

Electrochemical oxidation of sulfide ion at a boron-doped diamond anode

KATIE WATERSTON, DORIN BEJAN and NIGEL J. BUNCE*

Chemistry Department, University of Guelph, Guelph, Ontario, N1G 2W1, Canada

(*author for correspondence, fax: +1-519-7661499, e-mail: nbunce@uoguelph.ca)

Received 9 June 2006; accepted in revised form 16 October 2006

Key words: boron-doped diamond anode, sulfate formation, sulfide oxidation, zero-order kinetics

Abstract

The goal of the present research was the direct conversion of sulfide, an important contaminant in geothermal brines, to sulfate, whose discharge limits are much less stringent than those for sulfide. By the use of a novel anode material boron-doped diamond (BDD), we achieved near-quantitative electrochemical conversion of sulfide ions to sulfate with current efficiency of 90%. Kinetically, the reaction is first order in current density and zero-order in sulfide concentration. The current efficiency becomes essentially quantitative in the presence of chloride ion; under these conditions the reaction is chloride-mediated, at least in part, through the electrochemical formation of hypochlorite ion. Control experiments showed that hypochlorite oxidizes sulfide to sulfate quantitatively under the same conditions.

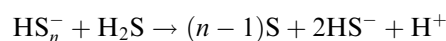
1. Introduction

Hydrogen sulfide – or, at alkaline pH, sulfide ion – is a significant contaminant in the geothermal brines that are by-products of oil and gas extraction; sulfide is also present in certain oil refinery waste streams. Removal of hydrogen sulfide from these aqueous streams is a high priority because of its toxicity and the corrosive properties of sulfide solutions, which cause “sour brines” to foul metal pipes through deposition of sulfidic scale [1]. In the past, remediation has been effected by a combination of precipitation (e.g., as ZnS) and oxidation (e.g., with chromates) in alkaline solution. These treatments are costly in terms of both the chemicals used and the disposal of the resulting toxic sludge. In the gas fields of Alberta, Canada, sour brines are often disposed of by reinjection at a geologically suitable site. This carries heavy costs in terms of transportation from the producer well to the reinjection well while maintaining the sour brine under pressure to prevent the release of H₂S (M. Weeks, Interactive Industrial Solutions, Edmonton, Alberta, personal communication).

Mao et al. [2] reviewed the electrochemistry of the sulfide system in the context of sweetening sour natural gas. Sulfide can be removed from aqueous solution, without producing metallic sludge, by oxidation either to elemental sulfur or to oxyanions such as sulfate SO₄²⁻, which is environmentally benign and is the subject of this research. Most previous work has focused on conversion of sulfide to sulfur, with or without

co-production of hydrogen, with some interest expressed in using hydrogen sulfide as the fuel in a fuel cell [3]. Mao et al. [2] also discussed various electrochemical methods for converting hydrogen sulfide to its elements, including high temperature electrolysis in alkaline solution and a number of electrocatalytic approaches that have not apparently been subsequently investigated. Szpyrkowicz et al. [4] found that sulfide ion in tannery wastewater was electrochemically oxidized at various Ti/metal oxide anodes, but did not report what oxidation product was formed.

The objective of Mao et al. [2] was to convert H₂S to sulfur and hydrogen, with sulfur precipitation occurring as far away as possible from the electrode surface in order to minimize anode passivation. Shih and Lee [5] had suggested the use of an organic solvent to remove sulfur from the anode surface as it was formed, but this approach increased the cell resistance and reduced the current efficiency. Alternatively, sulfur can be precipitated by passing H₂S into a sulfide solution that has been partly electrolyzed to polysulfide [6].



However, Mao et al. [2] noted that when sulfur dissolves in alkaline sulfide solutions to form polysulfide, disproportionation to thiosulfate occurs as a side reaction, especially at elevated temperatures.

Ateya and Al-Kharafi [1] studied the electrochemical oxidation of sulfide to sulfur, which deposited on the surface of their graphite anodes. In subsequent work, Ateya et al. [7] achieved oxidation of sulfide in a synthetic geothermal brine that contained 3.5% by mass of NaCl. X-ray photoelectron spectroscopy revealed that elemental sulfur was deposited on the surface of the carbon felt anode, causing passivation. Although the large surface area of the anode was claimed to alleviate this problem, it would presumably lead to failure of the method in long-term operation. The authors argued that further oxidation of elemental sulfur to sulfur oxyanions must be much slower than the oxidation of sulfide to the element under these conditions, because they observed no other species sorbed to the graphite felt. However, it is not clear whether the material balance for sulfur was investigated. The reaction rate increased at higher temperatures and at higher concentrations of sulfide, although the likely first-order dependence was not demonstrated.

Miller and Chen [8] found that the oxidation of sulfide at a $\text{Ti}/\text{Ta}_2\text{O}_5\text{-IrO}_2$ anode gave galvanic voltammograms whose potential showed large periodic excursions over a wide range of applied currents. Similar behaviour has been observed at platinum anodes [9]. The oscillations were explained in terms of deposits of elemental sulfur, which repeatedly formed on the anode surface and either flaked off [8] or was dissolved as polysulfide by the action of excess sulfide ion [10].

In the work of Ateya et al. [7], no sulfur was deposited on a titanium anode; with a stainless steel anode, pitting of the electrode occurred [11]. The latter observation is consistent with the report that sulfide can be removed from wastewaters by electrocoagulation at iron or aluminum sacrificial anodes [12], in the former case with the formation of FeS [13]. At aluminum, much of the anion removal occurred through chemisorption at pH values at which the precipitate of $\text{M}(\text{OH})_3$ was positively charged.

A major question to address is whether the objective of treating a solution polluted by sulfide is to recover sulfur and/or hydrogen from H_2S , or to convert toxic sulfide to a benign form such as sulfate. Mitigating the first approach, elemental sulfur is available at low cost and high purity from the Claus process in the sweetening of natural gas. Regarding the complete oxidation of sulfide to sulfate, Allison et al. [14] noted that the success of this conversion with conventional oxidizing agents requires that elemental sulfur does not precipitate from the solution. They achieved this condition by using surface active agents to prolong contact between the sulfide ion and the oxidant. This is consistent with the conclusion of Ateya et al. [11] that in the electrolysis of sulfide at graphite anodes, the deposited sulfur was stable with respect to further oxidation on kinetic rather than thermodynamic grounds.

The work of our laboratory is focused on electrochemical methods for the remediation of aqueous wastes that are recalcitrant to conventional treatments. An

attraction of electrochemical remediation is that electricity is far cheaper than any chemical reagent. Economic operation requires high current efficiency, meaning that almost all the electrons are used productively [15]. In this work we focus on the conversion of sulfide to sulfate, using synthetic solutions of sulfide in water with and without the addition of chloride ion.

2. Materials and methods

2.1. Materials

Sodium sulfide nonahydrate (ACS reagent, 98%), sodium sulfate (anhydrous, 99.9%), sodium thiosulfate volumetric standard, iodine volumetric standard, and starch indicator used in iodometric titrations were supplied by Sigma-Aldrich (Oakville, ON). Sodium chloride, sodium hydroxide, and barium chloride were supplied by Fisher Scientific Company (Toronto, ON). Solutions were prepared using distilled water and reagent grade chemicals.

The anode was a boron-doped diamond electrode (BDD), supplied by Swiss Center for Electronics and Microtechnology, Inc., Neuchâtel, Switzerland. A graphite rod supplied by Alfa Aesar, Ward Hill, MA, USA was used as cathode.

2.2. Apparatus

Electrolyses were performed in a Pyrex beaker for open reactions and in a glass cell built in our laboratory for closed reactions. The latter contained four openings in the top: two for insertion of the electrodes, one for escape of gas to a NaOH trap, and the fourth for admission of argon to sweep out gases after electrolysis was complete. Both cells held 80 ml of solution. The anode surface area was 40×15 mm. The cell was operated with the electrodes in a vertical configuration to allow the escape of gases evolved during electrolysis. Power to the electrochemical reactor was supplied by an EG&G Model 363 potentiostat/galvanostat.

2.3. Experimental procedures

The reactor was operated in batch mode with 80 ml of solution that was constantly stirred. The solutions contained sodium sulfide (range 15–60 mM) with 0.25 mM sodium hydroxide and in some cases 1–5% (w/v) sodium chloride as supporting electrolyte. All electrolyses were run galvanostatically at currents of 100–800 mA. Total electrolysis times ranged from 200 to 400 min. Concentrations of sulfide and tetrathionate were determined using iodometry [16, 17]. Concentrations of sulfate were determined using turbidimetric measurements [16] using a Pharmacia LKB Novaspec II UV/Vis spectrometer set to 420 nm to measure the apparent absorbance of the samples.

3. Results and discussion

Electrolysis of 30 mM sulfide in an open undivided cell at a BDD anode in alkaline solution, using a graphite rod cathode and 0.25 mM NaOH as supporting electrolyte, led to rapid loss of sulfide from solution (Figure 1). Residual sulfide was determined by iodometric titration. A heavy white precipitate formed upon addition of Ba(OH)₂ solution to the electrolyzed solution, suggesting the formation of sulfate as the product. No precipitation of elemental sulfur occurred during the reaction, and although a small amount of deposit was occasionally observed on the anode at intermediate stages of electrolysis, the anode surface was clean by the end of the reaction. The solution often became yellow early in the electrolysis, consistent with the presence of polysulfide ion, but the final solutions were invariably clear and colourless. Visual inspection showed copious gas evolution (H₂) at the cathode, but very little gas production at the anode. Unexpectedly, the loss of sulfide ion followed zero-order kinetics (current-controlled electrolysis), with a linear relationship between residual sulfide concentration and time at all stages of conversion. Electrolyses carried out in the presence of 1% w/v NaCl were also kinetically zero-order in substrate, and almost indistinguishable in rate. Although the chloride-assisted reaction probably involves the intermediacy of hypochlorite ion (see below), there is little difference in rate or efficiency between the assisted and unassisted reactions, because both chloride and sulfide ions are oxidized very efficiently at BDD anodes.

Zero-order behaviour was confirmed by carrying out the electrolysis at 200 mA and different starting concentrations of sulfide, and obtaining identical reaction rates of 0.18 mmol l⁻¹ min⁻¹ (Figure 2). Similar reac-

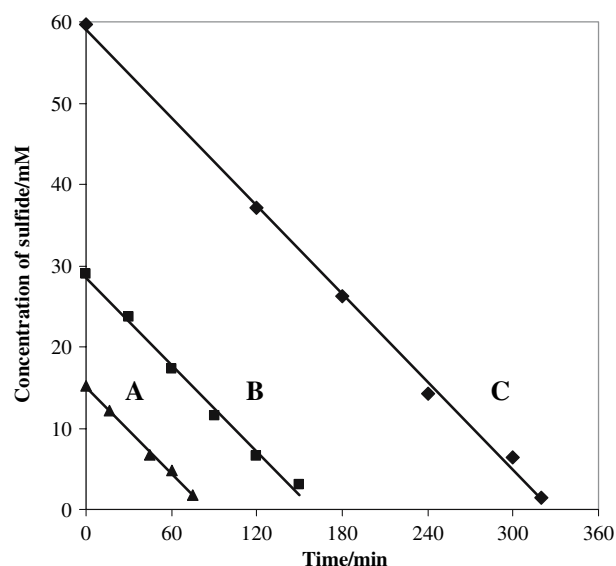


Fig. 2. Electrolysis of sulfide in the absence of chloride at applied current of 200 mA with initial sulfide concentrations 15 mM (A), 30 mM (B), and 60 mM (C), using BDD anode and graphite rod cathode.

tions in the presence of 1% NaCl (w/v) had rates 0.19, 0.20 and 0.21 mmol l⁻¹ min⁻¹ for initial concentrations 15, 30, and 60 mM, respectively. The reaction was first order in applied current (Figure 3) with reaction rates 0.09, 0.18, and 0.31 mmol l⁻¹ min⁻¹ for applied current 100, 200, and 400 mA. Similar experiments in the presence of 1% NaCl (w/v) had rates 0.09, 0.20 and 0.41 mmol l⁻¹ min⁻¹. The reaction rate responded only slightly to changes in the concentration of NaCl; for applied current 200 mA and concentrations 0.0, 1.0, 3.0, and 5.0% NaCl w/v, the reaction rates were 0.18, 0.20, 0.22, and 0.23 mmol l⁻¹ min⁻¹, respectively.

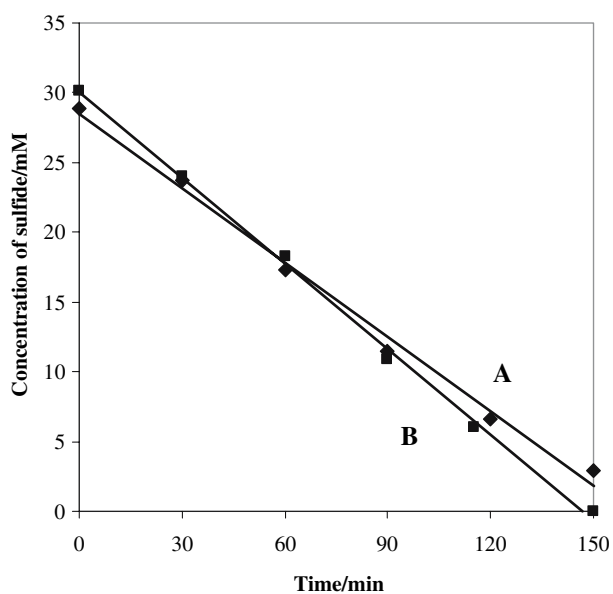


Fig. 1. Electrolytic remediation of sulfide in the absence (A) and presence (B) of 1% NaCl. BDD anode, graphite cathode, current 200 mA.

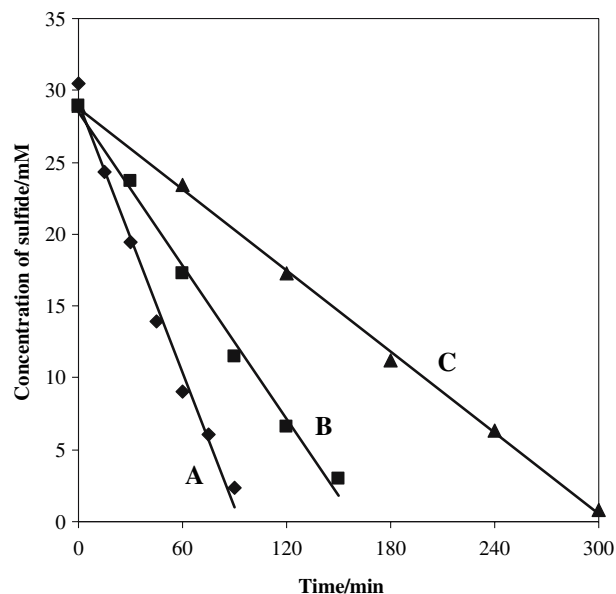
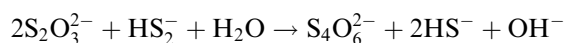
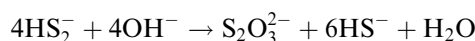


Fig. 3. Electrolysis of sulfide in the absence of chloride at applied currents of 400 mA (A), 200 mA (B), and 100 mA (C), using BDD anode and graphite rod cathode.

Turbidimetric analysis showed the formation of sulfate ion to be linear with time over most of the course of the reaction, eventually reaching a chemical yield of approximately 90% (Figure 4). In experiments using a closed cell, with H₂S swept out into an alkaline trapping solution, approximately 5% of the initial sulfide was volatilized at the pH of the experiment. Various sources were sought for the remaining 5–10% of the material, the exact amount of which varied from experiment to experiment. The complete disappearance of sulfide at the end of the experiment (i.e., complete loss of reducing titer) ruled out intermediate products of oxidation such as sulfite or hydrosulfite. No oxidizing titer was obtained when the electrolyte was treated with acidified KI, ruling out over-oxidation to persulfate. Instead, the missing material was analyzed as tetrathionate, S₄O₆²⁻ [17]; this forms by disproportionation of polysulfide in alkaline solution [2], followed by oxidation with further polysulfide ion (which we have written as HS₂⁻).



Based on an 8-electron oxidation of sulfide to sulfate, the current efficiency was approximately 90% in chloride-free solution and essentially quantitative in the presence of 1% NaCl, thus explaining the minimal evolution of gas at the anode through the parasitic oxidation of water.

The observation of zero order kinetics with respect to substrate implies that sulfide must be scavenged very efficiently from solution onto the BDD anode, and the lack of observable intermediates and high final sulfate

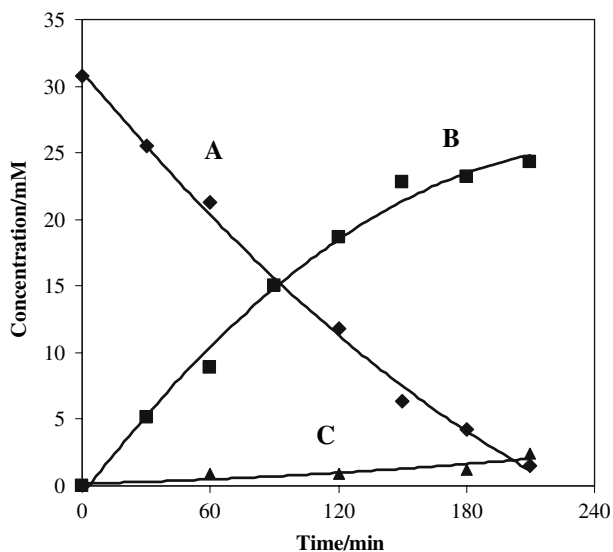


Fig. 4. Material balance in the oxidation of sulfide. Symbols: Sulfide (diamonds); sulphate (squares); volatilized hydrogen sulfide (triangles). BDD anode, graphite rod cathode, current 200 mA.

concentration indicates that sequential oxidation must be faster than release of any such intermediates into solution. Assuming Langmuir type adsorption, the fraction of occupied active sites on the BDD anode is given by $K[\text{S}^{2-},\text{aq}]/\{1 + K[\text{S}^{2-},\text{aq}]\}$, where K is the adsorption equilibrium constant. Zero-order behavior requires $K[\text{S}^{2-},\text{aq}] > 1$; in the middle of our concentration range, ~ 10 mM, $K > 10^2 \text{ M}^{-1}$. As the BDD electrodes aged over dozens of oxidation runs, their kinetic behavior gradually changed so that curvature was observed late in the run, suggesting that the nature of the electrode surface had changed in such a way as to reduce the value of K , i.e., weaker binding of sulfide and an approach to first order kinetics.

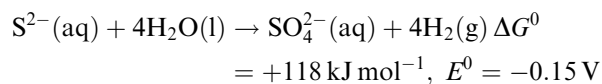
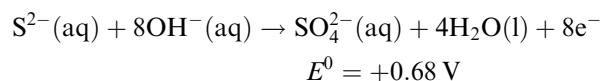
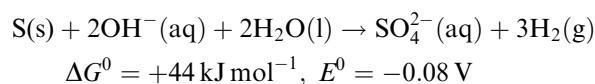
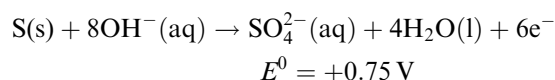
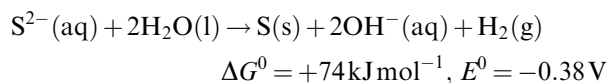
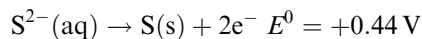
Another way of expressing the explanation for zero-order kinetics is that the rate of scavenging sulfide from solution onto the BDD anode must be much faster than the rate of oxidation at the electrode. Therefore under our conditions, the electrochemical oxidation is not diffusion-controlled, otherwise first order behaviour would have been observed. In seeming contrast, Lawrence et al. [18] found that sulfide could be quantified in sub-mM concentrations at a BDD microelectrode at pH 10. They observed a linear relationship between peak current of a cyclic voltammogram and concentration, suggesting diffusion-limited oxidation. This was attributed to the two-electron oxidation of sulfide to sulfur, but it is not clear whether this chemistry was actually observed as opposed to inferred. Tafel plots (E vs. $\log I$) had slope 120 mV per decade, suggestive of an irreversible oxidation with removal of the first electron being rate determining. The Randles-Sevcik plot of peak current vs. (scan rate)^{1/2} was linear, suggesting a diffusion-limited process with no electrode fouling. In the middle of the concentration range employed by Lawrence et al., $\sim 10^{-5}$ M, the observation of first order kinetics suggests $K[\text{S}^{2-},\text{aq}] < 1$, thereby bracketing the value of K between 10^2 and 10^5 M^{-1} . There is thus no conflict between our results and those of Lawrence et al. [18]; the latter authors worked at lower concentrations than we did, and used a microelectrode, which promotes depletion of substrate in the vicinity of the microelectrode. Both these differences favour a diffusion-limited replacement of sulfide at the electrode surface and hence first order kinetics with respect to substrate as observed by Lawrence et al. [18].

Lawrence et al. [18] also observed that the oxidation potential for sulfide was electrode-dependent: E values (vs. SCE) were +1.30, +0.76, +0.45, and +0.36 V for BDD, gold, glassy carbon, and platinum, respectively. Sulfur species are known to associate strongly with at least some of these anodes (Au, Pt) [19–24]. The high E value at BDD explains why oxidation all the way to sulfate is favoured at this anode.

An alternative explanation for the lack of precipitation of elemental sulfur at the BDD anode involves the overpotential for formation of S(s). Thermodynamic calculation [25] gives $E^0 = +0.44$ V vs. SHE (0.2 V vs.

SCE) for the reaction $S^{2-}(aq) \rightarrow S(s)$. Thus according to the data of Lawrence et al. just cited [18], glassy carbon and Pt have small overpotentials, Au a moderate overpotential, and BDD a large overpotential for this reaction. Parenthetically, Lawrence et al. [26] lowered the overpotential further at carbon nanotubes, observing $E_{1/2}$ near +0.2 V vs. Ag/AgCl, close to the thermodynamic value.

The calculated thermodynamic values for the relevant oxidation and overall cell reactions are as follows.



These data show that oxidation of $S(s)$ to $SO_4^{2-}(aq)$ in alkaline solution is more spontaneous than partial oxidation of $S^{2-}(aq)$ to $S(s)$. The outcome of the oxidation therefore depends on kinetic factors as noted by Ateya et al. [11], such as whether the elemental sulfur formed in the initial oxidation either precipitates as a solid phase or is dissolved from the anode by residual sulfide ion before it has time to be oxidized further. The large overpotential for the initial reaction at BDD therefore favours complete oxidation to sulfate.

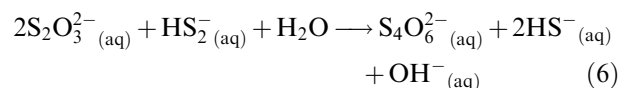
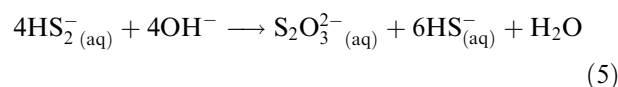
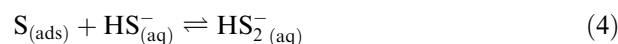
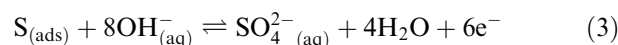
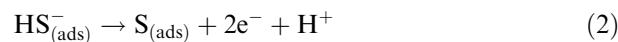
Lawrence et al. [18] also found that the oxidation of $S^{2-}(aq)$ to $S(s)$ is catalyzed by the ferrocyanide/ferricyanide couple, which has $E^0(\text{reduction}) = +0.36 \text{ V}$, allowing spontaneous oxidation of $S^{2-}(aq)$ to $S(s)$. Writing the oxidation of sulfide as $S^{2-}(aq)$ to $S(s)$ is an oversimplification, because elemental sulfur dissolves in sulfide solutions to give polysulfides, the more so as the concentration of sulfide increases (especially under our conditions of mM sulphide, rather than their conditions of μM sulphide). Thus when Lawrence et al. [18] report that the pH dependence of peak potential for the oxidation of sulfide at BDD, which had the value 20 mV/pH unit, was “consistent with a two electron,

one proton irreversible electrochemical process occurring”, the chemistry was presumably $S^{2-}(aq) \rightarrow HS_n^-(aq)$.



The foregoing chemistry has been investigated in the electrolysis of the “white liquor” used in the pulp and paper industry, because it has been found that increasing the concentration of polysulfide ion HS_n^- increases the yield of the process [27]. At a Pt anode, oxidation occurred at $E_{1/2} \sim -0.3 \text{ V}$ vs. SCE, and involved the formation of sulfur on the electrode surface and its subsequent dissolution. The dissolution is autocatalytic, because sulfur is dissolved more effectively from the anode by HS_n^- than by HS^- .

The complete scheme for the reactions leading to sulfate and tetrathionate as the oxidation products of sulfide ion is given in Reactions 1–6. At pH 11–12, sulfide is initially present as HS^- , and we have elected to write polysulfide as HS_2^- .

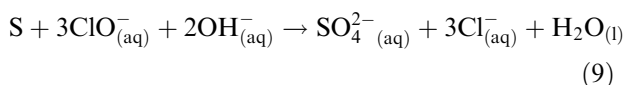
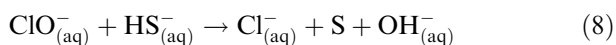
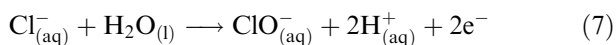


Reaction (1) represents the initial adsorption of sulfide on to the BDD anode, as discussed above. Reaction (2) is the initial stage of electrochemical oxidation to elemental sulphur. Further oxidation to sulfate (Reaction (3)) is faster than precipitation of sulfur, although there is always some tendency for residual unoxidized sulfide ion to extract elemental sulfur from the anode as polysulfide (Reaction (4)). When this happens, some of the polysulfide disproportionates, yielding thiosulfate (Reaction (5)) and hence tetrathionate (Reaction (6)). Polysulfide (yellow colour) was observed only in the early stages of the reaction, when significant concentrations of unreacted sulfide were still available.

The relative rates of Reactions (3) and (4) could be altered by adjusting the experimental conditions. High applied current (800 mA) increased the rate of Reaction

(3), and at initial sulfide concentrations < 30 mM, Reaction (4) was suppressed; quantitative conversion of sulfide to sulfate was observed and no tetrathionate was formed. Conversely, concentrations of sulfide > 80 mM and low applied current allowed Reaction (4) to compete, and up to 10% of tetrathionate was observed, with a concomitant reduction in the yield of sulfate.

In the case of the chloride-assisted oxidation, direct oxidation of sulphide is in competition with a hypochlorite-mediated oxidation, along with competition from Reactions (4)–(6).



Because the electrochemical oxidations of both chloride and sulfide (Reactions (2) and (7)) occur with high current efficiency, there is little increase in the rate of oxidation in the chloride-assisted reaction compared with the unassisted reaction (Figure 1). However, when the chloride-assisted reaction was mimicked by treating a solution of 30 mM sulfide with small aliquots of sodium hypochlorite solution over a time scale comparable with that of the electrolysis (3 h), the solution immediately became brightly coloured due to the formation of polysulfide, and remained yellow until the last aliquot of hypochlorite was added. Under these conditions, the yield of sulfate was only 10%, tetrathionate having been formed at its expense. Conversely, when the stoichiometric amount of hypochlorite was added in a single aliquot, no yellow colour was observed, no tetrathionate was formed, and the yield of sulfate was quantitative. Thus if the intermediately formed sulfur is oxidised fast enough so that it does not dissolve into the sulfide solution and form polysulfide, the complete 8-electron oxidation is the dominant oxidation pathway and little or no tetrathionate is formed.

4. Conclusion

By the use of the novel anode material boron-doped diamond (BDD), we have achieved near-quantitative electrochemical conversion of sulfide to sulfate with current efficiency of 90%. Kinetically, the reaction is first order in current density and zero order in sulfide concentration. The current efficiency rises to essentially quantitative in the presence of chloride ion; under these conditions the reaction is chloride-mediated, at least in part, through the electrochemical formation of hypochlorite ion. Control experiments showed that

hypochlorite oxidizes sulfide to sulfate quantitatively under the same conditions.

As a final comment we consider the possibility of developing electrochemical oxidation of sulfide to sulfate as a technology. In one respect, this system appears to be a nearly ideal candidate for environmental remediation because of the zero-order kinetics and because both the chemical and current yields are nearly quantitative. One prospective disadvantage is that in waters that also contain calcium ion, calcium sulfate might precipitate when the remediated water is pumped into a receiving well. Another is that sulfide ion to sulfate ion is an 8-electron oxidation; energy costs would be correspondingly reduced if the 2-electron oxidation of sulfide ion to elemental sulfur could be achieved with comparable efficiency. Further work in our laboratory is directed towards the latter possibility.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References

1. B.G. Ateya and F.M. Al-Kharafi, *Electrochem. Commun.* **4** (2002) 231.
2. Z. Mao, A. Anani, R.E. White, S. Srinivasan and A.J. Appleby, *J. Electrochem. Soc.* **138** (1991) 1299.
3. J. Zaman and A. Chakma, *Fuel Process. Technol.* **41** (1995) 159.
4. L. Szpyrkowicz, S.N. Kaul, R.N. Neti and S. Satyanarayan, *Water Res.* **39** (2005) 1601.
5. Y.S. Shih and J.L. Lee, *Ind. Eng. Chem. Process Des. Devel.* **25** (1986) 834.
6. Q. Yi, Q. Chen, P. Zhang and J. Zhou, *Aust. J. Chem.* **53** (2000) 557.
7. B.G. Ateya, F.M. Al-Kharafi, R.M. Abdallah and A.S. Al-Azab, *J. Appl. Electrochem.* **35** (2005) 297.
8. B. Miller and A. Chen, *Electrochim. Acta.* **50** (2005) 2203.
9. H. Helms, E. Schloemer and W. Jansen, *Monats. Chem.* **129** (1998) 617.
10. A. Chen and B. Miller, *J. Phys. Chem. B.* **108** (2004) 2245.
11. B.G. Ateya, A.S. Al-Azab and A.M. Abdullah, *Int. J. Chem.* **15** (2005) 113.
12. M. Murugananthan, G.B. Raju and S. Prabhakar, *J. Hazard Mater. B* **109** (2004) 37.
13. N.A. Bykovskii, L.N. Bykovskaya, N.S. Shulaev, V.F. Abromov and R.G. Ryskulov, Russian Patent, RU99-122118 (2001), through *Chem. Abstr.*, **136** (2002) 374439.
14. J.D. Allison, S.A. Thomas and K. Yang, U.S. Patent. 4,839,154 (1989).
15. K. Rajeshwar and J.G. Ibanez, 'Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement' (Academic Press, San Diego CA, 1997), Chapters 2 and 5.
16. APHA; AWWA; WEF, 'Standard methods for the examination of water and wastewater', 19th edn. (American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 1995).
17. W. Ciesielski, U. Zlobinska and A. Krenc, *Chem. Anal. (Warsaw)* **46** (2001) 397.

18. N.S. Lawrence, M. Thompson, C. Prado, T.G.J. Jones R.G. Compton, *Electroanalysis* **14** (2002) 499.
19. Y.-E. Sung, W. Chrzanowski, A. Zolfaghari, G. Jerkiewicz and A. Wieckowski, *J. Am. Chem. Soc.* **119** (1997) 194.
20. T. Loucka, *J. Electroanal. Chem. Interfacial Electrochem.* **36** (1972) 369.
21. N. Ramasubramanian, *J. Electroanal. Chem. Interfacial Electrochem.* **64** (1975) 21.
22. A.N. Buckley, I.C. Hamilton and R. Woods, *J. Electroanal. Chem.* **216** (1987) 213.
23. I.C. Hamilton and R. Woods, *J. Appl. Electrochem.* **13** (1983) 783.
24. A. Briceno and S. Chander, *J. Appl. Electrochem.* **20** (1990) 506.
25. Thermodynamic data from R.C. Weast (ed.), 'Handbook of Chemistry and Physics', 64th edn. (CRC Press, 1984), pp. D52–D93, except for the value for ΔG_f^0 for $S^{2-}(aq) = +86.2 \text{ kJ mol}^{-1}$ from J.W. Kury, A.J. Zielen and W.L. Latimer, US Atomic Energy Commission, Technical Information Service, Report UCRL-2108 (1953), pp. 3–11.
26. N.S. Lawrence, R.P. Deo and J. Wang, *Anal. Chim. Acta.* **517** (2004) 131.
27. M. Behm and D. Simonsson, *J. Appl. Electrochem.* **27** (1997) 507.