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Accurate Potentials of Hg/HgO Electrodes: Practical Parameters for Reporting Alkaline Water Electrolysis Overpotentials

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Alkaline water electrolysis (AWE) at a low temperature (<100 °C) is one of the most promising sustainable technologies for green hydrogen production.[1] The AWE process is composed of the hydrogen evolution reaction (HER: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$) and oxygen evolution reaction (OER: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$). By designing and synthesizing highly active electrocatalysts for both the HER and OER, high energy efficiency for AWE can be achieved. In typical lab-scale AWE experiments, the activity of an electrocatalyst for each half-cell reaction can be evaluated in a standard three-electrode system in which three electrodes (i.e., working, counter, and reference electrodes) are placed in an alkaline electrolyte (as typified by the following concentrations: 0.1, 0.5, and 1 M NaOH/KOH). A mercury/mercuric oxide (Hg/HgO) electrode has been utilized for many electrochemical studies involving alkaline electrolytes[2−17] and is also typically used as a reference electrode for electrocatalytic water splitting in alkaline media.[18] The internal aqueous solution within this Hg/HgO electrode is usually either 1 M NaOH or 1 M KOH (see the left side of Figure 1). In alkaline overall water splitting research, overpotentials required to deliver a given current density (e.g., 10 mA·cm^{-2}) for the HER and OER half-reactions are measured with respect to the Hg/HgO reference electrode.[18,19] It is then common practice to convert the potential values from V vs Hg/HgO ($E_{Hg/HgO}$) to V vs the reversible hydrogen electrode (RHE) (E_{RHE}) using the Nernst equation.[18] The widely used equation (simplified Nernst equation) for the Hg/HgO (1 M NaOH/KOH)-to-RHE potential conversion is shown below:[18,20−27]

$$E_{RHE} = E_{Hg/HgO} + \left(2.303 \times \frac{RT}{F}\right) \times \mathrm{pH} + E^{\circ}_{Hg/HgO} = E_{Hg/HgO} + 0.0592 \times \mathrm{pH} + E^{\circ}_{Hg/HgO} \quad (1)$$

where $E^{\circ}_{Hg/HgO}$ is the half-cell standard reduction potential of the Hg/HgO electrode [0.0983 V vs SHE (standard hydrogen electrode) at 25 °C],[28] R is the ideal gas constant (8.31432 J·K^{-1}·mol^{-1}), T is the temperature [298.15 K (= 25 °C)], and F is the Faraday constant (96485 C·mol^{-1}). In eq 1, the Hg/HgO electrode potential is denoted as $E^{\circ}_{Hg/HgO}$. However, according to previous reports,[3,14,15,17] it has already been found that this electrode potential tends to vary depending on the components of the internal solution in the Hg/HgO electrode and their concentrations. To better understand this phenomenon, one must first take a look at the Hg/HgO half-cell reaction[28] and corresponding Nernst equation[17] as shown below:

$$\mathrm{HgO}(s,\ \text{yellow}) + \mathrm{H_2O}(l) + 2e^- \leftrightarrow \mathrm{Hg}(l) + 2\mathrm{OH}^-(aq) \quad (2)$$

$$\begin{aligned} &E_{[\text{Hg/HgO with internal solution }(x\,M\,M\text{OH}):\,M=\text{Na or K}]} \\ &= E^{\text{real}}_{\text{Hg/HgO}(x\text{M}M\text{OH})} = E^{\circ}_{Hg/HgO} - \frac{RT}{2F}\ln\frac{a_{Hg}a_{OH^-}{}^2}{a_{HgO}a_{H_2O}} \\ &= E^{\circ}_{Hg/HgO} - \frac{RT}{2F}\ln\frac{a_{OH^-}{}^2}{a_{H_2O}} \end{aligned} \quad (3)$$

where x M is the solute concentration in molarity (M: mol·L^{-1}) and $E^{\text{real}}_{\text{Hg/HgO}(x\text{ M }M\text{OH})}$ is the Hg/HgO electrode potential with the internal alkaline solution at a given solute concentration. As indicated in eq 3, the Hg/HgO electrode potential can be altered mainly by a change in the activities of OH^- (a_{OH^-}) and H_2O (a_{H_2O}). The solute/solvent activity is given by

$$a = \gamma \times C \quad (4)$$

where γ and C are the activity coefficient and concentration (M), respectively. At 25 °C and relatively low NaOH/KOH concentrations (e.g., 0.1, 0.5, and 1 M), the H_2O activity is nearly equal to one (see Table S1), while the NaOH/KOH concentration change (e.g., 0.1 → 1 M) leads the OH^- activity change from 0.782/0.789 to 0.677/0.748, respectively.[29] Hence, in eq 3, the OH^- activity mainly contributes to the deviation from the standard potential of the Hg/HgO electrode. Additionally, as the activities of pure substances in condensed phases (i.e., solids or liquids) at 1 atm are one by definition,[30] the activities of Hg and HgO become one. All things considered, the potential of the Hg/HgO electrode (1 M NaOH/KOH) should not become equal to $E^{\circ}_{Hg/HgO}$. This

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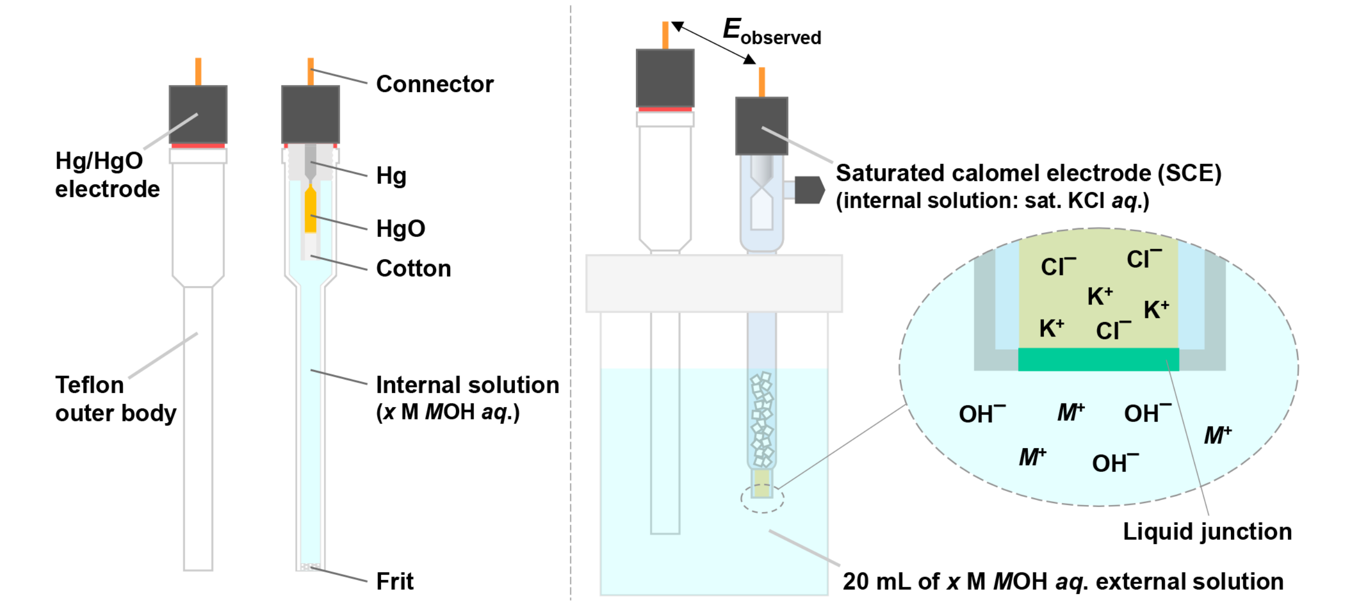

Figure 1. Left: External and internal views of the Hg/HgO reference electrode. Right: Two-electrode system for the Hg/HgO reference electrode potential determination.

Table 1. Theoretical and Experimental Hg/HgO Electrode Potentials [$E^{real}_{Hg/HgO(x\ M\ MOH)}$] with Different Internal Aqueous Solutions at 25 °C

Hg/HgO electrode potential: $E^{real}_{Hg/HgO(x\ M\ MOH)}$ (mV)						
	internal solution					
	0.1 M NaOH	0.5 M NaOH	1 M NaOH	0.1 M KOH	0.5 M KOH	1 M KOH
calc. potential	163.7	125.4	107.9	163.5	124.1	105.3
exp. potential [SCE (No. 1)]	148.5 ± 1.8	128.0 ± 1.7	108.9 ± 1.4	141.5 ± 1.2	126.7 ± 1.7	103.4 ± 2.3
exp. potential [SCE (No. 2)]	148.7 ± 1.5	127.0 ± 1.4	107.8 ± 0.6	141.4 ± 2.7	125.6 ± 1.7	102.7 ± 2.6
exp. potential[3]	169.0[a]		113.5[a]			110.0[a]

[a]The potentials of the Hg/HgO electrodes were determined by using the calomel electrode with a 0.1 or 1 M KCl internal aqueous solution.[3]

misconception of the Hg/HgO electrode potential values may hinder the accurate determination of the HER and OER overpotentials as these values are directly measured with respect to the Hg/HgO reference electrode and converted to V vs RHE based on the standard reduction potential of the Hg/HgO electrode.

There are several works that have experimentally and theoretically obtained the potentials of Hg/HgO electrodes with NaOH, KOH, $Ca(OH)_2$, and $Ba(OH)_2$ used as internal aqueous solutions at different concentrations.[3,31,14−17] However, most of these previous reports only considered internal solutions with concentrations in molality (m: mol·kg^{-1})[14,15,17] and percent composition (%)[31] rather than in molarity (M: mol·L^{-1}). More generally, few reports have provided experimentally measured potentials of the Hg/HgO electrodes having internal solutions with concentrations in molarity.[3] Nowadays, as molarity is most frequently used in the field of electrocatalytic water splitting, we urgently need the calculated potential values of the Hg/HgO electrodes (*x* M *M*OH, M = Na or K) that can be utilized for the Hg/HgO-to-RHE potential conversion and can also act as benchmarks for judging the reliability of each user's Hg/HgO electrode. To address these concerns, we herein discuss three points: (i) calculating the potentials of the Hg/HgO electrodes containing NaOH/KOH internal aqueous solution with different molar concentrations (M), (ii) how to calibrate/check the Hg/HgO electrode potentials, and (iii) additional instructions/precautions that should be considered when using Hg/HgO reference electrodes.

Hg/HgO ELECTRODE POTENTIAL CALCULATION

Since 0.1−1 M NaOH/KOH aqueous electrolytes are typically used for testing electrocatalysts for the HER and OER, we recommend the readers use the same electrolytes as the internal solutions (this point will be discussed in detail later in this Viewpoint).[32,33] Here, we attempted to calculate the potentials of the Hg/HgO electrodes with 0.1, 0.5, and 1 M NaOH/KOH internal aqueous solutions at 25 °C. For calculating the Hg/HgO electrode potentials, we used eq 3 and also calculated all the necessary parameters [i.e., γ_{OH^-} (the stoichiometric activity coefficient of OH^-) and a_{H_2O}] through the Excel spreadsheet tool created by Hausmann et al.[29] The as-calculated parameters are available in Table S1. Here, a_{OH^-} can further be calculated through eq 4 ($a_{OH^-} = \gamma_{OH^-} \times C_{OH^-}$). Importantly, since the as-calculated γ_{OH^-} is a stoichiometric activity coefficient,[29] C_{OH^-} becomes equivalent to the molar solute concentration (M) of sodium/potassium hydroxide. The as-calculated potentials of Hg/HgO electrodes (0.1, 0.5, and 1 M NaOH/KOH) are listed in Table 1. Within the concentration range from 0.1 to 1 M, all the as-calculated potential values are higher than the standard potential ($E^{\circ}_{Hg/HgO}$) value (98.3 mV) of the Hg/HgO electrode. Of the

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internal solution concentrations evaluated, the Hg/HgO electrodes with 1 M NaOH and KOH exhibited the calculated potentials closest to the standard potential at 9.6 and 7.0 mV higher than 98.3 mV, respectively. Thus, when one conducts the Hg/HgO (1 M NaOH/KOH)-to-RHE potential conversion using eq 1 to determine the overpotential for the HER and OER, one may underestimate and overestimate overpotential values. Instead of using eq 1, we recommend the readers use the Nernst equation with the Hg/HgO electrode potential [$E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$], keeping the internal solution (1 M NaOH/KOH) for the potential conversion in mind [see eq 5].

$$E_{\mathrm{RHE}} = E_{\mathrm{Hg/HgO}} + 0.0592 \times \mathrm{pH} + E^{\mathrm{real}}_{\mathrm{Hg/HgO(1\,M\,NaOH/KOH)}} \tag{5}$$

Hg/HgO ELECTRODE POTENTIAL CALIBRATION

In this section, we provide a facile experimental procedure for obtaining the real Hg/HgO electrode potential (additional details are available in the Supporting Information). For this measurement, a two-electrode system consisting of the Hg/HgO electrode of interest and a saturated calomel electrode (SCE) was used (see the right side of Figure 1). In this system, 0.1, 0.5, and 1 M NaOH/KOH aqueous solutions were used as both the external and internal electrolytes. To evaluate the measurement's reliability and reproducibility, three Hg/HgO electrodes (Nos. 1−3) and two SCEs (Nos. 1 and 2) were used (see Scheme S1 and Figure S1), and each SCE was utilized to measure the potential of each Hg/HgO electrode with the same internal solution type and concentrations. The potential difference (E_{observed}) between the Hg/HgO electrode and SCE was monitored using a multimeter for 2 h at 25 °C (see Figure S2), and the E_{observed} value was recorded every 10 min. All the resultant time−potential (E_{observed}) curves can be found in Figures S3−S8. The E_{observed} values recorded at 2 h were used for calculating the Hg/HgO electrode potentials. Note that the as-observed E_{observed} value expresses the potential difference between the Hg/HgO electrode and SCE because of the presence of a liquid junction potential (E_{LJP}). Since the internal solution of the SCE [saturated KCl aqueous solution (KCl sat.)] and the external electrolyte (x M NaOH/KOH) were different, a liquid junction potential at the KCl sat.|x M MOH interface exists and must, therefore, be considered for the Hg/HgO electrode calculation (see the right side of Figure 1). An E_{LJP} is present if one or more of the following cases are true:[34] (1) solutions A and B have the same constituents but at different concentrations, (2) solutions A and B have different constituents at the same concentrations, and (3) solutions A and B have different constituents at different concentrations. As indicated in Table 2, the E_{LJP} values for the different KCl sat.|x M MOH interfaces were calculated through two different methods: the Henderson equation[35] [see eq S1 and Table S2] and the stationary Nernst−Planck equation[36] (LJPcalc software: https://swharden.com/LJPcalc). When one takes the E_{LJP} into consideration, the as-obtained E_{observed} can be expressed by

$$E_{\mathrm{observed}} = E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\,\mathrm{M}\,M\mathrm{OH})} - E^{\circ}_{\mathrm{SCE}} + E_{\mathrm{LJP}} \tag{6}$$

where E°_{SCE} is the half-cell standard reduction potential of the SCE (0.2412 V vs SHE at 25 °C).[37] Using eq 6, each $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ value was obtained. For the true potential calculation, the E_{LJP} values determined by the LJPcalc software were used. By using the as-obtained triplicate $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values, means ± standard deviations were determined as shown in Table 1. To check whether the results of two sets of potential measurements can agree within experimental error or not, we conducted two-sample t-tests (see more details in the Supporting Information) and compared the results from two different SCEs for each internal solution case.[28] As indicated in Table S3, in all the internal solution cases, the calculated t values became smaller than a critical t value at a 95% confidence level. Therefore, it can be concluded that there is no statistically significant difference between the two measurements using two different SCEs. Furthermore, by computing the 95% confidence intervals for all the experimentally obtained $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values [see eq S4], we also confirmed whether the experimental $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values agree with the calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values or not. All the computational results are demonstrated in Figure 2. Each point and bar represent the mean of triplicate $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values and their corresponding 95% confidence interval, respectively. At the higher NaOH/KOH concentrations of 1 and 0.5 M (Figure 2a−d), the ranges of the as-computed 95% confidence intervals contain the calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values (dashed orange lines). Thus, for 1 and 0.5 M NaOH/KOH internal solutions, the experimentally obtained and calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values agree with each other within experimental error: the experimentally obtained results are not significantly different from the calculated results. In contrast, at the lower NaOH/KOH concentration of 0.1 M (Figure 2e,f), the calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values are outside of the ranges of the 95% confidence intervals, implying that our measurements provided different $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values from the calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values. In 1911, Donann et al. observed a different result when they also measured the potentials of three Hg/HgO electrodes with three different internal solutions (i.e., 0.1 M NaOH, 1 M NaOH, and 1 M KOH). Their resultant $E^{\mathrm{real}}_{\mathrm{Hg/HgO}(x\ \mathrm{M}\ M\mathrm{OH})}$ values are similar to our calculated values in both the higher and lower concentration cases (see Table 1).[3] As shown in Figure S9a, a commercially available Hg/HgO electrode contains a cotton absorbent at the Hg/HgO|internal solution interface, whereas the Hg/HgO electrode prepared by Donann et al.[3] did not contain cotton. Accordingly, there is a possibility that the as-observed potential deviations from the calculated $E^{\mathrm{real}}_{\mathrm{Hg/HgO(0.1\ M\ NaOH/KOH)}}$ might be caused by some chemical species (e.g., K^+, Na^+, OH^-, etc.) being unintentionally trapped in the cotton absorbent. To investigate this hypothesis, we prepared the Hg/HgO electrode main body preimmersed in 1 M KOH, washed it with deionized (DI) water, and then

Table 2. Calculated Liquid Junction (KCl sat.|x M MOH) Potentials (E_{LJP}) at 25 °C

junction: solution A|solution B	E_{LJP} (mV)[a]	E_{LJP} (mV)[b]
KCl sat.|1 M KOH	6.4	6.8
KCl sat.|1 M NaOH	8.0	8.5
KCl sat.|0.5 M KOH	3.7	4.0
KCl sat.|0.5 M NaOH	4.8	5.1
KCl sat.|0.1 M KOH	−0.1	0.0
KCl sat.|0.1 M NaOH	0.2	0.3

[a]Liquid junction potentials were calculated through the Henderson equation.[35] [b]Liquid junction potential was calculated according to the stationary Nernst−Planck equation[36] using LJPcalc software (https://swharden.com/LJPcalc).

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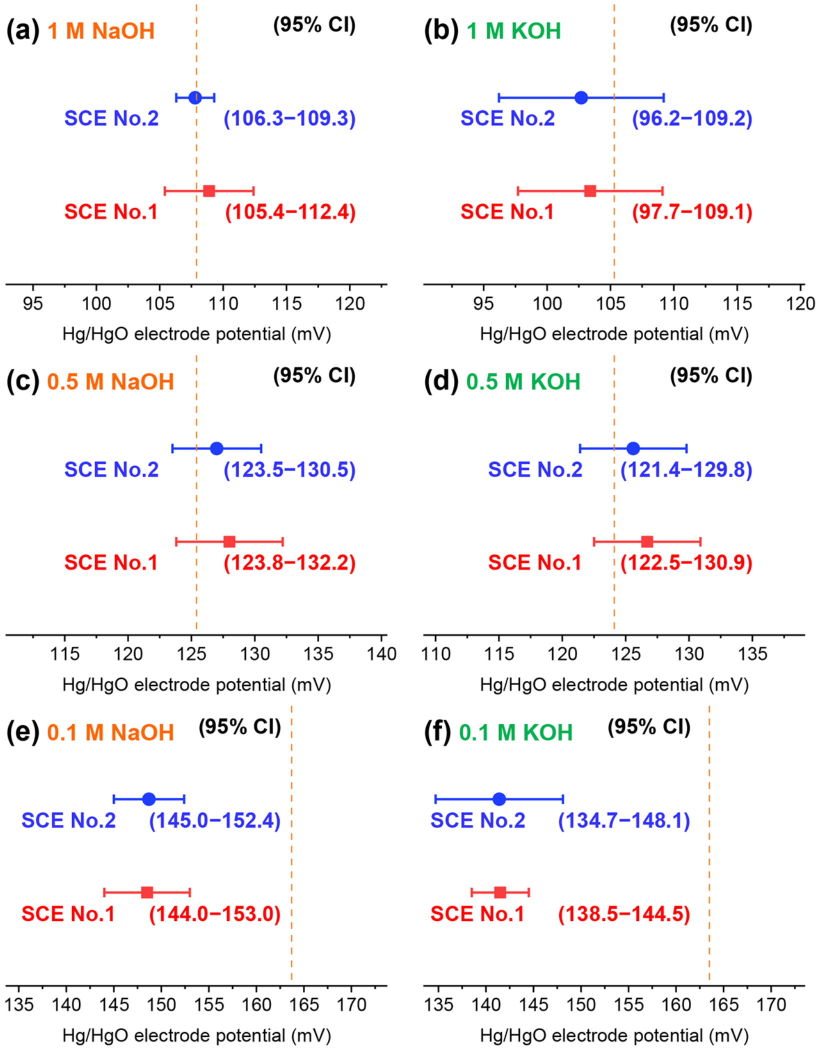

Figure 2. 95% confidence interval (CI) plots for the experimentally obtained potentials of Hg/HgO electrodes with different internal solutions (0.1−1 M NaOH/KOH). Dashed orange lines indicate the calculated Hg/HgO electrode potentials. Here, 95% probability experiment objective values lie in these as-calculated intervals. Note that experimental values are statistically compared with calculated values (≈ true values) in these figures.

performed SEM-EDX analysis of the cotton absorbent after immersing the as-washed Hg/HgO electrode main body in DI water for 50 h (see Figure S9b, details are available in the Supporting Information). Figure S9c shows the SEM image of the cotton absorbent after the 50 h DI water immersion. The cotton absorbent possessed a random micrometer-scale structure. The EDX elemental mapping images and corresponding EDX spectra are displayed in Figures S10 and S11. Surprisingly, even after the 50 h DI water immersion, the presence of potassium species in the cotton absorbent was confirmed. This result tells us that it is difficult to remove cations (i.e., Na^+ and K^+) from the cotton absorbent using concentration gradient as a driving force. In the $E^{real}_{Hg/HgO(0.1\ M\ NaOH/KOH)}$ measurement, the cotton absorbent probably retains Na^+/K^+ species from the previous experiments using the internal solutions with the higher NaOH/KOH concentrations. Presumably, OH^- can also be trapped due to the presence of Na^+/K^+ species, which induces charge neutralization. Consequently, the remaining Na^+/K^+ species might cause the local pH change near the Hg/HgO|internal solution interface, resulting in the Hg/HgO potential decrease.

Based on the above observations, we strongly recommend the readers calibrate their own Hg/HgO electrodes before performing any electrochemical tests, especially when they exchange the internal alkaline solution from high concentration to low concentration (e.g., 1 M → 0.1 M).

■ ADDITIONAL INSTRUCTIONS/PRECAUTIONS

Finally, we provide several instructions and discuss precautions when using the Hg/HgO electrode as a reference electrode in a standard three-electrode system.

- As seen in Table 3, if one uses two different alkaline solutions as internal and external electrolytes, undesired liquid junction potentials will be established at the Hg/HgO electrode frit. Moreover, during a long-term electrochemical test, internal/external solution may flow through the frit pores, resulting in the cation (Na^+/K^+) contamination and the concentration change of internal and external solutions.[38] Thus, one should use alkaline solutions with the same constituents at the same concentrations for both internal and external electrolytes.

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Table 3. Calculated Liquid Junction (x M M_1OH|y M M_2OH) Potentials (E_{LJP}) at 25 °C

junction: solution A|solution B	E_{LJP} (mV)[a]	E_{LJP} (mV)[b]
1 M KOH|1 M NaOH	2.3	2.3
0.1 M KOH|0.1 M NaOH	2.3	2.3
1 M KOH|0.1 M KOH	−27.1	−27.1
1 M NaOH|0.1 M NaOH	−35.3	−35.2
1 M KOH|0.1 M NaOH	−27.3	−26.8
1 M NaOH|0.1 M KOH	−34.9	−35.4

[a]Liquid junction potentials were calculated through the Henderson equation.[35] [b]Liquid junction potentials were calculated according to the stationary Nernst−Planck equation[36] using LJPcalc software (https://swharden.com/LJPcalc).

- Since yellow HgO is highly soluble in aqueous solutions at low pH values (<4),[12,39] the use of Hg/HgO electrodes in acidic media should be avoided.
- A small amount of yellow HgO can also dissolve into alkaline solutions.[40] Thus, laboratory safety regulations with instructions for mercury-containing wastes should be followed when disposing of external electrolytes and especially internal solutions.
- As the Hg/HgO electrode can be electrochemically stable under temperatures up to 90 °C,[13,15−17] one can use the Hg/HgO electrode for electrochemical studies that require relatively hot environments (e.g., alkaline fuel cells,[41] methane electrooxidation systems,[42] etc.).

SUMMARY

In this Viewpoint, we discussed computational and experimental methods for obtaining accurate potentials for Hg/HgO reference electrodes having NaOH/KOH solutions with different molar concentrations (0.1, 0.5, and 1 M) that are often used. By applying an accurate Hg/HgO electrode potential to the Hg/HgO-to-RHE potential conversion equation, one can report more accurate overpotential values for the HER and OER. We hope this study will improve the fundamental interpretation of the Hg/HgO electrode potential as well as the accuracy of reporting performance parameters in energy conversion devices involving alkaline media.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c05655.

Experimental details, a scheme (experimental design), calculation details, digital photographs, tables (calculation parameters and results), time−potential curves (SCE vs Hg/HgO), SEM and EDX elemental mapping images, and EDX spectra (PDF)

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Notes

The authors declare no competing financial interest.

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