Electrochemical reactions of H_2S in molten sulphide

ERNEST K. BANKS*, JACK WINNICK

*Georgia Institute of Technology, Atlanta, GA 30332, USA*

The reactions involving H_2S in molten alkali sulphides are essential to the operation of a novel electrochemical gas-cleaning device. These reactions are studied in free-electrolyte in order to elucidate the mechanism. Partial carbonation of the melt, as would occur in contact with wet, CO_2-containing gases, is also explored. The effect is seen to be a significant enhancement of the H_2S removal rate.

1. Introduction

Lim and Winnick [1] have demonstrated on a laboratory scale a scheme for electrochemically removing H_2S at high temperatures. Fig. 1 shows conceptually the cell used. Process gas containing H_2S flows past the working electrode of an electrochemical cell, where it is reduced:

$$H_2S + 2e \longrightarrow H_2 + S^{2-} \qquad (1)$$
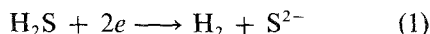
The S^{2-} ions produced migrate through the alkali sulphide electrolyte to the counter electrode. If a nitrogen stream flows past the counter electrode, sulphide ions are oxidized according to the reaction:

$$S^{2-} \longrightarrow 1/2S_2 + 2e \qquad (2)$$
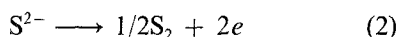
Alternately, a hydrogen stream may flow past the counter electrode, in which case the following reaction occurs:

$$H_2 + S^{2-} \longrightarrow H_2S + 2e \qquad (3)$$
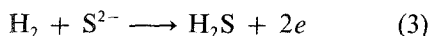
The direct electrochemical oxidation of sulphide, Reaction 2, is preferred for an industrial application. In this situation, a stack of cells is constructed, much like a fuel cell assembly. The H_2S is removed from a process gas, as coal gasification product, with a small hydrogen enrichment of the gas. The sulphur is removed at the anode as a vapour and condensed elsewhere.

An economic analysis based on Lim's feasibility experiment [1] was extremely encouraging,

however, many questions were left unanswered. Because this experiment was performed with porous electrodes and paste electrolyte (hot pressed matrix plus electrolyte powders), no fundamental parameters could be determined. Further, the effect of other gaseous components was not fully explored. A thermodynamic study [1] showed that CO_2 and H_2O may cause partial carbonation of the sulphide electrolyte:

$$CO_2 + H_2O + S^{2-} = CO_3^{2-} + H_2S \quad (4)$$
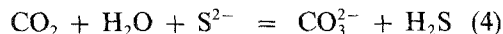
However, no other changes in the electrolyte except for polysulphide composition changes, would be possible.

A more basic study was carried out by White and Winnick [2] in free electrolyte (Fig. 2) using a three-electrode system with smooth graphite working and counter electrodes sheathed in alumina tubes. The reference was a silver–silver sulphate electrode in a eutectic alkali sulphate melt housed in a mullite tube. The main objectives here were to determine the kinetic currents and reaction orders in H_2S. This information is necessary to assure design for current densities limited only by gas-phase diffusion and operation to p.p.m. levels of H_2S. White's results did indeed show very high exchange currents ($\sim 40\,\text{mA cm}^{-2}$) on smooth graphite electrodes, confirming the design basis. Reaction orders in both cathodic and anodic directions were low, less than 0.5, permitting high kinetic rates at low H_2S levels.

The reaction pathways however, were not

* *Present address*: Monsanto Co., St. Louis, MO, USA.

$$H_2S + 2e \longrightarrow S^{2-} + H_2$$

N$_2$, CO$_2$, CO
H$_2$O, H$_2$

N$_2$, CO$_2$, CO
H$_2$O, H$_2$, H$_2$S,
COS

Porous Cathode

Electrolyte + Matrix

Porous Anode

H$_2$ or N$_2$

H$_2$S (with H$_2$)
S$_2$ (with N$_2$)

$$S^{2-} \longrightarrow \tfrac{1}{2}S_2 + 2e \quad (\text{with N}_2)$$
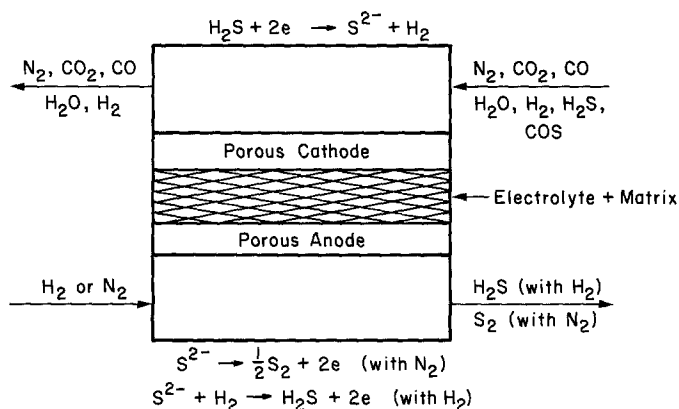$$S^{2-} + H_2 \longrightarrow H_2S + 2e \quad (\text{with H}_2)$$

Fig. 1. Electrochemical desulphurization cell.

determined, nor was the carbonation reaction explored. For these reasons the study was extended in these directions.

2. High-temperature sulphur electrochemistry

Although no prior work in these electrolytes at temperatures above 600° C has been reported, some studies performed in the 300 to 400° C range are relevant. Interest in the sodium–sulphur battery has stimulated a significant effort in the electrochemistry of polysulphide

melts at these temperatures as reviewed recently by Tischer [3].

The earliest relevant report is by Selis [4]. In sulphide–polysulphide melts at 350° C, graphite was found to be a stable, effective electrode material. Oxidation appeared to take place via:

$$2S^{2-} \longrightarrow S_2^{2-} + 2e \qquad (5)$$
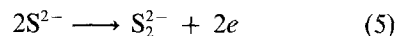
in the sulphide-rich phase. The kinetics were fast, and the rate diffusion-controlled, as determined by the linear response of peak voltammetry currents to the square-root of scan rate
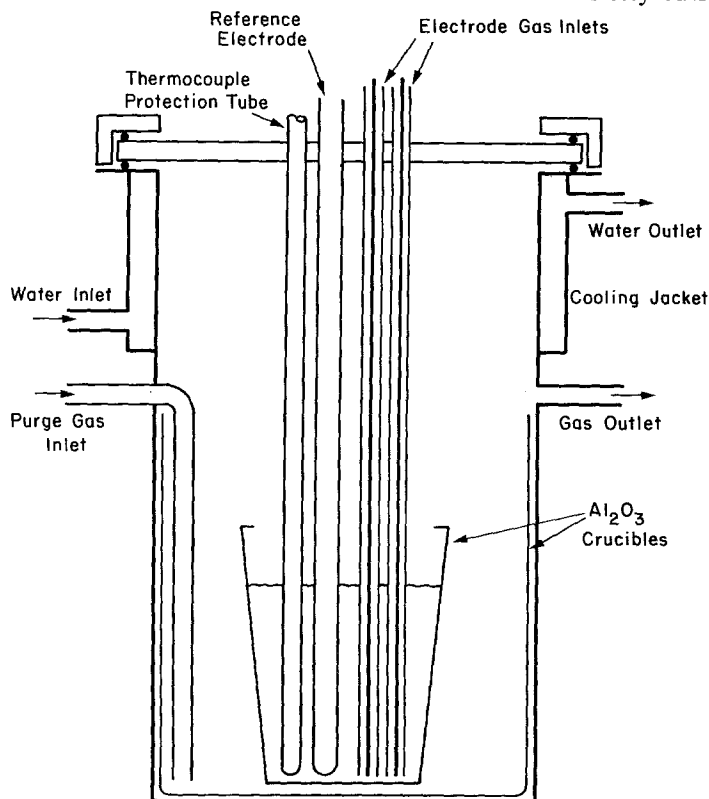

Fig. 2. Reaction furnace.

(v). These currents were also linear with the sulphide content of the phase as expected for diffusion control. The cathodic currents were high, but although the linearity with $v^{1/2}$ was again seen, no dependence on composition was observed.

South et al., in a later paper [5], discerned a 'catalytic' reduction path, due to the upturn in the current function, $i_p/v^{1/2}$, at low scan rates:

$$O + e = R$$

$$R + Z \longrightarrow O \qquad (6)$$
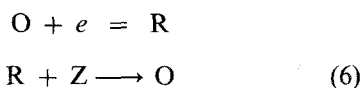
where i_p is peak current, O is the oxidized species, R is the reduced species and Z is a species in solution. South also found no effect on cathodic currents of melt composition. Selis [4] concluded that the reduction wave observed is due to polysulphide:

$$S_2^{2-} + 2e = 2S^{2-} \qquad (7)$$
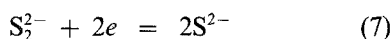
Ludwig [6] also concluded that a catalytic mechanism is responsible for the high cathodic currents in polysulphides. His cyclic voltammograms showed distinct features: limiting currents without a clear peak at low scan rates, a lack of hysteresis, and a normal peak at high scan rates. A two-step charge-transfer, with two, reversible, single-electron transfers superimposed, is suggested. Ludwig also found a catalytic mechanism for the oxidation; the current function, $i_p/v^{1/2}$, falls as scan rate rises.

Sulphide oxidation has been examined in some high-temperature supporting electrolytes on graphite electrodes [7, 8]. Here again S_2^{2-} is involved in the electrochemistry. At 1023 K, in fluoride, the reaction appears diffusion-controlled. However, at 1323 K, in cryolite, there is a mix of diffusion with charge-transfer resistance.

It thus seemed possible that similar reactions were occurring in the sulphide melt near 1000 K. The concentrations of polysulphide will be smaller than those in the 300 to 400° C melts. Thus, the current densities would be lower, but the basic features would be the same.

3. Experimental details

The apparatus of White and Winnick [2] was modified to provide for simultaneous gas analysis and galvanostatic operation. The modification consisted of sheathing the electrode tubes in Fig. 2 with larger diameter alumina tubes which capture the gases after passage over the wetted electrodes.

Two Hewlett-Packard 5840A gas chromatographs (GC) were used to analyse the composition of the various gas streams. The GC is a digital processor-based instrument operated from a terminal. The terminal was connected to the main-frame module which housed the injection port, column oven, detectors, gas-flow systems and the electronics. One GC was fitted with a thermal conductivity detector (TCD) to analyse for CO_2 composition, while the other was equipped with a flame photometric detector (FPD) to examine for sulphur levels.

A 60 mol % K_2S and 40 mol % Na_2S mixture was used as electrolyte by White [2]. Sufficient quantities of the alkali sulphide constituents had to be initially purified since the most pure source of K_2S commercially available is only 44% pure (Alfa Chemical) (the remainder is polysulphide) while commercially available Na_2S is 99% pure (Alfa Chemical). The method of purification involved heating each alkali sulphide separately up to 1260 K in a 75 ml porcelain crucible in a hydrogen atmosphere. The hydrates and excess polysulphides were reduced as these conditions were maintained for at least 24 h.

Once a sufficient quantity of the alkali sulphides had been purified, weighed amounts of K_2S and Na_2S were placed in a 250 ml Al_2O_3 crucible. This resulting mixture was heated beyond its melting point and left at an elevated temperature for some time to assure a homogeneous mixture. After cooling, the mixture was crushed into small chunks with a clean hammer and loaded into a Bluer Mill to grind the electrolyte into a fine powder. The whole assembly was lowered into the furnace and the furnace was sealed. After the proper gas connections were made, the furnace was purged with hydrogen and the furnace was slowly heated.

During the heating process, the melting point of the electrolyte was observed visually and with an a.c. bridge. After the melting point was noted, the cell was heated to an operating temperature of 1000 K. This is 100 K lower than that

used by White [2]. Gas flow to the electrodes was checked visually by observing the reaction crucible for bubbling. If vigorous bubbling was not evident, the furnace was cooled to room temperature and more electrolyte was added. In general, a sufficient quantity of electrolyte was added by the second or third attempt to ensure proper cell performance. After the particular gas flow to the electrodes had stabilized and the system had reached thermal equilibrium, the cell resistance, R_s was measured. To estimate double-layer capacitance C_{dl}, a current step I_{APP}, was applied to the cell using the galvanostat and the voltage response was recorded as an oscilloscope trace. The value of the double-layer capacitance was estimated from the slope of the voltage response in the first $50\,\mu s$:

$$C_{dl} = \frac{I_{APP}}{(\mathrm{d}E/\mathrm{d}t)_{t=0}} \qquad (8)$$

As an aid to determining the slope, a Polaroid picture of the oscilloscope trace was taken using an Oscilloscope Camera (Tektronix C-5C).

The experiments were divided into two main parts: those conducted in a sulphide melt equilibrated with gases containing no CO_2 or water vapour, and those in a sulphide melt equilibrated (and partially carbonated) with a gas containing CO_2 and water vapour at coal-gas levels. Each main part consisted of cyclic voltammetry followed by galvanostatic operation with effluent gas analysis.

The cyclic voltammetry experiments were run with the following gases:

A. 1.5% H_2S, 50% H_2, balance N_2.
B. 0.3% H_2S, 50% H_2, balance N_2.
C. 0.65% H_2S, 20% H_2, 5.8% CO_2, 25% CO, balance N_2.

Sweeprates of 250, 500, 750, 1000, 1250, 1500, 1750 and $2000\,\mathrm{mV\,s^{-1}}$ were used for each of the gases. Once it was certain that the electrolyte was saturated with the particular process gas, typically overnight, the gas to the electrode was shut off and the excess pressure between the gas lines and the electrolyte (due to a pressure drop associated with gas bubbling through the electrolyte) was released. A cyclic voltammogram was then run at the given sweeprate. After the sweep, the gas was again bubbled at the elec-

trode. The system was allowed to return to equilibrium (approximately 30 min) before the next sweeprate was run. When all the sweeps had been run with the particular gas of the day, the function generator was reconnected to the potentiostat so that it would sweep in the positive direction first before sweeping negatively. The above procedure was also used for this set of runs.

All galvanostatic experiments were run with gas bubbling past the working electrode with no gas flow at the counter electrode. Both the inlet and outlet streams of the working electrode were sampled daily at open circuit with a $50\,\mu l$ syringe. The working/counter (W/C), working/reference (W/R) and counter/reference (C/R) open circuit voltages were daily and continuously recorded to observe the equilibrium potential of the cell.

Currents of ± 10, ± 25, ± 50 and $\pm 100\,\mathrm{mA}$ were applied to the cell. The inlet and outlet streams of the working electrode were sampled on the FPD. After sufficient data had been collected with the diluted H_2S gas, a new process gas was introduced to the working electrode which contained 0.65% H_2S, 8% CO_2, 25% CO, 20% H_2 and a balance of N_2. (The water-gas shift reaction will produce water, see Appendix.) This new gas was bubbled through the electrolyte for several days to assure carbonate–sulphide equilibrium. During the transient period the inlet and outlet gases were sampled hourly for CO_2 and H_2S content.

After equilibrium was attained, cyclic voltammetry and galvanostatic removal experiments were performed.

4. Results

Table 1 reports values of the open-circuit voltages for the four different gases reported in this work. Each gas containing H_2S was run for approximately a week; the reported values are an average of the voltages observed during that time period. The temperature is 1000 K; the results are similar to those at 1100 K [2].

Values of the cell resistance, R_s, were constant for different applied currents during a particular day. The average value of R_s was $1.0\,\Omega$. Determination of the double-layer capacitances C_{dl},

Table 1. Open-circuit voltages

Gas	H_2 (%)	H_2S (%)	CO_2 (%)*	W/C (mV)	W/R (V)
1	100	0	0	− 10.8	− 1.898
2	50	0.26	0	− 17.0	− 1.911
3	50	0.42	0	+ 25.0	− 1.830
4	20	0.47	5.8	+ 68.8	− 1.928

*Corrected for water-gas shift reaction, (see Appendix).

was dependent upon finding the slope of a tangent to a curve and was therefore subject to lack of precision. It averaged somewhat higher than the values found by Armstrong *et al.* [9] in Na_2S_3 ($\sim 30\,mF\,cm^{-2}$) at 350°C by a more accurate a.c. impedance technique.

Fig. 3 shows cyclic voltammograms at 250 and $2000\,mV\,s^{-1}$ sweeprates, using Gas A. Use of Gas B caused no significant change. The characteristics of the plots are very similar to those obtained in the polysulphide melts and solutions [3–5].

The effect of galvanostatic operation on gas H_2S content with currents up to 100 mA (cathodic) is shown in Table 2. It can be seen that the H_2S removal, with Gases 2 and 3, reaches a limiting value at relatively low currents. This limit is nearly proportional to inlet gas H_2S content and is linked to diffusional mass-transfer limitations [10].

Some H_2S removal from the gas, ~ 5 to 10%, was always observed at open-circuit. This effect was greater immediately after a galvanostatic experiment. Its cause is discussed later.
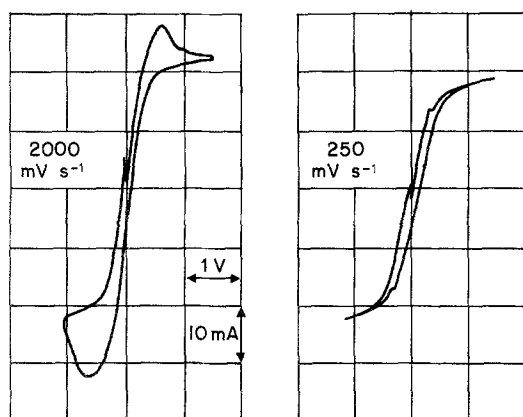
The fractional carbonation of the melt was calculated by monitoring the inlet and effluent H_2S during the equilibration with gas No. 4, a period of 49 h, through use of Equation 4. The conversion to carbonate was calculated to be 4.1 mol %. A chemical analysis of the frozen melt (Atlantic Microlab) indicated 3.3 mol % carbonate. A conversion of 4% implies an equilibrium constant (k_{eq}) for Reaction 4 of 0.11, in good agreement with available thermodynamic data [11], $K_{eq} = 0.12$, with the assumption of ideal liquid mixing.

Cyclic voltammograms obtained after saturation, and partial carbonation of the melt, with Gas C are shown as Fig. 4. While the peak currents are similar to those in Fig. 3, they are displaced considerably away from the equilibrium voltage.

The H_2S removal in the carbonated melt was most surprising. The last row in Table 2 shows a removal rate more than three times greater than with Gas No. 3. This large removal of H_2S, a reduction by more than half of the inlet concentration, was immediate on application of current and disappeared immediately on its interruption. This experiment was replicated several times with no significant change in results. Application of current caused no noticeable change in the CO_2 content of the effluent from the working electrode.

Table 2. Effect of applied current on H_2S removal

Gas	I (mA)	H_2S removal rate,* $(g\,mol\,s^{-1} \times 10^8)$	Current efficiency (%)
2	50	1.1	4.4
2	100	1.2	2.4
3	10	2.3	44.0
3	25	2.6	20.0
3	100	4.0	7.7
4	100	13.0	25.0

Fig. 3. Cyclic voltammograms: Gas A.
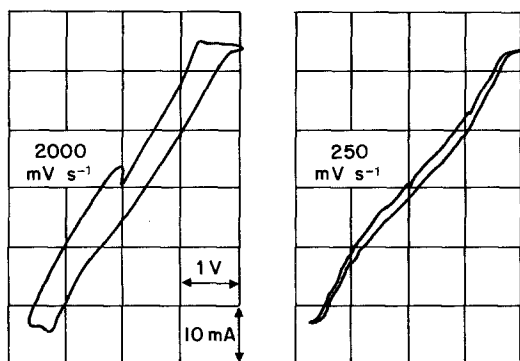
*In excess of that at open-circuit.

Fig. 4. Cyclic voltammograms: Gas C.

5. Discussion

The cyclic voltammetry results in the sulphide melt, Fig. 3, are strongly suggestive of a 'catalytic' reaction, Case VII of Nicholson and Shain [12], Reactions 6. The indicators are: (1) anodic and cathodic sweeps are symmetric, with $i_a/i_c \cong$ 1.0 for all scan rates, (2) a plot of peak current, i_p, versus $v^{1/2}$, Fig. 5, and (3) a plot of $i_p/v^{1/2}$ versus $\log v$, Fig. 6, are distinctive of this sequence [12]. This is in agreement with the conclusions of South et al. [5] and Ludwig [6] in polysulphide melts. South et al. [4] and Selis [5] saw no change in peak current with polysulphide content, an effect analogous to the lack of H_2S effect here.
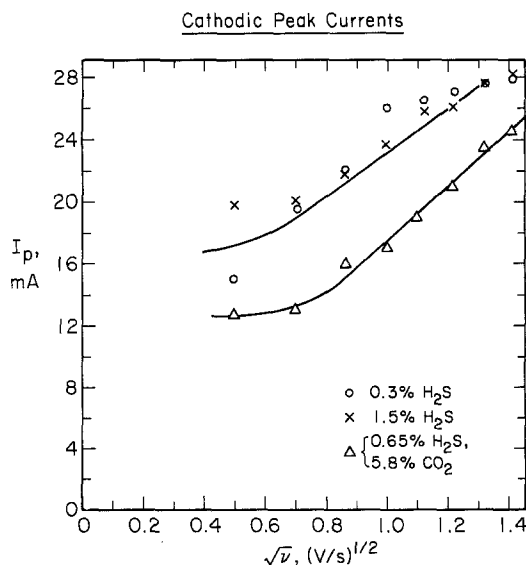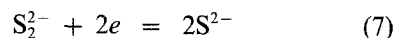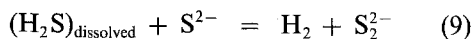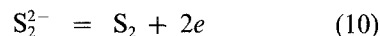
Cathodic Peak Currents

Fig. 5. Peak current dependency on scan rate.

The nearly equal currents indicate the same electrochemically active species:

$$S_2^{2-} + 2e = 2S^{2-} \qquad (7)$$

cathodic:

$$(H_2S)_{dissolved} + S^{2-} = H_2 + S_2^{2-} \qquad (9)$$

and

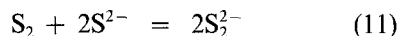$$S_2^{2-} = S_2 + 2e \qquad (10)$$

anodic:

$$S_2 + 2S^{2-} = 2S_2^{2-} \qquad (11)$$

The role of polysulphide as active species has other semi-quantitative supporting evidence. The peak current dependence on scan rate [13];

$$i_p = 0.4463nFAC_0^* \left(\frac{nF}{RT}\right)^{1/2} v^{1/2}D_0^{1/2} \qquad (12)$$

where D_0 is diffusivity and A is area; exhibits a slope corresponding to a concentration C_0^* of the order $10^{-5} \, mol \, cm^{-3}$ if the diffusion coefficient is of the order $10^{-5} \, cm^2 \, s^{-1}$ [7]. The concentration of S_2^{2-} at equilibrium can only be estimated from Equation 9, since the standard free energies of our Na/K sulphide and polysulphide are not available. Using the values for the Na_2S and Na_2S_2 reported in Barin and Knacke [11], the S_2^{2-} concentration is predicted to be of the order $10^{-5} \, mol \, cm^{-3}$ in rough agreement with that from the peak currents. Finally, the exchange currents measured by White and Winnick [2] are about two orders lower than those found in polysulphide melts at $350°C$ [6], where polysulphide concentrations would be two to three orders higher than in our sulphide melt [14].

The H_2S removal at open-circuit, which was greatest following extended current application, is likely due to its reaction, via Equation 9, with the excess sulphide generated electrochemically, Reaction 7. This delayed effect is caused by the relatively poor mass-transfer; a porous-electrode cell does not exhibit this behaviour [1].

The effect of partial melt carbonation is evident in the voltammogram, Fig. 4, and in the enhanced removal of H_2S, Table 2. A 'catalytic' mechanism is still indicated by the shapes of the voltammogram and the current function, Fig. 6. The cathodic wave is displaced in the cathodic direction, as compared with the carbonate-free
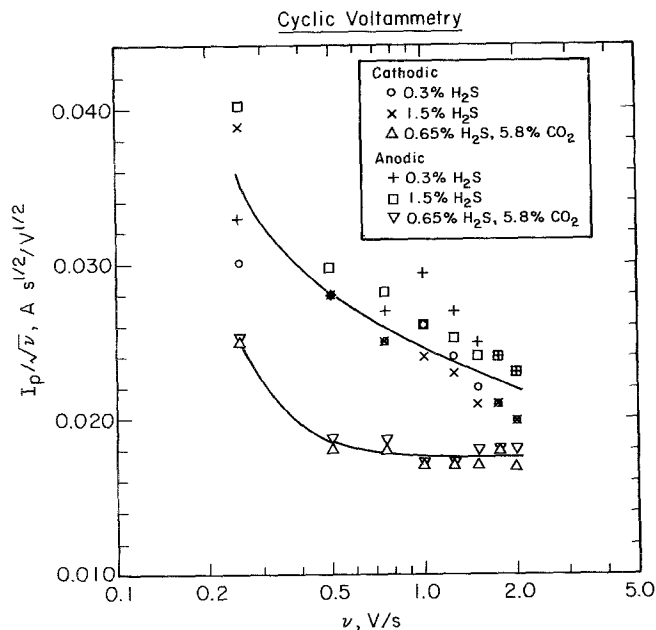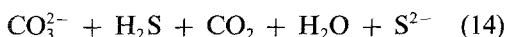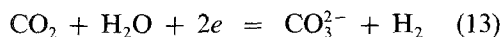
Fig. 6. Current function dependency on scan rate.

melt, Fig. 3, and a limiting current is reached. This is consistent with a sharply increased rate of the chemical reaction step [15]. It may be that a somewhat different 'catalytic' reaction scheme occurs with CO_2, H_2O and carbonate present.

$$CO_2 + H_2O + 2e = CO_3^{2-} + H_2 \quad (13)$$

$$CO_3^{2-} + H_2S + CO_2 + H_2O + S^{2-} \quad (14)$$

while Reactions 7 and 9 are also occurring to some extent. The limiting current behaviour, independent of scan rate, seen in the voltammograms is characteristic of a rapid chemical step. This may explain the sharply increased rate of H_2S removal in the carbonated melt.

The anodic reactions occurring in a practical device, schematically as Fig. 1, would remain as Equations 10 and 11, since no hydrogen would be used as depolarizer. In this situation, the oxidation of carbonate requires more than one volt higher potential than does sulphide, as determined from thermodynamic data [11].

6. Conclusion

A 'catalytic' mechanism has been proposed for the reactions of H_2S in a sulphide melt at 1000 K. It appears that polysulphide is the active agent, as seen at lower temperatures. The rate of

hydrogen reaction is strikingly increased in the presence of CO_2 and H_2O. While the sequence is not clear in this more complex situation, the enhanced rate of electrochemical H_2S removal from realistic coal-gas compositions is highly encouraging as regards the commercial application of the technique.

Acknowledgements

Appendix

The process gas used to indicate the consequences of bubbling CO_2 into the cell had a composition of 0.65% H_2S, 8% CO_2, 25% CO, 20% H_2 and a balance of N_2 at room temperature. The actual composition varies at the operating temperature of 1000 K because of the water-gas shift equilibrium:

$$H_2 + CO_2 = H_2O + CO \quad (A1)$$
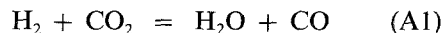
The kinetics of this reaction are assumed to be rapid at the cell operating temperature. Table A

Table A. Process gas composition at 1000 K

Component	Theoretical (%)	Experimental (%)
CO_2	5.7	5.8
CO	27.3	27.2
H_2	17.7	17.8
H_2O	2.3	2.2
H_2S	0.65	0.65
N_2	Balance	Balance

compares the theoretical process gas composition calculated at 1000 K versus the composition of the gas determined by a TCD analysis of the gas after being heated to 1000 K in a Thermolyne Furnace.

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