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Getting the Basics Right: Preparing Alkaline Electrolytes for Electrochemical Applications

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The electrolyte represents a vital component of every electrochemical system that determines the fundamental properties of the electrode interface and relevant performance metrics. Remarkably, alkaline aqueous electrolytes (e.g., KOH and NaOH) are essential to numerous electrochemical energy devices, including alkaline electrolyzers, fuel cells, supercapacitors, and alkaline batteries. Alkaline electrolytes also affect the thermodynamic properties and kinetics of electrocatalytic reactions, such as the oxygen evolution reaction (OER), the hydrogen evolution reaction (HER), the oxygen reduction reaction (ORR), and the CO_2 reduction reaction (CO2RR).[1−5] The number of studies focusing on these electrochemical systems has experienced significant growth in the past decade. However, the lack of consistency among numerous interdisciplinary research groups working in this field has led to the misinterpretation of different processes and the overestimation of performance metrics, which previous Viewpoints have debated.[6−14]

Recent studies have shown that alkaline electrolyte concentrations and compositions should not be considered trivial because, for example, the presence of metal impurities and imprecise pH estimations have resulted in inaccurate descriptions of the electrochemical performance.[5,6,15−17] Therefore, there is a need for standardized protocols to improve and examine the quality of alkaline electrolytes so that electrochemical energy systems can be objectively evaluated and compared.[12,13] In this Viewpoint, we describe six practices to prepare, characterize, and validate the quality of alkaline electrolytes used in electrochemical energy systems (Figure 1). By adapting previous procedures and performing specific measurements, we provide a unified protocol to prepare and purify alkaline electrolytes, standardize their concentrations, determine their elemental compositions, provide statistical metrics, and examine their electrochemical properties.

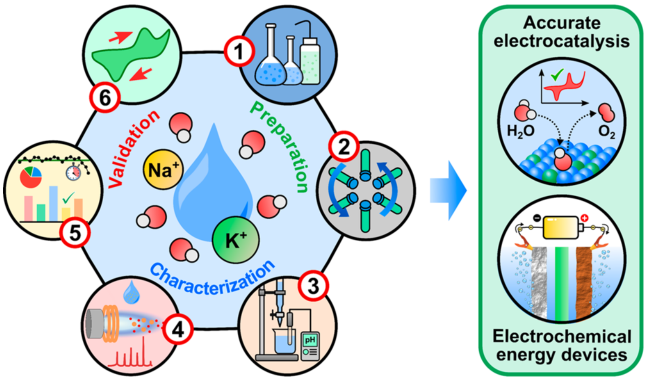

Figure 1. Preparing, characterizing, and validating the quality of alkaline electrolytes through systematic protocols enables consistent evaluation and comparison of electrochemical systems.

Step 1: Best Practices for Alkaline Electrolyte Preparation. The preparation of alkaline electrolytes needs to meet specific requirements to achieve accurate concentrations and minimize impurities. We summarize some essential practices based on traditional procedures presented in well-known textbooks and our experience. We describe these practices in detail in the Supporting Information (Section S1).

First, inaccurate alkali concentrations can lead to erroneous pH estimation and, therefore, questionable reports of voltage efficiency and overpotentials of electrocatalysts.[6] This problem is mainly caused by (1) CO_2 absorption that modifies the effective molarity due to dissolved carbonate, (2) incorrect weighing due to the hygroscopic nature of alkali solids, and (3) incorrect calculations caused by improper use of compositions given by companies (see Table S1). CO_2 absorption can be prevented by boiling deionized (DI) water before use and sparging electrolytes with inert gases. Handling hygroscopic solids can be improved if measurements are done in low-humidity environments. Correct solid calculations are done when accurate alkali purities are retrieved from certificates of analysis from the manufacturer. Moreover, these three problems can be effectively controlled by standardizing the final electrolyte concentration (see Step 3).

Second, impurities induce detrimental effects and impact reproducibility when studying electrocatalytic materials.[10,18−20] For instance, glass etching products and metal impurities can deactivate electrocatalysts,[4,12,21−24] whereas Fe impurities enhance the OER activity.[15,19,25−27] Fe impurities can also form hydroxyl radicals that poison and degrade critical components such as cation exchange membranes.[28] Al impurities are also responsible for significant performance degradation due to changes in the ORR mechanism.[29]

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Importantly, some of these effects occur only after long-term tests. Therefore, special attention must be given to stability examinations when impurities are present in electrochemical energy devices.

Alkaline electrolytes can be easily contaminated with impurities if not prepared and handled correctly. For instance, it is well-known that strong bases etch glasses, including borosilicate glass, resulting in unwanted impurities.[21,30,31] These can also originate from incorrect cleaning of glassware or using chemicals with low purities.[22] Thus, we recommend replacing glassware (i.e., volumetric flasks, beakers, stir rods, vials, and bottles) with plasticware whenever possible, especially when concentrated alkaline electrolytes are used for long periods.[21] Cleaning glassware and plasticware with strong acid solutions is also highly recommended. Researchers must carefully select acids with high purity to avoid a systematic error. We recommend using trace-metal grade nitric acid, although other mixtures, such as aqua regia, can be used to wash electrodes and cells.[32] Finally, we encourage the use of glass-free components in electrochemical cells. For instance, previous studies have used PTFE cells to avoid glass etching in alkaline media.[15,19,21,25,33,34] Note that Fe, Ti, Mn, and other metal impurities have been found in other materials often regarded as "metal-free," such as 3D printing filaments and other polymers.[35,36] Therefore, we encourage future studies to always examine the impact of impurities, especially after prolonged testing.

Step 2: Removing Fe Impurities. The work by Trotochaud et al. revealed a worrying fact: numerous studies of Ni-based electrocatalysts showing "outstanding" OER activities were likely affected by Fe impurities.[15] Thus, this field urgently needs to recognize and account for the effect of impurities in electrochemical energy systems. However, through an exhaustive literature survey using SciFinder, we found that roughly ~6% of the publications mention using some electrolyte purification routine. Hence, it is likely that a large number of studies on electrochemical energy devices report erroneous performance metrics, impeding the advancement of the field.

The Boettcher group proposed an effective method to remove Fe from KOH electrolytes,[15,37] alleviating the challenges of comparing electrocatalytic activity. Although this method has proven reliable, we have observed that reproducibility varies when some steps are not performed systematically. Thus, we adapted the Fe purification protocol from the Boettcher group by adding specific steps to improve reproducibility and maximize Fe removal. The routine is detailed in Section S2, and a suggested workflow is shown in Scheme S1. Certain variables were optimized to validate the effectiveness of our protocol (see Step 4). Still, this is not the only method to remove Fe. Electrochemical purification methods or removal assisted by chemical agents and resins have been reported.[19,22,32,38] Note, however, that specific electrochemical setups could be hard to replicate, and adding chemicals could potentially interfere with tests.[18,39] Thus, we recommend limiting their use to studies where superior removal is needed. In Steps 4 and 6, we experimentally demonstrate that our routine meets satisfactory impurity levels with minimal impact during electrochemical tests, making it adequate for most studies. Nevertheless, we know that the performance of this routine could vary if alkaline electrolytes with different compositions are used. Therefore, we encourage determining the exact composition after purification (see Step 4).

Step 3: Alkaline Electrolyte Standardization. Once the alkaline electrolyte has been purified, the exact concentration must be determined. Knowing precise alkali concentrations provides reliable pH values and, therefore, an accurate description of the electrode potentials (e.g., conversion to the reversible hydrogen electrode, RHE).[8] This is a critical step because most studies typically round concentrations, although this may not be true due to the problems discussed in Step 1. A simple but rigorous method to determine the alkali concentration is the weak acid−strong base volumetric titration, which is widely described in classical chemistry textbooks. Our group uses a protocol to standardize monoprotic alkaline electrolytes (e.g., NaOH, KOH) against a nonhygroscopic primary standard (see Section S3 and Figure S1). We demonstrate the accuracy of this method by both conventional volumetric titrations and a pH probe (Figure S3). Both approaches exhibit comparable repeatability.

We found that 1 M KOH solutions prepared from different varieties and manufacturers exhibited different molarities (Figure S4). This lack of accuracy results from different alkali compositions and water absorption, demonstrating the importance of standardizing alkaline electrolytes and following the guidelines from Step 1. Figure S5 shows the effect of rinsing the $Ni(OH)_2$ precipitate with KOH after washing with deionized water during Fe purification. When the precipitate is washed with 5 mL of KOH three times, the alkali concentration after purification remains close to the concentration of unpurified KOH (Figure S5a). However, when the precipitate is not washed, the resulting purified electrolyte is diluted due to water remaining in the precipitate (Figure S5b). Hence, it is essential to perform purification systematically to avoid changes to the final composition and to determine the exact alkali concentration via titration.

To assist in applying these standardization routines in the field, we provide a spreadsheet to estimate alkaline electrolyte molarities (~1 M) using volumetric and pH titrations. Notably, the Menezes group published a Viewpoint highlighting the relevance of determining accurate pH values of alkaline electrolytes. They provided a convenient spreadsheet to calculate pH values using activity coefficients (e.g., from concentrations in mol/kg or mol/L).[6] Once the electrolyte pH is known, accurate reference potentials can be estimated by calibrating the reference electrode with the standard hydrogen electrode as described elsewhere.[40] Thus, we recommend combining these resources to ease the conversion of electrode potentials. Finally, note that estimating alkali concentrations would improve not only the reproducibility of electrochemical tests but also the description of the electrocatalytic activity because reactions such as the OER and the CO2RR are highly sensitive to the electrolyte pH.[5,16,41,42]

Step 4: Determining Compositions through ICP-MS. Determining the exact composition of alkaline electrolytes is critical to examine the effects of impurities on electrochemical energy systems. Inductively coupled plasma mass spectrometry (ICP-MS) is a robust elemental analysis technique for quantifying trace metal ions. However, analyzing strong base solutions is challenging due to the complex ion matrix and high total dissolved solids (TDS), often requiring additional separation methods.[19,43,44] Our group developed a solution-mode ICP-MS method to analyze ~1 M KOH and NaOH electrolytes without affecting the detection limits necessary for trace-metal analysis. As detailed in Section S4, this method uses a simple dilution routine (Scheme S2) to decrease TDS levels and a collision/reaction cell to remove polyatomic interferences, resulting in detection limits below 1 ppb for all trace-metal impurities (Table S2). We used this method to determine the composition of these electrolytes under different conditions. Figures 2 and S6 show the concentrations of major elements found in unpurified and purified electrolytes. Detailed compositions are shown in Table S3. Remarkably, concentrations as low as 1 ppb were estimated. After following our purification protocol, the Fe concentration in the unpurified KOH electrolyte (~60 ppb) decreased nearly six times (~9 ppb). The concentrations of other elements remain almost constant, and only Ni, Cu, B (KOH) and Zn, Li (NaOH) exhibit significant differences before and after purification.

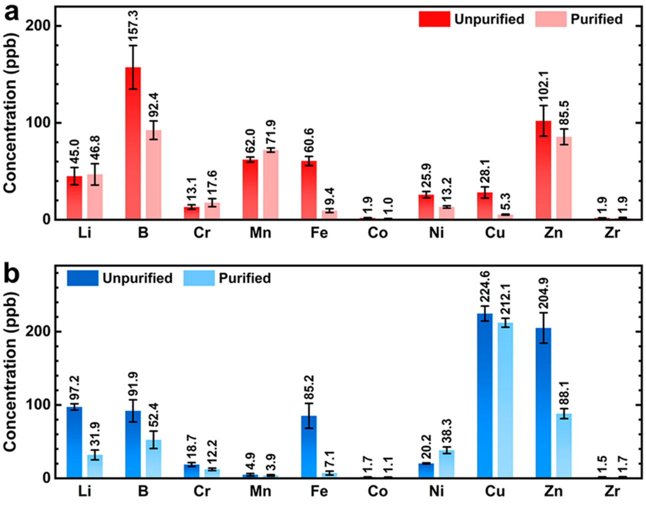


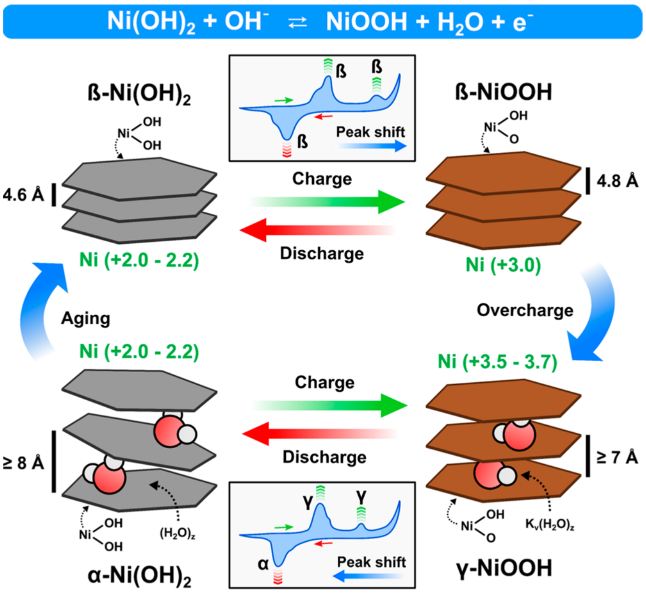
Figure 2. Concentrations of primary elements in unpurified and purified alkaline electrolytes from solution-mode ICP-MS analysis: (a) 1 M KOH and (b) 1 M NaOH.

We also examined the effects of the practices discussed in previous steps. Using glassware to prepare alkaline electrolytes increases the concentration of B, Al, and Si compared with electrolytes prepared using plasticware (Figure S7). Fe and Ni concentrations in KOH electrolytes from different manufacturers vary significantly (Figure S8). Even ultrahigh purity (UHP) KOH is not entirely free from Fe (~18 ppb). Furthermore, we examined the effect of the resting time and KOH concentration during Fe purification. Figure S9a shows that Fe remains constant below 10 ppb only after 48 h of resting. Figure S9b reveals that the Fe concentration increases with the KOH concentration, suggesting that Fe removal efficiency decreases with concentrated KOH, and thus, more $Ni(OH)_2$ precipitate is needed to remove Fe effectively. Overall, estimations of trace impurities can be made in ~1 M KOH and NaOH electrolytes using ICP-MS. We encourage future studies to examine metal contents not only in electrocatalysts but also in alkaline electrolytes.

Step 5: Statistical Quality Control. Due to the growth of interdisciplinary research in this field, we urge the community to adopt analytical quality control measures. The fifth step involves using statistics to describe the accuracy, repeatability, and reproducibility of electrolyte preparation. We recommend using the following (see Section S5 and the spreadsheet in the Supporting Information): (1) descriptive statistics (e.g., mean, standard deviation, relative standard deviation) and standard uncertainties, (2) performing the Grubbs' test to identify outliers, (3) control charts to track changes in electrolyte compositions, and (4) Student's *t* tests to compare means and determine statistical significance among groups. We also encourage the readers to report uncertainties properly.[20,45] Adopting these guidelines will improve reproducibility and enable meaningful comparisons in the field.

Step 6: Validation through Electrochemical Testing. Although elemental analysis provides precise electrolyte compositions, such analysis may not be readily available for everyone. However, conventional electrochemical tests, such as cyclic voltammetry (CV), can be used to detect Fe impurities on Pt, Au, and Ni electrodes.[4,15,19,25,32,38] Remarkably, the electrochemical behavior of Ni in alkaline media has been extensively examined. Activation of Ni electrodes in alkaline media results in a thin $Ni(OH)_2$ film, while subsequent charging results in an NiOOH-type structure, which is the OER-active phase.[25] As described by Bode,[46] pure $Ni(OH)_2$ and NiOOH have ordered (β) and disordered (α/γ) phases, and their populations can be changed via aging or redox transformations (e.g., charge/discharge and overcharge), resulting in characteristic redox peaks (Scheme 1). We examined the electrochemical behavior of Ni foam electrodes using purified and unpurified electrolytes (experimental details in Section S6; see Supporting Note 1 and Figure S10 for important electrode considerations).

Scheme 1. Bode Scheme of the Ni^{2+}/Ni^{3+} Redox Transition Illustrating the Different Phases of the Layer Stacking and Expected Voltammogram Shapes



Cycling in purified and unpurified KOH results in different CV shapes (Figure 3). As depicted in Figures 3a and S11 (see Supporting Note 2 for detailed peak description), redox peaks at ~1.4 and ~1.6 V vs. RHE increase in intensity due to promotion of the ordered β/β phase during aging in Fe-purified KOH (~9 ppb Fe).[15,25] As depicted in Figures 3b and S12, aging in unpurified KOH (~60 ppb Fe) obscures redox peaks at ~1.6 V vs. RHE due to a significant decrease of the OER overpotential and anodic shift of $Ni^{2+/3+}$ redox peaks due to suppression of the $Ni^{2+/3+}$ redox reaction by Fe (see

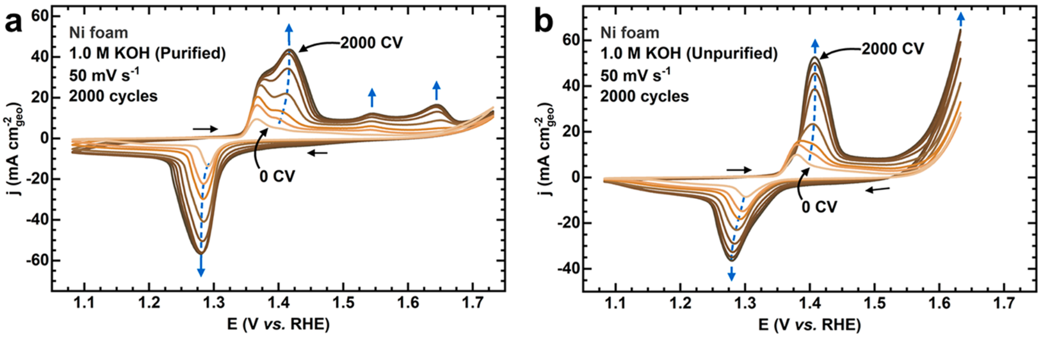


Figure 3. Extended cycling of Ni foam electrodes in 1 M KOH: (a) purified and (b) unpurified.

Supporting Note 3).[25,33] As shown in Figure S13, anodic Ni redox peak and OER overpotential changes can be easily tracked using CV. We also examined the activation of Ni foam in UHP KOH (~18 ppb Fe) using CV (Figure S14). Although peaks characteristic of the ordered β/β phase were seen, we found a subtle decrease of the OER overpotential after an additional 2000 cycles (see Figure S15 and Supporting Note 4). Purified and unpurified NaOH electrolytes also exhibited distinct CV shapes and Ni redox peak shifts (Figures S16 and S17). Finally, electrochemical impedance spectroscopy (EIS) was utilized to complement these tests (see Figure S18, Table S4, and Supporting Note 5). Although the double-layer capacitance (C_{dl}) of Ni foam after CV increases in all electrolytes, only activation in unpurified KOH results in lower charge transfer resistance (R_{ct}) due to improved OER kinetics.[26]

Fe incorporation also affects bimetallic electrocatalysts if tested in unpurified KOH, resulting in inaccurate descriptions due to varying Fe contents.[25,27,33,34] Thus, we tested NiFe foam electrodes (Fe ~ 2.5%) in unpurified KOH (~60 ppb Fe). Figure S19 shows a distinct decrease in the OER overpotential and anodic peak shifting after CV (see Supporting Note 6). Physicochemical characterization of the NiFe foam electrode before and after CV aging reveals an increase in the Fe content on the electrode surface (Figure S20). Similarly, EIS analysis shows differences in the R_{ct} values caused by the increase of the OER activity (Figure S21 and Table S5). Thus, further Fe incorporation can occur even if the material already contains Fe, making the estimation of reliable electrocatalytic metrics difficult. As shown in Figure S22, the anodic peak for the α/γ phase shifts anodically with the Fe content and decreases the OER overpotential, hindering the β/β phase (see Supporting Note 7).

Hence, we recommend monitoring the redox peaks of the β to γ phase transition at ~1.6 V vs. RHE (i.e., $\mathbf{a}_3$ and $\mathbf{a}_4$ peaks in Figure S11) via CV activation as a convenient method to detect Fe incorporation. Prolonged CV scans of Ni electrodes in Fe-purified electrolyte could be reported in the supporting information by researchers to confirm the absence of Fe impurities when ICP-MS is unavailable. However, we strongly encourage complementing both methods whenever possible. We also encourage researchers to detect trace impurities using other methods, especially when other electrode materials are tested (e.g., Pt and Au).

We highlight three essential aspects of metal incorporation. First, Fe-purified electrolytes should be used to study Ni-based electrocatalysts, including those already containing Fe, to avoid variation in Fe compositions. However, Fe dissolution into purified electrolytes also occurs, leading to changes in Fe concentrations, especially during prolonged tests.[19] Therefore, electrolyte and surface composition analysis after electrochemical tests is encouraged. Second, note that metal impurities could also affect the energy storage capabilities of redox capacitors and alkaline batteries.[27,47] More studies are needed because this problem has not been widely examined. Third, metal incorporation might be inevitable even after purification or when using UHP electrolytes (see Supporting Note 4). However, researchers must constantly examine its extent and impact on electrochemical systems so that fair comparisons and accurate descriptions of electrocatalytic activity/stability can be made.[4,19]

Studies on other electrochemical systems, such as CO_2 and N_2 reduction, also depend on alkaline electrolytes and Ni-based anodes to perform the OER and therefore need to follow these guidelines.[5,12] Note, however, that the effect of other impurities in these systems remains unclear, and practices such as electrolyte standardization must consider the presence of other species (e.g., carbonates when studying the CO2RR). Therefore, we urge the community to adopt and modify the practices from this Viewpoint, so that general practices are established in developing fields and adopted by the community. Importantly, these effects must be carefully examined during extended periods so that the electrochemical description is accurate and reproducible.

In conclusion, alkaline electrolyte properties are often considered trivial, although their impact on electrochemical energy systems is critical. Even slight changes and assumptions of the electrolyte concentration can result in erroneous and inaccurate descriptions of the electrocatalytic activity (see Figure S23 and Supporting Note 8). In this Viewpoint, we show six essential practices to improve the preparation, characterization, and validation of common alkaline aqueous electrolytes that research groups can easily apply in the future. We believe that generalizing these practices would significantly improve the evaluation and comparison of electrochemical energy materials and devices operating with alkaline electrolytes.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c02847.

Detailed experimental protocols, supporting figures, and tables: electrolyte molarities from titrations, detailed elemental compositions from ICP-MS, electrochemical characterization of Ni and NiFe electrodes, and NiFe foam characterization (PDF)

Excel spreadsheet for volumetric and pH titrations of ~1 M KOH/NaOH electrolytes (XLSX)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Notes

Views expressed in this Viewpoint are those of the author and not necessarily the views of the ACS.
The authors declare no competing financial interest.

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