Electrochemical oxidation of H₂S on polycrystalline Ni electrodes

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Abstract

We have evaluated the applicability of Ni anodes in electrochemical conversion of H₂S to form sulfur (polysulfides) and H₂. Two different electrolytes containing sulfide were evaluated: a buffered solution of Na₂HPO₄ at pH 9.2, and a NaOH solution at pH 13. At pH 9.2, deposition of sulfur on the Ni anode was observed, resulting in a significant decrease in electrochemical performance. The composition, morphology, and thickness of the sulfur deposit, as determined by Raman spectroscopy and SEM, was found to strongly depend on the applied potential, and ranged from dense S₈ films to highly porous spherical sulfur structures. Oxidation of the anode was also observed by conversion of Ni to NiS₂. The formation of the sulfur film was prevented by performing the reaction at pH 13 in NaOH in the range of −1.0 V to +0.6 V versus Hg/HgO. It is proposed that at these highly basic pH values, sulfur is dissolved in the electrolyte in the form of polysulfides, such as S₂^{2−} or S₈^{2−}. When using Ni anodes some oxygen evolution was observed at the anode, in particular at pH 13, resulting in a Faradaic efficiency for sulfur removal of ~90%.

Graphic Abstract

Keywords H₂S · Ni anode · Sulfide oxidation · Sulfide selectivity · Basic conditions · Phosphate buffer · Anode deactivation

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1 Introduction

Hydrogen sulfide is largely produced in the so-called hydrogen desulfurization (HDS) process for purification of oil [1, 2], but also present in significant concentration in industrial off-gas of, e.g., steel manufacturing. Hydrogen sulfide is highly toxic and odorous [3, 4]. Efficient and safe isolation using absorption, followed by desorption and conversion in the (super) Claus process, is therefore crucial [5]. H₂S absorption is energy intensive and costly,

and a disadvantage of the Claus process is that water is the coproduct of formation of elemental sulfur:

It is much more appealing to utilize the chemically bound hydrogen in H_2S to electrochemically form H_2 . This requires anodic electrochemical oxidation of the sulfide ion, which has been investigated for purification of geothermal brines that accompany oil and gas extraction [4]. Bunce et al. [6] reported that the oxidation of sulfide ion at a boron-doped diamond (BDD) anode forms sulfate, with near quantitative chemical yield and current efficiency, in both the absence and presence of chloride ion. However, as Bunce et al. [6] argue, there are certain disadvantages in developing this chemistry into a prospective technology. First, BDD is still a rather exotic material that is not available at low cost. Second, the 8-electron oxidation of sulfide to sulfate is four times as energy intensive as the 2-electron oxidation to elemental sulfur. Dimensionally stable anodes based on iridium dioxide, such as $\text{Ti}/\text{IrO}_2\text{--Ta}_2\text{O}_5$, have also been investigated in oxidation of sulfide [3, 7], and were found to promote the 2-electron oxidation of sulfide to elemental sulfur, rather than the 8-electron oxidation to sulfate. Unfortunately, this requires the rare and expensive IrO_2 . Ateya and Al-Kharafi [8] found that use of graphite anodes leads to deposition of sulfur, as confirmed by X-ray photoelectron spectroscopy, rapidly decreasing the performance of such electrode. The authors show that further oxidation of elemental sulfur to sulfur oxyanions did not occur under their electrochemical conditions.

A significantly cheaper alternative for IrO_2 in electrochemical oxidation of water in basic conditions, is known to be NiO , in situ forming highly effective catalytic surfaces of $\text{Ni}(\text{O})\text{OH}$ (nickel-oxy-hydroxide), promoted by small quantities of Fe [9, 10]. To the best of our knowledge, $\text{Ni}(\text{oxide})$ has not been evaluated in the electrochemical oxidation of sulfide, which would be much more attractive as compared to the use of expensive noble metals [11] or BDD [6]. We have therefore investigated the effect of various process conditions on the electrochemical oxidation of sulfide over Ni electrodes, with focus on the pH of the applied electrolyte. In particular, mildly basic, phosphate-buffered conditions (pH 9) were compared to highly basic conditions, to determine the stability of the anode which is likely affected by sulfur deposits. Cyclic voltammetry and chronoamperometry measurements were combined with gas chromatography (GC) to identify gas formation during sulfide oxidation. Raman spectrometry, scanning electron microscopy (SEM), and energy-dispersive X-ray spectrometry (EDX) were used to characterize the composition and structure of thin solid films that were formed on the Ni electrodes, in particular at conditions of relatively low pH (< 10).

2 Experimental

All experiments were carried out in Milli-Q water. NaOH (Sigma Aldrich, 99.99%) and Na_2HPO_4 (Sigma Aldrich, 99.0%) were used to prepare solutions of pH 9 to 13. Ni electrodes (surface area $\approx 0.265 \text{ cm}^2$, diameter $51 \pm 1 \text{ mm}$) were prepared from Ni sheets (Alfa Aesar, 99.95%) and polished with an alumina suspension paste (1, then $0.3 \mu\text{m}$, respectively). The experiments were conducted in a stirred, undivided cell, using platinum gauze as the counter electrode (cathode), to minimize the over-potential for hydrogen evolution. All potentials were measured against a commercially available Hg/HgO reference electrode.

The effect of electrolyte composition on solubility of H_2S was determined in a gas-tight reactor [12]. The feed rate of the gas mixture of 5 vol% H_2S in Ar to the reactor was set to a constant 2.5 mL min^{-1} , introduced through a Teflon-made tube immersed in solution, and the concentration of H_2S in the reactor effluent was determined by gas chromatography, using a RestekTM sulfur column [13]. The volume of electrolyte solution was set to 100 mL, and the head-space of the reactor amounted to about 25 mL. For the 0.5 M NaOH solution, H_2S was undetectable for 10 h, which is explained by the large capacity of such solution for absorption of H_2S , induced by the chemical reaction of H_2S with NaOH . The breakthrough curve for the 0.5 M Na_2HPO_4 solution, is shown in Supplementary Fig. S1 illustrating that even after hours of operation, a steady state had not been reached. Phosphate buffer was initially used to minimize acidification of the solution when H_2S is purged through. Only in purified water, the gas flow exiting the reactor reached the inlet concentration after 24 h of purging, indicating saturation.

Since feeding H_2S to the electrochemical cell will thus typically induce variations in sulfide concentrations, Na_2S (Sigma Aldrich, 99.0%) was used to conduct voltammetry measurements. A flow of H_2S (5 vol% in Ar) was only used for the combined electrolysis/gas chromatography measurements, using 0.5 M Na_2HPO_4 , or 0.1 M NaOH solutions, respectively, to determine the anode selectivity for oxidation of sulfide, as compared to oxidation of water forming oxygen.

Raman spectroscopy was carried out by exposing the samples at ambient conditions to laser excitation at wavelengths of 532 nm (20 mW) and 785 nm (40 mW), using a Bruker Senterra Raman microscope. Before each measurement, the thin film formed on the electrode was carefully rinsed with Milli-Q water and dried in a desiccator for 10 min.

HR-SEM images were recorded using an accelerating voltage ranging of 2.00 kV to 10.00 kV. The microscope allowed energy-dispersive X-ray analysis (EDX) for mapping of the elemental composition of the samples.

3 Results and discussion

3.1 Electrochemical oxidation of sulfide at pH 9.2

Cyclic voltammograms of the oxidation of sulfide at pH 9.2 in Na_2HPO_4 solution are shown in Fig. 1.

A positive potential scan for the 0.2 M Na_2HPO_4 solution (pH 9.2) starting from -0.8 V versus Hg/HgO , in the absence of sulfide (dashed line), did not show any significant increment in current up to 0.7 V, suggesting that oxidation of the Ni surface, nor water oxidation occurs significantly in this potential range. A significant oxidative response was found starting at approximately 0.9 V (not shown), which besides to the oxidation of water, might be attributed to the simultaneous oxidation of the Ni electrode. The Pourbaix diagram reported in literature [14] suggests that oxidation of Ni to Ni^{2+} , followed by deposition of a (passivating) film of $\text{Ni}(\text{OH})_2$, is quite feasible at 0.9 V and at a pH of 9.2.

When sulfide was present in the same electrolyte, starting from -1.0 V versus Hg/HgO (scanning in the positive direction), electrochemical oxidation of sulfide to sulfur initiated at around -0.4 V on the Ni electrode, while two maxima can be observed at -0.2 V and 0.1 V. The anodic current rising exponentially at potentials higher than $+0.2$ V is likely due to continued deposition of sulfur, since the reference scan in the absence of sulfide hardly showed a current response at these potentials. The high selectivity of the electrode for oxidation of sulfide at 0.65 V is also

Fig. 1 Cyclic voltammograms of sulfide (10 mM Na_2S) oxidation on a polycrystalline Ni electrode in a 0.2 M Na_2HPO_4 buffer solution (pH 9.2). The dashed line in the main panel shows the electrochemical response in the absence of Na_2S . The main panel also shows the effect of variations in the final potential of the scan, starting at -1.0 V and ending at -0.5 V (green, short dash), $+0.2$ V (red, long dash), and $+0.6$ V (black, solid line). Scan rate 20 mV s^{-1} . The inset shows a response to a series of identical scans starting at -0.5 V and ending at $+0.6$ V. S values (S1–S4) denote the scan sequence, showing a decreasing electrochemical response at approximately $+0.1$ V. (Color figure online)

demonstrated in Supplementary Fig. S2, by analyzing the products of electrolysis of a 0.5-M Na_2HPO_4 solution to which a constant flow of 2.5 mL min^{-1} H_2S (5% in Ar) was supplied. The steady-state hydrogen concentration amounted to ~ 1300 ppm, in good agreement with a measured current of ~ 0.4 mA (see Supplementary Table S3). This also suggests soluble polysulfides (if any) were not reduced cathodically by the Pt Gauze. On the basis of oxygen evolution (~ 250 ppm), the anode selectivity for sulfide oxidation amounts to $\sim 60\%$. It should be mentioned that this $\sim 60\%$ is likely a lower limit, considering comparable amounts of O_2 were also detected in the absence of electrochemical conversion (not shown), likely due to residual oxygen in the applied electrolyte. The limited water oxidation efficiency is in agreement with the thermodynamically and kinetically (lower over-potential) more favorable oxidation of sulfide.

When the potential was scanned in the reverse direction, a reduction peak was observed at around -0.6 V, indicative of the reaction of sulfur to sulfide. When the potential was again increased, maximum values were observed at -0.2 V and 0 V, with identical current densities as compared to the first scan. Now limiting the positive scan to $+0.2$ V (red curve in Fig. 1), the minimum value and width of the peak at -0.6 V in the reverse scan shows an obvious difference: a lower upper limit results in a shallower current minimum and less wide sulfur reduction peak to sulfide. This suggests lower quantities of sulfur are deposited, as compared to scanning up to $+0.7$ V, demonstrating sulfur deposition is indeed continued at potentials larger than $+0.2$ V. When the positive scan was limited to -0.4 V, the reduction peak was absent (Fig. 1, green line), showing sulfur deposition requires electrode potentials more positive than -0.4 V. In addition, when the *negative* potential scan was limited to a value of -0.5 versus Hg/HgO , to prevent reductive stripping of surface-sulfur deposits (forming sulfide), the oxidation peak around 0 V was significantly stronger in the initial scan than in subsequent scans (see the inset curves displayed in Fig. 1). This suggests that the electrode rapidly deactivates for sulfide oxidation, likely caused by the formation of a film of sulfur of significant thickness, deposited on the electrode in the first scan.

To investigate the dependence of the quantity of Sulfur deposited, on the applied potential of sulfide oxidation, chronoamperometry measurements were performed at different potentials (see Supplementary Fig. S4), followed by a reductive scan from -0.35 to -1.0 V. The electrochemical response is shown in Fig. 2.

Clearly, the deposited sulfur amount increases as a function of applied potential for oxidation of sulfide, the highest quantity being deposited at $+650$ mV, and the lowest at -150 mV. The shape of the reductive wave does not change significantly, although the minimum shifts to more reductive potential, and two minima at -0.6 V and -0.8 V, become

Fig. 2 Cyclic voltammograms of reductive stripping of oxidized thin films of sulfur on a Ni-polycrystalline electrode in a 0.2-M Na_2HPO_4 solution (pH 9.2) containing 10 mM Na_2S . Scan rate 10 mV s^{-1} . The highest quantity is deposited at 650 mV, and the least at -150 mV

Fig. 3 Charge Q (mC) required to reductively remove sulfur from the Ni electrode, formed by the oxidation of sulfide at variable potentials in chronoamperometry measurements (see Fig. S4)

apparent. The origin of the broadening (and potentially two minima) is not exactly known, but could be induced by the thickness, and different morphology of the film when formed at more positive potential ($+650 \text{ mV}$), as is evident from the film characterization by SEM (see Figs. 6, 7).

The total charge required to reductively remove sulfur from the surface of nickel as a function of applied potential of sulfide oxidation, is shown in Fig. 3. The required charge for removal of sulfur, clearly increases as a function of increasing oxidative potential during sulfur deposition.

When comparing the charge calculated for reductive stripping of the film to the charge of sulfide oxidation at constant potential, these results are inconsistent. The charge accumulated in the oxidative process is significantly larger. This

suggests some sulfur is converted to soluble polysulfides, which may occur simultaneously to the sulfur deposition in phosphate buffer solutions.

3.2 Characterization of the electrode surface after sulfide oxidation at pH 9.2

The nature of the film deposited on the nickel electrodes is visually significantly different, when the potential applied for oxidation of sulfide is increased from 250 to 1250 mV versus Hg/HgO, as shown in Fig. 4.

There is a clear change in the color of the film on the Ni electrode when the applied potential is increased. The surface deposit initially is grayish-white, while it becomes significantly darker in color at higher potentials. At 1250 mV the sample shows a rough and completely black film. This suggests a significant change in the morphology and composition of the film. Raman spectroscopy was used to identify the chemical composition of the surface deposits.

Raman spectroscopy was carried out using 532 nm and 785 nm excitation. Before each measurement, the thin film formed on the electrode was carefully rinsed with Milli-Q water and dried in a desiccator for 10 min. As shown in Fig. 5, the compound formed at 250 mV results in three main Raman peaks, located at 150 cm^{-1} , 210 cm^{-1} , and 580 cm^{-1} . These peaks can be assigned to elemental sulfur (S_8). However, for the sample obtained from electrolysis at 1250 mV (Fig. 5b), additional peaks can be observed, in particular in a range between 300 and 400 cm^{-1} using the excitation wavelength of 785 nm, which peaks are indicative of the formation of a NiS_x phase, most likely NiS_2 . Apparently, at potentials higher than 1.0 V versus Hg/HgO, oxidation of the Ni electrode is significant.

3.3 The ex situ characterization of the film by SEM and EDX

The morphology and composition of the film was further characterized by scanning electron microscopy (SEM), combined with elemental analysis (EDX).

Initially, sulfur deposition appears to result in a rather homogeneous, porous film. On top of this initial film, spherical sulfur structures are formed, which appear to cluster at certain areas of the Ni electrode. The EDX results show the surface deposit primarily consists of elemental sulfur, along with remnants of the sodium phosphate solution used, explaining the peaks (of weak intensity) of Na, P, and O. Upon increasing the potential, the concentration of the spherical structures observed in SEM increases, while the chemical composition remains predominantly sulfur, with traces of sodium phosphate (not shown). Above 850 mV, the morphology significantly changes, as is illustrated by the SEM image shown in Fig. 7.

Fig. 4 Photos of thin films formed by electrochemical oxidation of sulfide on polycrystalline Ni electrode by applying different potentials for 2 h. The films were formed in 10 mM Na_2S dissolved in a 0.2-M Na_2HPO_4 buffer solution (pH 9.2)

Fig. 5 Raman spectra of the films formed at 250 mV, and 1250 mV versus Hg/HgO on polycrystalline Ni electrode

At an applied potential of 1250 mV versus Hg/HgO, the (black) films were found to be highly porous in structure (Fig. 7), with a morphology consisting of agglomerated spherical particles. The film thickness was estimated to be around 24 μm . The EDX data show remnants of the phosphate solution, but in addition, Ni peaks of significant intensity (Fig. 7) show up at 850 mV and above, the potential at which both water oxidation and Ni surface oxidation can take place. It is worth noting that all Ni detected by EDX must be in the film rather than of the electrode itself, as an electron beam of the energy applied here, cannot penetrate a film of this thickness of $> 20 \mu\text{m}$. Since Ni-oxide (or hydroxide hydrate) phases were not detected by Raman

spectroscopy, Ni-oxide species (if formed at all) are likely transformed by chemical reaction with sulfide, possibly at the same time when sulfur deposition is taking place. This is in accordance with the Raman spectra, showing the formation of Ni sulfides after chronoamperometry at relatively high oxidation potential.

3.4 Sulfide oxidation in 0.2 M NaOH

Since polysulfides have been reported to be soluble at high pH, sulfide oxidation was also investigated in 0.2 M NaOH at pH 13.

Fig. 6 SEM images of the films formed at 250 mV, including elemental analysis of the roughened surface. EDX shows this primary film likely consists of residual, crystallized Na-Phosphate, as well as sulfur

Fig. 7 SEM and EDX results of the film obtained during electrolysis at 1250 mV on a Ni-electrode in a 0.5 M Na_2HPO_4 solution with 50 mM Na_2S

In 0.2 M NaOH solution (pH 13), again the upper potential limit was increased and set at 0.58 V or 0.8 V (see Fig. 8). Compared to the Na_2HPO_4 solution, sulfide oxidation occurs with much higher current, while the maxima in the Voltammogram shift to higher potential (0 and 0.4 V in NaOH, versus -0.2 V and 0.1 V in NaH_2PO_4). In particular, at potentials larger than 0.6 V versus Hg/HgO, a significant exponential increase in current is observed, which is very likely the result of oxidation of Ni and extensive formation of oxygen from water oxidation.

In contrast to the Na_2HPO_4 solution, a peak corresponding to sulfur reduction at low potential is not present in the reverse scan. This is in agreement with visual inspection of the electrodes after reaction, which did not show deposition of sulfur species alike the electrodes used in Na_2HPO_4 solution. This might be due to a fast chemical reaction between elemental sulfur and NaOH, resulting in the formation of an alkaline solution of polysulfide, such as S_8^{2-} . Indeed, the

electrolyte turned yellowish after extended periods of electrolysis. Furthermore, the nickel electrode did not turn blackish (indicative of the formation of $\text{Ni}(\text{O})\text{OH}$), suggesting nickel remains in a low oxidation state during sulfide oxidation at relatively low potentials and in alkaline conditions.

H_2 electrolysis was also carried out in a 0.5-M NaOH solution at 800 mV for more than 10 h to determine the anode selectivity for oxidation of sulfide (See Supplementary Fig. S5). This potential was chosen to have significant current, with minimized oxygen evolution. The steady-state hydrogen concentration amounted to $\sim 15,000$ ppm, in good agreement with a measured current of ~ 5 mA (on the basis of comparable calculations shown in Supplementary Table S3). The closure of the H_2 and electron balance demonstrates polysulfide reduction is less favored at the cathode than production of hydrogen, and a membrane is principally not necessary to obtain high Faradaic efficiency for hydrogen evolution on a Pt-Gauze electrode. On the basis of oxygen

evolution (~750 ppm), the selectivity towards sulfide of the anode amounts to ~90%. This value is remarkably high, given the absence of sulfur deposits to inhibit the water oxidation reaction towards oxygen, and confirms the oxidation of Sulfide is thermodynamically and kinetically favored over production of oxygen when polycrystalline Ni electrodes are used.

4 Discussion

The mechanism for the electrochemical oxidation of sulfide is complicated since sulfur has a number of different oxidation states such as -2 , 0 , $+4$, and $+6$. Anodic oxidation of sulfide can produce elemental sulfur, polysulfides, or sulfur oxyanions depending on the electrode composition, potential, pH, and temperature of the electrolyte. Moreover, on Pt anodes, current oscillations have been observed in two regimes of potential. [11]

In this study, Ni anodes showed remarkable changes in behavior in the conversion of sulfide, when the pH was increased from 9.2 to 13. Polycrystalline Ni electrodes form sulfur deposits in buffered Na_2HPO_4 electrolyte, while soluble sulfur species are formed in NaOH solution. Sulfide oxidation on Ni seems to occur in three stages, based on the current response in voltammetry, with some minor evolution of O_2 in the last regime of high potential. To the best of our knowledge, sulfide oxidation on Ni has not been previously discussed in literature, so we will base our discussion on the knowledge available for carbon and Pt metal, as well as a review paper on H_2S conversion [15].

In general, when hydrogen sulfide is dissolved in alkaline solution, sulfide ion is formed:

Sulfur is formed at the anode and hydrogen is liberated at the cathode according to the following electrochemical reactions:

Sulfur rapidly dissolves in the alkaline media forming polysulfides (only disulfide is shown in the equation):

Incidentally, removal of polysulfates from the electrolyte can most likely be achieved by refreshing the electrolyte, and in a separate vessel induce sulfur formation by acidification, according to the reverse of reaction (5):

Polysulfides, which are highly soluble in alkaline water, may also directly form at the anode:

As is obvious from cyclic voltammetry, sulfide oxidation appears to occur in three stages. We propose initially sulfide adsorbs on the surface of Ni (both at pH 9.2 and pH 13), followed by oxidation of these adsorbates to sulfur (Ni does not change oxidation state):

This likely forms the initial (rather homogeneous) film at pH 9.2, as observed in the SEM images (Fig. 6), while sulfur dissolves at pH 13 according to reaction (5). We propose the second, stronger current response is likely due to occurrence of reaction (3), presumably forming the spherical structures of sulfur at pH 9.2, which are again rapidly dissolved at pH 13 according to reaction (5). The most dramatic and effective oxidation of Sulfide is observed above a potential of approximately 800 mV, leading to a thick film of porous sulfur (reaction 3), formation of NiS_2 , and likely polysulfide at pH 9.2, and exclusively polysulfide (reaction 6) at pH 13, accompanied by some oxidation of water.

The above indicated mechanism of reaction is rather speculative, and we propose to perform additional experiments to provide evidence for the various sulfide oxidation processes. In particular, use of an electrochemical Quartz Crystal Microbalance (e-QCM) is recommended, allowing to determine weight changes as a function of applied potential, and to accurately determine the selectivity of the Ni anode for sulfide over water oxidation. We also recommend to perform spectrophotometric (ICP) measurements of the concentration of Ni in solution, since in particular at pH below 11–12 instability (dissolution) can be expected. Finally, in situ Raman measurements appear valuable to further study the intriguing phenomena of sulfur deposition reported here, varying applied electrode, applied potential, and pH of solution.

For large-scale sulfur removal it is highly unlikely to use expensive Pt cathodes; cheaper cathodes, such as graphite-based materials or MoS_2 -based cathodes, need to be used, which are also effective in reducing protons (water) to hydrogen. If a membraneless cell configuration is desired, the tendency of these materials to reduce polysulfides needs to be assessed.

5 Conclusions

Using Ni anodes in a Na_2HPO_4 solution at pH 9.2, electrochemical oxidation of sulfide results in the formation of sulfur deposits at potentials of -0.4 V to $+0.4$ V versus Hg/HgO, predominantly consisting of a primary porous film, with spherical structures superimposed. Such films can be removed by reductive stripping. A significant amount of oxidized Ni (likely NiS_2) was found in samples exposed

Fig. 8 Cyclic voltammograms of sulfide oxidation (10 mM Na_2S) in a 0.2-M NaOH solution on a polycrystalline Ni electrode in a wide potential range. Scan rate 20 mV s^{-1} . The black solid line was recorded without sulfide, the red line (long dash) up to a maximum of 580 mV, and the green line (short dash) up to a maximum of 800 mV

to potentials higher than 0.8 V versus a Hg/HgO reference electrode, accompanied by a thick, highly porous film of sulfur, and likely formation of polysulfides. The latter are not reduced at the Pt cathode, resulting in Faradaic Efficiency towards hydrogen being $\sim 100\%$.

In NaOH solution, formation of a sulfur film was not observed in the potential range investigated (-0.4 V to $+0.8 \text{ V}$ versus Hg/HgO), as determined by visual inspection, and the absence of a reductive current at negative potentials. At an applied potential of 800 mV, oxygen evolution was observed, although a FE towards sulfide oxidation of $\sim 90\%$ could still be maintained at these potentials (Fig. S5).

In conclusion, to effectively oxidize sulfide, NaOH solutions (high pH) are clearly preferred over Na_2HPO_4 solutions, since sulfur deposition is prevented and higher current densities can be achieved. Corrosion of Ni to Ni sulfides at high pH has not been evidenced in the present study at potentials smaller than $+0.8 \text{ V}$ versus Hg/HgO, but should be evaluated in future studies.

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References

1. Hensen EJM, Kooyman PJ, van der Meer Y, van der Kraan AM, de Beer VHJ, van Veen JAR, van Santen RA (2001) The relation

- between morphology and hydrotreating activity for supported MoS_2 particles. *J Catal* 199(2):224–235. <https://doi.org/10.1006/jcat.2000.3158>
2. Reinhoudt HR, Boons CHM, van Langeveld AD, van Veen JAR, Sie ST, Moulijn JA (2001) On the difference between gas- and liquid-phase hydrotreating test reactions. *Appl Catal A* 207(1–2):25–36. [https://doi.org/10.1016/S0926-860X\(00\)00612-8](https://doi.org/10.1016/S0926-860X(00)00612-8)
3. Haner J, Bejan D, Bunce NJ (2009) Electrochemical oxidation of sulfide ion at a $\text{Ti}/\text{IrO}_2\text{--Ta}_2\text{O}_5$ anode in the presence and absence of naphthenic acids. *J Appl Electrochem* 39(10):1733–1738. <https://doi.org/10.1007/s10800-009-9873-7>
4. Hastie J, Bejan D, Bunce NJ (2011) Oxidation of sulfide ion in synthetic geothermal brines at carbon-based anodes. *Can J Chem Eng* 89(4):948–957. <https://doi.org/10.1002/cjce.20454>
5. van Yperen R, van Dillen AJ, Geus JW, Boellaard E, van der Horst AA, van der Kraan AM (1995) Regenerable sorbent for high-temperature desulfurization based on iron–molybdenum mixed oxides. Preparation of catalysts VI: scientific bases for the preparation of heterogeneous catalysts. Elsevier, Amsterdam
6. Waterston K, Bejan D, Bunce NJ (2007) Electrochemical oxidation of sulfide ion at a boron-doped diamond anode. *J Appl Electrochem* 37(3):367–373. <https://doi.org/10.1007/s10800-006-9267-z>
7. Chen AC, Miller B (2004) Potential oscillations during the electrocatalytic oxidation of sulfide on a microstructured $\text{Ti}/\text{Ta}_2\text{O}_5\text{--IrO}_2$ electrode. *J Phys Chem B* 108(7):2245–2251. <https://doi.org/10.1021/jp036639h>
8. Ateya BG, Al-Kharafi FM (2002) Anodic oxidation of sulfide ions from chloride brines. *Electrochem Commun* 4(3):231–238. [https://doi.org/10.1016/S1388-2481\(02\)00254-0](https://doi.org/10.1016/S1388-2481(02)00254-0)
9. Gorlin M, Chernev P, de Araujo JF, Reier T, Dresch S, Paul B, Krahnert R, Dau H, Strasser P (2016) Oxygen evolution reaction dynamics, faradaic charge efficiency, and the active metal redox states of Ni–Fe oxide water splitting electrocatalysts. *J Am Chem Soc* 138(17):5603–5614. <https://doi.org/10.1021/jacs.6b00332>
10. Trotochaud L, Young SL, Ranney JK, Boettcher SW (2014) Nickel–iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation. *J Am Chem Soc* 136(18):6744–6753. <https://doi.org/10.1021/ja502379c>
11. Miller B, Chen AC (2006) Oscillatory instabilities during the electrochemical oxidation of sulfide on a Pt electrode. *J Electroanal Chem* 588(2):314–323. <https://doi.org/10.1016/j.jelechem.2006.01.006>
12. Kas R, Kortlever R, Yilmaz H, Koper MTM, Mul G (2015) Manipulating the hydrocarbon selectivity of copper nanoparticles in CO_2 electroreduction by process conditions. *ChemElectroChem* 2(3):354–358. <https://doi.org/10.1002/celec.201402373>
13. Mul G, Wachs IE, Hirschoen AS (2003) Catalytic synthesis of methanethiol from hydrogen sulfide and carbon monoxide over vanadium-based catalysts. *Catal Today* 78(1–4):327–337. [https://doi.org/10.1016/S0920-5861\(02\)00309-7](https://doi.org/10.1016/S0920-5861(02)00309-7)
14. Ciesielczyk F, Bartczak P, Wieszczycka K, Siwinska-Stefanska K, Nowacka M, Jesionowski T (2013) Adsorption of Ni(II) from model solutions using co-precipitated inorganic oxides. *Adsorption* 19(24):423–434. <https://doi.org/10.1007/s10450-012-9464-5>
15. Zaman J, Chakma A (1995) Production of hydrogen and sulfur from hydrogen sulfide. *Fuel Process Technol* 41(2):159–198. [https://doi.org/10.1016/0378-3820\(94\)00085-8](https://doi.org/10.1016/0378-3820(94)00085-8)

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