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Electrolysis of liquid hydrogen sulphide

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Electrolysis of liquid hydrogen sulphide has been investigated. Pyridine was used to provide conductivity. The cathodic current efficiency for hydrogen production was 99.7 ± 0.5%; sulphur was the major anodic product with a current efficiency of 84.2 ± 4.5%. Ohmic losses in the solution were the largest source of voltage drop.

1. Introduction

The electrolysis of liquid H_2S has received virtually no previous attention. In their surveys of conducting solutions, some researchers electrolyzed liquid H_2S [1–3] and liquid H_2S solutions [2, 4, 5] but did not identify products.

In this study liquid H_2S was electrolyzed at room temperature and elevated pressure. Pyridine was added to provide the supporting electrolyte.

2. Experimental

2.1. *Electrolysis apparatus*

A Parr Model 4760 pressure bomb, equipped with a thermocouple, pressure gauge, lines for filling and sampling and electrical connections was used for the electrolyses. Initially, the electrode design shown in Fig. 1 was employed. The two electrodes were machined from aluminium-7075, chosen because of its excellent corrosion resistance to H_2S and sulphur and its relatively low hydrogen overvoltage in aqueous systems. Small glass pegs supported the aluminium electrodes and flared glass tubes fitted through the openings in the electrodes insulated the thermocouple and filling tube. Geometric criteria for the electrode design included large active area, short current path, and ease of product separation. Large bubbles of gaseous product were buoyed up the inclined space between the electrodes and out of the liquid space.

In later experiments the graphite electrodes shown in Fig. 2 were used. The space-fillers permitted the electrodes to be completely submerged in only 10 ml of liquid.

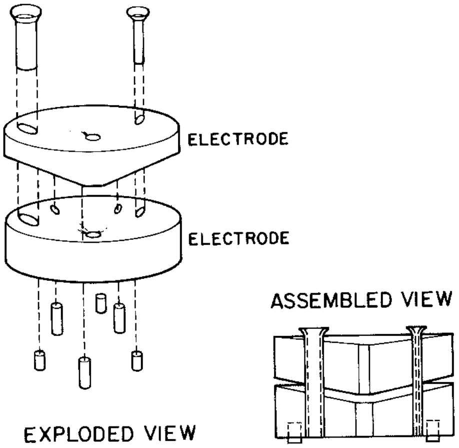


Fig. 1. Electrode design 1.

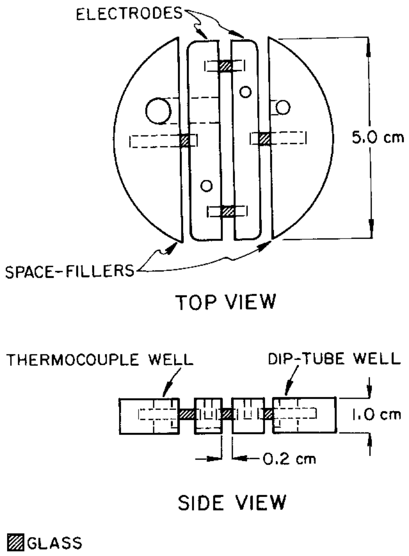


Fig. 2. Electrode design 2.

2.2 *Experimental and analytical procedures*

The desired amount of pyridine was first placed in the cell. The cell was then sealed, evacuated and placed in an ice-water bath. H_2S (99.6% minimum liquid purity) was condensed into the cell. The amount of H_2S fed was determined by weighing the supply bottle before and after addition. The ice bath was removed and the cell allowed to reach room temperature. After electrolysis, the pressure was released and the remaining H_2S was allowed to evaporate and vent through a solution of $KMnO_4$, which oxidized the H_2S to sulphur.

Gas analysis was done with a Carle Analytical Gas Chromatograph Model 111 H, specifically designed for hydrogen analysis. Solid products were extracted into carbon disulphide, which was then filtered, evaporated and weighed. Remaining solids were scraped from the electrodes and cell surfaces. The mass of the solids was determined to within 0.1 mg.

Conductivity measurements were taken with a Barnstead Model PM-70CB conductivity bridge. Through calibration with KCl standards, specific conductivities could be determined.

3. Results

3.1. *Product identification and current efficiencies*

Every sample of gas taken from the cell after electrolysis contained hydrogen. There was no evidence of minor gaseous product formation. Results of the measured yields are summarized in Table 1. The current efficiency for electrochemical hydrogen production was 99.7 ± 0.5%.

At the conclusion of electrolysis and after evaporation of the remaining H_2S, a yellow solid was found in the cell and on the electrodes. Microscopic examination of the solid revealed finely divided rhombic crystals with an average diameter of 0.1 mm. A Debye–Scherrer powder diffraction pattern of the solid was identified through the ASTM files as α-sulphur (rhombohedral). The anodic current efficiency for sulphur production is summarized in Table 2.

Table 1. Hydrogen production efficiency

Case	*Cathode*	*Hydrogen yield (%)*
1	Aluminium	99.3*
2	Aluminium	100.3*
3	Graphite	99.5
	Average:	99.7 ± 0.5%

* Corrected for $2Ag + H_2S = Ag_2S + H_2$ reaction on silver wires in the cell.

Table 2. Sulphur production efficiency

Case	*Anode*	*Sulphur yield (%)*
1	Aluminium	82.7
2	Aluminium	86.7
3	Aluminium	78.7
4	Graphite	89.1
	Average:	84.2 ± 4.5%

In electrolysis experiments using aluminium electrodes, a brown gummy substance was formed. The amount increased with increasing current density. When produced in large quantities, the substance lost its gummy texture.

Four blank runs were performed to ensure that product formation was due to the electrolysis. Operating conditions, experimental procedures and times were the same as those used for electrolysis runs, except that no current was passed through the solution. No hydrogen or sulphur was observed in any blank run. These runs also produced the gummy material, but only in very small quantities and only after a reaction period of about three days.

Elemental analysis of the side products from blank and electrolysis runs was performed with the results shown in Table 3. Some of the carbon,

Table 3. Composition of side product

Component	*Wt% in sample*	
	Blank run	*Electrolysis run**
Carbon	6.46	2.08
Hydrogen	0.94	3.72
Nitrogen	0.68	0.42
Oxygen	Not analyzed	33.73
Sulphur	6.15	8.64
Ash	~ 77	59.48
Metals	Not analyzed	Major: aluminium magnesium Minor: silicon

* Aluminium electrodes

hydrogen, nitrogen, and sulphur may have come from traces of electrolyte and solvent remaining in the solid. However, these results indicate that the side products probably originated from corrosion of the aluminium electrodes. This is consistent with the increase in the amount of side product formed with increasing current density and the pitted surface of the aluminium anode following electrolysis, especially in regions of higher current densities.

3.2. *Solution conductivities*

The specific conductivity of the H_2S used in this study was found to be $9.3 \times 10^{-9} \Omega^{-1} cm^{-1}$ at 0° C and $1.8 \times 10^{-8} \Omega^{-1} cm^{-1}$ at 10° C. These values compare favourably with the values reported in the literature [1–3, 6, 7]. The specific conductivity of pyridine/H_2S mixtures exhibited a maximum of $1.81 \times 10^{-4} \Omega^{-1} cm^{-1}$ at a pyridine mole fraction of about 0.30 and temperature of 25° C. Pyridine concentrations up to 0.3 mole fraction were used in the electrolyses. Apart from the different solution resistivities, no difference in results at different concentrations was noted.

The rather low conductivity obtainable with pyridine led to several attempts to find better electrolytes. The addition of anhydrous sodium sulphide to liquid H_2S caused only a very slight rise in conductivity. The specific conductivity at 0° C was only $4.5 \times 10^{-8} \Omega^{-1} cm^{-1}$ at an Na_2S concentration of 1.8 moles l^{-1} (mole fraction: 0.057), and appeared to be relatively insensitive to concentration. Addition of elemental sulphur to H_2S/Na_2S mixtures in the ratio of 2.9 moles S to 1 mole Na_2S increased the conductivity slightly and caused a conductivity maximum to appear, as shown in Fig. 3.

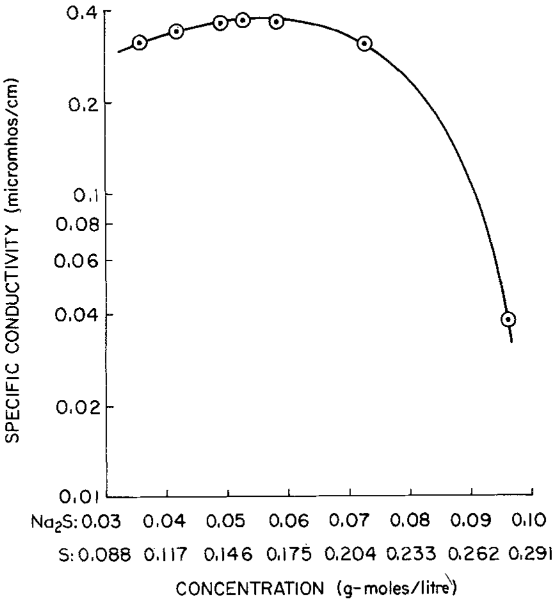


Fig. 3. Specific conductivity of $Na_2S/S/H_2S$ mixtures at 0° C.

The addition of CO_2 to $H_2S/Na_2S/S$ mixtures caused a marked decrease in solution conductivity. A liquid composition of 44.9 mol% H_2S, 54.9 mol% CO_2, 0.17 mol% S, and 0.06 mol% Na_2S gave a specific conductivity of only $1.37 \times 10^{-9} \Omega^{-1} cm^{-1}$ at 0° C.

3.3 *Voltammetry*

Voltammetric measurements were made; however, since no reference electrode was used, only information about the coupled electrode pair could be obtained. The sum of the overpotentials for both electrodes can be calculated from overall voltammetric data provided that the solution ohmic loss can be accurately measured. This was done using the current interrupter technique. A Tafel plot for electrolysis at 0° C on graphite electrodes is shown in Fig. 4. At low current densities, the total overpotential was a few hundred millivolts, indicating that most of the voltage loss in the electrolysis arose from ohmic loss in the solution.

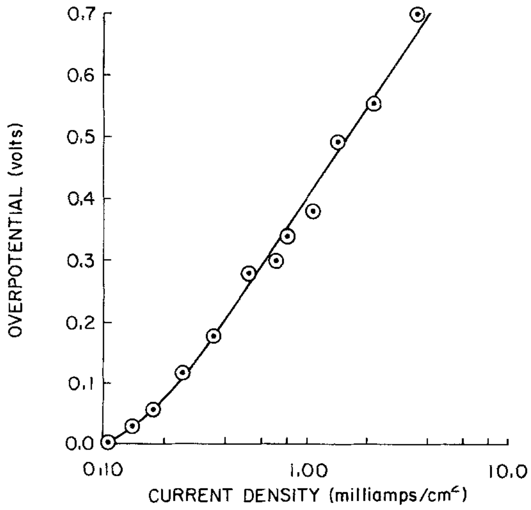
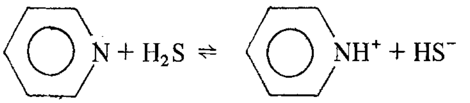


Fig. 4. Tafel plot for H_2S electrolysis on graphite electrodes at 0° C.

4. Discussion

4.1. *Electrolysis*

Superfically, similarities between the electrolysis of H_2S and H_2O would be expected. However, the conductivity of pure liquid H_2S, 10^{-8} to $10^{-9}\,\Omega^{-1}\,cm^{-1}$ [1–3, 6, 7] is much less than that of water. The low dielectric constant of H_2S, 10.2 [8], compared to that of H_2O, 78, ensures that H_2S will be a much poorer solvent for ionic compounds. Hydrogen sulphide can be made conductive by the addition of organic amines [2, 4–7]. (Pyridine was used in this study, but many others act similarly.) Presumably the conductivity is induced by an acid–base reaction as postulated by Cotton and Waddington [7]:



No direct evidence for the presence of these ions was obtained in this study, however.

The formation of sulphur or polysulphides could lead to the formation of an insulating layer on the anode, should the local concentration of the sulphur exceed its solubility limit. The small, but significant, solubility of S in H_2S (0.6 mol% at 0° C) [9] was apparently sufficient to prevent deposition of sulphur on the anode at the conditions of these experiments. At higher current densities, forced convection of the solution past the electrodes might be required to aid diffusion of sulphur away from the anode.

4.2. *Current efficiencies*

It is not known why the sulphur yields were less than 100%. The measured amounts of sulphur were probably biased downward somewhat by losses in the extraction process. The occurrence of other anodic reactions forming products not extracted with the sulphur is also a possibility. Furthermore, sulphur may have been either physically or chemically included with the side product. However, it is unlikely that a significant amount of sulphur diffused to the cathode and was reduced, since this would have resulted in a low hydrogen yield.

4.3. *Solution conductivities*

The low conductivity of H_2S/Na_2S mixtures indicated that the Na_2S did not ionize to an appreciable extent. This may be predicted by the Bjerrum parameter, given the low dielectric constant of H_2S. The decrease of solution conductivity with the addition of CO_2 is not surprising because of the low dielectric constant of liquid CO_2 (1.60 at 20° C).

4.4 *Applications*

Electrolysis of H_2S has been proposed as a possible alternative to conventional H_2S disposal schemes such as the Claus process [10–12]. The value of the recovered product, especially H_2, could possibly offset the cost of the required electrical energy. Because of the great differences in free energies of formation of H_2O and H_2S [+ 56.69 and + 7.89 kcal (g mol)$^{-1}$ respectively], it is conceivable that an H_2S electrolysis process operated in conjunction with an H_2–air fuel cell could be a net energy producer. However, the results presented here indicate much higher solution conductivities must be obtained before the process can be made practical.

Acknowledgement

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