Unveiling hydrogen evolution dependence on KOH concentration for polycrystalline and nanostructured nickel-based catalysts

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Abstract
Nickel-based hydrogen evolution reaction (HER) electrodes have been widely used in alkaline and anion exchange membrane water electrolysis. Therefore, understanding the activity dependence on the KOH concentration (pH) of alkaline electrolytes is essential for designing durable and active HER catalysts. In this work, the HER activity and kinetics of polycrystalline and nanostructured nickel-based catalysts are evaluated in various pH and KOH concentrations. The results for nanostructured NiMo catalyst indicate that both electrochemical active surface area and reaction order have a promoting region under various pH's and KOH concentrations (0.01–1.0 M, pH 12–14) accompanied by better HER activity (a lower overpotential for achieving −10 mA cm⁻²) and Tafel slope decreases from around 180 mV dec⁻¹ to 60 mV dec⁻¹ in the same pH and KOH concentration range. The change in the Tafel slope indicates that the HER rate-determining step for HER at NiMo/C changes with pH and KOH concentration. The polycrystalline Ni displays different behaviours where a promoting (0.01–0.10 M, pH 12–13), stabilizing (0.1–1.0 M, pH 13–14), and an inhibiting region (2 M, pH > 14) are present. However, Tafel slopes of around 120 mV/dec are obtained for polycrystalline Ni at all KOH concentrations. The HER characteristics are inhibited at 2.0 M KOH for both catalysts due to slower OH* transport kinetics. The results confirmed the importance of tuning catalyst-pH/KOH concentration for better HER activity and kinetics.

Graphical abstract

Keywords Hydrogen evolution reaction (HER) · Nickel · Catalyst-electrolyte interaction · KOH effect · Alkaline electrolysis

1 Introduction
The hydrogen evolution reaction (HER) kinetics is sluggish in an alkaline environment being two orders of magnitude slower than that in an acidic environment [1, 2]. The large
energy ($E_a$) of the $H_{ads}$ intermediate formation (Volmer reaction) and water dissociation process in alkaline HER induces an additional energy barrier and controls the overall reaction rate [3, 4].

Nickel (Ni) is a promising HER catalyst for cathode electrodes in alkaline and anion exchange membrane (AEM) water electrolysis [5–7]. Thus, understanding the electrolyte pH/KOH concentration dependence on the HER and electrochemical surface area (ECSA) of nickel-based electrodes has recently become one of the key issues in nickel electrocatalysis. The HER on nickel occurs at an applied negative potential ($E < 0.00$ V vs. RHE) where the water is reduced to hydrogen and the surface of the electrode is metallic nickel [8, 9]. When nickel is scanned in the positive potential direction ($0 \leq E_{app} \leq +0.50$ V vs. RHE), the Ni surface is converted into $\alpha$-Ni(OH)$_2$ when reacted with OH$^-$ ions [9]. When the electrode is scanned in a reverse direction, $\alpha$-Ni(OH)$_2$ is easily reduced to Ni [8, 9]. The ECSA is an important parameter in defining catalyst intrinsic HER activity [10, 11] and the surface area of the catalyst in contact with the electrolyte [12, 13]. Machado and Avaca introduced a method for determining the ECSA of Ni by polarizing the Ni electrode cathodically to remove any traces of surface oxides/hydroxides and then recording a cyclic voltammogram for the Ni electrode or catalyst in the $\alpha$-Ni(OH)$_2$ potential region ($\approx -0.15 \leq E_{app} \leq +0.50$ V) [14].

In the case of platinum (Pt), fundamental HER studies have indicated that the catalyst-electrolyte interaction on single/polycrystalline Pt depends upon the pH of the electrolyte. The HER kinetics in alkaline and high-pH conditions are sluggish and two orders of magnitude slower than in acidic due to pH-dependent $H$-adsorption energy and/or water dissociation energy barrier which suppress their practical applications [15–19]. However, these studies are limited to single/polycrystalline Pt and certain types of electrolytes and concentrations such as 0.1 M KOH (pH 12.8–13) and buffer solutions for pH (7–10) without going to higher pH/KOH concentrations.

Recently, Li et al. found that on polycrystalline Pt, the HER activity increased as the NaOH concentration increased from 0.01 (pH 12) to 1.0 M (pH 14) [20]. Wang et al. showed that Pt catalyst-electrolyte interaction is dependent upon catalyst morphology with the HER activity of nanostructured Pt-based electrocatalysts being better in high-pH (0.1–1.0 M KOH, pH 13–13.5) electrolytes than in less alkaline environments (0.01 M KOH to neutral buffer, pH 12–7.1). Polycrystalline Pt showed the opposite trend [19]. Kuznetsov et al. noted that the anodic charge (for $\alpha$-Ni(OH)$_2$ formation charge and electrochemical $H_{ads}$ oxidation) and ECSA of NiCu/C CVs depend on the NaOH concentration and HER activity of partially oxidized Ni disc electrode increased with the pH/NaOH concentration below $-0.18$ V vs. RHE [21]. Cossar et al. also mentioned that current densities in CVs can change with electrolyte concentration, meaning that the apparent active surface areas can change with the electrolyte concentration [22].

However, apart from the aforementioned studies on Pt, there are no detailed reports and information dealing with Ni-based catalyst-alkaline electrolyte interaction and how the ECSA or the HER activity of polycrystalline and nanostructured nickel-based catalyst change with pH/KOH concentration. Polycrystalline Ni and nanostructured NiMo are widely studied as HER catalysts in traditional alkaline and AEM water electrolysis, respectively [20].

In this work, the influence of pH/KOH concentration on HER performance, ECSA, Tafel slope, and reaction order for two model catalysts (polycrystalline Ni and nanostructured NiMo) are evaluated. The catalyst stability under various pH concentrations is beyond the focus of this communication. The results indicate that KOH electrolyte catalyst interaction relies on the composition and morphology of Ni-based catalysts.

### 2 Experimental methods

All electrochemical experiments were carried out using a potentiostat/galvanostat (BioLogic-SP 150) in a three-electrode configuration. The working electrodes (WE) were nickel-based catalysts (either polycrystalline nickel (Ni-poly) disc ($\Theta = 5$ mm) or nanostructured NiMo) of a geometric surface area of $A_g = 0.196$ cm$^2$. The nanostructured NiMo has been synthesized with a modified process of chemical reduction using sodium borohydride reported by Faid et al. [7]. The reference electrode (RE) was a homemade reversible hydrogen electrode (RHE). All potential values in this work are reported against the RHE. A Ni mesh (40 mesh woven from 0.13 mm diameter wire, 99.99% metal basis, Alfa Aesar, Germany) was cut out in a rectangular shape ($20.67 \times 10.76$ mm$^2$) and used as a counter electrode (CE). The loading of nanostructured NiMo was kept at 0.25 mg cm$^{-2}$. The ohmic ($IR$) drop was compensated at 85% of the ohmic resistance measured by the electrochemical impedance spectroscopy (EIS) technique at $-0.3$ V vs. RHE. The EIS test was collected in a frequency range of $0.1$–$10^5$ Hz with an amplitude of 10 mV alternative current (AC) perturbation.

The electrolytes were prepared by mixing KOH pellets (Sigma-Aldrich, 99.99% in purity) in ultra-high purity water (Millipore, 18.2 MΩ cm in resistivity). All KOH electrolytes (0.01, 0.10, 0.5, 1.0, and 2.0 M KOH) were outgassed using ultra-high purity $N_2(g)$ (99.999% in purity) before each experiment.

The HER experiments were investigated by a series of linear sweep voltammetry (LSV) in the potential region of $0.00 \leq E_{app} \leq -0.60$ V vs. RHE at the potential scan rate of...
\( \nu = 0.30 \text{ mV s}^{-1} \). Cyclic voltammetry experiments were carried out at a potential scan rate of \( \nu = 20, 50, \) and \( 100 \text{ mV s}^{-1} \) in the potential region of the formation and reduction of \( \alpha-\text{Ni(OH)}_2 \) (\( -0.15 \leq E_{\text{app}} \leq +0.50 \text{ V vs. RHE} \)).

The structure and surface of Ni-poly disc electrode and nanostructured NiMo were studied using scanning electron microscopy Zeiss-Ultra/Supra 55-FEG-SEM.

### 3 Results and discussions

#### 3.1 Effect of KOH concentration on the HER performance

Figure 1a and b show SEM images of polycrystalline Ni.
and nanostructured NiMo. The SEM image of polycrystalline Ni is a relatively smooth surface while the nanostructured NiMo has nanoparticle morphology.

Figure 1c and d show LSV curves of the HER activity of polycrystalline Ni and nanostructured NiMo in various KOH concentrations (0.01–2.0 M). The nanostructured NiMo resulted in higher HER performance than polycrystalline Ni. Both polycrystalline Ni and nanostructured NiMo have similar trends with HER activity increasing as the pH/KOH concentration increases from 0.01 to 1.0 M (pH 13.8) and then the HER performance slightly decreased in 2.0 M (pH 14.2) KOH. Figure 1e displays the overpotential required to achieve −10 mA cm−2 for polycrystalline Ni and nanostructured NiMo in various KOH concentrations (0.01–2.0 M). Nanostructured NiMo achieves −10 mA cm−2 at an overpotential of 160 mV compared to 360 mV for polycrystalline Ni. For all pH/KOH concentrations, nanostructured NiMo has nanoparticle morphology.

3.2 Effect of KOH concentration on ECSA

Figure 2a and b show the CV transients of α-Ni(OH)2 formation and reduction at various KOH concentrations (0.01–2.0 M) of polycrystalline Ni and nanostructured NiMo. The anodic and cathodic features correspond to the formation and reduction of a surface layer of α-Ni(OH)2. The shape of the oxidation and reduction peaks is characteristic of the formation of α-Ni(OH)2 and its reduction to metallic Ni, respectively.

The CVs of polycrystalline Ni and nanostructured NiMo at the same scan rate displays a higher peak current for the formation of α-Ni(OH)2 in 0.01 to 1.0 M KOH concentration increases from 0.01 to 1.0 M then decreases at 2.0 M. The increase of the α-Ni(OH)2 formation current is in the order of 0.01 < 0.1 < 0.5 < 2.0 < 1.0 M.

The ECSA is calculated using the following equation:

\[
\text{ECSA} = \frac{Q}{514}\]  

(1)

where \(Q\) is the experimentally determined charge of α-Ni(OH)2 formation in µC. The theoretical charge value (514 µC cm−2) is the charge required to form one monolayer of α-Ni(OH)2 [23].

When considering ECSA based upon α-Ni(OH)2 charge, for polycrystalline Ni, the ECSA increased by 50% from 0.01 to 1.0 M KOH while for nanostructured NiMo, the ECSA increased more than 8 times from 0.01 to 1.0 M KOH as shown in Fig. 2c.

3.3 Effect of scan rate on the CV behaviour and ECSA

Figure 2d and e show the CV transients obtained in the potential region of the α-Ni(OH)2 formation and reduction in 0.10 M and 1.0 M aqueous KOH on nanostructured NiMo and polycrystalline Ni and were acquired at different potential scan rates \(ν = 20, 50,\) and 100 mV s⁻¹.

The oxidation (anodic) peak potential (\(E_{p,ox}\)) and the recombination (cathodic) peak potential (\(E_{p,red}\)) correspond to the oxidation and reduction peak current (\(I_{p,ox}\) and \(I_{p,red}\)) change with scan rate. For polycrystalline Ni and nanostructured NiMo, in both concentrations, \(E_{p,ox}\) shifted towards higher potentials upon increasing the value of \(ν\), while potential \(E_{p,red}\) shifted towards negative values. Furthermore, \(I_{p,ox}\) and \(I_{p,red}\) values increased upon increasing the value of \(ν\). The results illustrate that there is a linear relationship between \(I_{p,ox}\) and \(ν\). On the other hand, while there appears to be a linear relationship between \(I_{p,red}\) and \(ν\), a careful analysis of this relationship is more complicated due to overlapping contributions from the reduction of α-Ni(OH)2 and HER.

As can be seen in Fig. 2, by decreasing the potential scan rate, the \(I_{p,ox}\) in 0.10 M and 1.0 M aqueous KOH solution decreased. As described earlier, this peak corresponds to the formation of α-Ni(OH)2 and is used to determine the electrochemical surface area of Ni electrodes.

The ECSA values at different scan rates in 0.10 M and 1.0 M aqueous solutions obtained from CVs are shown in Fig. 2f. The figure displays a very minor dependence on potential scan rate for polycrystalline Ni and nanostructured NiMo in 0.1 and 1.0 M KOH. For polycrystalline Ni, at the same pH/KOH concentration, the ECSA-scan rate dependence displays that ECSA will vary only \(3 ± 1\%\) when the scan rate increases from 20 to 100 mV s⁻¹ in 0.1 and 1 M KOH as in Fig. 2f. At the same scan rate \(ν = 100\) mV s⁻¹, the ECSA of polycrystalline Ni in 1.0 M aqueous KOH solution is only \(2.6\%\) greater than in 0.10 M aqueous KOH solution.

The nanostructured NiMo showed a higher degree of ECSA dependence on potential scan rate at 0.1 M KOH than 1.0 M KOH. The ECSA-scan rate dependence displays that ECSA varies \(20 ± 2\) and \(5 ± 1\%\) when the scan rate increases from 20 to 100 mV s⁻¹ in 0.1 and 1.0 M KOH, respectively as in Fig. 2f.

3.4 Effect of KOH concentration on the HER kinetics

Figure 3a and b display Tafel slopes of polycrystalline Ni and nanostructured NiMo in (0.01–2.0) M KOH concentrations. Tafel slopes of around 120 mV dec⁻¹ are obtained for polycrystalline Ni at all studied KOH concentrations, indicating that HER is controlled by the first electron transfer step (Volmer step), which is governed by the barrier of the electrochemical water dissociation.
Nanostructured NiMo displays Tafel slopes dependence on KOH concentration with Tafel slope of around 180, 145, 110, 62, and 70 mV dec\(^{-1}\) in 0.01, 0.1, 0.5, 1.0, and 2.0 M KOH, respectively. Tafel slope of 120 mV dec\(^{-1}\) indicates a Volmer step as a rate-determining step (rds) at lower concentration (0.01–0.5 M KOH) while a Tafel slope of around 60 mV dec\(^{-1}\) corresponds to a rds of second electron transfer Heyrovsky step implying that the HER mechanism for nanostructured NiMo changes with KOH concentration to

\[
\text{H}_2\text{O} + e^- + * \rightarrow \text{H}^* + \text{OH}^- \quad \text{(Volmer)}
\]

Nanostructured NiMo displays Tafel slopes dependence on KOH concentration with Tafel slope of around 180, 145, 110, 62, and 70 mV dec\(^{-1}\) in 0.01, 0.1, 0.5, 1.0, and 2.0 M KOH, respectively. Tafel slope of 120 mV dec\(^{-1}\) indicates a Volmer step as a rate-determining step (rds) at lower concentration (0.01–0.5 M KOH) while a Tafel slope of around 60 mV dec\(^{-1}\) corresponds to a rds of second electron transfer Heyrovsky step implying that the HER mechanism for nanostructured NiMo changes with KOH concentration to
Volmer-Heyrovsky mechanism. This change in the reaction mechanism suggests that the cation concentration plays an important role in how accessible the surface is for hydrogen adsorption.

\[ \text{H}^* + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^- + * \] (Heyrovsky)

Tafel slopes of 120, 40, and 30 mV dec\(^{-1}\) observed for the Volmer, Heyrovsky, and Tafel determining rate steps, respectively, are widely accepted for kinetic models. However, for Heyrovsky as a rate-determining step, at higher coverage region (\(\theta_H > 0.6\)), a Tafel slope of 120 mV dec\(^{-1}\) was observed. Therefore, a Tafel slope of 120 mV dec\(^{-1}\) may originate from either the Volmer or the Heyrovsky rate-determining step with high adsorbed hydrogen atom coverage [24].

It is proposed that massive \(\text{H}_3\text{O}^+\) intermediates generated at high-pH/KOH concentration electrolytes (1.0 M KOH) would create a unique acid-like local environment on the surface of nanostructured catalysts, which facilitates the overall HER kinetics. In low-pH/KOH concentration electrolyte or bulk materials surface, such an anomalous enriched \(\text{H}_3\text{O}^+\) layer is absent, so a poorer HER activity is observed [19].

The increase in Tafel slope and overpotential to achieve \(-10\) mA cm\(^{-2}\) when moving from 1.0 to 2.0 M KOH suggested a detrimental effect on HER when using 2.0 M KOH concentration due to high local alkalinity, high viscosity, and low \(\text{OH}^-\) transport.

Figure 3c and d display reaction order plots of polycrystalline Ni and nanostructured NiMo. The current is reported for 50 mV potential steps (vs. RHE) plotted as a function of the logarithm of the current density on the y-axis and the logarithm of the cation concentration on the x-axis. The slopes extracted from the linear fit of the current response (reaction orders) are shown next to the plots. The figure shows positive reaction orders for both polycrystalline Ni and nanostructured NiMo.

For polycrystalline Ni, positive reaction order increase with applied HER potential, however, at higher KOH...
concentration (2.0 M), the reaction order trend reversed, indicating an inhibiting effect on HER due to higher local alkalinity and the concentration of weakly hydrated cations at the reaction interface.

For nanostructured NiMo, the positive reaction order is almost constant at around 0.33 ± 0.02 and stabilizes at higher KOH concentrations up to 2.0 M KOH. It should be noted that we do not see here the inhibition effect of higher KOH concentration (2.0 M) as in polycrystalline Ni suggesting KOH concentration (cation effect) dependence on the catalyst (polycrystalline Ni vs. nanostructured NiMo).

Based upon our results above, we show that the KOH concentration (pH) effect in HER in alkaline media depends upon the catalyst composition and morphology (polycrystalline Ni vs. nanostructured NiMo). For polycrystalline Ni, the catalyst has three regions depending upon the local KOH concentration: a promotion (0.01–0.1 M, pH 12–13), stabilization (0.1–1.0 M, pH 13–14), and an inhibition region (2.0 M, pH > 14). In the promotion region, KOH through pH and cation effect accelerates HER kinetics. In stabilization region, the promotion region stabilizes, and HER properties do not change so much in this region. At the inhibition region, it is proposed that at higher KOH concentration (2.0 M), OH* transport kinetics are slower than water dissociation rate [19], and hence HER may have a negative reaction order dependence on KOH concentration in this region.

For nanostructured NiMo, there is typically a promotion region under various pH/KOH concentrations (0.01–1.0 M, pH 12–14) and then it turns to inhibition region at 2.0 M (pH > 14). The pH/KOH concentration has an essential role for nanostructured NiMo HER activity and kinetics (as we can see from the overpotential values achieved at −10 mA cm−2 and Tafel slope changes).

The difference in KOH electrolyte-activity and kinetics trends are strongly dependent upon the catalyst morphology, composition, and “strength” of the catalyst-water-cation (K+) interactions. Our findings have important application for HER cathodes in alkaline and AEM electrolysers where using weak KOH electrolyte concentrations is essential. Tuning the cathode composition/morphology with KOH concentration can therefore enhance the performance and stability.

4 Conclusions

The influence of pH/KOH concentration on Ni-based catalyst HER activity depends upon the catalyst composition and morphology. For polycrystalline Ni, the catalyst performance and kinetics have three regions depending upon the KOH concentration: (1) a promoting (0.01–0.10 M, pH 12–13), (2) stabilizing (0.1–1.0 M, pH 13–14), and (3) an inhibiting region (2.0 M, pH > 14). While for nanostructured NiMo, there is typically a promoting region under various pH/KOH concentrations (0.01–1.0 M, pH 12–14), and then it turns into inhibiting region at 2.0 M (pH > 14). The pH/KOH concentration has an essential role for nanostructured NiMo HER activity and kinetics, as observed from the overpotential values to achieve −10 mA cm−2 and Tafel slope changes. The difference in pH/KOH concentration trend with polycrystalline Ni and nanostructured NiMo confirmed the importance of optimizing the electrode–electrolyte interface for optimum HER performance and kinetics.

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