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Dissolved Iron in Alkaline Media: Techniques and Insights for Understanding its Effects on Water Splitting Reactions

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Abstract

Dissolved iron in alkaline media is an important topic influencing a wide array of electrochemical reactions and most notably those occurring in alkaline water electrolyzers (AWE). This work compiles the study techniques and strategies that have been used in the past few years to help tackle this challenging issue. Focus is made on iron solubility in the studied medias, the importance of using a quality reference electrolyte, where and how to measure iron content in the system and also on what is agreed and what is debated concerning the influence of dissolved iron on the Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER), notably in the way these electrolyte impurities do enhance or alter the reactions kinetics.

Keywords

Dissolved cations; Alkaline Electrolyte Impurities; Alkaline Water Electrolysis; Hydrogen Evolution Reaction; Oxygen Evolution Reaction.

Highlights

- Iron is dissolved in alkaline electrolytes of industrial applications

- Dissolved iron must be studied with properly-tuned electrolytes
- Methods to quantify dissolved iron are proposed
- The effect of dissolved iron on water electrolysis reactions is detailed

1. Introduction

Alkaline Water Electrolysis (AWE) is one of the eldest technologies for hydrogen production. In the last ten years, interest in AWE has rekindled as green hydrogen perspectives using transition metals instead of costly and scarce noble metals appeared relevant for energy transition. Close attention has been paid towards cathode and anode materials and their fine characterisation and performance assessment. The diaphragm/electrode package represents 25.7 % of the cost of a 1 MW Alkaline Water Electrolyser placing it high for the potential cost reduction of the technology [1]. Major catalysts for Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) in alkaline media have been developed and reviewed extensively [2]. However, the electrolyte had not drawn as much attention until recently, as work showing how iron impurities significantly decrease the OER overpotential on nickel anodes in KOH 30 wt.% [3] regained interest [4]. This has led to numerous researches on the influence of iron impurities in alkaline media [5][6] and its effect on water splitting reactions [7]. Various metals turned out to be sensitive to iron impurities for the OER (Ni [8]–[15], Pd [16], Co [13][15], Cu [15], Pb [17], Au [15][18], Ag[15]) and for the HER (Ni, Ag, Au, Cu) [19]. Other electrochemical reactions have been studied (Urea Oxidation Reaction (UOR) [20] and Glucose Oxidation Reaction (GOR) [21]) and proved sensitive to iron as well. Additionally, iron is a widespread impurity that may originate from an electrolyser's balance of plant or from make-up water, inducing more global effects on electrochemical devices. For instance, CO₂ reduction electrolysers may simultaneously show increased anodic performance and degraded ionomers/membranes and cathode performance in the presence of iron [22]. Therefore, it appears essential to study iron impurities closely in a wide range of applications.

However, no methodological consensus exists yet. Research teams use different iron precursors, purification methods and iron concentration measurement techniques. These differences may impact the conclusions, as electrochemistry is extremely trace sensitive. Therefore, this article focuses on the diverse methods involved in the study of iron impurities in alkaline media, as well as on their effect on AWE reactions, and aims at informing both newcomers and experienced scientists about the challenges surrounding this growing topic.

2. On the Effect of Iron Impurities for Water-splitting Reactions

2.1. Choice of KOH Concentration and Dissolved Fe Concentration

As shown in Table 1, most research teams use 0.1 or 1 M KOH electrolytes at room temperature, which are better suited to laboratory standards but have significantly lower Fe solubility than KOH 30 wt.%, 80°C, encountered in industrial AWE systems. Research teams usually add iron to the desired concentration by using precursor salts in dilute KOH, such as: $\text{Fe}(\text{NO}_3)_3$ [23], $\text{Fe}(\text{ClO}_4)_3$ [24], $\text{Fe}_2(\text{SO}_4)_3$ [25] and K_2FeO_4 [14]. However, this has two drawbacks: these salts may precipitate as the solubility of iron is low and additional anions are introduced in the media. These additional supporting anions can have their own effects on the global water-splitting performance of the system, blurring the specific influence of dissolved iron.

Table 1: Overview of the experimental conditions used for electrochemical studies of dissolved iron in alkaline media

Reaction studied	Electrode material	Fe precursor	KOH Purification method	Fe monitoring in electrolyte (technique)	[KOH] (mol/L) (* = NaOH)	[Fe] As received (ppm)	[Fe] After purification (ppm)	[Fe] added (ppm)	Susceptible metal traces	Monitored metal traces	Refs
Studies on the presence of iron											
OER	Ni	High purity iron foil exposition overnight	Pre-electrolysis 1 mA, 5 days, 1 kg Hg cathode, 3 cm ² Ni anode	Yes (UV vis ²)	5.9	0.55	< 0.02	1	Hg, Ni	-	[3]
OER	Ni	Traces in commercial KOH	Ni(OH) ₂	None (ICP-OES of digested electrodes ¹ , XPS ¹)	0.1 and 1	-	unknown	unknown	Ni	-	[26]
OER	NiFe	Traces in commercial KOH and $\text{Fe}(\text{NO}_3)_3$ (l)	Ni(OH) ₂ with filtering step	None (Just CVs ?)	1	-	unknown	unknown	Ni	-	[23]
OER	Ni	$\text{Fe}(\text{NO}_3)_3$ (s)	5-day pre-electrolysis with Ni electrodes – No specified conditions	None (Use CV on Pt)	0.1	-	unknown	0.1	Ni	-	[27]
OER	Ni	$\text{Fe}(\text{NO}_3)_3$ (l)	Ni(OH) ₂	None (ICP-OES ¹)	1	-	unknown	55.8	Ni	-	[8]
OER	Ni	Traces in KOH	Ni(OH) ₂	None (XPS ¹ , GIXRD ¹ , SEM ¹)	1	0.036	unknown	0.04 – 1.00	Ni	-	[4]
OER	CoFe	$\text{Fe}(\text{NO}_3)_3$ (l)	Ni(OH) ₂ with filtering step	Yes (ICP-OES ²)	1	0.055	0.005	11	Ni	-	[28]

OER	Ni	Fe(NO ₃) ₃ (s)	Ni(OH) ₂ with filtering step	Yes (GIXRD ¹ , XPS ¹ , SEM ¹ , ICP-MS ²)	1	0.0664	0.006	0.1-1.0	Ni	-	[29]
OER	Ni	Fe(ClO ₄) ₃ ·6 H ₂ O (s)	Ni(OH) ₂ and pre-electrolysis with gold electrodes – <i>patented</i>	Yes (ICP-MS ²)	0.1	1.2	< 0.03	12	Au	-	[24]
UOR	Ni	Fe ₂ (SO ₄) ₃ (l)	Ni(OH) ₂	No (XPS ¹)	0.1*	-	unknown	0.00 – 0.25	Ni, Pt	-	[20]
Studies on the concentration of iron											
OER	Ni, Cu, Ag, Au	Fe(NO ₃) ₃ (l)	-	No (XPS ¹)	1	-	-	16.50	-	-	[15]
OER	Ni	-	-	No (XPS ¹)	-	-	-	unknown	-	-	[30]
OER	Ni	K ₂ FeO ₄ (s) and (l)	-	No (XPS ¹ , XRD ¹ , SEM ¹)	0.1	-	-	14 -700	-	-	[14]
HER and OER	Ni	Fe ₂ (SO ₄) ₃ (l)	-	Yes (ICP-OES ²) and XPS ¹ , SEM/EDX ¹	6.9	0.1	-	0 – 9	-	-	[25]
HER	Ni	Traces in KOH	Pre-electrolysis <i>no specified conditions</i>	Yes (AAS ²)	6.9	3.00	-	0.03 – 3.00	-	-	[31]
HER	Ni	Traces in KOH	-	-	6.9	0.5	-	0.5	Ni	-	[32]
HER	Ni, Ag, Au	Traces in NaOH	Pre-electrolysis <i>no specified conditions</i>	-	0.1*	-	-	unknown	unknown	-	[19]
1 : Techniques used for <i>post mortem</i> analysis of electrodes, 2 : techniques used for electrolyte analysis											

The former issue has been underlined once: when using Fe₂(SO₄)₃ at higher concentrations than 8.95 ppm in KOH 30 wt.% at room temperature, dark red FeOOH solid precipitates appear [25]. This likely also occurs in other experiments of Figure 2, especially considering many of them are done in dilute media, meaning iron is less soluble. Iron may seem solubilised but is bound to precipitate over time if added in larger quantities than its solubility value [33] meaning the actual iron concentration may not be equal to the quantity introduced in the media. For K₂FeO₄, no precipitation is observed as iron is added as FeO₄²⁻, a much more soluble species in alkaline media [14], making it ideal for higher concentrations studies. However, FeO₄²⁻ is a Fe(VI) species, whereas other salts yield Fe(III) species meaning the effects observed must be compared with care.

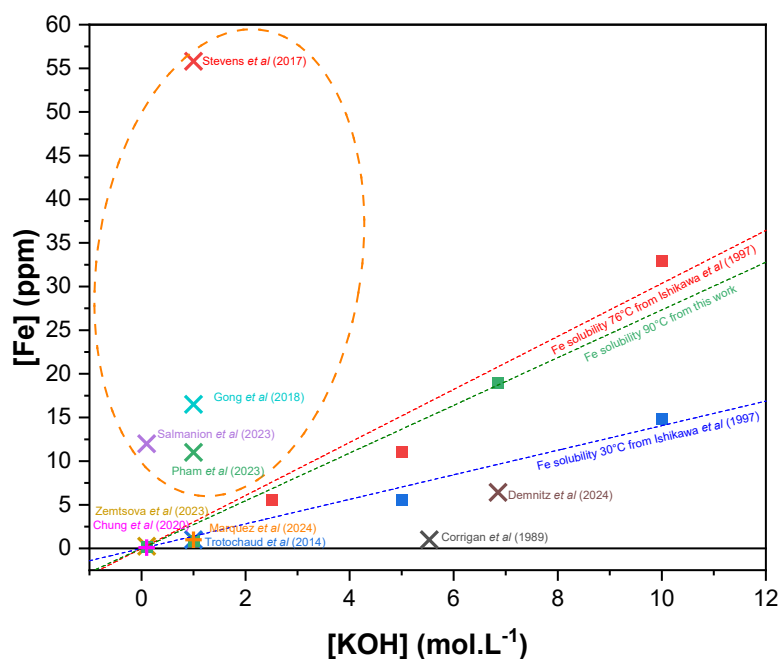


Figure 1: Crosses indicate iron concentrations used in studies conducted at room temperature with respect to the KOH concentration by Stevens et al [8], Gong et al [15], Salmanion et al [24], Pham et al [28], Zemtsova et al [20], Trotochaud et al [4], Corrigan et al [3], Demnitz et al [25], Chung et al [27] and Marquez et al [29]. The dashed orange circle indicates data for which it is suspected that the real dissolved iron concentration is below the targeted value. Squares indicate experimental iron solubility at different temperatures for comparison and the matching coloured dashed lines are linear regressions to guide the eye. Green squares indicate Fe solubility data from this work that was obtained by heating samples containing iron powder at 90°C for 76 hours. The final concentration was measured by ICP-MS.

To our knowledge, the second issue is not discussed in studies on iron impurities and NO_3^- , ClO_4^- , SO_4^{2-} anions are not mentioned in a recent review on impurities effect on water electrolysis [34]. Interestingly, former studies on the subject used iron foils [3] or iron anodes [35][36], allowing Fe to be introduced in the media without anions and to concentrations lower than its solubility. Adjusting iron concentration should be done by diluting a mother iron-saturated KOH solution with a purified KOH solution in that case [3].

Based on this, future research on the topic may consider:

- Adding iron to concentrations that are relevant to iron solubility in the chosen media. If the desired concentration is higher, consider using a more concentrated electrolyte. If the aim is to study iron influence on water electrolysis, conditions should be industrially relevant [37], with iron concentration comprised between 2 and 20 ppm.

- When adding iron salts to the media, anion traces have also been added to the media and may also influence the electrochemical results. Alternative methods that do not introduce anions, such as iron dissolution, should be chosen.

2.2. Deciding on a Reference Electrolyte

An important aspect of studying iron impurities is to have a reference electrolyte solution: one must differentiate studies investigating the simple presence of iron in alkaline media and studies investigating the influence of iron concentration. When investigating the effect of the presence of iron, the blank solution should be completely iron-free. When studying on the concentration of iron, knowing the initial amount of iron in solution is enough. As iron impurities in alkaline media originate from the commercial product [4], making a blank solution requires a purification step or an iron concentration measurement step.

Purifying the solution may remove iron while introducing other impurities, which could lead to erroneous conclusions [30]. It is recommended to add a trace-metal measurement step after purification to assess iron has been removed and to ensure other impurities were not introduced in the solution.

Three approaches have been used successfully to purify alkaline solutions: pre-electrolysis, absorbents and ion-exchange membranes. These techniques have also been combined sometimes [24]. To our knowledge, the third method has only been reported in one paper, with little detail on the efficiency of the purification [38], which is why focus is made on the two other methods. The first method is pre-electrolysis; usually done in a two-electrode setup, it consists of applying a potential difference sufficient to remove metallic impurities by electrodepositing them on the cathode as drawn on the scheme of Figure 2, b). Pre-electrolysis was adopted with different electrode materials: Corrigan *et al* used a 1 kg Hg cathode, a 3 cm² Ni anode and applied 1 mA for 5 days [3]; Spanos *et al* used MoS₂ deposited on Ni foam as electrodes and applied 100 mA for 12 h [39]; Weber *et al* employed a 24 h long pre-electrolysis step with Pt mesh electrodes [40]; Chung *et al* used a 5-day electrolysis with Ni-wire electrodes [27]. The second method, introduced by the Boettcher group, consists of using a α -Ni(OH)₂ suspension to absorb iron impurities [4], as iron incorporates into the lattice of Ni(OH)₂ at

anodic polarisation in KOH and also at open-circuit potential. The suspension is made by precipitating α -Ni(OH)₂ with a Ni salt in alkaline media. Once the precipitate is obtained, it is added to the KOH solution to purify, homogenised by centrifugation and the phases are finally separated. The detailed procedure is shown on Figure 2, a). Recent works underlined the presence of Ni impurities in the electrolyte after the numerous purification steps and strongly recommended to add a filtering step [30][41] and a 48 h decanting step [41] to avoid them. Marquez *et al* have quantified the iron removal in 1 M KOH and report an iron concentration of 9.4 ppb after purification with α -Ni(OH)₂ [40]. Spanos *et al* have also quantified the iron content after pre-electrolysis and found no iron within the detection range of the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), which is within the 10 ppb range [38]. Hence, sufficiently long pre-electrolysis seems to be the best compromise, as it has the advantage of being a single-step process, limits the addition of Ni impurities and purifies Fe to equivalent ranges as a Ni(OH)₂ suspension as detailed in Figure 2, c).

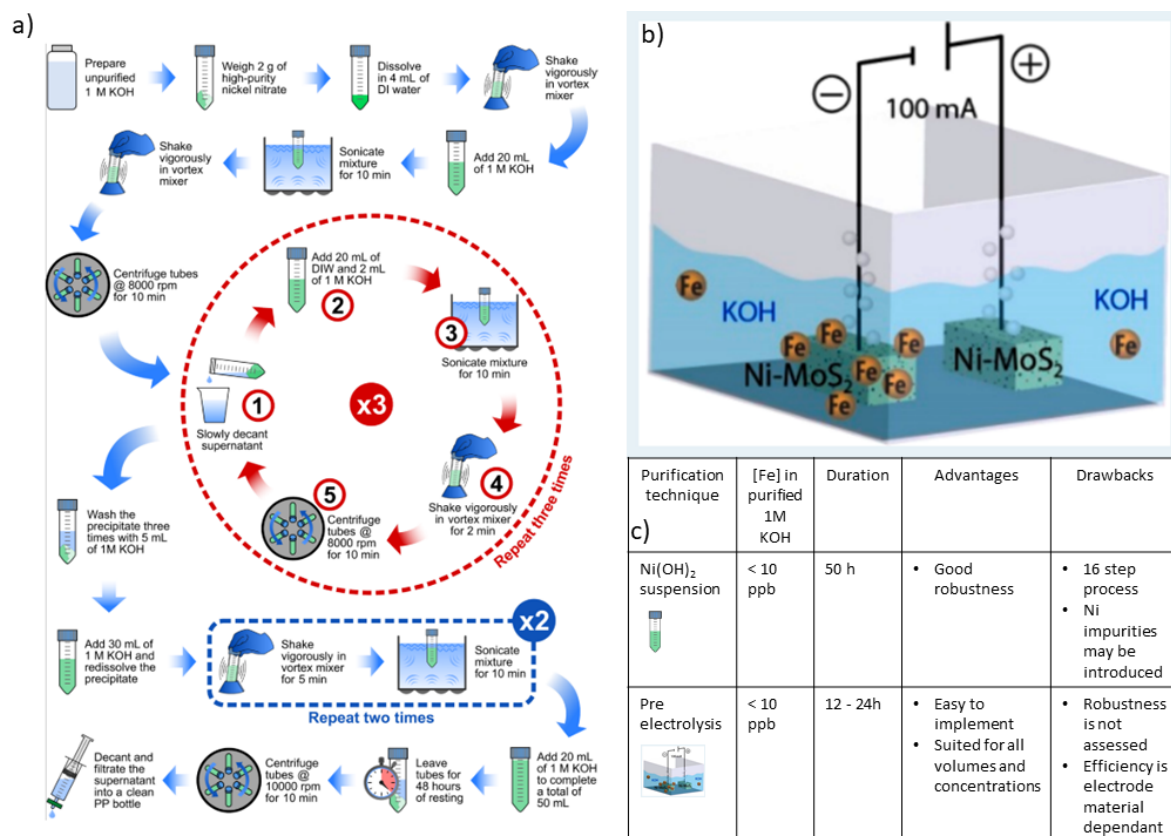


Figure 2: Iron purification methods. a) from reference [41], b) from reference [39], c) Comparative table on the purification methods.

Some research teams made the choice of not purifying their electrolyte to avoid introducing additional impurities. This approach is effective when studying the effects of iron concentration. Even if the suppliers give an impurity analysis certificate, it is safer to measure the iron content of the solution. In table 1, one can see many works rely on such information for their iron content data. We recommend doing this measure in the lab whenever possible, as described hereafter.

2.3. Monitoring Iron Concentration in the Electrolyte

A number of works have investigated the effect of iron impurities without measuring iron content in the electrolyte but rather by *post mortem* analysis of the electrodes. Klaus *et al* used X-ray Photoelectron Spectroscopy (XPS) and ICP-OES of digested electrodes to assess no iron was found on the electrodes when used in purified electrolyte [26]. Trotochaud *et al* used XPS and to a lesser extent Scanning Electron Microscopy (SEM) and Grazing incidence X-Ray Diffraction (XRD) *post mortem* to ensure no Fe had been incorporated in the electrode during OER in purified KOH [4]. Pham *et al* used ICP-OES pre and post purification to assess purification was efficient [28]. Farhat *et al* assumed no Fe was in the electrolyte based on electrochemical results [23] and so did Chung *et al* based on the cyclic voltammetry response of a Pt electrode [27].

However, it is important to monitor dissolved iron concentration in the electrolyte before, during, after the experiment or even *operando*. Iron concentration may change throughout the experiment for numerous reasons: precipitation of dissolved Fe, reduction of Fe on the electrode (mainly for HER), electrolyte evaporation during long experiments and iron leaching from the experimental setup [25]. Techniques that have been used successfully include ICP-OES [8][28][25] and ICP-Mass Spectroscopy (ICP-MS) [24][41]. ICP-MS allows precision up to the 0.01 ppb range but may be challenging to conduct properly, given the probable interferences, especially with high potassium concentrations [42]. Marquez *et al* have made recommendations on how to conduct such measures [41]. However, for high potassium loading, ICP-OES seems to be the best candidate as it has a higher tolerance to total dissolved matter even though its precision is in the 10 ppb range. Other techniques used successfully in earlier works include ultraviolet-visible (UV-vis) [3] and Atomic

Adsorption Spectroscopy (AAS) [31] measures. These methods have lower precision and detection thresholds than ICP-OES/ICP-MS, but have the advantage of being easy to implement as a verification routine for solutions containing iron in the ppm unit range. Finally, there are very little *operando* measurements in literature [26], which could be of great interest in the field [43].

Coupling iron concentration measurement with *post mortem* analysis of electrodes to have a clear view of the system's evolution during experiments is recommended; all techniques are not equal and must be chosen based on the operating conditions of the system (electrolyte concentration, temperature and iron concentration variation range throughout the experiment) and the aimed precision level.

2.4. Effects on OER

Studies of iron dissolved in the electrolyte and its effects on nickel anodes for OER have led to consensus on some aspects of the so-called "Fe effect". The presence of iron impurities in alkaline electrolyte is favourable for the OER on nickel anodes (Figure 3, a): iron is present on the Ni anode after the experiments and the gains are due to catalytic enhancement rather than a surface effect, as illustrated on the scheme of Figure 3, b) and the SEM image of Figure 3, e) showing a flat surface comparable to the initial state of the anode. This has been systematically reported by research teams [3][4] and summarised [5][6]. Iron can also spontaneously be integrated into Ni-rich oxyhydroxide layers that form during electrochemical activation of Ni-Fe alloys, both from electrolyte impurities and from the underlying Fe-containing alloy [44]. The activity enhancement seems sustainable in time, given that iron is present in the electrolyte: as evidenced by Figure 3, c), the electrode deactivates when cycled in Fe-free electrolyte. Isotopic labelling has confirmed the dynamic behaviour of iron continuously dissolving in the electrolyte and redepositing on the anode [27] illustrated on Figure 3, d). This is encouraging for AWE industrial systems operating in Fe-rich environments [7]. This also raises the question of using "activated" commercial anodes in the AWE system. Indeed, compared to simple Ni material, these activated anodes are by essence more complex, expensive, difficult to recycle and less resistant to degradation (continuous degradation over the years, or start/stop degradation). A basic comparison of performances at

initial state would of course give absolute advantage to the activated anodes, but given some time operating inside the system the simple Ni electrode might “self-activate” from the iron dissolved in the lye, reaching steady-state performances close to the initially activated anode. Note that most of the academic works presenting novel anode catalyst materials benchmarked at initial state, without a break-in period in relevant lye composition and temperature (and without durability study in such conditions) are not usable by the industry [45].

However, some points concerning the electrocatalytic mechanisms behind such an enhancement remain unclear in the community. Is the active site Ni or Fe? What is the oxidation number of Fe during the OER? As Stevens *et al* have shown, the effect of incorporated iron from the electrolyte is equivalent to that of co-deposited iron [8], meaning fundamental electrocatalytic studies of model NiFe oxyhydroxides are relevant to understand the mechanism behind the “Fe effect”. Also, the quantification of this effect may be imprecise due to the introduction of various counter anions throughout the studies as well as concentrations above solubility value. Recent studies are also not done in industrial conditions for OER. From a scientific and industrial point of view, these two aspects need to be further studied to quantify the gains obtained from the presence of iron in the electrolyte and compare different materials in iron-containing electrolytes as iron is almost inevitable in an industrial electrolyser. It seems crucial to evaluate the change in performance of new catalysts in the presence of iron.

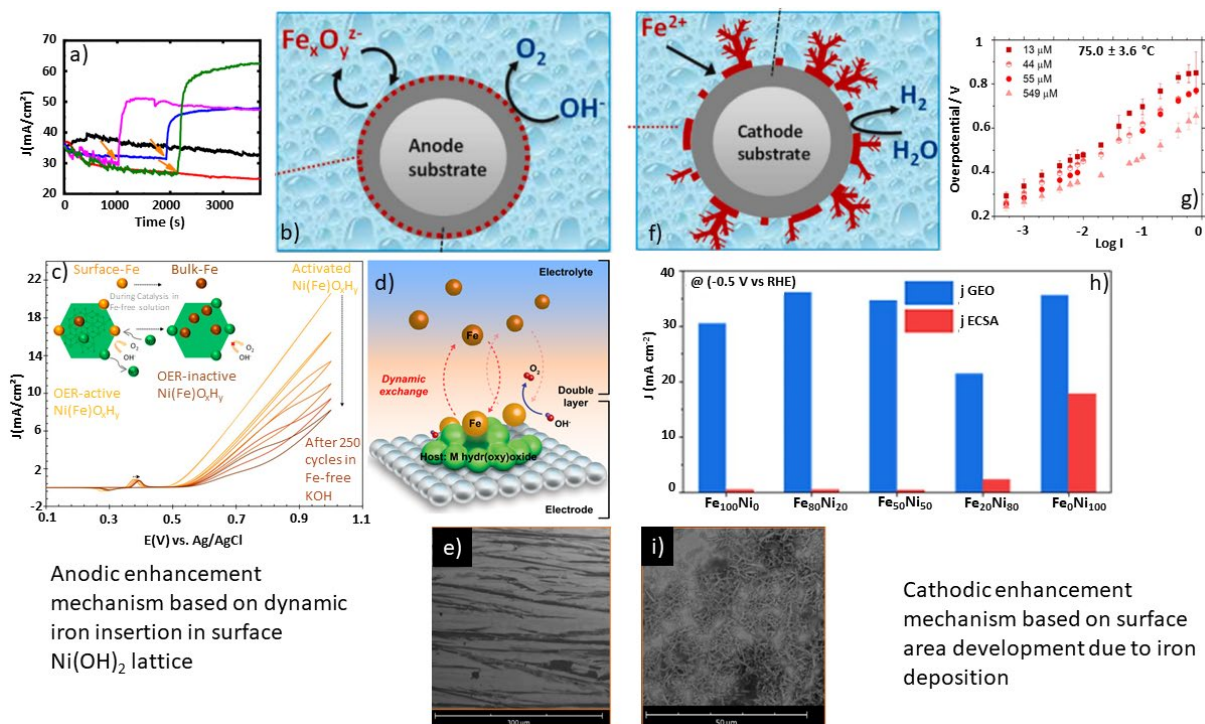


Figure 3: Dissolved iron influence on HER and OER in industrial AWE. a) Chronopotentiometry measures on nickel electrodes in 1 M KOH polarised at 1.5 V vs RHE from reference [24] orange arrows indicate addition of iron chloride, b) Scheme illustrating iron incorporation in nickel anodes in industrial AWE from reference [25], c) Scheme and cyclic voltammeteries illustrating the deactivation of $\text{Ni}(\text{Fe})\text{O}_x\text{H}_y$ in KOH devoid from Fe impurities from reference [23], d) Scheme illustrating the dynamic interaction between dissolved and incorporated iron during OER on nickel electrodes from reference [27], e) SEM image of Ni anode having incorporated Fe after use in KOH, iron is not visible at this scale, from reference [25], f) Scheme illustrating iron electrodeposition on nickel cathode in industrial AWE from reference [25], g) Tafel plots of nickel cathodes in KOH with different iron concentration, the higher the concentration the lower the overpotential, from reference [25], h) Bar plot illustrating how electrode roughness may enhance geometric current density while ECSA current density decreases from reference [46], i) SEM image of Ni cathode with electrodeposited Fe dendrites after use in KOH, from reference [25]

2.5. Effects on HER

The effect of iron impurities on HER have been studied to a lesser extent than OER, even though iron does influence the cathodic performance in industrial AWE [47]; however the majority of iron in solution is electrodeposited on the cathode rather than inserted in the anode [25].

Authors agree on a number of aspects of HER in the presence of dissolved iron (Figure 3). Electrodeposition occurs during HER, illustrated on Figure 3, g), forming elemental Fe, as detected by macro observations [47] and SEM analysis of used cathodes [25][31][48]. The morphology of the deposit varies from droplets to full dendrites, depending on the applied charge. An example of such a deposit is visible on the SEM image of Figure

3, i). Although Fe is less catalytically active for HER than Ni, strong evidence of iron deposits diminishing cathodic overpotential have been provided [25]; the effect may be largely attributed to surface enhancement, rather than a synergetic effect between nickel and iron as shown by Perez Bakovic *et al* [46] and illustrated on Figure 3,h). However, it is still unclear if there is a limit to this surface enhancement, as suggested by the Tafel plots of Figure 3, g); experiments of at least a several hundred hours are needed to conclude clearly. Also, some authors have claimed that iron prevents nickel cathode from hydride deactivation [49]. The deactivating effect was observed at constant surface area, meaning it is different from the previously-mentioned enhancing effect. The nickel hydrides supposedly deactivating the cathode were not identified due to its *ex situ* instability and the surface area was checked optically.

The effect of iron on the cathode is globally positive in the cited studies but may be negative for long-term operation of industrial electrolysers and we recommend to study this in industrially-relevant conditions with a relevant iron concentration. Again, it may be very interesting to evaluate how different cathode catalysts are modified by the presence of iron in the electrolyte.

3. Conclusions and perspectives

This overview on the studies of dissolved iron in alkaline media demonstrates numerous electrochemical reactions may be impacted; relevant guidelines to study this topic were proposed. We stressed how iron solubility in alkaline media varies with concentration and temperature and the importance of using iron concentrations that are lower than the solubility in the studied media. Methods to obtain a reference electrolyte were proposed, which can be done by purifying the electrolyte from Fe impurities or by assessing the initial iron concentration. Moving on to the actual experiments, it is recommended to measure iron content in the electrolyte with methods such as ICP-MS/ICP-OES, UV-vis or AAS throughout the experiments and to complement these measures with *post mortem* electrode analysis such as XPS, SEM, XRD to track iron movements in the whole system. *Operando* studies would also be of high interest. Finally, the way iron influences the OER and HER reactions on nickel-based electrodes was stressed. Both may benefit from the

presence of iron. OER may benefit from the dynamic interaction between absorbed iron in the Ni(OH)₂ lattice of the anode and the electrolyte. HER may benefit from the surface-enhancing deposition of iron in the form of dendrites but this positive effect could become detrimental with time. Experimental data is missing to quantify this time dependency. Dissolved iron would however have a negative effect on PGM-based cathodes [7].

Future work may focus on studying the effect of other dissolved metallic cations, and also the possible synergetic effect between them. These ideas have begun emerging in recent works. Ye *et al* [30] and Salmanion *et al* [24] have investigated the impact of dissolved Ni on OER, reaching contradictory conclusions. Meanwhile, Marquez *et al* have initiated research on the influence of dissolved Cu, Co, and Mn [29], paving the way for the examination of potential synergistic effects among these elements. More generally, we invite the scientific community to consider the water-splitting electrocatalyst as a dynamic surface in interaction with the lye. This lye could, by extension, be also considered as being part of the “electrode” system thus relevant monitoring of its composition during experiment should be raised at the same level of importance as the conventional characterization of the electrocatalyst material. Future work may take advantage of this conceptual change and put more effort on tuning the composition of the electrolyte which is not usually optimised as much as the electrode.

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Author contributions

All authors have contributed equally.

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* Paper of special interest

** Paper of outstanding interest.

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