. The exchange current density is the current recorded at zero overpotential and no electrolysis. Lower i_o values are directly proportional to a weaker metal-hydrogen interaction and lead to higher HER overpotentials (η), or less H₂ outgassing. The Tafel equation is used to define the relationship between η and i_o :

$$\eta = b \log (i/i_o)$$

where $b = RT/\alpha F$ (or Tafel slope), i = current density, α = charge transfer coefficient, and F = Faraday number. The Tafel slope is a useful indicator of a metal or additive's influence over the hydrogen outgassing. Table 3 ranks metals and their HER Inhibition property based on their hydrogen exchange current density (i_o). The first tier HER Inhibitors exhibit low i_o values whereas HER *catalysts* (Rh, Pd, Pt) have much greater i_o values. An HER overpotential range is also listed for each metal, with the overpotential measured across a current density range of 1 to 1,000 mA/cm².

Based on Table 3, and using the Zn²⁺/Zn(s) electrolyte as an example, Zn has an i_o of 3.16×10^{-11} A/cm². Based on this metric alone, Mn, Pb, and Cd would be the first additives of choice for HER Inhibition based on their lower i_o values (second choices may include In, Ga, and Nb due to their proximity). Factoring in η adds Bi and Sn to consideration: Bi and Sn exhibit overpotentials of 0.78 V and 0.86 V, respectively, at a current density of 1 mA/cm². Both values are greater than the 0.72 V overpotential of Zn and would push the HER onset voltage to deeper reducing potentials.

When incorporated into an electrolytic solution, the metal additives would act as kinetic HER inhibitors, filling active sites on the Zn electrode to prevent the e⁻ transfer from Zn to H_{ads} that would result in H₂ gas evolution. By inhibiting H₂ gas formation, the HER inhibitors also increase the overall HER overpotential of the cell, widening the stability window of the aqueous electrolyte and enabling greater output voltages.

Table 3. Exchange current density⁷ (i_0) for metal electrodes in acid matrix and corresponding overpotential⁵ (η), where available. Red: 1st tier HER inhibitors (lowest i_0). Yellow: 2nd tier HER inhibitors. Blue: HER catalysts

Metal	i_0 (A/cm ²)	$-\log i_0$ (A/cm ²)	η (V) ($1 \leq i \leq 1000$ mA/cm ²)	Electrolyte
Hg	5.01E-13	12.30	0.9 – 1.1	7.5 M H ₂ SO ₄
Cd	2.51E-12	11.60	0.98 – 1.25	1 M H ₂ SO ₄
Pb	3.98E-12	11.40	0.52 – 1.26	1 M HCl
Mn	1.26E-11	10.90		0.05 M H ₂ SO ₄
Zn	3.16E-11	10.50	0.72 – 1.23	1 M H ₂ SO ₄
Tl	2.51E-10	9.60		0.1 M H ₂ SO ₄
In	3.16E-10	9.50		0.1 M H ₂ SO ₄
Ga	3.98E-09	8.40		1 M H ₂ SO ₄
Nb	3.98E-09	8.40		0.5 M H ₂ SO ₄
Ti	5.01E-09	8.30		H ₂ SO ₄ (pH = 2.2)
Al	1.00E-08	8.00	0.57 – 1.29	1 M H ₂ SO ₄
Ag	1.26E-08	7.90	0.5 – 1.1	0.1 M H ₂ SO ₄
Sn	1.58E-08	7.80	0.86 – 1.23	1 M H ₂ SO ₄
Bi	1.58E-08	7.80	0.78 – 1.23	1 M H ₂ SO ₄
Cu	1.58E-08	7.80	0.48 – 1.25	0.5 M H ₂ SO ₄
Mo	5.01E-08	7.30		0.1 M H ₂ SO ₄
Cr	1.00E-07	7.00		0.5 M H ₂ SO ₄
Au	3.16E-07	6.50	0.24 – 0.8	0.5 M H ₂ SO ₄
Fe	2.51E-06	5.60		0.5 M H ₂ SO ₄
Co	5.01E-06	5.30		0.5 M H ₂ SO ₄
Ni	5.62E-06	5.25	0.56 – 1.24	0.5 M H ₂ SO ₄
Sb	7.94E-06	5.10		1 M H ₂ SO ₄
Rh	0.0003	3.50		0.5 M H ₂ SO ₄
Pd	0.0008	3.10	0.1 – 1	1 M H ₂ SO ₄
Pt	0.0010	3.00	0.015 – 0.048	1 M H ₂ SO ₄

It is important to note that the HER Overpotential is especially sensitive to pH, temperature, electrolyte composition, and chemical additives. The formation of various oxides and other ionic complexes from the electrolyte across acidic, neutral, or alkaline conditions may also influence the exchange current density and alter the overpotential. MERGE Chemistry can help identify HER inhibitors for your electrolyte based on careful consideration of these factors. The best additive package will likely involve a combination of multiple inhibitors that are carefully tailored for compatibility with the electrolyte matrix.

6. CONTACT US

Visit www.mergechem.com to review the full scope of our products and services and schedule a discovery call with our team to discuss how we can support your EAS needs.

If you have suggested edits or general feedback regarding this article, please email us directly at info@mergechem.com.

7. REFERENCES

The following references were consulted for this article and are listed in alphabetical order based on lead author:

1. Beard, K. W. (ed.), Reddy, T. B. (ed.), *Linden's Handbook of Batteries*, fifth edition, McGraw-Hill Education, 2019
2. Harris, D. C., *Quantitative Chemical Analysis*, 7th ed. W. H. Freeman and Company, 2007
3. Housecroft, C. E., Sharpe, A. G., *Inorganic Chemistry*, 3rd ed. Pearson Education Limited, **2008**
4. Juarez, F., Santos, E., Schmickler, W. "Volcano plots used in hydrogen electrocatalysts – uses and abuses", *Beilstein J. Nanotechnol.* **2014**, *5*, 846-854
5. Knobel, M. "Overvoltage", *International Critical Tables*, **1929**, *6*, 339-340
6. Lingane, J. J., *Electroanalytical Chemistry*, 2nd ed. Interscience Publishers, Inc. **1958**
7. Sangaranarayanan, M. V., Harinipriya, S. "Hydrogen evolution reaction on electrodes: Influence of work function, dipolar adsorption, and desolvation energies", *J. Phys. Chem. B.*, **2002**, *106*, 8681-8688
8. Sawyer, D. T., Sobkowiak, A., and Roberts, J. L., *Electrochemistry for Chemists*, John Wiley, **1995**
9. Sui, Y., Xiulei, Ji. "Anticatalytic Strategies to Suppress Water Electrolysis in Aqueous Batteries" *Chem. Rev.* **2021**, *121*, 6654-6695
10. Zhang, X. G., *Corrosion and Electrochemistry of Zinc*, Plenum Press, **1996**