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# *An investigation of sulphite ion oxidation as an alternative anodic reaction in fluidized bed electrowinning or other high rate electrolysis cells*

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The oxidation of sulphite ion to sulphate ion appears to offer attractions as an anodic reaction for cells operated at high current density such as those used in the fluidized bed electrodeposition of metals. In the present investigation several anodes were tried in a cell where the anolyte was aqueous ammonium sulphite solution and copper was electrowon from acidified aqueous cupric sulphate solution onto a fluidized cathode. The cell voltage was determined as a function of current density and a porous anode consisting of reticulated vitreous carbon with a lead coating was found to yield low cell voltages as did a DSA anode. The former anode did not evolve oxygen in the current density range up to 5500 A $m^{-2}$ whereas the latter showed the onset of oxygen evolution as the current density was raised. Some effects of anolyte flow rate and extent of conversion of sulphite to sulphate, as well as the distribution of potential drops in the cell were determined. Below 3500 A $m^{-2}$, sulphite ion oxidation using the reticulated vitreous carbon anode resulted in cell voltages below those of conventional commercial cells for copper electrowinning.

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## 1. Introduction

The fluidized bed electrode (FBE) has been investigated in the past because of its high mass transfer coefficient and because of its high active surface to volume ratio. These properties allow large amounts of current to be efficiently passed in a relatively small cell.

The investigation described here was aimed at reducing the electrical energy consumption for electrowinning of metals using a fluidized bed cathode; however it is thought that the results are relevant to other cells where cathodic reactions are to be carried out at high rates and the electrolyte is aqueous. Attempts to lower the energy consumption in fluidized bed copper electrowinning have been made by Ziegler [1] and by Dubrovsky *et al.* [2]. These workers have both noted that the major part of the electrical energy was consumed in the anodic chamber of the cell. In their studies, as well as in this one, a microporous partition separated the anodic and cathodic chambers of the cell.

One approach to reducing the anodic energy consumption is to reduce the ohmic potential drop in the anode chamber. Dubrovsky placed the anode directly against the diaphragm and used an excess of supporting electrolyte. Another approach is to use an anodic reaction which uses less energy than the traditional anodic evolution of oxygen. Previous investigators have studied various alternative anodic reactions [1, 3, 4].

In this study the oxidation of sulphite was used in place of the anodic evolution of oxygen. Many investigators have studied the electrooxidation of various reducing sulphur species in aqueous solutions [4–7]. In fact, the use of sulphur dioxide as a depolarizer in copper electrowinning was first patented in 1878 [8].

Fig. 1 shows plots of oxidation potential

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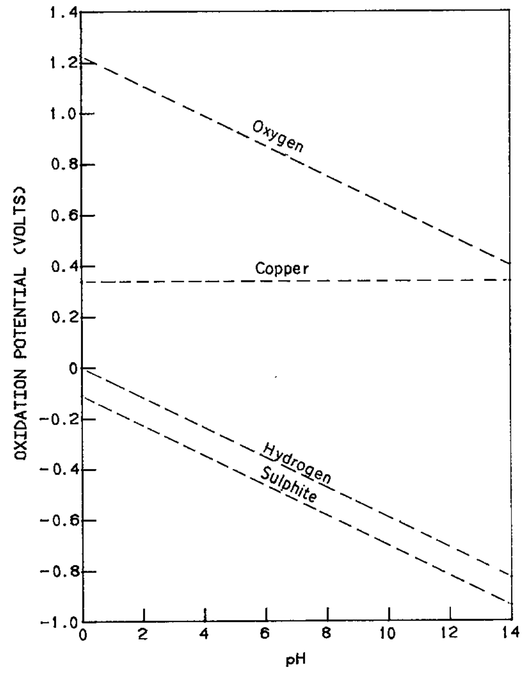

Fig. 1. Oxidation potential versus pH for species of interest in this investigation.

(calculated using thermodynamic data in [9]) versus pH for several reactions, assuming unit activity. For oxygen evolution as the anodic reaction and cupric reduction to copper metal as the cathodic reaction the standard cell potential is positive for the entire pH range. A positive standard cell potential indicates that an energy input would be required for the reaction to proceed. However, if sulphite oxidation occurs in place of oxygen evolution then the standard cell potential is negative over the pH range. Hence, thermodynamically, the sulphite oxidation–cupric reduction reactions should occur spontaneously. In practice, it is necessary to supply electrical energy to the cell so that the reactions proceed at useful rates.

Lu and Ammon [4] recently investigated the catalytic effect of various materials on the electro-oxidation of sulphur dioxide in electrolytes containing sulphuric acid. Their study found palladium to be the best catalyst for the oxidation of sulphur dioxide.

Palladium and other materials were used in this study. The approach attempted was to develop anode systems that would minimize anodic overpotentials as well as reduce mass transfer limitations. For this process to be commercially feasible, a readily available form of sulphite would be necessary. Ammonium sulphite was chosen for this study for two reasons: (1) Ammonia scrubber technology for removal of sulphur dioxide from gas streams exists. The effluent scrubber solution can be controlled to yield ammonium sulphite [10], and (2) the oxidation product of ammonium sulphite is ammonium sulphate which can be used as fertilizer. The ammonium sulphate can also be used as an intermediate in the production of phosphate fertilizers [10]. If a copper sulphide ore is to be processed, then a scheme represented by the overall plant reaction

$$\begin{aligned} &Cu_2S + 2NH_3 + 3/2O_2 + H_2O \\ &= (NH_4)_2SO_4 + 2Cu \qquad (1) \end{aligned}$$

is conceivable.

## 2. Experimental apparatus and procedure

### 2.1. *Apparatus*

A cell equipped with a rectangular fluidized cathode of the 'side by side' design (current flow perpendicular to electrolyte flow) was used, as shown in Fig. 2. The cell, similar in design to that of Dubrovsky *et al.* [2], consisted of two halves separated by a microporous plastic

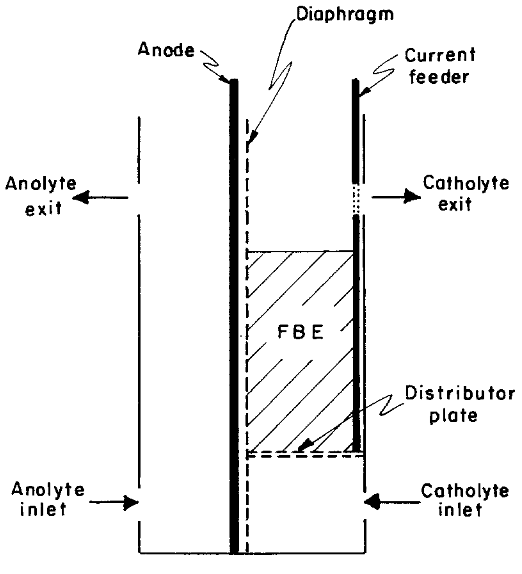

Fig. 2. Schematic diagram of cell equipped with fluidized cathode of side by side configuration.

diaphragm (Daramic, W. R. Grace Corporation). This diaphragm had pores of approximately 0.1 μm, and was virtually impermeable to electrolyte at the pressure differentials encountered in this investigation. By screening the rest of the diaphragm with silicone cement a 'window' 45 mm wide by 100 mm tall was created in the diaphragm. In this way current and metal deposition were restricted to regions of the cathode that were well fluidized. The cathode consisted of copper particles (approximately 500 μm diameter) connected by a current feeder, consisting of a copper strip, to the external circuit. When fluidized, the bed was approximately 220 mm high, and 70 mm by 28 mm, the latter being the dimension perpendicular to the diaphragm.

Seven different types of anodes were used in this study. The anodes fall into two groups, two-dimensional (planar) and three-dimensional (porous). The planar anodes were all approximately 70 mm wide, 2 mm thick and 490 mm long. They were either made of a mesh type material or a sheet material with an array of holes drilled opposite the window. The purpose of the mesh openings, or holes, was to facilitate the removal of oxygen bubbles and the arrival of fresh reactant at the anode–window interface. One of the planar anodes tested was a titanium mesh which was coated with a catalyst for anodic oxygen evolution. This anode is referred to as DSA and was supplied by a division of Diamond Shamrock Corporation (now Eltech Corporation). Another anode was a platinum coated titanium mesh. The platinum was electrodeposited. A 316 stainless steel sheet anode was also used. It had an 8 x 9 array of 4 mm diameter holes drilled opposite the window. The last planar anode used was a lead–6% antimony sheet also with an array of holes drilled opposite to the window.

The first porous anode used was made of graphite. This anode restricted the anolyte flow excessively and yielded high cell voltages; the details of its construction are therefore omitted here. Two other porous anodes were used, both fabricated from reticulated vitreous carbon (RVC). RVC is a glassy carbon material which is highly porous, has a high specific surface, is electrically conductive, and offers little resistance to fluid flow (see Table 1). Both RVC anodes were 6.5 cm wide, 2.5 cm thick and 13.5 cm long. One of these anodes was electroplated with lead from a standard lead fluoro-borate plating bath. The other RVC anode was also plated with lead from the same bath. An attempt was made to plate palladium over the lead from a proprietary plating bath. Palladium would not plate directly onto the RVC and there was doubt concerning the efficacy of its deposition onto the lead coated RVC.

*Table 1. Selected properties of RVC used in this investigation*

| *Property* | *Value* |
|---|---|
| Pores per inch | 30 |
| Porosity | 97% |
| Specific surface | 16.5 $cm^2$ $cm^{-3}$ |
| Resistivity | 50 $\times 10^{-4}$ ohm cm |

The RVC anodes were centred opposite the window area. The anodes were mounted with a thin layer of glue to the back wall of the anode chamber. The glue also minimized possible channeling of the anolyte flow along the back wall. Electrical connections were made to the anodes by lead foil which was soldered to the side of the RVC material.

After the experiments were completed, the lead coated RVC anode was cut in half to examine its interior. Lead was visually observed to be deposited all the way through the RVC; however, the deposit was not uniform.

Fig. 3 shows the cell and its support system. Power was supplied by a Hewlett Packard 6260B regulated dc power supply. The current was measured by a shunt resistor. The current signal and cell voltage were simultaneously recorded on a dual channel chart recorder. The anolyte and catholyte each had separate reservoirs and pumping systems. Flowmeters and sampling ports were placed in the electrolyte inlet streams. Stainless steel heat transfer coils were placed within each reservoir. The coils were connected to a temperature controlled bath. A Luggin capillary and a silver chloride reference electrode were used to measure the potential drop in the cathode chamber. The cathode chamber potential drop was measured on a Beckman 3500 high impedance milivolt/pH meter.

*Table 2. Experimental conditions*

| Run | Anode | Catholyte ($g\,l^{-1}$) | | Catholyte pH | | Anolyte (M) | | Anolyte pH | | Temperature (° C) | | Flow rate ($l\,min^{-1}$) | | Bed expansion (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cu | $H_2SO_4$ | initial | final | $(NH_4)_2SO_4$ | $(NH_4)_2SO_4$ | initial | final | catholyte | anolyte | catholyte | anolyte | |
| A1 | SS | 30 | 50 | 1 | 1 | 2 | – | 7 | 7 | 33.7 | 32.5 | 6.9 | 4.0 | 20 |
| A2 | PG | 30 | 50 | 1 | 1 | 2 | – | 7 | 6.5 | 30 | 33.3 | 6.9 | 4.0 | 20 |
| A3 | PG | 32.1 | 50 | 1 | 1 | 2 | – | 6.5 | 6.2 | 31 | 31.8 | 1.0 | 4.0 | 20 |
| A4 | DSA | 30 | 50 | 1 | 1 | 2 | – | 7 | 6 | 34.1 | 36.8 | 6.9 | 4.0 | 20 |
| A5 | DSA | 30 | 50 | 1 | 1 | 2 | – | 7 | 6 | 35.7 | 36.8 | 6.9 | 4.0 | 20 |
| A6 | DSA | 30 | 50 | 1 | 1 | 1 | 1 | 7 | 5 | 37.8 | 38.6 | 6.9 | 4.0 | 20 |
| A7 | DSA | 30 | 50 | 1 | 1 | – | 2 | 5 | 3 | 32.1 | 34.5 | 6.9 | 4.0 | 20 |
| B1 | DSA | 29.3 | 50 | 0.8 | 0.6 | 2 | – | 7.3 | 6.0 | 28.8 | 30.9 | 0.4 | 4.0 | 20 |
| B2 | DSA | 29.3 | 50 | 0.8 | 0.6 | 2 | – | 7.3 | 6.0 | 28.7 | 30.5 | 1.0 | 4.0 | 20 |
| B3 | DSA | 29.3 | 50 | 0.8 | 0.6 | 2 | – | 7.3 | 6.0 | 28.2 | 30.5 | 2.0 | 4.0 | 20 |
| B4 | DSA | 29.5 | 50 | 0.65 | 0.62 | 2 | – | 8.2 | 7.4 | 28.9 | 30.3 | 2.0 | 4.0 | 20 |
| B5 | PL | 30 | 50 | – | – | 2 | – | – | – | 30.2 | 31.1 | 0.4 | 4.0 | 20 |
| B6 | PTM | 27.8 | 50 | 1.3 | 1.2 | 2 | – | 7.1 | 3.5 | 28.5 | 29.5 | 0.4 | 4.0 | 20 |
| B7 | PTM | 27.8 | 50 | 1.3 | 1.2 | 2 | – | 7.1 | 3.5 | 28.5 | 29.5 | 1.0 | 4.0 | 20 |
| B8 | *RVC* Pb | 29.9 | 50 | 0.83 | 0.93 | 2 | – | 7.99 | 7.14 | 27.9 | 30.2 | 0.4 | 4.0 | 17 |
| B9 | *RVC* Pb | 28.3 | 50 | 0.93 | 0.93 | 2 | – | 7.96 | 6.76 | 27.7 | 29.8 | 0.4 | 4.0 | 17 |
| B10 | *RVC* Pd | 30.0 | 50 | 0.82 | 0.83 | 2 | – | 8.2 | 6.92 | 27.3 | 31.2 | 0.4 | 4.0 | 17 |
| B11 | *RVC* Pd | 29.0 | 50 | 0.83 | 0.85 | 1 | 1 | 7.94 | 7.14 | 25.7 | 29 | 0.4 | 4.0 | 17 |

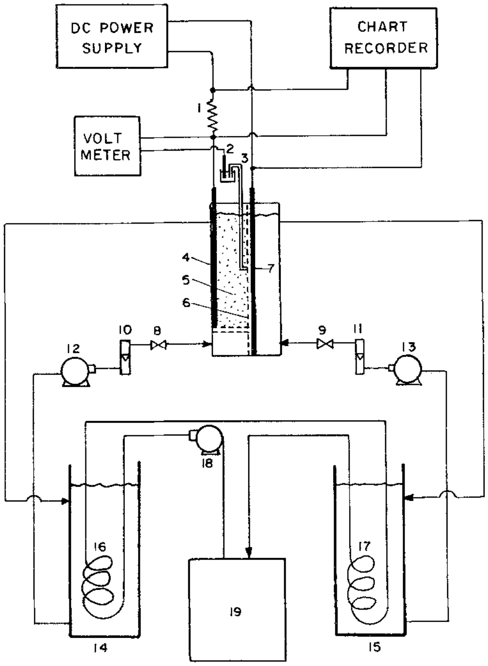

Fig. 3. Cell shown connected to apparatus supplying current, catholyte and anolyte. 1 – shunt, 2 – reference electrode, 3 – Luggin capillary, 4 – current feeder, 5 – FBE, 6 – diaphragm, 7 – anode, 8 and 9 – sample ports, 10 and 11 – flowmeters, 12 and 13 – electrolyte pumps, 14 and 15 – catholyte and anolyte reservoirs, 16 and 17 – heat exchange coils, 18 – coolant pump, 19 – constant temperature bath.

### 2.2. *Procedure*

A cleaned anode was installed in the cell together with a cleaned current feeder and the diaphragm. The two halves of the cell were joined and the cell connected to the support system. Anolyte and catholytes were then mixed. The ammonium sulphite monohydrate used was either MCB ‘purified crystals’ or ALPHA 97%. The anolyte volume for all these experiments was 3 l. Analytical reagent grade ammonium sulphate was used in some of the experiments and was supplied by Mallinckrodt, Inc.

The catholyte was made from CITCO 99% copper sulphate pentahydrate and Mallinkrodt reagent grade sulphuric acid. The catholyte volume was either 5 or 8 l.

Distilled water was used for mixing all electrolytes. The salts were first dissolved and poured into the reservoirs. The electrolytes were then diluted to the proper volume by using calibration marks on the reservoirs. After the electrolytes were mixed, a Luggin capillary was installed in the cathode chamber. The capillary tip just touched the centre of the window area on the diaphragm. The pumps were then started and approximately 1750 g of 28 x 35 mesh copper particles were poured into the cathode chamber. After adding the particles, the temperature was allowed to stabilize.

Throughout the experiment, the temperatures, cathode chamber potential drop, cell voltage, applied current, and electrolyte flowrates were controlled and/or measured. In addition, anolyte and catholyte samples were taken periodically for concentration and current efficiency determinations.

At the nominal currents and electrolyte flowrates employed, less than 1.4% of the entering reactant species could be converted per pass through the reactor. Furthermore, in any one experiment less that 10% of the reacting species was converted. Hence a condition of constant composition was approximated. The power supply was operated in constant current mode; voltage fluctuations occurred but were typically less than ± 5%. The cathodic potential drop was measured against a silver chloride reference electrode. The silver chloride reference electrode was calibrated against a calomel electrode.

Further details concerning the apparatus, anodes and experimental procedure are given elsewhere [11].

## 3. Experimental results

### 3.1. *Preliminary comparison of anodes*

The experimental programme began by generating polarization curves for the cell using different anodes and operating conditions (see Table 2).

Fig. 4 shows the polarization curves obtained with an anolyte flowrate of 0.4 $\mathrm{l\,min^{-1}}$, the catholyte flowrate was held constant at 4.0 $\mathrm{l\,min^{-1}}$ for the entire investigation. The ‘superficial current density’ is defined here as the current per unit area of window. It should be noted that conventional copper electrowinning cells operate at voltages of approximately 2 V at 50–200 $\mathrm{A\,m^{-2}}$. The anodes compared were: planar lead (PL), platinized titanium mesh (PTM), DSA, palladium

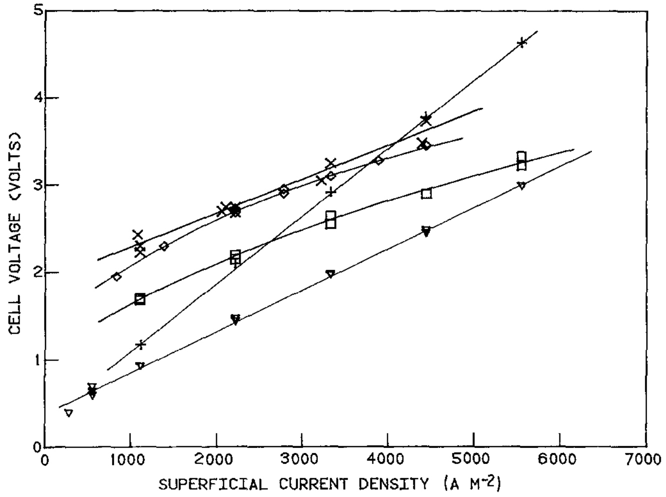

Fig. 4. Comparison of several anodes used in this investigation. X – planar lead, ◇ platinized titanium mesh, □ Diamond Shamrock dimensionally stable anode, + – palladium coated reticulated vitreous carbon RVC/PD, ▽ – lead coated RVC (RVC/PB). Anolyte flowrate = 0.4 l min$^{-1}$.

coated RVC (RVC/Pd), and lead coated RVC (RVC/Pb). As can be seen from Fig. 4, the RVC/Pb anode had the lowest cell voltage. The RVC/Pb anode will be further discussed in the porous anode subsection. The polarization curves were found to be reproducible to better than 5%.

Fig. 5 compares polarization curves obtained with an anolyte flowrate of 6.9 l min$^{-1}$ and at slightly higher temperatures. The anodes compared were: planar 316 stainless steel (SS), porous graphite (PG), and DSA. Here we see that the DSA anode gave the lowest cell voltage.

Fig. 6 shows that as the anolyte flowrate was reduced the anode voltage increased. Also, as the anolyte flowrate decreased, the superficial current density at which oxygen evolution was observed decreased. When the anolyte flowrate was lower than 2.0 l min$^{-1}$ oxygen evolution was observed for the entire range of current densities. This behaviour indicated that the oxidation of the sulphite species was partially mass transfer controlled.

A set of runs was performed to simulate the effect of extent of reaction on cell performance. Fig. 7 shows the results using the DSA anode. Here the anolyte flowrates were kept the same, but the anolyte compositions were varied at constant ionic strength. The bottom curve is for an anolyte which was 2 M in ammonium sulphite; the middle curve is for an anolyte 1 M in ammonium sulphite, and the top curve is for a 2 M ammonium sulphate anolyte. Apparently, the cell voltage

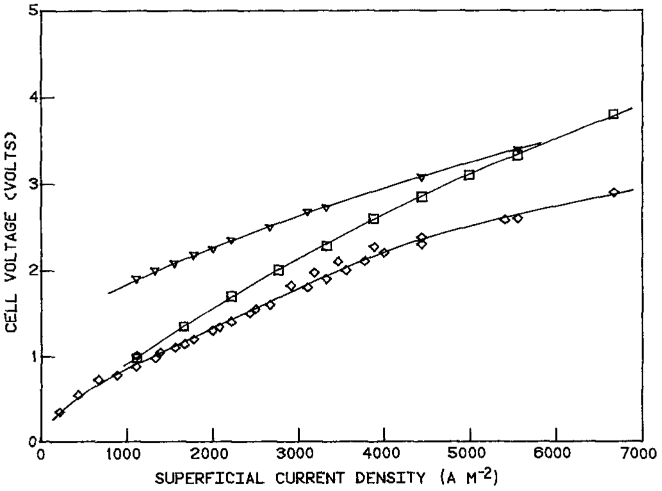

Fig. 5. Comparison of the ▽ – stainless steel (SS), □ – porous graphite (PG) and ◇ – DSA anodes at anolyte flowrate of 6.9 l min$^{-1}$.

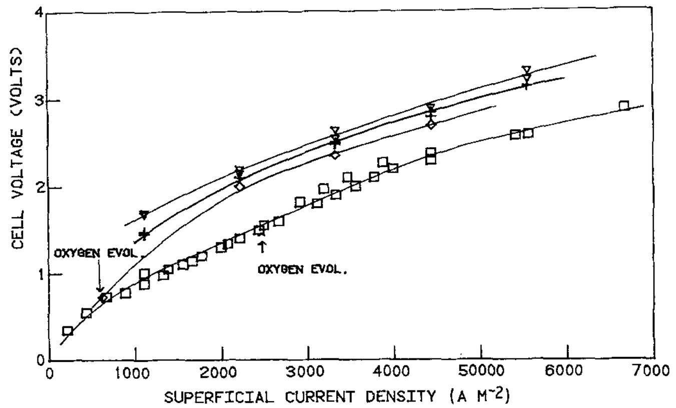

Fig. 6. Effect of anolyte flowrate on cell voltage and oxygen evolution using the DSA anode in sulphite ion oxidation. Anolyte flowrate (l min$^{-1}$); ▽ – 0.4, + – 1.0, ◇ – 2.0, □ – 6.9.

increased with an increase in the sulphate to sulphite ratio. Also, the superficial current density at which oxygen evolution began decreased with an increase in the sulphate to sulphite ratio. However, the electrolyte conductivities are within a few percent of each other. This indicated that as the anodic reaction shifted from sulphite oxidation to oxygen evolution then a higher cell voltage was required, which is consistent with expectations from thermodynamics.

### 3.2. *Porous anodes*

Porous anodes were examined because they offer a large surface area per unit volume of material. Using porous anodes would result in actual current densities which would be low and hence reduce surface overpotentials and concentration overpotentials which might be present with a comparable planar anode. This type of anode was ideally suited as a counterelectrode for fluidized bed cathode because of relatively large current per unit volume passed in the fluidized bed reactor. Packed bed anodes have been suggested in the literature [1, 3]; however, problems were sometimes encountered due to poor interparticle conductivity.

The performance of the porous anodes employed in this investigation is compared in Fig. 8. The poor response of the porous graphite anode was thought to be due to the lack of a catalytic surface for the sulphite oxidation to occur [4] and to the low permeability of the graphite which caused an excessive pressure drop in the anode side of the cell and forced the diaphragm away from the anode surface.

The reticulated vitreous carbon anode (RVC) was very permeable and did not restrict flow to nearly the same extent as the porous graphite. From Fig. 8 it can be seen that the lead plated RVC performed better than the 'palladium' plated RVC. No oxygen evolution was observed for either anode over the range of superficial current densities studied.

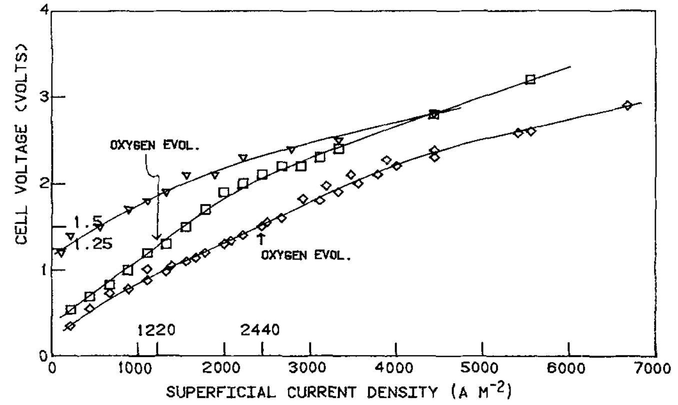

Fig. 7. Effect of sulphite to sulphate molar ratio on cell voltage and oxygen evolution using DSA anode. Oxygen evolved throughout current density range for sulphate ion alone. $SO_3 : SO_4$/ Run; ▽ – 0:2/A7, □ – 1:1/A6, ◇ – 2:0/ A4 and A5.

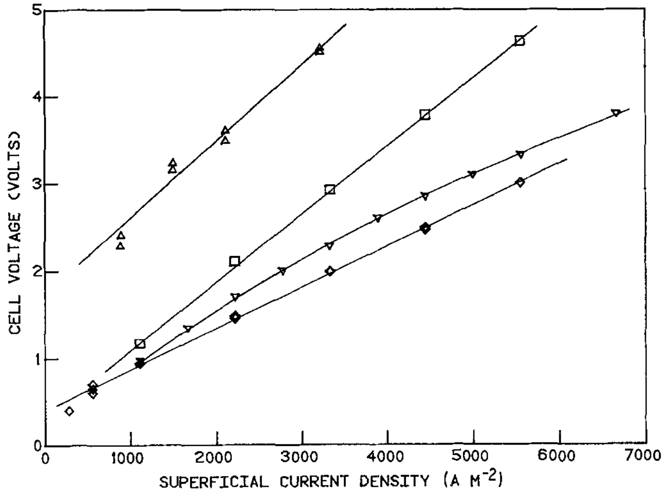

Fig. 8. Comparison of porous anodes used in this investigation. Anolyte flowrate (l min$^{-1}$)/Anode: △ – 1/PG, □ – 0.4/RVC/PD, ▽ – 6.9/PG, ◇ – 0.4/RVC/PB.

The cell voltage was found to be unchanged on varying the anolyte flow rate from 0.4 to 2.0 l min$^{-1}$ when using the RVC/Pb anode. This would seem to indicate that mass transfer was not rate controlling and agrees with the concept that a large amount of the internal surface was active.

The distribution of the voltage drops in the cell when using the RVC–Pb anode is shown in Fig. 9. The voltage drop across the diaphragm in this figure was calculated from measurements of the resistance of the diaphragm, saturated with 1 M sodium chloride solution, corrected by the mean conductivity of anolyte and catholyte. The cathode chamber voltage drop is the result of measurement using the Luggin capillary, and the anode chamber drop is obtained by difference.

It was found impossible to analyse for sulphite ion in the presence of ammonium ion by the technique available in this laboratory (iodometric titration). The only guide to anodic current efficiency is therefore the absence of oxygen evolution when using either of the RVC anodes. Cathodic current efficiencies were determined by withdrawing samples from the known catholyte volume and analysing for copper by iodometric titration. Measured values ranged from 89 to 98%, being higher when splashing and air entrainment (which can lead to chemical oxidation of the deposited copper) were avoided in the catholyte reservoir.

## 4. Discussion

It is appropriate to contrast the requirements for anodes used in high rate electrolysis cells (e.g. cells with fluidized cathodes) with those of anodes for conventional cells using planar cathodes. In electrowinning with the latter cells,

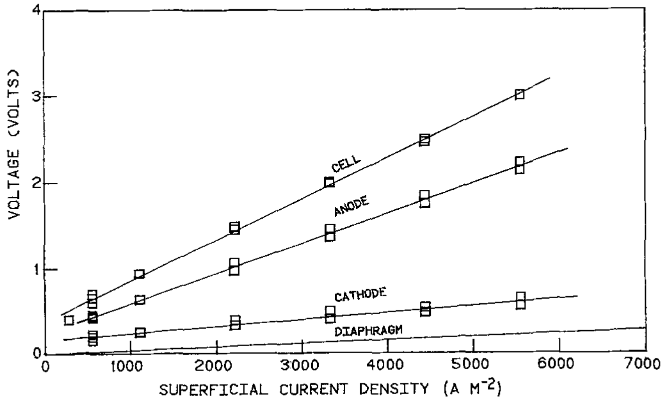

Fig. 9. Distribution of voltage within the cell using the lead coated reticulated vitreous carbon anode. Anolyte flowrate = 0.4 l min$^{-1}$.

current densities are typically a few hundred A m$^{-2}$. Accordingly there is little opportunity for the introduction of an anode of any complexity or capital cost. Furthermore, the electrolyte is sufficiently conductive that the ohmic potential drop therein is a small part of the total cell voltage and the anode–cathode spacing has little effect on cell voltage. In contrast, current densities in fluidized bed electrowinning are more than an order of magnitude greater, and potential drop in the anolyte can become a large part of the cell voltage. This is particularly true if the anodic reaction is the evolution of oxygen; at the high current densities employed the gas evolution rate is high and so is the gas holdup in the anolyte, resulting in an anolyte of high effective resistivity.

It becomes clear that a conventional planar anode will yield an excessive cell voltage if used in conjunction with a fluidized cathode, particularly if that anode is located some distance from the cell diaphragm. Unfortunately many previous investigations of fluidized bed electrowinning have employed a planar anode in such a location. Fig. 10 depicts the work of many previous studies. The lines are for copper electrowinning, and in some instances the energy consumption has been calculated from published cell voltages assuming 100% cathodic current efficiency (which can be achieved by taking care to exclude air from the catholyte). Where possible the date of publication of the results has been included. The rectangle represents the commonly encountered range of values for conventional electrowinning of copper. All but one of the lines are for investigations in which the anodic reaction was oxygen evolution and, in those investigations carried out prior to 1981, the anode was placed some distance from the cell diaphragm. The resulting high cell voltages and energy consumptions may explain why the fluidized bed electrode has won little commercial acceptance. The results of Ziegler *et al.* [12] and of Dubrovsky *et al.* [2] show that a cell can be operated with a fluidized cathode and an oxygen evolving anode at moderate energy consumptions. The former investigators employed a double layer of titanium mesh with the DSA coating; the latter employed a single layer placed directly in contact with the cell diaphragm. The line shown for the present study is for sulphite oxidation at the reticulated vitreous carbon anode with the lead coating and is calculated assuming 100% cathodic current efficiency. It is seen that the avoidance of gas evolution and the use of a reaction of lower electrode potential might lead to considerable benefits in terms of electrical energy consumption.

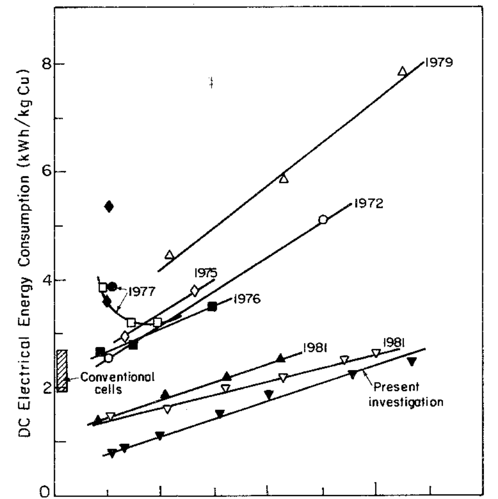

Fig. 10. Comparison of energy consumption rates obtained in this investigation of sulphite ion oxidation with those obtained in previous investigations of fluidized bed electrodes where oxygen evolution has been the anodic reaction. Also shown is the range for conventional electrowinning cells. Numbers are year of publication: △ = reference [13], ● = [14], □ = [15], ○ = [16], ■ = [17], ▲ = [12], ▽ = [2], ◆ = [18], ◇ = [19], ▼ = present investigation.

This investigation has been oriented towards cells in which metal is electrowon onto a fluidized cathode. However, it appears that the results might be exploited in other cells operated at high space–time yields.

## 5. Concluding Remarks

Several anodes were examined for their suitability in the oxidation of sulphite ion to sulphate ion in aqueous ammonium solutions. The investigation was concerned with cells in which a fluidized cathode was used for copper deposition from acidified sulphate solutions but the results are thought to be of wider applicability. A reticulated vitreous carbon anode which had been coated externally and internally with electrodeposited lead was found to perform well in this application. It yielded cell voltages lower than conventional electrowinning cells (where oxygen evolution is the anodic reaction and current densities are 100–200 $\mathrm{A\,m^{-2}}$) at superficial current densities up to approximately 3000 $\mathrm{A\,m^{-2}}$.

## Acknowledgement

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