



Towards an electrochemical process for recovering sulphur dioxide

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Abstract

Research is reported on the development of a process to electrochemically oxidise sulphur dioxide gas, absorbed into sulphuric acid solutions. This process is aimed at the recovery of potentially valuable sulphur species, from waste and effluent gases, as sulphuric acid. A small pilot scale sieve-plate electrochemical reactor (SPER) is used for the oxidation of SO₂. The SPER is an undivided cell using, in this case, monopolar connected electrodes. The anode material was platinised titanium or lead dioxide and the cathode material was zirconium metal or Ebonex[®], both materials do not form sulphur in the electrolysis of SO₂ in solutions of sulphuric acid. Typical current efficiencies are above 80% at current densities of 10–20 mA cm⁻². Energy consumptions are between 1.8 and 2.4 kWh kg⁻¹. Production of sulphuric acid at concentrations of 6 mol dm⁻³ by anodic oxidation of SO₂ is demonstrated. The mass-transfer behaviour of the sieve-plate reactor is particularly good for this reaction involving relatively low concentrations of dissolved SO₂ concentration. The behaviour of the sieve-plate reactor is mathematically modelled. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Sulphur dioxide; Oxidation recycling; Electrochemical; Electrocatalytic; Reactor design; Model; Plate

1. Introduction

The development of the processes for the removal of sulphur dioxide from flue and waste gases has been stimulated by the increasing importance of sulphur dioxide pollution control. There has been significant interest in the use of electrochemical processes which do not require the continuous use of chemical reagents [1]. Sulphur dioxide can be oxidised electrochemically to species such as sulphate and dithionite and can be reduced electrochemically to sulphur. The electrochemical oxidation of SO₂ has been investigated both as a pollution control method and as part of hybrid processes for hydrogen produced by water electrolysis at low cell voltages [2]. The oxidation of SO₂ using noble metal electrocatalysts was realised in the Westinghouse process for hydrogen production [2,3]. Indirect processes based on the bromide–bromine and iodine–iodide redox couples have also been developed [4,5].

The main products of electrochemical oxidation and reduction of SO₂ in acid solution are sulphuric acid and sulphur, respectively. The formation of sulphur can represent a significant solids handling problem and can lead to problems in cell operation. In many applications, for example, in the chemical process industries, sulphuric acid is a

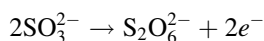
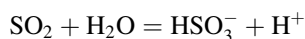
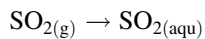
favourable product as it can be used in house in chemical manufacture and is readily transported.

The present work is concerned with the direct anodic oxidation of SO₂ to produce sulphuric acid. The overall reaction for the oxidation of SO₂ can be written as

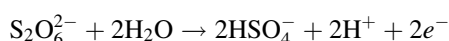
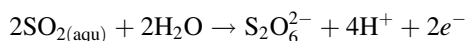


where hydrogen is formed at the cathode.

The mechanism of SO₂ oxidation in aqueous sulphate solutions is complex and depends significantly on anode material and the solution pH [6]. The absorption of sulphur dioxide into aqueous solution is followed by several possible equilibrium processes.



In acidic solution, the electrochemical oxidation of dissolved sulphur dioxide has been extensively studied on platinum, gold and graphite anodes [7–10]. At pH < 2, the mechanism leading to sulphate formation is suggested.



Other studies [11] have suggested the involvement of indir-

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ect mechanisms involving surface oxide (of Pt and Pb) reaction with an activated SO_3^{2-} species.

Direct oxidation of SO_2 has typically necessitated the use of membrane electrolyzers to avoid the formation of elemental sulphur at the cathode which deactivates the system. An undivided cell electrolysis, which can operate without cathodic sulphur formation, is potentially an attractive alternative to a divided cell electrolysis in terms of lower cell cost and energy consumption and lower reactor installation cost. A further potential reduction in installation cost may result from performing the absorption of SO_2 and its electrochemical oxidation in one unit.

An electrochemical system which performs the absorption and oxidation in one is the sieve-plate electrochemical reactor (SPER) [12]. The SPER consists of a bank of undivided cells situated above a sieve plate located in an absorption column. The SPER is a unit in which simultaneous electrolysis and gas absorption occurs (see Fig. 1). The absorption of SO_2 , occurs in the gas sparged region, above the sieve plate, in the inter-electrode spaces formed between the cell electrode assemblies. Electrolyte flows through the cells, above the sieve plate, located between a pair of weirs to maintain an appropriate liquid electrolyte level. The SPER has been previously used in the epoxidation of alkenes [12] where the excellent interfacial mass-transfer characteristics have proven beneficial in the oxidation of these gases which have low solubility in the aqueous electrolyte used. The oxidation of sulphite ions in a sieve-plate cell using nitrogen for gas sparging to simulate sieve-plate operation, has been reported previously [13].

This paper reports data on the performance of the sieve-plate cell with a gas mixture which contains sulphur dioxide in low concentrations. The performance of the SPER system is mathematically modelled as a continuous recycle stirred tank reactor for the gas phase.

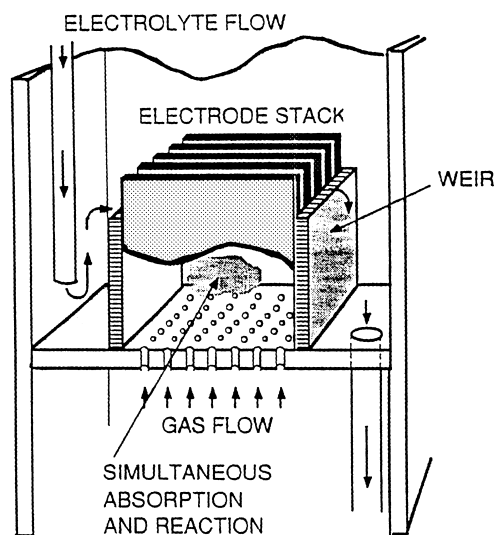


Fig. 1. Schematic representation of the sieve-plate reactor.

2. Experimental

Linear sweep voltammetry was performed in a sealed, magnetically stirred H-type glass cell, 250 cm³ in volume. All electrodes had surface areas of 1 cm². Anode materials were platinised titanium (Magneto-Chemie) and lead dioxide, prepared by anodic oxidation from lead nitrate solution, and cathodes were zirconium metal (Goodfellow Metals) and Ebonex[®] (Atraverda). Ebonex[®] is a conducting ceramic, magneli phase suboxide (predominately Ti_4O_7). Electrical power to the batch cell was supplied by a computer controlled VERSASTAT manufactured by EG&G Princeton App. Research. Electrolyte solutions of sodium sulphite in 0.5 mol dm⁻³ sulphuric acid were freshly prepared prior to each experiment. The sulphite concentration present in the solution was determined iodometrically. Prior to each run, the electrodes were washed with diluted sulphuric acid and then rinsed in doubly distilled water. Anodes were pre-treated anodically at 0.3 V for 5 min in the electrolyte solution prior to commencing each preparative experiment.

The small-scale pilot sieve-plate electrochemical reactor used anodes of platinised titanium (supplied by Magneto-Chemie) and zirconium metal or Ebonex[®] cathodes (Atraverda). The size of each electrode plate was 15 cm high × 5 cm wide. The cells were connected in a monopolar arrangement with cathode and anode plates connected to separate titanium rods which acted as current feeders. The anodes and cathodes were interleaved to form a series of nine monopolar connected cells. The set of cells was located inside an acrylic box (cell holder) which contained two weirs, which maintained the electrolyte at a level such that each electrode plate had an exposed area of 50 cm².

The electrical power to the cells was supplied by a Farnell Instrument stabilised DC power supply. The SPER cells were located inside the main pilot absorption tower constructed of 10 cm internal diameter QVF glass. The column contained a gas sparging ring to feed the gas to the base of the sieve plate and the base of the column was fitted with a 2 cm³ reservoir to hold the electrolyte.

The SPER was located in a gas and electrolyte flow circuit as shown in Fig. 2. Further details of the equipment can be found in Ref. [13]. The gases SO_2 (30% in air) and N_2 were supplied from a cylinder through a sequence of control valves to reduce the input pressure to the SPER to the operational level (≈ 1 bar). SO_2 could be mixed with nitrogen prior to introduction into the SPER. The total flow rate of gas entering the SPER was typically 60 cm³ min⁻¹ (1 bar, 20°C).

The electrolyte used in this work was sulphuric acid (0.5–5) mol dm⁻³ (M), unless otherwise stated. Temperatures of operation were maintained at 20°C. The electrolyte flow rate through the reactor was constant at 67 cm³ s⁻¹ and the gas flow rate was 0.92 cm³ s⁻¹ (1 bar, 20°C) through the sieve plate. The operating pressure of the reactor was nominally 1 bar absolute. These conditions resulted in an electrode area of 50 cm² exposed to electrolysis for each plate. The

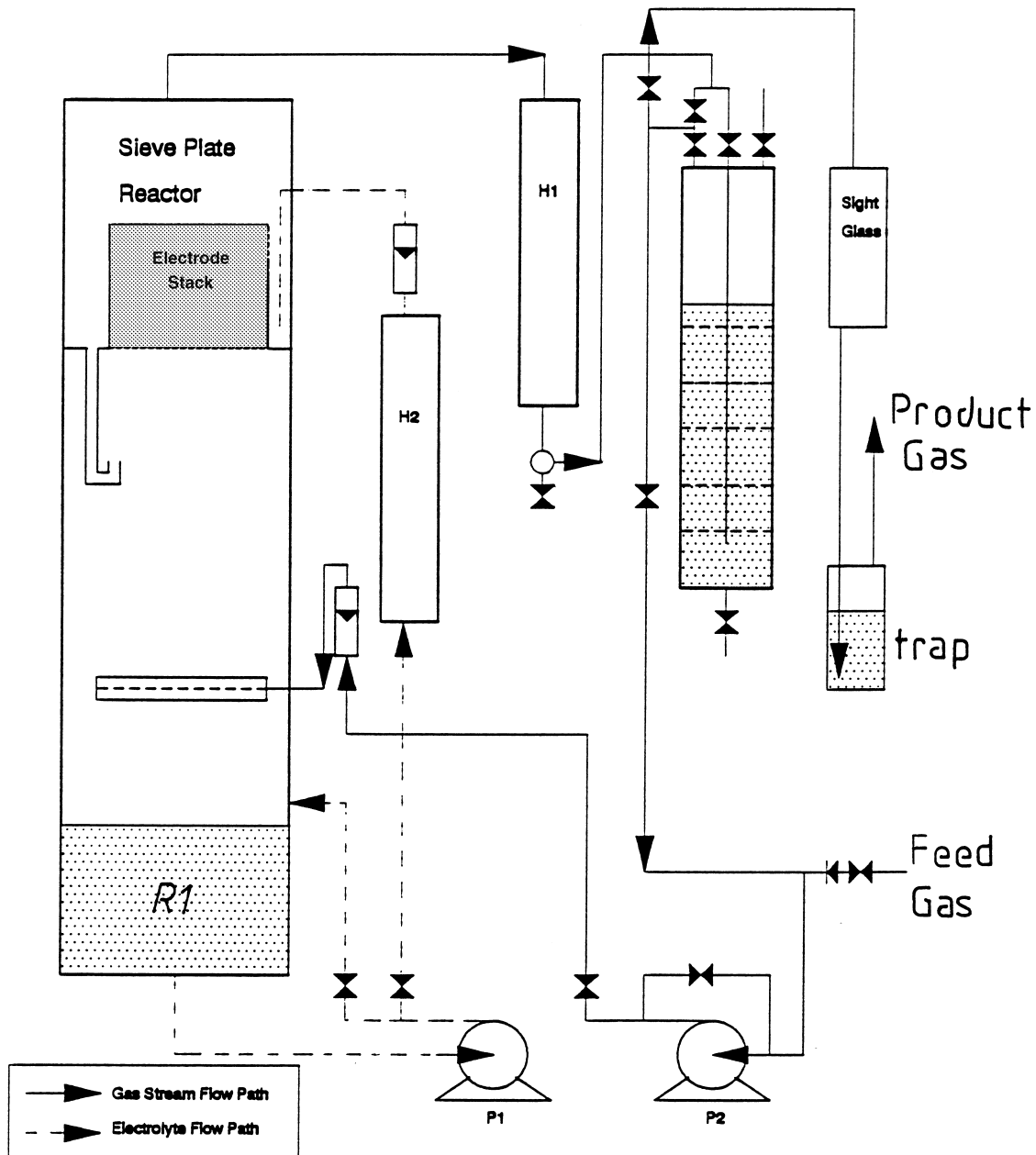


Fig. 2. The experimental equipment for sulphur dioxide oxidation in the sieve-plate reactor.

flow conditions of operation were selected on the basis of previous mass-transfer studies of the SPER to be reported.

The analysis of SO_2 in solution was carried out iodometrically. The experimental study for the oxidation of SO_2 in sulphuric acid using the SO_2 -air mixture diluted with nitrogen gas to a composition of 3.0% by volume feed. The electrolyte was pre-saturated to a concentration of 8.25 mol/m^{-3} prior to electrolysis. Any loss of SO_2 in the exit gas was monitored by absorption in iodine solution. The extent of gas stripping of SO_2 from solution was determined by a series of blank runs (without electrolysis) in which the concentration of SO_2 in solution was continuously monitored. All current efficiency data quoted in

this work is corrected for the loss of SO_2 in the exit gas using the above two procedures.

3. Mathematical model

The mathematical model of the SPER is based on the recycle flow configuration shown in Fig. 3. This is essentially an absorption recycle reactor which accommodates electrochemical reaction and inter-phase and intra-phase mass transport. Electrolyte circulates from a reservoir to the cell stack continuously. The volume of electrolyte in the reservoir is much greater than that in the cell stack and thus,

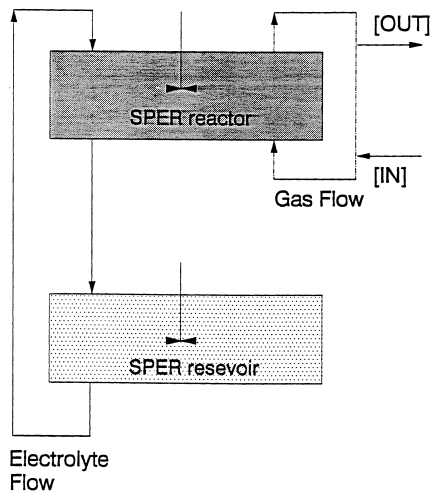


Fig. 3. The model of the sieve-plate gas-liquid operation.

as a quasi-steady-state approximation, the material balance for reactive species in the liquid phase is

$$V_{\text{cell}} \frac{dC}{dt} + k_e A_e C = K_g A [P_0 - mC] \quad (3)$$

where V_{cell} is the total electrolyte volume, m the equilibrium constant of SO_2 in the solution, A_e the electrode area, A the interfacial gas/liquid area, P_0 the bulk partial pressure of SO_2 in the gas phase, m the equilibrium (Henry) constant, C the concentration of SO_2 in the electrolyte and k_e (m s^{-1}) the overall rate constant, which is function of mass transport at the electrode and electrode kinetics.

The overall gas-phase mass-transfer coefficient is given in terms of the individual mass-transfer coefficient by

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{m}{K_c} \quad (4)$$

The mass-transfer coefficient values have been measured by reactive absorption of O_2 into sulphite solutions and by stripping of SO_2 with nitrogen gas sparging. A material balance on the gas phase, which is in recycle around the cell is

$$K_g A [mC - P_0] = \frac{Q}{RT} [P_0 - P_i] + \frac{V_r}{RT} \frac{dP_0}{dt} \quad (5)$$

where V_r is the reactor gas volume, Q the gas flow rate into and out the cell (assumed constant), P_0 and P_i the partial pressures of SO_2 in the reactor exit and inlet, respectively. Absorption of SO_2 gas is approximately equal to the generation of hydrogen gas at the cathode. The inlet and exit partial pressures are related through the gas recycle ratio, r , according to $P_i = (rP_0 + P_g)/(1+r)$ where P_g is the partial pressure of SO_2 in the feed which has a total flow rate, $Q_g = Q(1+r)$.

The solution to Eqs. (3) and (5) can be obtained analytically when k_e remains constant. For example, in the case of a mass-transport controlled oxidation of SO_2 in solution

where $k_e \cong k_L$, the liquid-to-electrode mass-transport coefficient. The value of the reaction rate constant k_e can also include the influence of dissolved oxygen on the oxidation of sulphur dioxide in solution. Prior to electrolysis dissolved oxygen and SO_2 will achieve concentrations as defined by the relative rates of absorption and reaction in solution, as defined by the balances above for a second order reaction between the species [14].

$$\frac{d\text{O}_2}{dt} = -1.4 C_{\text{SO}_3^{2-}} C_{\text{O}_2} \text{ mol dm}^{-3} \text{ s}^{-1} \quad (6)$$

Assuming that during electrolysis the rate of absorption of oxygen is equal to the rate of chemical reaction then the chemical rate is first order in dissolved sulphur dioxide, i.e. equal to $k_e C_{\text{SO}_2}$. Hence, the total 'reaction rate' for SO_2 is $(kA_e + k_e V_{\text{cell}})$.

The solution to the model Eqs. (3) and (5), which combine to give a linear second-order differential equation, is straightforward and is given by

$$C = A_1 e^{m_1 t} + A_2 e^{m_2 t} + \left(\frac{g}{b}\right) \quad (7)$$

$$\frac{m_1}{m_2} = \frac{-1}{2} [(a+d) \pm \sqrt{(a+d)^2 - 4b}]$$

where

$$a = \frac{k_e A_e}{V_{\text{cell}}} + \frac{K_g A m}{V_{\text{cell}}}$$

$$d = \frac{Q}{V_r(r+1)} + \frac{K_g A R T}{V_r}$$

$$b = \frac{k_e A_e d}{V_{\text{cell}}} + m g / P_g$$

$$g = \frac{K_g A Q P_g}{V_r V_{\text{cell}}(1+r)}$$

where P_g is the partial pressure of SO_2 in the feed, and r the gas recycle ratio,

$$A_2 = \frac{K_g A P_g / V_{\text{cell}} - m_1 (C_0 - g/b) - C_0 (K_g A m + k_e A_e) / V_{\text{cell}}}{(m_2 - m_1)}$$

$$A_1 = C_0 - A_2 - \frac{g}{b}$$

C_0 is the initial solution concentration of SO_2 .

P_0 is obtained from Eq. (3) as

$$P_0 = \frac{V_{\text{cell}}}{K_g A} [A_1 e^{m_1 t} (m_1) + A_2 e^{m_2 t} (m_2)] + (k_e A_e / K_g A + m) C \quad (8)$$

At the steady state, the concentration of SO_2 in solution is given by

$$C = \frac{P_g}{m(1.0 + RTDa\{1.0 + T_g K_g a RT\})} \quad (9)$$

where T_g is the residence time of gas in the sieve-plate cells, $K_g a$ the specific gas-phase mass-transfer coefficient and Da

a modified Damkohler number given by

$$Da = \frac{k_e A_e}{K_g A R T}$$

which is the ratio of the liquid-to-electrode mass-transport rate and the gas-to-liquid mass-transport rate.

4. Results and discussion

The objective of this research project was to investigate the performance of a monopolar SPER for gas–liquid reaction systems for the direct electro-oxidation of sulphur dioxide to sulphuric acid in an undivided cell electrolysis. This application is to enable the recovery of SO₂ from industrial and waste gas and its recycling in the form of sulphuric acid.

The sieve-plate reactor combines the function of gas absorption and electrochemical reaction in one unit. The design provides good liquid cross flow and good inter-phase and intra-phase mass transport. These mass-transfer characteristics have been determined and correlated as a function of both gas and liquid flow rates [15].

Prior to this study the SPER had only been operated as a bipolar electrode unit. The monopolar electrode connection offers the following advantages:

1. the application of highly conducting solutions, without loss of efficiency due to current bypass;
2. greater flexibility in electrode materials and in electrode geometry;
3. improvement in gas distribution and mass transport; and
4. improved electrolyte flow distribution.

The extent of current bypass around bipolar electrodes has been demonstrated [12] to be very significant with even dilute electrolyte solution. With more concentrated electrolytes much greater current bypass is expected. Bipolar electrodes impose limitations in material compatibility and coating requirements. Damage to either anode or cathode requires disposal of both. Bipolar electrodes must be made from flat sheet material and cannot, for example, be expanded.

The research study of the SPER required first identification of suitable anode and cathode materials for undivided cell electrolysis. The anode for effective oxidation of SO₂ and the cathode for no (or negligible) reduction of SO₂, i.e. a dominant hydrogen evolution reaction.

4.1. Anode and cathode materials

Preliminary screening of cathode materials was performed using nickel, stainless steel, natural graphite and glassy carbon, zirconium and Ebonex[®]. Linear sweeps voltammetry was performed at 20°C using an electrolyte solution of 0.05 mol dm⁻³ sodium sulphite in 3.0 mol dm⁻³ sulphuric acid. Nickel, stainless steel, graphite and glassy

carbon are active towards the reduction of sulphite ions to sulphur, exhibiting a pre-reduction wave at approximately -0.25 V (vs. SCE) prior to hydrogen evolution. The formation of elemental sulphur was visible for all the four electrode materials.

Linear sweep voltammograms at 100 mV s⁻¹ for zirconium and Ebonex[®] (porous and non-porous) are shown in Fig. 4 for solutions of 0.5 mol dm⁻³ sulphuric acid with 0.05 mol dm⁻³ sodium sulphite. The data for zirconium shows a relatively slow rise of current density with potential. Comparison of the LSVs for zirconium with and without sulphite ions shows a depression of the current density response when sulphite ions are present. This would indicate a blocking of sites for hydrogen evolution by an adsorbed species. The formation of elemental sulphur was not observed with this cathode material. The LSV curves for Ebonex[®], exhibit a depression in current density response in the presence of sulphite ions, as in the case of zirconium. The generation of hydrogen gas becomes significant at potentials of 0.4 V (vs. SCE) which are significantly less cathodic than those for zirconium. As with zirconium, no sulphur formation was observed. Ebonex[®] and zirconium would appear to be suitable cathode materials for undivided cell oxidation of SO₂.

The anodic oxidation of sulphite and dissolved SO₂ has been reported on a range of materials including carbons, lead dioxide and precious metals such as gold, platinum and palladium. For this study, we investigated a commercially available electrode, platinised titanium, with expected stability under anodic oxidation in fairly concentrated sulphuric acid solutions. Other commercial, dimensionally stable coated titanium anodes (DSA) using, e.g. IrO₂, RuO₂ coatings, have been reported [2,3] not to be effective in sulphur dioxide oxidation. Fig. 5 shows a linear sweep voltammogram for the anodic oxidation of SO₂ in 0.5 mol dm⁻³ sulphuric acid, on Pt/Ti, and lead dioxide at 25°C. In the presence of sulphite the current rises rapidly at potentials of 0.3 V (vs. SCE) and greater, while in the absence of sulphite, there is no equivalent oxidation process at these potentials.

The LSV for lead dioxide coated platinum electrode shows a well-defined oxidation peak at 900 mV (vs. SCE) in the presence of sulphite ions, which is due to the oxidation of the species. There is no background oxidation peak with sulphuric acid in the absence of sulphite ions. In view of the above demonstrated suitability of lead dioxide as an anode material, the use of lead dioxide coated titanium were investigated. A series of cyclic voltammograms (sweep rate range 50–500 mV s⁻¹), for lead dioxide coated titanium is shown in Fig. 6 for the oxidation of 0.05 mol dm⁻³ SO₃²⁻ in 0.5 mol dm⁻³ sulphuric acid, demonstrating again the oxidation of SO₂ in solution.

The principle anticipated mechanism for the oxidation of sulphur dioxide in sulphuric acid solutions was by direct anodic oxidation. However, oxygen is known to be a suitable oxidant for dissolved sulphur dioxide species and this is a second mechanism for oxidation. Oxygen would be present

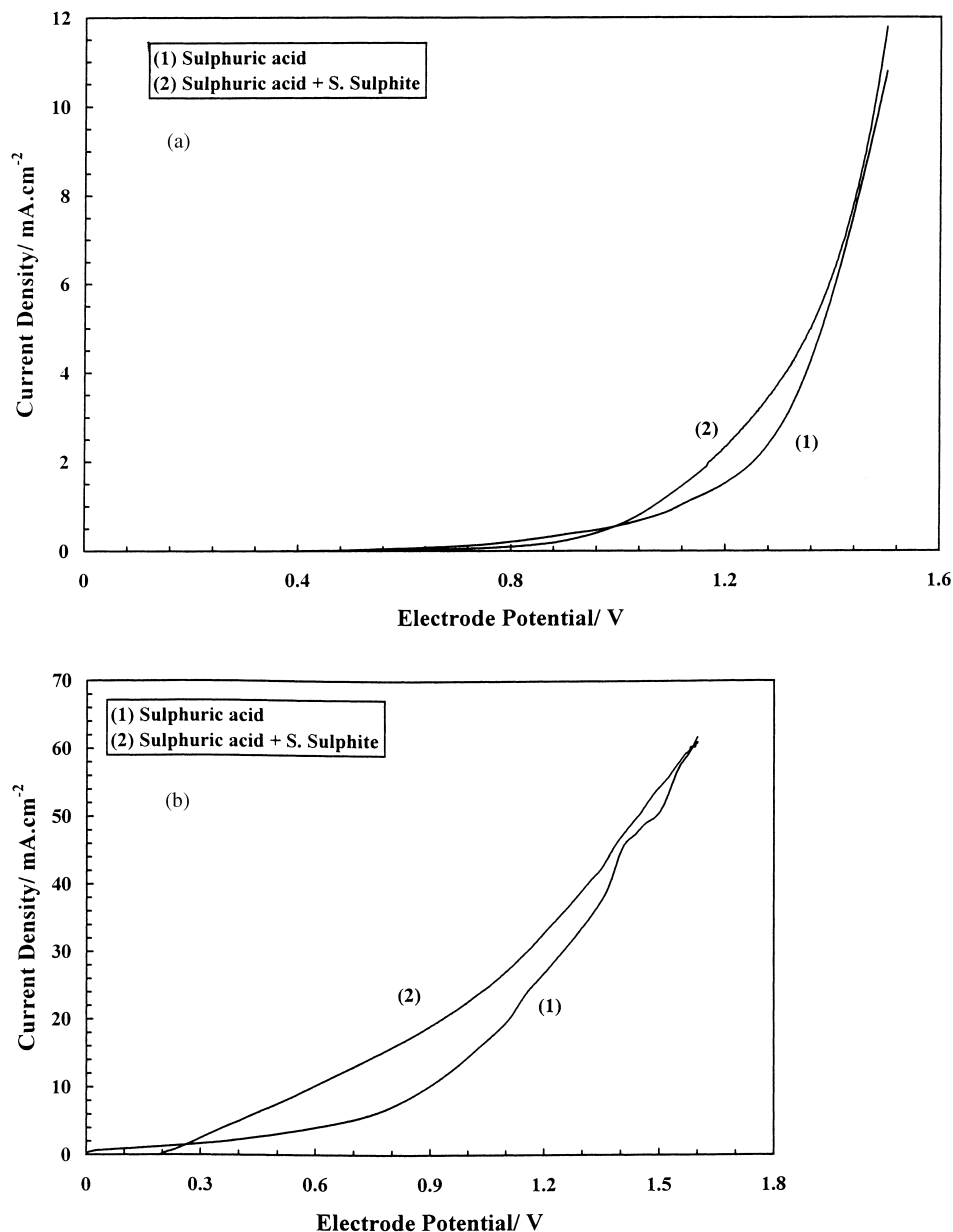


Fig. 4. Linear sweep voltammograms for reduction of $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ in 0.5 mol dm^{-3} sulphuric acid. (a) zirconium, (b) Ebonex[®].

in the feed gas, and would be potentially a byproduct from the anodic oxidation of water, a side reaction causing a loss in current efficiency. Additionally dissolved oxygen may be cathodically reduced to peroxy species which could also contribute to sulphur dioxide oxidation. However, the extent of this reaction is uncertain as peroxy species are rapidly catalytically destroyed by trace metals, leading to water production. Overall, in the SPER system, oxidation of sulphur dioxide could occur by a combination of electrochemical oxidation and chemical oxidation.

4.2. SPER performance

The oxidation of sulphur dioxide was performed continuously in the SPER using a simulated waste gas contain-

ing 3% SO_2 by volume in nitrogen (and 1.5% oxygen by volume). Prior to electrolysis the system was operated for 1 h to achieve 'saturation' of the electrolyte with SO_2 . The typical dissolved SO_2 concentration achieved was $8.25 \text{ mmol dm}^{-3}$. During electrolysis the system was operated with a continuous supply of feed gas at a rate which balanced the production of hydrogen gas at the cathode.

Fig. 7 shows the current efficiency performance of the reactor at two current densities and two sulphuric acid concentrations. Efficiencies of >80% over the duration of the experiments are achieved. The steady-state concentration of dissolved SO_2 was typically $5.5\text{--}5.6 \text{ mmol dm}^{-3}$, and $3.6\text{--}3.7 \text{ mmol dm}^{-3}$ at current densities of 10 and 20 mA cm^{-2} , respectively. Current efficiency is slightly

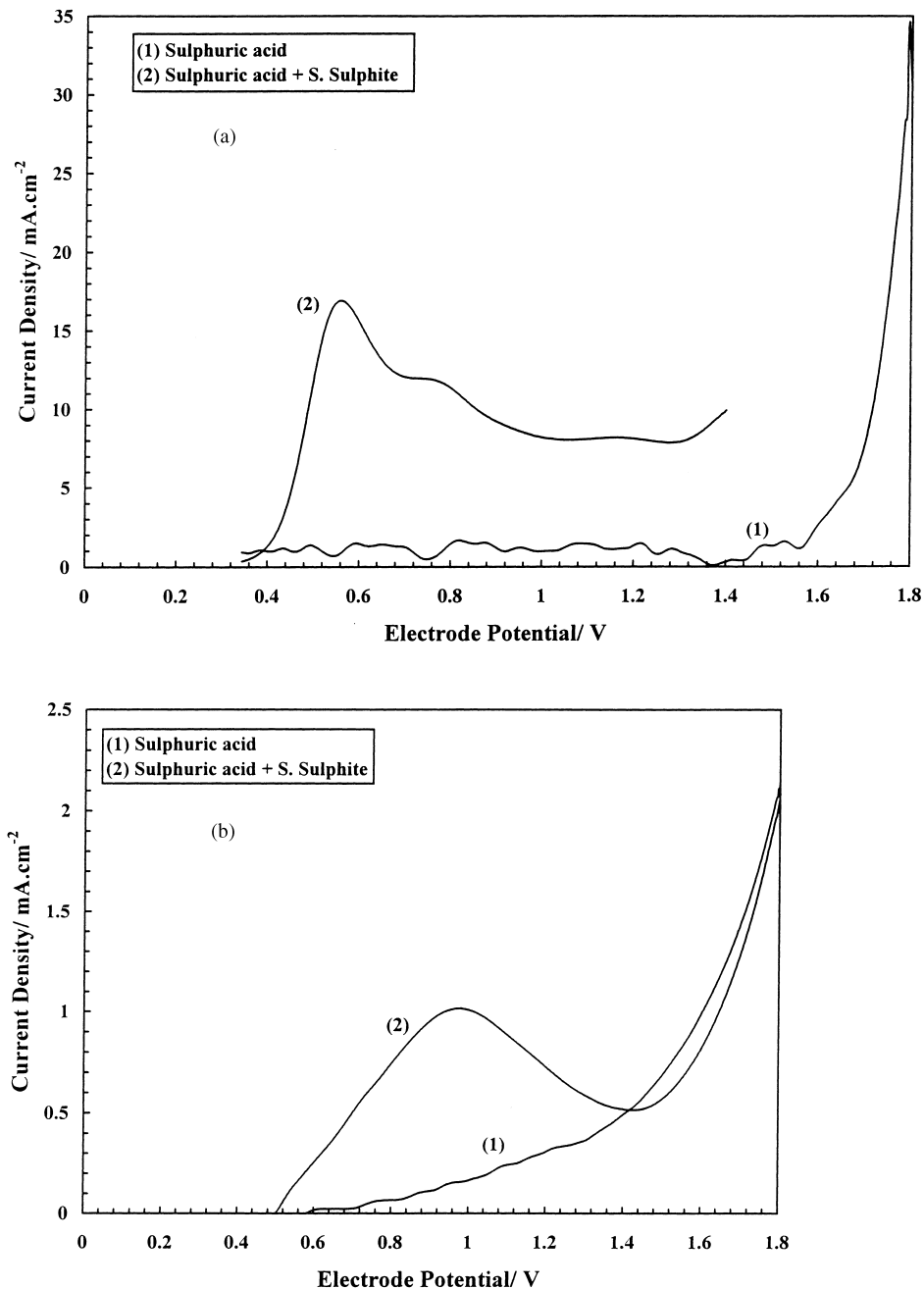


Fig. 5. Linear sweep voltammograms for oxidation of $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ in 0.5 mol dm^{-3} sulphuric acid in platinised titanium and lead dioxide anodes. (a) Platinised titanium, (b) Lead dioxide.

greater with the more concentrated sulphuric acid solution. The current efficiency is greater at the lower current density.

The cell voltages were 2.8 and 3.5 V at current densities of 10 and 20 mA cm^{-2} , respectively. These correspond to energy consumptions in the range of $1.8\text{--}2.4 \text{ kWh kg}^{-1}$. The formation of sulphur was not observed in solution or on the electrodes under any operating conditions used. The major contributing factor to the energy consumption in this system is the overpotential at the cathode. There is limited scope for selecting materials with lower overpotentials due to the requirement for a non-sulphur dioxide reducing

cathode. A second contributing factor to the energy consumption is that of the effective electrolyte resistivity. Although the electrical conductivity of the sulphuric acid solutions are relatively high, the gas sparging operation, plus the generation of hydrogen gas in situ, produces a relatively large gas fraction which significantly reduces the effective electrolyte conductivity.

Overall although the SPER is a relatively efficient unit for the direct anodic oxidation of sulphur dioxide having good electrolyte to electrode mass-transfer rates, there are a number of disadvantages associated with its operation.

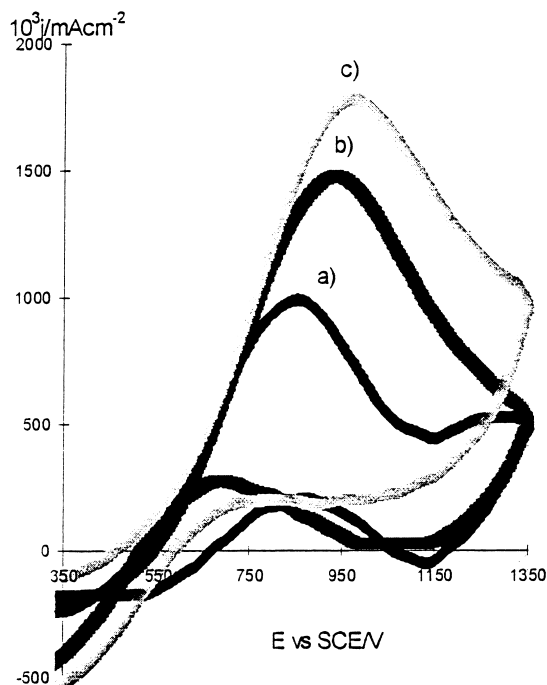


Fig. 6. Cyclic voltammograms for oxidation of $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ in 0.5 mol dm^{-3} on lead dioxide. (d) 50 mV s^{-1} , (e) 100 mV s^{-1} , (f) 200 mV s^{-1} .

1. Limitations in cathode materials selection. Even zirconium may present long term problems due to hydride formation during hydrogen evolution.
2. Limitation in the inter-electrode gap due to gas sparging requirements. However, the monopolar design enables much closer electrode spacing when, for example, expanded metal electrodes are used.
3. Generation of hydrogen in situ with the gas sparging removes the dissolved sulphur dioxide from solution.

The alternative to the SPER is to perform the anodic oxidation of pre-absorbed solutions of SO_2 in sulphuric acid. This operation although enabling a smaller inter-electrode gap and increased effective electrolyte conductivity does not have the benefit of the electrochemical reaction enhancing the rate of SO_2 absorption. Generation of hydrogen gas will still also remove from SO_2 solution. The alternative use of divided cells, although potentially resolving problems associated with in situ hydrogen generation, presuming that anodic oxygen evolution is small, carries with it a much increased capital cost and, potentially, a higher cell voltage. In addition, even with membranes, SO_2 will transport from anode to cathode either by diffusion or electro-osmosis (with solvated H^+ ions) and thereby be potentially reduced, at the cathode, to sulphur.

5. Mass transfer and model

The model presented in Section 3 predicts both the dynamic and steady-state performance of the SPER during

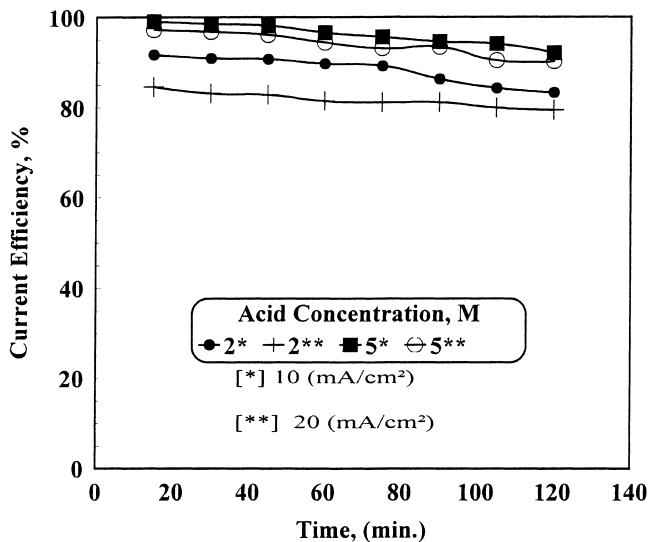


Fig. 7. Variation of current efficiency during continuous operation of the sieve-plate reactor during sulphur dioxide oxidation.

sulphur dioxide oxidation. Operation of the SPER focused on the steady-state performance which is modelled using Eq. (9). The influence of mass transfer is readily apparent in the model. There are essentially two major factors predicted by the model which influence performance, for a given reaction system,

1. the Da number which is the dimensionless group representing the ratio of liquid-to-electrode mass transport and gas-to-liquid mass transport and
2. the product of the gas residence time and gas-to-liquid mass-transport rate. In the latter case, as the gas residence time is increased, through a reduction in gas flow rate, the gas-to-liquid mass-transport rate will decrease. Measurements of the gas-to-liquid mass transport performed in a sieve-plate unit, to be reported in detail elsewhere [15], confirm this behaviour.

However, the additional factor with the SPER operation, when electrolysis occurs, is the generation of oxygen and hydrogen gas at the anode and cathode, respectively. This gas generation will effect the gas-to-liquid mass-transport rate and its influence is difficult to measure in the reaction system and is thus not possible to incorporate into the model.

The generation of oxygen and hydrogen gas has also a profound effect on the liquid-to-electrode mass-transport rate. Liquid-to-electrode mass transport in the SPER, in the absence of electrolytic gas generation, has been measured and correlated (see Fig. 8) as a function of liquid-phase and gas-phase Reynolds numbers [15]. However, this correlation does not give an accurate prediction of experimentally determined mass transport in the SPER during electrolysis. This mass transfer was measured during the oxidation of sodium sulphite solution with nitrogen gas sparging through the sieve plate. Fig. 9 shows the variation in the logarithm of

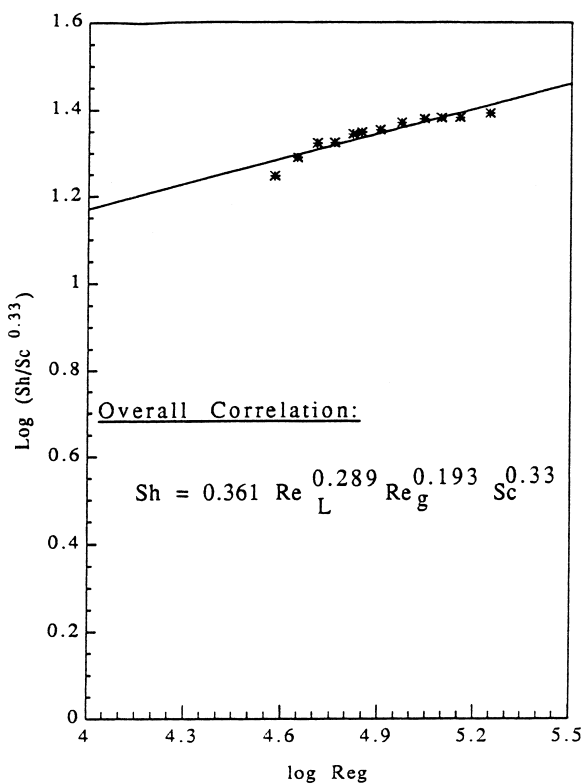


Fig. 8. Correlation of liquid-to-electrode mass transport in the sieve-plate electrochemical reactor. Re_g = gas-phase Reynolds number, Re_L = liquid Reynolds Number, Sc = Electrolyte Schmidt number, Sh = Sherwood number.

concentration of sulphite with electrolysis time as a function of current density for two different operating conditions. The linear correlation of the data in Fig. 9 conform with an approximate mass-transport limiting current model and the slope of the correlation gives the specific mass-transport coefficient k_1a for each current density. Within the current density range the mass-transport coefficient is almost proportional to current density (Table 1). It should be noted that the extent of oxidation by electrogenerated oxygen and other species, as discussed in Section 3, will also be included in this data.

The data in Table 1, together with estimations of the gas-to-liquid mass-transport rates in the sieve-plate reactor, are used to estimate the steady-state performance. Fig. 10 shows the influence of Da on the steady-state concentration of dissolved SO_2 , expressed as the ratio of final value to initial value prior to electrolysis, C^* . As the value of Da increases, i.e. the liquid-to-electrode mass-transport rate increases, the concentration of SO_2 in the liquid falls. This is due to an increased consumption of SO_2 by electrolysis. The experimental measured concentrations of SO_2 are in general agreement (see Fig. 10) with the model predictions. It should be noted that in this system the extent of oxidation of SO_2 by electrogenerated oxygen and other species, may be a significant factor influencing performance.

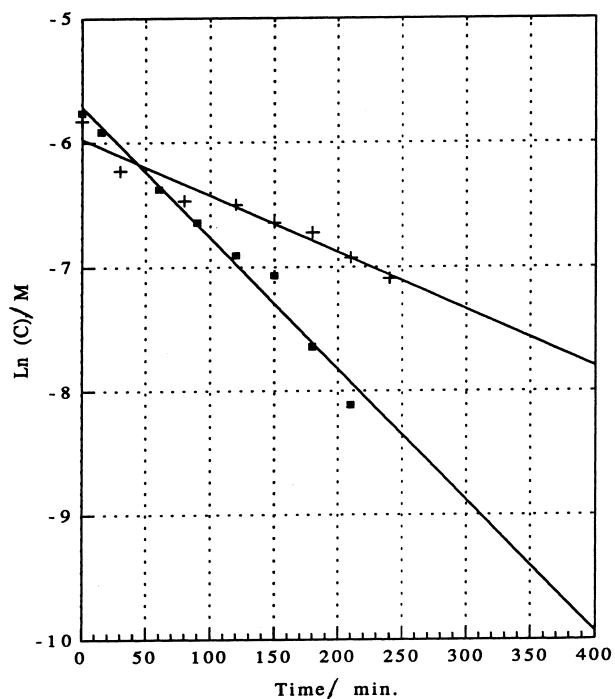
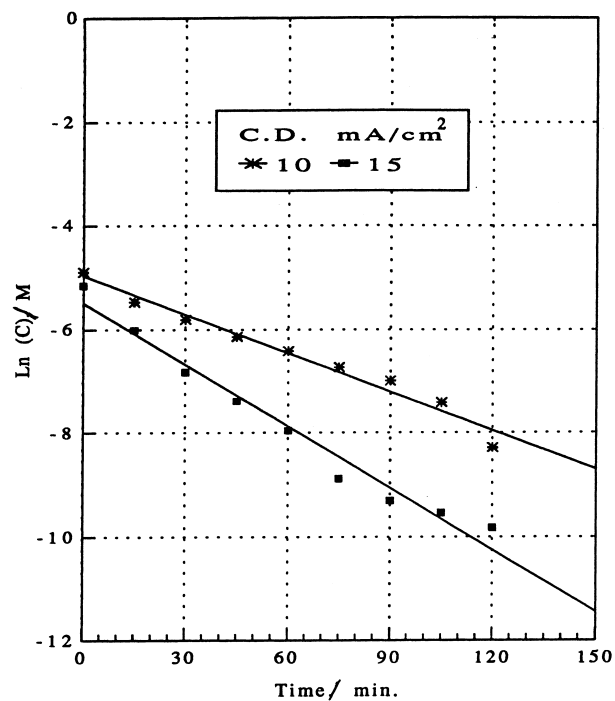


Fig. 9. Variation in the concentration of dissolved sulphur dioxide with electrolysis time for oxidation in the sieve-plate reactor. (a) 5.0 mol dm^{-3} sulphuric acid, 10 cell stack, * 10 mA cm^{-2} , ■ 15 mA cm^{-2} . (b) 2.0 mol dm^{-3} sulphuric acid, 5 cell stack, + 10 mA cm^{-2} , ■ 25 mA cm^{-2} .

6. Conclusions

The results of this research have shown that platinised titanium and lead dioxide coated titanium are suitable anode materials for sulphite oxidation, which can be used in the

Table 1
Effect of current density on mass-transport coefficient

Current density (mA cm^{-2})	10	15	25
Mass-transport coefficient (ms^{-1})	2.1×10^{-5}	3.3×10^{-5}	4.8×10^{-5}

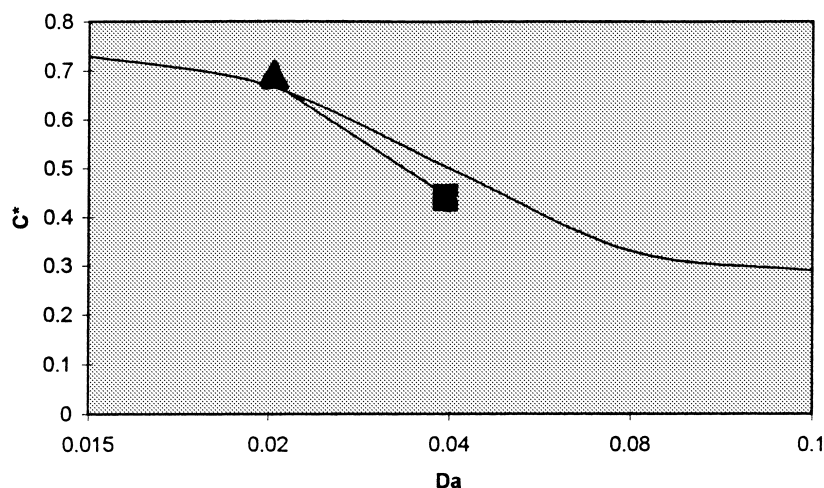


Fig. 10. Variation in steady-state sulphur dioxide concentration with Da number, gas-liquid equilibrium coefficient $m = 0.36$ (kNm^{-2}) (mol m^{-3}). $K_g aRT = 0.45 \text{ s}^{-1}$. $T_g = 6.0 \text{ s}$. Temperature 298 K. Experimental data: \blacktriangle —10 mA cm^{-2} ; \blacksquare —20 mA cm^{-2} .

oxidation of sulphur dioxide effluent gases in the sieve-plate electrochemical reactor. The sieve-plate reactor has good mass-transfer characteristics for gas-liquid electrochemical reactions and can be used with good performance in the anodic oxidation of SO_2 . The direct oxidation can be performed in undivided cells utilising Ebonex or Zr cathodes without the formation of elemental sulphur at the cathode. Current densities of operation with low SO_2 concentration (mmolar) are relatively high at 10–20 mA cm^{-2} . The use of high sulphuric acid concentrations gives good current efficiency and energy consumption.

The direct anodic oxidation of SO_2 is an alternative to the use of chemical oxidants such as bromine and hydrogen peroxide. The use of hydrogen peroxide, at high concentrations sufficient to produce concentrated sulphuric acid by oxidation, is significantly more costly (by a factor of six) than the use of the electron.

7. Nomenclature (units: mol m, s, K)

A	electrode area
A_e	interfacial gas, liquid area
C	concentration
C_0	initial solution concentration
Da	modified Damkohler number
k_c	overall liquid-phase rate constant
k_e	overall electrochemical rate constant
k_g	gas-phase mass-transfer coefficient
K_c	overall liquid-phase mass-transfer coefficient
K_g	overall gas-phase mass-transfer coefficient

m	equilibrium constant
P_g	partial pressure of SO_2 in feed
P_i	partial pressure at the reactor inlet
P_0	bulk partial pressure of SO_2
Q	gas flow rate
Q_g	feed gas flow rate
r	recycle ratio
R	gas constant
t	time
T	temperature
T_g	residence time of gas in cells
V_{cell}	total electrolyte volume
V_r	reactor volume

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References

- [1] G. Kreysa, J.M. Bisang, W. Kochanek, G. Linzbach, *J. Appl. Electrochem.* 15 (1985) 639.
- [2] P.W.T. Lu, E.R. Garcia, R.L. Ammon, *J. Appl. Electrochem* 11 (1981) 347.
- [3] P.W.T. Lu, R.L. Ammon, *J. Electrochem. Soc.* 127 (1980) 2610.
- [4] B.D. Struck, R. Junginger, D. Boltersdorf, H. Neusmeister, *Int. J. Hydrogen Energy* 5 (1980) 487.
- [5] H.W. Nurnberg, J. Divisek, B.D. Struck, *Nuclear Technologies in a Sustainable Energy System*, in: G.S. Bauer, A. McDonnell (Ed.), Springer-Verlag, Berlin, Heidelberg, 1983, 155.

- [6] A.J. Appleby, B. Pichon, *J. Electroanal. Chem. Inter. Electrochem* 95 (1979) 59.
- [7] T. Hunger, F. Lapique, A. Storck, *J. Appl. Electrochem.* 21 (1991) 588.
- [8] E.T. Seo, D.T. Sawyer, *Electrochim. Acta* 10 (1965) 239.
- [9] K. Wiesener, *Electrochim. Acta* 18 (1973) 185.
- [10] T. Hunger, F. Lapique, *Electrochim. Acta* 36 (1991) 1073.
- [11] G. Kreysa, A. Storck, *Dechema Monograph*, vol. 123 VCH Verlagsgesellschaft, 1991.
- [12] K. Scott, W. Hui, *J. App. Electrochem.* 26 (1996) 10–17.
- [13] K. Scott, W. Taama, *J. Chem. Tech. Biotechnol.* 70 (1997) 51–56.
- [14] S. Yagi, H. Inoue, *Chem. Engng. Sci.* 17 (1962) 411–421.
- [15] W.M. Taama, K. Scott, to be submitted.