JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 23–26

Coproduction of sulphuric acid and hydrogen by sulphur-assisted water electrolysis process

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Received 17 March 1982

The addition of sulphur powder to the anode compartment of the sulphuric acid–water electrolysis cell resulted in the suppression of oxygen evolution rate; at a cell voltage of 2 V, there was an acceleration of the hydrogen production rate, and the anode reaction led to the production of sulphate ion (SO_4^{2-}) by the oxidation of the sulphur powder. The net equation for this sulphur-assisted water electrolysis system may be written as

$$S + 4\,H_2O \rightarrow H_2SO_4 + 3\,H_2$$

whose stoichiometry was proved experimentally using phosphoric acid as the electrolyte. The whole process can be rationalized if the anodic oxidation of sulphur occurs at a lower potential than oxygen evolution and hence the energy consumption is lower. Thus the addition of sulphur to the anolyte helps to improve the energy efficiency of the acidic water electrolysis system and generates, simultaneously, sulphuric acid and hydrogen.

1. Introduction

Both sulphuric acid (H_2SO_4) and hydrogen (H_2) are important chemicals. Sulphuric acid is mainly produced by two-stage air oxidation of sulphur to sulphur trioxide (SO_3) which is then absorbed in dilute sulphuric acid to yield concentrated sulphuric acid. The first stage of air oxidation is highly exothermic ($\Delta H^0 = -296.6$ kJ mole^{-1}) and the heat released is generally used to generate steam in the sulphur burning chamber with a thermal efficiency less than 30%. The net equation for the industrial contact process is expressed as Equation 1.

$$S + 3/2O_2 + H_2O \xrightarrow{\text{thermal}} H_2SO_4 + \Delta H \quad (1)$$

On the other hand, hydrogen is mainly manufactured by a natural gas steam reforming process. However, water electrolysis is still widely used to yield high purity product. This electrochemical water splitting system can be written as Equation 2,

$$H_2O + \Delta E \xrightarrow{\text{electrolysis}} H_2 + 1/2\,O_2 \quad (2)$$

where the applied voltage ΔE is usually about 2 V which is greater than the 1.23 V theoretical decomposition potential of water. The Gibbs free energy of water decomposition is estimated to be + 237.2 kJ mole^{-1} by $\Delta G^0 = -nFE$. Therefore, it is interesting to know whether it would be feasible to perform the water splitting process at lower potential when the anodic oxidation of sulphur is the anode reaction. It is also expected that the transfer of part of the exothermic sulphur oxidation energy to the energy demanding water electrolysis system may occur.

2. Coproduction concept

The addition of Equations 1 and 2 gives Equation 3,

$$S + 4\,H_2O + (3\Delta E - \Delta H) \xrightarrow{\text{electrolysis}} H_2SO_4 + 3\,H_2 \quad (3)$$

The calculated Gibbs free energy for Equation 3 is + 206.7 kJ mole^{-1} which is lower than the free energy for conventional water electrolysis. In other words, sulphur might be oxidized electro-

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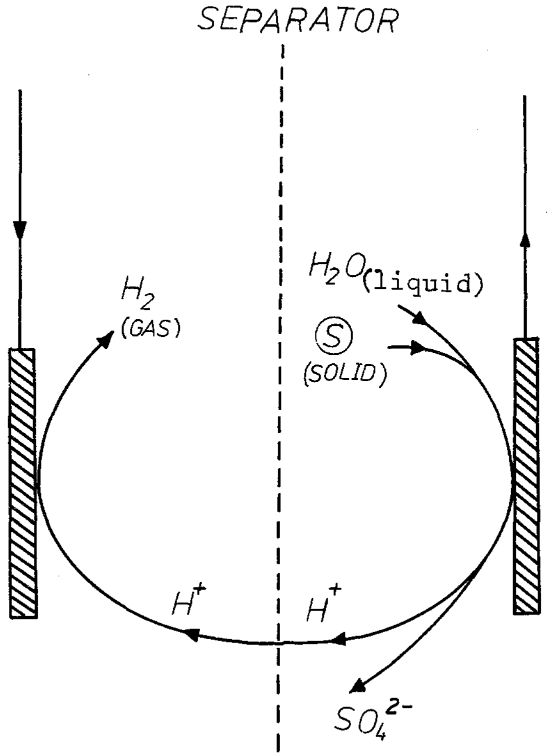

Fig. 1. Illustration of the coproduction of sulphuric acid and hydrogen by a sulphur-assisted water electrolysis process.

chemically in water so that the cell produces, simultaneously, sulphuric acid and hydrogen.

Since the standard potential of anodic oxidation of sulphur is 0.45 V [1] and that for the oxidation of H_2SO_3 to H_2SO_4 is 0.2 V, it is appropriate to write

$$S + 4\,H_2O \rightarrow H_2SO_4 + 6H^+ + 6\,e^- \qquad (4)$$

which is much lower than the water oxidation potential of 1.23 V.

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (5)$$

This fact implies that if the anode compartment of the conventional water electrolysis system is filled with sulphur powder, the electrooxidation of sulphur powder may take place instead of oxygen evolution. Meanwhile, the cathode keeps producing hydrogen ($H^+ + e^- \rightarrow 1/2\,H_2$). Since the oxidation product SO_2 is highly soluble in water forming sulphurous acid (H_2SO_3) which should be further oxidized to produce the desired sulphuric acid [2].

$$H_2SO_3 + H_2O \rightarrow H_2SO_4 + 2\,H^+ + 2\,e^-$$
$$E = -0.171\ \mathrm{V} \qquad (6)$$

The whole concept may be represented by Fig. 1 which illustrates the coproduction of sulphuric acid and hydrogen from the sulphur-assisted water electrolysis process.

3. Experimental procedure

Experimentally, an electrolytic slurry reactor was designed to test the proposed concept. The reactor system is composed of two 350 cm^3 three-necked chambers separated by a fine glass fritt as shown in Fig. 2. Tacussel potentiostat PRT 10-0, 5 and recorders TILOG-101 and TV 11 GD were used to monitor the electrolysis current and voltage respectively. The electrolyte was sulphuric acid and the electrodes were Pt gauze in both compartments. In a typical reaction, 5 g/350 cm^3 of sulphur powder was added to the anode compartment containing 4.13 mol dm^{-3} H_2SO_4 and the applied potential was 2 V to ensure significant reaction rate.

Table 1. Data for the various water electrolysis processes. 60° C, 2 V

	Electrolyte V (%)	*S* (g cm^{-3})	H_2 (m^3 kwh^{-1})	O_2 (m^3 kwh^{-1})	*$BaSO_4$ ppt.* (mole kwh^{-1})	H_2/SO_4^{2-} (mole $mole^{-1}$)
1	H_2SO_4 20	–	0.14	0.07	–	–
2	H_2SO_4 20	14	0.25	0	(3.4)*	3.0
3	H_3PO_4 50	20	0.007	not recorded	0.102	2.8 (≈ 3.0)

* estimated

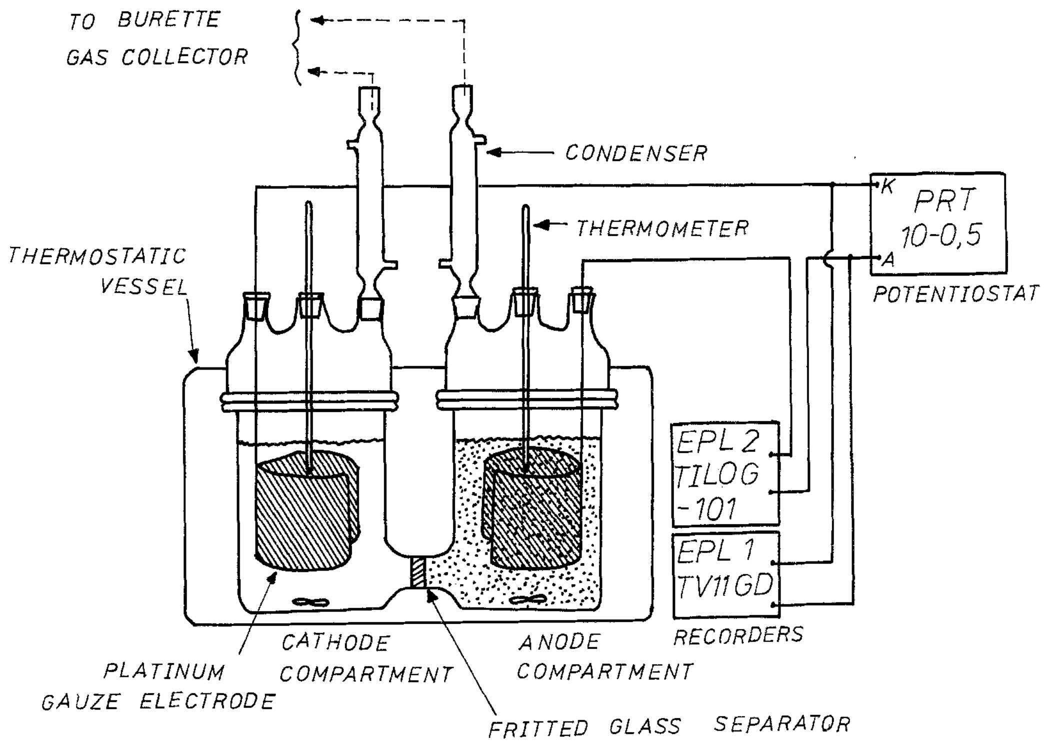

Fig. 2. Diagram of the electrolytic reactor and related equipment. Reactor volume, 700 cm³ (350 cm³ each). Electrodes 33.8 mm × 49.2 mm ($1\frac{3}{8}$ in × 2 in), 52 mesh Pt gauge.

4. Results

4.1. *Coproduction test*

The experimental results at 25–80° C indicate that oxygen gas was not formed at the anode but the hydrogen gas production rate increased as shown in Fig. 3 and Table 1 which also gives comparative data for different electrolysis conditions.

Nevertheless, the concentration of sulphuric acid in this system is too high to allow the detection of its incremental increase from the sulphur oxidation products. Sulphuric acid production was proved to occur by employing phosphoric acid as the electrolyte although the efficiency of the cell is then relatively poor. After a period of operation, the sulphur powder was filtered from the phosphoric acid solution which was subsequently analysed for sulphate by precipitation with barium nitrate to give barium sulphate. The data in Table 1 indicate that the mole ratio of hydrogen and sulphate ion (SO_4^{2-}) as estimated by this method was about 3 : 1 which satisfies Equation 3. This result is further evidence to support the coproduction concept.

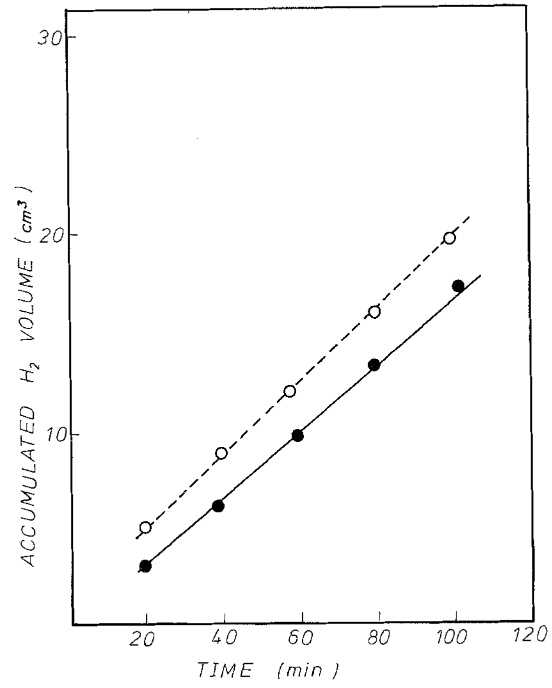

Fig. 3. Hydrogen production rate during acidic water electrolysis. Applied potential, 2 V; temperature 60° C. ——, 4.13 mol dm^{-3} H_2SO_4; ----- 4.13 mol dm^{-3} H_2SO_4 + 5g/350 cm³ S.

4.2. *Energy conversion and efficiency*

The energy efficiency of the sulphur-assisted water electrolysis system (at 60° C), defined as η (m^3 H_2 kwh^{-1}), was calculated to be 0.25 which is greater than for the conventional acidic water electrolysis system value of 0.14. This phenomenon proves that the proposed thermal-electrochemical energy conversion concept ($3\Delta E - \Delta H$) may indeed be working.

5. Conclusion

The engineering design of the proposed concept may be challenging. The whole system may be operated as a flow system by allowing the circulation of sulphur/sulphuric acid slurries which may be continuously pumped through the cell while the hydrogen gas evolves from the other chamber. The operation condition can be set at 60–70° C with 2 V applied potential to give 0.50 m^3 H_2 kwh^{-1} dm^{-2} and 6.86 mole khw^{-1} of sulphuric acid.

References

[1] H. Binder, A. Kohling and G. Sandstede, *Ang. Chem. Int. Ed.* 6 (1967) 884.

[2] C. S. Chang and G. T. Rochelle, *AIChE J.* 27 (1981) 292.