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Minimizing the Influence of Metal Contaminations for the Alkaline Hydrogen Evolution Reaction on Platinum

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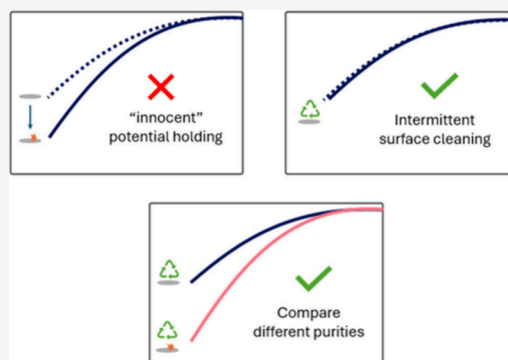


Article Recommendations



Supporting Information

ABSTRACT: The kinetics of alkaline water reduction on Pt can be strongly affected by the accumulation of impurities on the surface. Here, we demonstrate that such impurity effects can play a role even when the highest purity, pretreated NaOH electrolyte is used, which can lead to a misinterpretation of hydrogen evolution reaction (HER) activity trends. We show that the impurity accumulation time of a chosen electrochemical protocol plays a crucial role in the extent of surface contamination and the resulting drift in HER current. By incorporating intermittent surface cleaning into the measurement sequence, we effectively mitigated contamination accumulation effects. However, the HER activity still largely depends on the electrolyte impurity levels. We argue, therefore, that optimization of both the measurement method and the purity of the chemicals is essential for minimizing contamination effects and provide recommendations for employing this integrated approach to prevent systematic errors.



Green hydrogen produced via water electrolysis with renewable electricity will be an important part of the energy transition.¹ In addition, the relative simplicity of the hydrogen evolution reaction (HER) makes it a suitable candidate for developing and validating the fundamental models that lie at the heart of electrocatalysis.² However, the slow kinetics of HER in alkaline media, even on model surfaces such as platinum, remain incompletely understood.³

An important complication of kinetic assessments in alkaline media is the accumulation of metal impurities at the electrode surface. Previous studies, most notably by Subbaraman et al. and Weber et al., have demonstrated that metal (hydr(oxy)oxide) contaminations from commercially available electrolytes deposit on the cathode during measurements and considerably alter the HER reaction rate and voltammetric features of the surface.^{4–8} From a mechanistic point of view, small amounts of oxophilic elements are known to have a substantial effect on the HER activity of Pt in alkaline media. This cocatalytic effect has been attributed to an increased OH binding energy, or a decreased potential of zero charge (PZC).^{9–11}

Despite the evidence of the importance of metal impurities, appropriate measures to avoid their interference have rarely been reported in HER studies. For the oxygen evolution reaction (OER) and CO₂ reduction, the need to remove trace impurities from high-purity chemicals is more established.^{12,13} While

recommended by previous studies, electrolyte purification is not commonly performed for HER measurements.^{6,14} In addition, the role of the used electrochemical methodology in obtaining activity data on impurity accumulation is seldom evaluated or discussed, even though instability in the HER current over successive cycling has been reported.^{8,14}

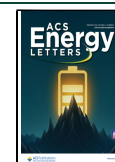
Building on this foundation, we construct an integrated approach for minimizing the effects of impurities on alkaline HER measurements using polycrystalline Pt as a model surface. We highlight that contamination accumulation is complex and can result in both activation and deactivation of the surface without clear indications in the blank cyclic voltammogram (CV), X-ray photoelectron spectroscopy (XPS) survey spectra, or inductively coupled plasma mass spectrometry (ICP-MS). As a result, metal impurities can lead to a hard-to-detect systematic error when an inappropriate method, with a long impurity accumulation time, is used. We mitigate the current drift in a series of measurements by avoiding the use of chronoamper-

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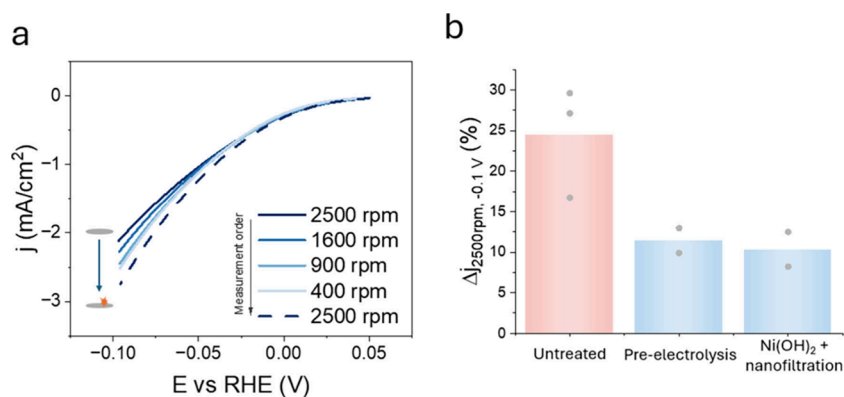


Figure 1. Increasing current in the measurement sequence during the case study on the rotation rate dependence of HER on Pt(poly) in high-purity 0.1 M NaOH (“Suprapur”). (a) LSV sweeps of HER measured consecutively at 2500, 1600, 900, and 400 rpm (solid) and again at 2500 rpm (dashed). Recorded at 10 mV/s, with 100% iR -compensation (85% during the measurement, 15% manual correction). Held for 2 min at 0.05 V_{RHE} in between every LSV sweep. (b) Effect of different pretreatment strategies (pre-electrolysis or a combination of cleaning the electrolyte with Ni(OH)₂ particles followed by nanofiltration) on the difference in current density between the first and last LSV at 2500 rpm at $-0.1 V_{\text{RHE}}$. Gray dots represent the individual data points.

ometry (CA) as an “innocent” waiting step and by incorporating intermittent surface cleaning. However, even with these precautions, the HER activity can still strongly depend on the electrolyte contamination levels. These findings emphasize the importance of considering both electrochemical methodology and chemical purity in obtaining reliable activity data.

The duration of an electrochemical measurement is an important factor for alkaline HER experiments as a result of the accumulation of impurities on the electrode surface. To demonstrate that the time-dependent impurity accumulation can lead to a misinterpretation of HER activity trends, we performed an illustrative study on the rotation rate dependence of HER on polycrystalline Pt in 0.1 M high-purity NaOH (“Suprapur”), as was previously done for Au.¹⁵ The effect of impurity accumulation (or other time effects) can be quantified by repeating the initial measurement in a consecutive series of measurements. Therefore, the HER activity was measured with LSV at 2500, 1600, 900, and 400 rpm and then again at 2500 rpm. Between each LSV sweep, a potential of 0.05 V_{RHE} was applied for 2 min, which was arbitrarily selected to reach steady state conditions,¹⁵ but prolongs the impurity accumulation time.

Figure 1a shows that, without taking the second 2500 rpm sweep into account, the LSV curves suggest high mass transport conditions inhibit HER, as the current density is highest for 400 rpm ($j_{-0.1\text{V}} = -2.5 \text{ mA/cm}^2$), and lowest for 2500 rpm ($j_{-0.1\text{V}} = -2.2 \text{ mA/cm}^2$). However, repetition of the first rotation rate, 2500 rpm (dashed, $j_{-0.1\text{V}} = -2.7 \text{ mA/cm}^2$), reveals that in the time frame of this experiment, the increase in the HER current ($\sim 25\%$) is larger than the rotation rate dependence. A similar current progression with a batch-dependent HER promotion or inhibition was previously observed by Subbaraman et al.⁸ The CV of the Pt surface only changes very slightly during this measurement (Figure S1), so the impurity accumulation is not immediately apparent.

By pretreating the high-purity NaOH with established cleaning methods, we demonstrate that purification can reduce the time-dependent current drift. In Figure 1b, we show the relative increase in current at $-0.1 V_{\text{RHE}}$ from the first to the last LSV sweep at 2500 rpm, for two different pretreatment options. Specifically, we used pre-electrolysis,^{4,6} or a combination of Fe-scavenging Ni(OH)₂ particles and nanofiltration.¹⁶ Both procedures target transition metal impurities and are not

expected to decrease the content of other impurities such as anions, alkali metal cations, and organics. The details of both procedures are described in the methods section, and the complete LSV series are available in the SI (Figure S2). ICP-MS demonstrates that the Ni(OH)₂ + nanofiltration method does not increase, but decrease the Ni content in the electrolyte (Table S4). We find that both purification strategies are successful in reducing the current drift from 25% to $\sim 10\%$, highlighting the significant role of trace transition metal impurities during this measurement. As a result, purified electrolytes allow for an extended time window of impurity accumulation in the method, before causing adverse effects. However, it is important to realize that some impurities remain in the electrolyte with the used purification methods, so this time is not infinite.¹⁶ The partial mitigation of the impurity effect with electrolyte purification is consistent with previous work by Weber et al. Absolute electrolyte purification seems to be a goal that is difficult to achieve. In our case study, the remaining drift is still too large to determine the rotation rate dependence. Hence, the electrochemical procedure is an additional factor that we address here.

We first establish more explicitly that the direction and magnitude of the activity change strongly depend on the electrolyte purity. Instability in the HER activity on Pt during long-term chronoamperometry was previously observed by Weber et al. in 0.1 M LiOH, NaOH, and KOH.⁶ Rather than demonstrating long-term poisoning, we highlight a transition from impurity-induced promotion at low coverages to inhibition at higher coverages. Figure 2 provides the data of long-term CA experiments at $-0.2 V_{\text{RHE}}$ in untreated 0.1 M NaOH of high (“Suprapur”), intermediate (99.99%), and low (99.99%) purity. The specifications of these NaOH purities are summarized in Table 1. Note that we consider a grade of 99.99% to be of low purity, even though this is generally regarded as a high-purity chemical.^{6,14}

In the high-purity NaOH solution, the current increases until a peak current density is reached after 1.5 h. This is followed by a decrease in current of roughly an order of magnitude over the next 10 h. Long-term electrochemical impedance spectroscopy (EIS) confirms that this is not caused by bubble accumulation (Figure S4). For the low-purity NaOH solution, only a steep decline in the current is observed. Within the first two h, the

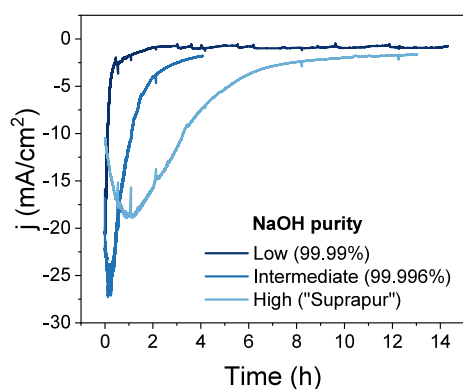


Figure 2. Long-term chronoamperometry recorded at $-0.2 V_{\text{RHE}}$ with 85% iR -correction at 900 rpm in 0.1 M NaOH of high (“Suprapur”), intermediate (99.996%), and low (99.99%) purity.

Table 1. Specification of the Different NaOH Purities, Including the Used Grades and the Fe Concentration in a 0.1 M NaOH Solution^a

NaOH purity	grade	[Fe] in 0.1 M solution (ppb)
low	99.99%	26.5
intermediate	99.996%	6.5
high	“Suprapur”	0.025

^aThe numbers are based on the certificates of analysis, which are included in the SI (Table S5). Fe is one of the contaminants that is expected to have a large contribution to the observed anomalous activities, as will be discussed later.

current reduces by an order of magnitude. Correspondingly, using NaOH with intermediate impurity levels results in a transient that is between the previous extremes. Subbaraman et al. previously attributed a gradual HER promotion on Pt(111) to high Co and Ni levels, and surface deactivation to a high Fe content.⁸ This correlation is not evident in our results (Tables S4 and S5), but a relation with the Fe concentration can be observed in Table 1. Assuming that the impurities accumulate gradually, these observations indicate that low coverages of contamination *enhance* HER activity, whereas higher coverages *inhibit* HER activity. Whether the enhancement is actually observed depends on the purity of the electrolyte (and, presumably, the real electrode surface area). As a result, the apparent HER activity evolves with time, and the trends observed depend on when the measurement is evaluated. For the particular experiment in Figure 2, at $t = 0$ h, the highest

current is observed for low \approx intermediate $>$ high purity. This trend is inverted at $t = 2$ h, where the order becomes high $>$ intermediate $>$ low purity.

Finally, we used voltammetric and spectroscopic characterization of Pt after long-term measurements to investigate more directly the accumulation of impurities and their possible identity. Figure 3a shows the CV of a polycrystalline Pt surface in 0.1 M NaOH (high purity, not purified) before and after applying a potential ($0.5 V_{\text{RHE}}$ or $-0.2 V_{\text{RHE}}$) for 2 h. Changes in the CV are a common identifier of impurities on the surface and were previously observed on polycrystalline Pt and Pt(111).^{6,8,17,18}

Before the measurements, we obtain the characteristic CV of polycrystalline Pt in alkaline media, featuring the hydrogen underpotential (H_{upd}) region ($0.05 V_{\text{RHE}}$ to $0.45 V_{\text{RHE}}$), the so-called “double layer” or “low-capacitance” region ($0.45 V_{\text{RHE}}$ to $0.7 V_{\text{RHE}}$),¹⁹ and the Pt oxidation region ($0.7 V_{\text{RHE}}$ to $1.2 V_{\text{RHE}}$). Holding the potential for 2 h at a value either below or above the onset of HER leads to identifiable changes in the voltammetric features. Applying $0.5 V_{\text{RHE}}$ for 2 h results in an increase in the capacitive current in the “double-layer” region, as well as a decrease in the current in the Pt oxidation region. The changes become even more pronounced after applying a potential in the HER range, $-0.2 V_{\text{RHE}}$, consistent with negative potentials facilitating the electrochemical deposition of metals.⁶ Additional peaks appear in the “double-layer” region, and the current shows a further decrease in the Pt oxidation region, suggesting surface-blockage. In addition, the peaks at $0.38 V_{\text{RHE}}$ corresponding to adsorption/desorption processes in $\{100\}$ steps, shift toward more negative potentials ($0.35 V_{\text{RHE}}$). These results confirm that impurities deposit on the Pt surface in a broad potential window, even in the cleanest available NaOH.

To identify the contaminations on the surface, ex-situ XPS spectra were obtained before and after applying $-0.2 V_{\text{RHE}}$ for 4.5 h in a 1 M high-purity NaOH solution. The longer time and higher NaOH concentration were used to increase the contamination coverage, to exceed the XPS detection limit. With the survey spectrum, which scans across a wide range of binding energies and indicates the surface composition, no contaminations could be identified (Figure S4), highlighting the challenges of detecting surface contamination from high-purity electrolytes. However, in the high-resolution spectral range of the Fe 2p peak (Figure 3b), we find a considerable difference between the clean and contaminated surface. Besides a Pt 4s peak at a binding energy of 725 eV, which is present in both cases, the contaminated sample displays an additional peak at

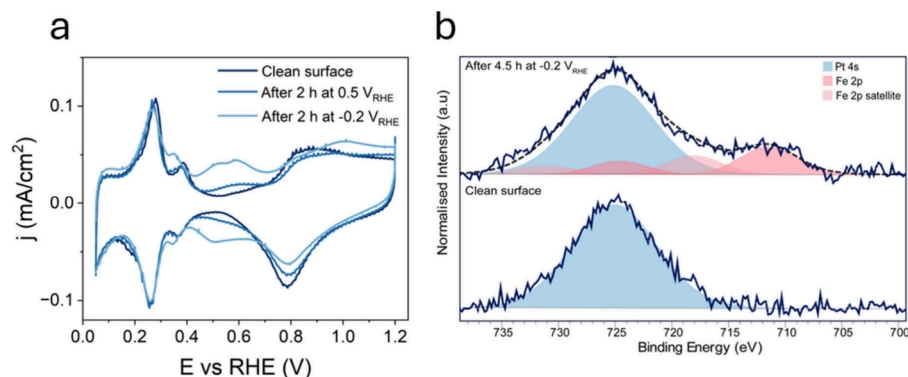


Figure 3. (a) Cyclic voltammogram of Pt disk in 0.1 M high-purity NaOH (“Suprapur”) before (clean surface) and after 2 h at $0.5 V_{\text{RHE}}$ or $-0.2 V_{\text{RHE}}$. (b) XPS spectrum in the Fe 2p region of a Pt disk surface before (clean surface) and after 4.5 h at $-0.2 V_{\text{RHE}}$ in 1 M high-purity NaOH (“Suprapur”).

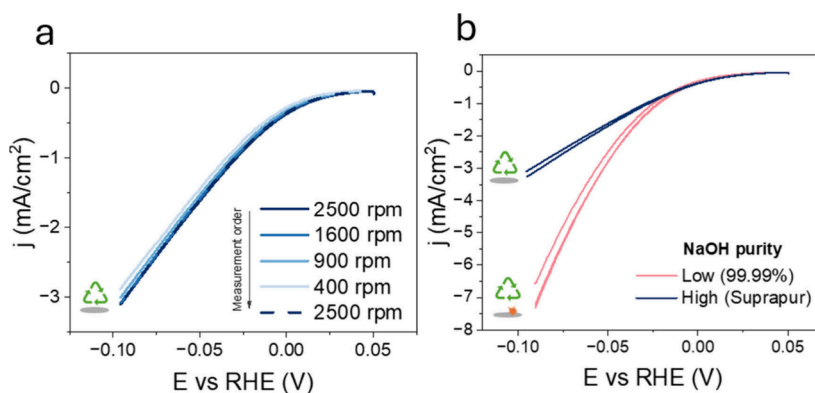


Figure 4. (a) LSV sweeps of HER measured consecutively at 2500, 1600, 900, and 400 rpm (solid) and again at 2500 rpm (dashed), with 10 CV cycles (0.05–1.2 V_{RHE} , 50 mV/s) in between every sweep as intermittent surface cleaning. Recorded at 10 mV/s in 0.1 M high-purity NaOH (“Suprapur”). (b) Comparison of first LSV sweeps at 2500 rpm in low (99.99%) and high (“Suprapur”) purity 0.1 M NaOH with 100% iR -compensation (85% during the measurement, 15% manually).

711 eV, corresponding to the Fe 2p_{3/2} peak.²⁰ The Fe 2p_{1/2} and Fe 2p satellite peaks overlap with the Pt 4s peak. This XPS measurement confirms the presence of metal impurities on the Pt surface after long-term chronoamperometry (4.5 h) in high-purity NaOH, where the Fe content is below the detection limit of ICP-MS (Table S4).

It is likely that a mixture of contaminants, which depends on the used grade and batch of chemicals, deposits on the electrode surface and affects the HER activity. In addition to Fe, Ni and Pb were sometimes detected in their respective high-resolution spectra during measurements with different exposure conditions (e.g., time or NaOH batch) and/or XPS settings (e.g., step size; Figure S5). Since these high-resolution measurements were only performed for elements observed in previous studies^{6,21} it is possible that other metals are present on the surface as well. However, considering the consistent detection of Fe in all XPS measurements, the correlation of the time-dependent HER promotion/inhibition to the Fe content (Figure 2 and Table 1), and the effectiveness of the Ni(OH)₂ + nanofiltration purification method (Figure 1b), which was designed to generate an Fe-free electrolyte, we suspect that Fe plays a large role in the observed anomalous activities. Additionally, spiking the electrolyte with Fe leads to the formation of a peak in a position similar to the peak observed in Figure 3a (Figure S6).

As discussed previously, Pt surface modification with metal hydroxides can both enhance and deteriorate the HER activity of bare Pt, similar to the behavior of impurities in our study.⁹ However, the remaining uncertainty in the identity of the relevant contaminants and their (in situ) oxidation state needs to be addressed before quantitative conclusions can be drawn regarding the specific role of impurities in HER promotion and inhibition. Ni, Co and Mn on Pt(111) are reported to be in hydroxide form at -0.1 V, whereas Fe consists of a mixture of Fe(II) and Fe(III) oxides and hydroxides at this potential.⁹ Especially for Fe, understanding the in situ oxidation state and its relation to HER activity will therefore be an interesting topic for future work.

Returning to our case study on the rotation rate dependence, we investigated whether modifying the electrochemical protocol could reduce impurity effects without being limited to only using the first scan, as previously recommended by the Markovic group for Pt(111).⁸ By avoiding CA as an “innocent” waiting step and incorporating an appropriate intermittent surface cleaning protocol into a series of measurements, we can

successfully mitigate the current drift. The main idea is that before every HER measurement in the sequence the surface must be cleaned or conditioned to a reproducible starting state.

To this end, we included 10 CV cycles from 0.05 to 1.2 V_{RHE} at 50 mV/s, and eliminated the CA's at 0.05 V_{RHE} between the measurements. We expect the CV cycling to be a cleaning step, because the observed changes in the CV as a result of impurity accumulation decrease with cycling in this potential window (Figure S7). By performing the CV cycling between every LSV sweep, and after EIS, which was recorded at the start of the measurement sequence to determine the solution resistance, we have bypassed the previously encountered time effects. As can be seen in the series of polarization curves in Figure 4a, the first and the last LSV sweeps at 2500 rpm overlap, in stark contrast to the measurements without the cleaning protocol in Figure 1. This shows that the method mitigates current drift in a measurement sequence while simultaneously allowing time for changing parameters, as the current remained stable for more than 45 min. Finally, the rotation rate dependence is revealed. A higher rotation rate leads to a slight increase in the current density, in agreement with previous observations on single-crystal surfaces.²²

Several other methods were attempted and are included in SI (Figure S8). Our method evaluation is based on the (lack of) overlap between the first and last LSV, which are recorded with the same settings. Without any waiting steps between the LSVs, the current decreases. This could be related to other processes rather than impurity accumulation, such as the accumulation of hydrogen at the surface. When fewer CV cycles (2 instead of 10) are used between the LSV sweeps, the stability is improved compared to the protocol that uses CA between the LSVs, but a small current drift remains that neutralizes the apparent rotation rate dependence. This potentially explains the absence of a rotation rate dependence of alkaline HER on Pt in several previous studies, although a relation to the choice of purging gas (Ar/H₂) cannot be excluded yet.^{22–25} We highlight that the upper potential of the CV needs to be sufficiently positive, presumably leading to the oxidation and subsequent dissolution of impurities, or recovery of clean Pt sites by electrochemical roughening, as evidenced by the increase in current when the upper limit is reduced to 0.8 V. Based on these assessments, we believe the method with 10 CV cycles between 0.05 V_{RHE} and 1.2 V_{RHE} approaches the “real” behavior of our system best, but

we acknowledge that a comparable stability could potentially be achieved with alternative methods as well.

By using this method, we were able to measure the HER activity reproducibly even in low-purity NaOH (Figure S9). However, the obtained current in low-purity NaOH differs significantly from the current in high-purity NaOH, as can be seen in Figure 4b. In this figure, we compare the HER current obtained in high and low purity 0.1 M NaOH for the first LSV sweeps recorded at 2500 rpm. The HER current in low-purity NaOH ($j_{-0.1V} \approx -7 \text{ mA/cm}^2$) is more than double the current in high-purity NaOH ($j_{-0.1V} \approx -3.2 \text{ mA/cm}^2$), also when the measurement is performed under stationary conditions (Figure S10). Note that in line with Figure 2, the apparent activity trend depends on when the measurement is evaluated. We observe a reversed trend when comparing the different grades of NaOH with the last LSV sweep of the protocol that uses CA in between the LSV sweeps. In that case, the current in low-purity NaOH is lower than the current in high-purity NaOH (Figure S11).

After purification of both electrolytes with Ni(OH)₂ particles + nanofiltration, the obtained currents closely approach each other in the first LSV sweep, demonstrating again that the purification method is highly effective (Figure S12a). Still, a (smaller than before) divergence is apparent during chronoamperometry (Figure S12b). This reasserts the importance of the measurement method, even in purified electrolytes, while simultaneously implying that the contamination levels of a purified solution depend on the initial purity of the used chemicals.

Because the observed current is highly dependent on both the method and the purity of chemicals, it is challenging to know what the “real”, intrinsic, kinetic behavior of the system is. Reproducibility is not enough for this evaluation, as becomes clear from Figure 4. Nevertheless, we think comparing different purities is an important step for revealing and quantifying impurity-induced systematic errors, which helps us approach the ‘true’ kinetic current.

While this paper is not the first to address the importance of controlling impurities, we think their effects might still be underestimated, especially in light of recent interest in electrolyte effects. After all, when changing the cation (concentration), one also changes the impurity content of the electrolyte,²⁶ which we showed affects the HER activity to a large extent. This has not been taken into account in previous reports on the cation identity effect for alkaline HER on Pt (Table S6), in contrast to studies on CO₂ reduction²⁷ and OER.²⁸ Interestingly, the HER/HOR activity on Pt in 0.1 M NaOH/KOH is reported to depend more on the impurities than on the respective cations.²⁶ In addition, on Cu electrodes, it was observed that the difference in steady-state HER activity between NaOH (99.99%) and CsOH (99.95%) disappears upon pretreating the electrolytes with electrolysis.¹⁴ These findings imply that part of the reported electrolyte effects in alkaline HER studies could be convoluted by impurity accumulation.

Of course, the relevance of considering impurities is not limited to electrolyte studies. For electrode studies, it is important to realize that the response of a surface to impurities can vary, which was a crucial insight for the benchmarking of Ni oxyhydroxide electrodes for OER.¹² Additionally, we observe that the current drift observed on polycrystalline Pt in Figure 1a is smaller on Pt (111), which might indicate that the effect of contamination for HER on Pt is facet-dependent (Figure S13). The differences in properties between different Pt facets (e.g.,

the OH-binding energy²⁹ or PZC^{19,30}) could potentially rationalize these findings and provide a useful tool in deriving a mechanistic picture of impurity effects, for which Pt(111) has been the predominant model surface so far.^{9,11,31}

Based on our work, we have several recommendations for minimizing the influence of contamination on alkaline HER measurements. The measures should be taken in addition to previously recommended practices (also targeting anion and organic impurities), including but not limited to avoiding glass cells for alkaline media,³² thorough cleaning of the cell, and electrode polishing with diamond particles instead of alumina particles.³³ For additional recommended practices on obtaining and extracting kinetically meaningful data (e.g., *iR* correction), the reader is referred to the works of Wei et al. and Van der Heijden et al.^{34,35} Moreover, if the experiment allows, reducing risk factors, such as high electrolyte concentrations, large electrolyte volumes, high mass transport (e.g., rotation),⁸ or small electrode surfaces, might be beneficial. Here, we specifically recommend the following:

- 1) Determining the response of a system to impurities by varying the purity of the chemicals used. In essence, this is a calibration step that reveals the magnitude of impurity effects with the used method, which helps prevent undetected systematic errors. This is the most important measurement that needs to be taken and reported. Presumably, some systems are less sensitive to impurities. This could, for example, be expected for high-surface-area electrodes. Still, it is important to perform and report a measurement with different purities to check the validity of that assumption.
- 2) Purifying chemicals if a sensitivity to impurities is detected with step 1. For XOH (X = Li, Na, K, e.g.) solutions, we recommend the Ni(OH)₂ + nanofiltration method (or pre-electrolysis, but that is more time-consuming and less versatile). As discussed before, the Ni(OH)₂ + nanofiltration method does not appear to increase the Ni impurity levels; surprisingly, it can even decrease the Ni impurity levels (Table S4). For pre-electrolysis, careful consideration of the electrode material is required to prevent the introduction of new impurities (e.g., using Pt electrodes during pre-electrolysis for an experiment on Au would be advised against). Chelex treatment had no effect in these alkaline conditions (Figure S2), but has been reported to be useful for other electrolytes.¹³ Note that even when chemicals are purified, it is important to perform the calibration step described in suggestion 1, as the final impurity levels likely depend on the initial purity (Figure S12). In addition, this step reveals the potential contribution of other variable impurities (organics, anions, alkali metal cations) that are not removed with the purification procedures.
- 3) Being conscious of the impurity accumulation time before HER measurements. This includes (I) minimizing potential holding (e.g., CA) as we have not been able to identify an “innocent” potential; (II) being cautious with CV cycling in a potential window with a low (<1 V) upper vertex potential; (III) avoiding leaving the working electrode in the electrolyte without potential control, i.e., “open circuit” (Figure S14). If possible, the above-mentioned steps should be reduced or substituted with CV cycling to 1.2 V. The effect of certain steps within a

sequence can be evaluated by performing a HER sweep before and after said step. In addition, the electrochemical methods should be reported in every detail (Table S1). In some cases, it might not be possible to have a short impurity accumulation time. For instance, spectroscopic studies could require a long acquisition time, which means checking the effect of this time, varying the purity (suggestion 1) and purification (suggestion 2) of chemicals become even more important.

- 4) Performing a surface cleaning step right before the HER measurement, because the above-mentioned steps are not completely avoidable. The exact protocol will need tailoring for different surfaces, setups, and reactions. For instance, CV cycling to 1.2 V cannot be used for single crystals, because this potential is outside their stability window.¹⁸ To check the effectiveness of the cleaning step, we suggest conducting a measurement sequence to evaluate the stability of the current. For Pt(111), the Markovic group suggests only using the first HER sweep and ensuring this is recorded within 1–2 min of contact with the electrolyte.⁸
- 5) Varying the method. Because HER currents are dependent on the employed electrochemical sequence, it is important to validate the obtained HER activity trends with different methods. We specifically recommend an additional evaluation of the stability of the HER current (and activity trend) with chronoamperometry (~20 min). While the reporting of consecutive CV cycles also leads to useful information regarding the stability,¹³ the short time scale may underestimate the consequences of impurity effects. We find CA to be clearer and more representative in this regard, especially when combined with recommendation 1.

Although our work focuses on the HER on Pt, the general insights can be transferred to other surfaces and reactions in alkaline media. The relevance of impurities on HER has already been established for Au, Ag, and Cu in low-purity solutions.^{4,5} Similarly, metal impurities have been found to affect a variety of electrochemical processes, including cathodic Au corrosion, the hydrogen oxidation reaction, the oxygen reduction reaction, CO₂ reduction, bicarbonate electrolysis, OER, and glycerol oxidation.^{8,12,13,36–39}

In conclusion, the findings of this study suggest that metal contaminations, already on the (sub)ppb scale, are a key variable for alkaline HER measurements. We have demonstrated that even when using the highest purity chemicals and electrolyte pretreatment, impurity accumulation time is an extremely important factor to consider. The current change due to the accumulation of impurities could lead to misinterpretation of a series of measurements, such as the rotation rate dependence, when an inappropriate method is used. Intermittent surface cleaning has been proven to be successful in mitigating this issue. Still, merely varying the chemical purity leads to a significant change in the HER current. As a result, conclusions drawn without explicitly controlling for or reporting these factors should be interpreted with caution. This is especially relevant for work on electrolyte effects for alkaline HER, as the variation in impurity levels is rarely accounted for. Future studies on the HER in alkaline media should incorporate measures, such as the ones described in our work, to ensure impurities do not interfere with the parameter of interest.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.5c03780>.

Experimental methods; Figures S1–S15 (CVs before and after measurements, LSV sequences in different electrolytes, with different methods, and on Pt(111), ICP-MS results and certificates of analysis, XPS spectra, LSV comparisons of (purified) high and low purity NaOH, Pt(111) blank CV) (PDF)

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Notes

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