

# Electrogenerative oxidation of sulphur dioxide

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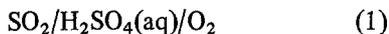
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Possible applications of a galvanic synthesis of sulphuric acid from sulphur dioxide and oxygen are discussed and preliminary results for a laboratory-scale reactor are presented. The use of active, fuel-cell electrodes enables relatively large current densities to be obtained at low cell voltages.

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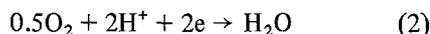
## 1. Introduction

The possibility of producing sulphuric acid with concomitant d.c. electrical-energy generation (i.e. electrogenerative production of sulphuric acid) has been recognized for some time [1]. A cell of the type

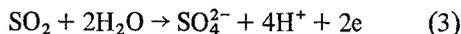


with the overall cell reactions

Cathode:



Anode:



has a standard potential of 1.06 V. Given the large tonnage of sulphuric acid produced each year (United States production alone was 42 million tons in 1979 [2]), a viable electrogenerative (EG) process, in theory, could recover a significant amount of useful energy [3]. This aspect would be particularly pertinent to pyrometallurgical operations where sulphur dioxide is generated during ore roasting (e.g. copper and zinc processing [4]), since d.c. electricity is required in the latter stages. However, the known irreversible nature of each electrode reaction [5] and the poor performance of working cells reported to date [6] have not been encouraging to the development of this concept.

With the refinement and advances in the fabrication of high-performance electrodes [7] available for electrogenerative processes and with rising energy costs, it is appropriate to re-examine EG sulphur dioxide oxidation. Recent half-cell work on  $\text{SO}_2$  oxidation with fuel-cell-type electrodes [8, 9] suggests that substantially better perform-

ance than that reported earlier by Schlatter [6] could be obtained. Here we report encouraging preliminary operating results for the  $\text{SO}_2/\text{O}_2$  undivided electrogenerative reactor.

## 2. Experimental

The electrogenerative reactor used in this study was a static, free-electrolyte cell of similar design to those described earlier [10, 11]. Porous, Teflon-bonded, fuel-cell electrodes containing  $10 \text{ mg cm}^{-2}$  of platinum black (United Technologies Corporation) served both as anode and cathode. Pure streams of  $\text{SO}_2$  (Matheson) and  $\text{O}_2$  (Chemetron) at approximately atmospheric pressure were passed over the anode and cathode, respectively. An electrolyte chamber (0.635 cm thick), which contained about  $5 \text{ cm}^3$  of electrolyte, separated the electrodes. Sulphuric acid solutions were prepared from reagent-grade sulphuric acid and distilled water.

In order to obtain reproducible results, it was necessary to electrochemically activate the electrodes before each experiment. This was done by alternately polarizing them anodically and cathodically with a constant current of  $10 \text{ mA cm}^{-2}$ , reversed every two minutes. This procedure lasted ten minutes.

Polarization curves were obtained by discharging the cell through a decade resistance box in series with an ammeter (Sensitive Research Instruments, Model S). Cell voltages were measured with a high-impedance digital voltmeter (Hewlett Packard, Model 3430A) connected directly to the cell. The cell was discharged, starting at open circuit, to obtain an initial polarization curve. A

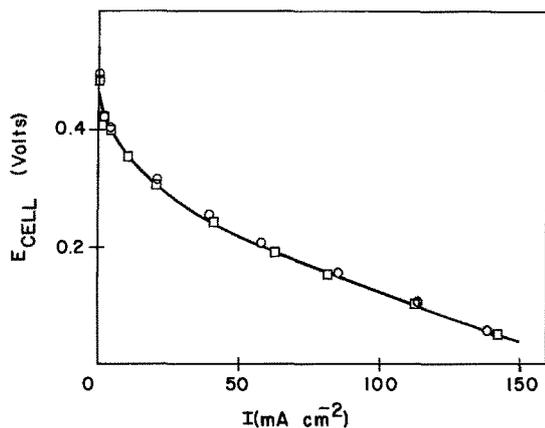


Fig. 1. Performance of an  $\text{SO}_2/\text{O}_2$  electrogenerative reactor. Initial sulphuric acid concentrations: □, 0.5 M; ○, 3.0 M. The apparent electrode area was  $5.0 \text{ cm}^2$ .

second polarization curve was then obtained, again starting from open circuit, in which voltage and current readings were allowed to stabilize for two minutes. The first and second polarization curves took approximately 40 and 90 minutes, respectively, to generate. The second polarization curves are presented as the results of each experiment. The open-circuit voltages were obtained after the second polarization curves.

Cell resistances were determined before and after each experiment with a Keithley Model 503 milliohmmeter, with hydrogen passing over both electrodes. After measuring the cell resistance, the hydrogen was removed by purging with argon for at least 15 minutes before the reactant gases were introduced. Reported cell voltages are not corrected for the resistive potential drop.

### 3. Results and discussion

Fig. 1 shows the results from two typical experiments with initial electrolyte concentrations of 0.5 M and 3.0 M  $\text{H}_2\text{SO}_4$ . Polarization curves were fairly reproducible provided that the electrodes were pretreated as described above. Cell polarization behaviour is similar for both electrolyte concentrations; a dramatic decrease in performance is expected for acid concentrations greater than 7.5 M [8], presumably due to the sharp fall in the activity of water at higher acid concentrations. Open-circuit voltages are much lower than those predicted; this was expected since neither elec-

trode operates reversibly [5]. The rapid drop in cell potential upon drawing current can be associated with the irreversible nature of the cell reaction. Concentration polarization arising from depletion of  $\text{SO}_2$  or  $\text{O}_2$  at the electrodes is probably negligible with the use of pure gases and gas-permeable electrodes. The solubility of  $\text{SO}_2$  in sulphuric acid may be detrimental to cell performance because  $\text{SO}_2$  can chemically short the cell at the oxygen electrode. However, an experiment with an ion-exchange membrane (Du Pont de Nemours and Co., Nafion 125) did not improve overall cell performance, but did significantly increase the internal resistance.

With the large currents and small electrolyte volume used, the concentration of sulphuric acid increased appreciably during the course of each experiment. The measurements of cell resistance made before and after each experiment reflected this variation for the experiments with an initial acid concentration of 0.5 M (for the polarization curve shown, the initial cell resistance was  $0.85 \Omega$  and the final value was  $0.43 \Omega$ ). With an initial concentration of 3.0 M  $\text{H}_2\text{SO}_4$ , the cell resistance remained constant at about  $0.3 \Omega$ .

The most interesting feature of the polarization curves for these cells is the large current densities obtained, albeit at low cell voltages. These current densities,  $\sim 100 \text{ mA cm}^{-2}$ , are orders of magnitude greater than those reported earlier [6], and are a consequence of the use of efficient fuel-cell electrodes which can probably be improved significantly. Thus there is incentive for further investigation into the use of  $\text{SO}_2/\text{O}_2$  electrogenerative cells where low voltage d.c. electricity is produced.

Further work is continuing in order to determine the effect of  $\text{SO}_2$  and  $\text{O}_2$  concentrations on cell performance. Such information should allow an assessment of the potential applications of the  $\text{SO}_2/\text{O}_2$  electrogenerative reactor.

### Acknowledgement

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