

# Low temperature electrochemical oxidation of sulfur dioxide

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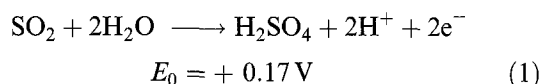
Received 26 May 1995; revised 10 December 1995

The low temperature electrochemical oxidation of sulfur dioxide on carbon gas diffusion electrodes modified with cobalt phthalocyanine (CoPc) was studied. It was found that when operating with mixtures of air containing up to 20% by volume SO<sub>2</sub> a basic problem of the electrooxidation of SO<sub>2</sub>, namely its permeation into the electrolyte, can be resolved. It is demonstrated that sulfur dioxide can be oxidized in the presence of air on active carbon, modified with cobalt phthalocyanine without external current at room temperature. The electrocatalytic character of the process is established and the rate dependence on the concentrations of H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub> up to 0.30 vol % in air is displayed. An original method for the 'cold oxidation' of SO<sub>2</sub> to sulfuric acid is proposed.

## 1. Introduction

The properties of sulfur dioxide, and more specifically its oxidation to sulfur trioxide, have been well studied [1]. Electrochemical oxidation of SO<sub>2</sub>, usually on noble metals electrodes and their oxides, has been studied since the early 1930s [2–4]. The mechanism of the electrochemical oxidation of sulfur dioxide was investigated on platinum [5], gold [6] and graphite [7] electrodes. The investigations on platinum revealed two possible oxidation mechanisms; first, a direct electron transfer at low anodic polarization; and second, oxidation of the sulfur dioxide by the surface metal oxides at higher anodic polarization.

Using model carbon gas diffusion electrodes (g.d.e.) catalysed with cobalt dibenzotetraazaanulene (CoTAA), Tarasevich *et al.* [8] have shown that at low SO<sub>2</sub> concentrations in sulfuric acid solutions (1–10 N H<sub>2</sub>SO<sub>4</sub>) the oxidation reaction order is close to 1. At medium concentrations the reaction order becomes fractional. Tarasevich *et al.* assumed that, in the potential range 0.2–1.0 V vs RHE, the most probable reaction, leading to the formation of sulfuric acid, is



The oxidation of SO<sub>2</sub> on carbon g.d.e. catalysed with cobalt chelates was studied in this laboratory [9]. The results revealed that these electrodes possess good electrochemical characteristics. A substantial drawback is their considerable permeability with respect to SO<sub>2</sub>. Attempts to remove this defect by modification of the electrode design [10] or by adding KI to the electrolyte [11] were not successful.

The aim of the present work is to resolve the problem for the complete oxidation of SO<sub>2</sub> on g.d.e. when using SO<sub>2</sub> gas mixtures.

## 2. Experimental details

The carbon g.d.e. used in the present investigation were developed in the Central Laboratory of Electrochemical Power Sources [10]. The electrode is bilayered and consists of diffusion layer of hydrophobic carbon black, (XC-30), with a loading of 100 mg cm<sup>-2</sup> and an active layer containing 40 mg cm<sup>-2</sup> of catalyst and 18 mg cm<sup>-2</sup> of XC-30. The carbon black is hydrophobized with Teflon [12]. The catalyst used was either CoPc, deposited on activated carbon [13] or pure Norit-NK.

The measurements were carried out in a three-electrode cell (Fig. 1) with 4.5 N H<sub>2</sub>SO<sub>4</sub> either under potentiostatic or galvanostatic conditions using a 'Radelkis' potentiostat. The geometric surface area of the electrodes was 10 cm<sup>2</sup>. In some cases a filter-press type cell, where the anode and cathode spaces were separated by a Nafion<sup>®</sup> membrane, was used. Larger electrodes of 200 cm<sup>2</sup> were applied for the more accurate measurements of the concentrations of the sulfur dioxide at the inlet and the outlet of the gas chamber of the electrochemical cell, as well as the concentration of the sulfuric acid. During the latter measurements the electrolyte was circulating with the aid of a peristaltic pump and its volume was comparatively small, 400 ml.

The counter electrode was of tungsten carbide–WC [14], and the reference was (Hg/Hg<sub>2</sub>SO<sub>4</sub>) in 4.5 N H<sub>2</sub>SO<sub>4</sub>. The potential was measured by a digital voltmeter or recorded on a Servogor RE 511 instrument. All potentials in this paper are referred to the potential of the hydrogen electrode in the same solution. Sulfur dioxide was used either in the pure state or as gaseous mixtures with air or argon. When working with SO<sub>2</sub>–Ar mixtures the electrolyte was bubbled with argon to avoid the effect of dissolved oxygen. The gases were supplied from cylinders and mixed in

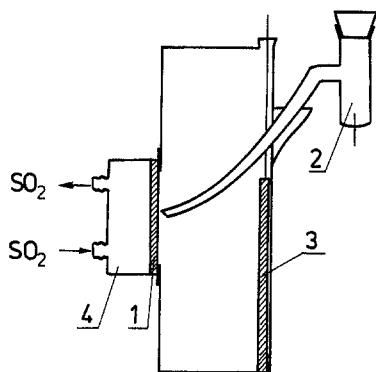


Fig. 1. Design of the electrochemical cell used in testing gas diffusion electrodes. Key: (1) gas diffusion electrode; (2) reference electrode; (3) counter electrode; (4) gas chamber.

a 'Brooks 5850' device which ensures the necessary constant  $\text{SO}_2$  concentration in the gas mixture. All measurements were carried out at room temperature.

### 3. Results and discussion

The degree of oxidation (DO) is defined as the ratio of the amount of oxidized  $\text{SO}_2$  on the g.d.e. to the total amount of  $\text{SO}_2$  entering the electrode (there is a difference between the amount of  $\text{SO}_2$  introduced to the gas chamber of the cell and the amount entering the electrode — only part of the  $\text{SO}_2$  enters the g.d.e.):

$$\text{DO} = \frac{M_{\text{ox}}}{M_{\text{tot}}} \times 100\% \quad (2)$$

The amount of oxidized  $\text{SO}_2$  is determined by the number of faradays passed through the g.d.e. during the experiment, assuming a 100% coulombic efficiency.  $M_{\text{tot}}$  is the sum of  $M_{\text{ox}}$  and the amount of  $\text{SO}_2$  passed into the electrolyte, which is assessed by iodometric titration.

Figure 2 presents the current density and the oxidation degree as a function of the  $\text{SO}_2$  concentration in the gas mixture (air +  $\text{SO}_2$ ) at constant potential,

$E = 750 \text{ mV vs RHE}$ , at which the electrodes show stable performance during long term tests [10]. It is seen that at  $\text{SO}_2$  concentrations of 25 and 50 vol % the current densities attained are 50 and  $80 \text{ mA cm}^{-2}$ , respectively. The second curve in Fig. 2 reveals that for up to 20 vol %  $\text{SO}_2$  the DO is 100%. This result is very important since it makes it possible to solve the basic problem in the oxidation of  $\text{SO}_2$  on the g.d.e., that is, to eliminate the permeation of  $\text{SO}_2$  in the catholyte. This is accompanied by a decrease in the current density at constant potential.

As mentioned above, the capability of the g.d.e. to operate at low partial  $\text{SO}_2$  pressures is of practical significance from the ecological point of view. Since the  $\text{SO}_2$  concentration in the waste gases of many chemical processes is below 1% by volume detailed measurements were performed at these low concentrations. Figure 3 presents the polarization curves for the oxidation of  $\text{SO}_2$  at 0.24 and 1% by volume on g.d.e. catalyzed with Norit + CoPc and with Norit only. At  $E = +750 \text{ mV vs RHE}$  the current density is 1.5 to  $2.0 \text{ mA cm}^{-2}$  for both catalysts. Norit + CoPc has high catalytic activity, the above cited current density being attained at  $\text{SO}_2$  concentrations which are four times lower than in the case of the pure Norit catalyst. These polarization curves demonstrate the capability of the g.d.e. to operate at low  $\text{SO}_2$  concentrations, whereby the penetration of  $\text{SO}_2$  into the electrolyte (see Fig. 2) is avoided. In this way definite amounts of waste gas (at selected low flow rates of the gas in the gas chamber) can be purified. Figure 4 shows the relationship between the degree of  $\text{SO}_2$  removal by a g.d.e. with  $200 \text{ cm}^2$  surface area and the flow rate of the gas mixture ( $\text{SO}_2 + \text{air}$ ) supplied to the electrode. The degree of  $\text{SO}_2$  removal, or the purification of the gas mixtures from  $\text{SO}_2$ , is defined as

$$x = \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}}\right) \times 100\% \quad (3)$$

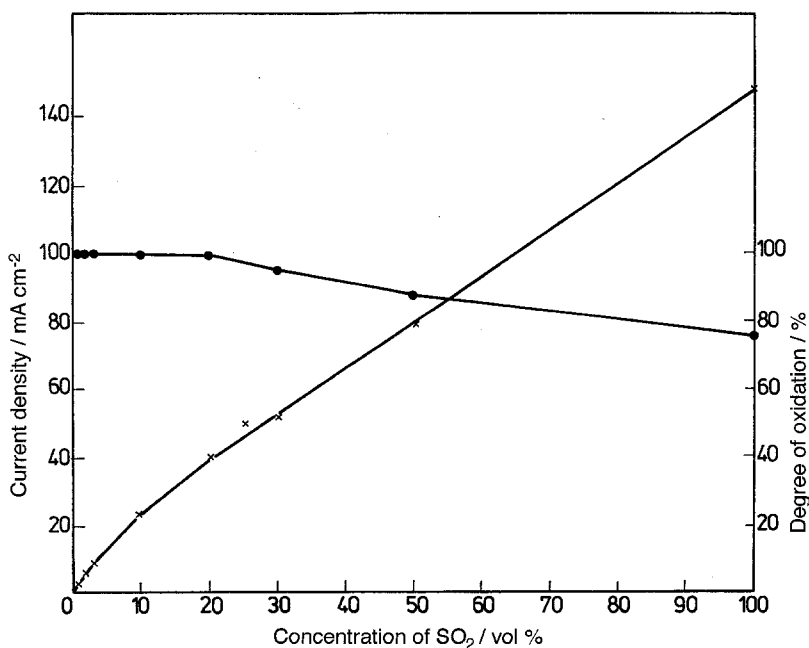


Fig. 2. Dependence of the current density (x) and the degree of oxidation (●) on the  $\text{SO}_2$  concentration in the gas mixtures (air +  $\text{SO}_2$ ) at a constant potential;  $E = 750 \text{ mV vs RHE}$ ;  $t = 25^\circ\text{C}$ ;  $4.5 \text{ N H}_2\text{SO}_4$ ; catalyst: Norit-NK/CoPc.

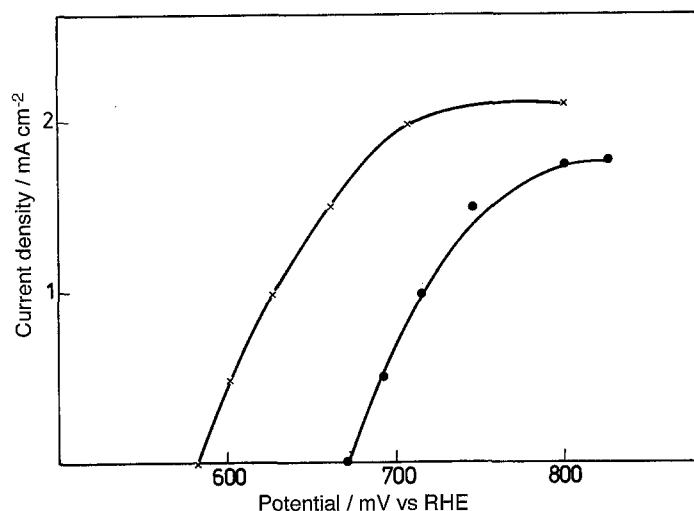


Fig. 3. Polarization curves of gas diffusion electrodes operating with  $\text{SO}_2$  + air mixtures;  $t = 25^\circ\text{C}$ ;  $4.5\text{N H}_2\text{SO}_4$ ; (●) Norit-NK + CoPc,  $0.24\text{ vol } \%$   $\text{SO}_2$ ; (x) Norit-NK,  $1\text{ vol } \%$   $\text{SO}_2$ .

where  $C_{\text{out}}$  is the  $\text{SO}_2$  concentration at the outlet of the gas chamber and  $C_{\text{in}}$  at the inlet. The electrode potential was maintained at  $750\text{ mV vs RHE}$ . The attained current density of about  $2\text{ mA cm}^{-2}$  varied insignificantly with the flow rate of the gas mixture. It is seen that under these conditions the electrode removes 50 to 70% of  $\text{SO}_2$  from the waste gas with an initial concentration of  $1\%$   $\text{SO}_2$ . This represents a considerable ecological effect, even when using the less active catalyst Norit-NK. Detailed information on the performance of the mixed catalyst Norit + CoPc in the removal of  $\text{SO}_2$  from waste gases were reported earlier [15].

An interesting result was observed during the above experiments: namely, that there was no quantitative relationship between the amount of the oxidized  $\text{SO}_2$  and the electric charge passed through the electrode for a certain period of time. It was found that the  $\text{H}_2\text{SO}_4$  concentration in the electrolyte increased at a rate higher than that corresponding to the amount of the oxidized  $\text{SO}_2$  by the external applied current. This suggests, that part of the  $\text{SO}_2$  entering the cell is oxidized by another mechanism, that is, not by the applied external current.

To elucidate this phenomenon the experimental polarization curve was compared with the polarization

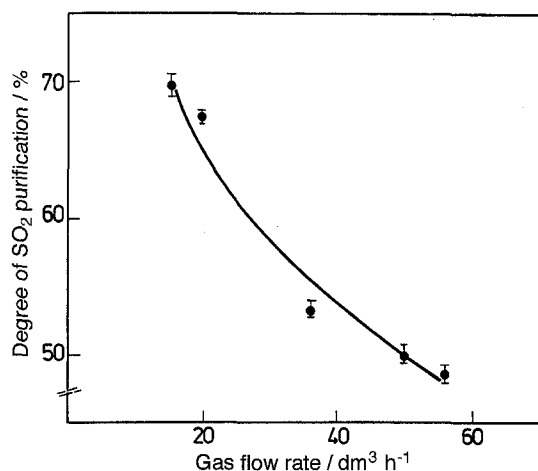


Fig. 4. Dependence of the degree of  $\text{SO}_2$  purification on the low rate of the gas mixture supplied to the electrode at a constant potential;  $E = 750\text{ mV vs RHE}$ ;  $t = 25^\circ\text{C}$ ;  $4.5\text{N H}_2\text{SO}_4$ ; g.d.e.:  $S = 200\text{ cm}^2$ ;  $1\text{ vol } \%$   $\text{SO}_2$  in air;  $i \approx 2\text{ mA cm}^{-2}$ .

curve in which the current was calculated from the rates of the oxidation of  $\text{SO}_2$  determined by chemical analysis. The two curves are shown in Fig. 5 where (a) is from the experimentally obtained  $I/E$  curve and (b) is from calculated current values. The current corresponding to the total amount of  $\text{SO}_2$  oxidized at the g.d.e. was determined by two independent methods:

(i) by the difference of the  $\text{SO}_2$  concentration in the gas mixture at the inlet and outlet of the gas chamber of the cell at a constant gas mixture flow rate,  $50\text{ dm}^3\text{ h}^{-1}$ , using Faraday's laws:

$$I = \frac{\Delta N_{\text{SO}_2} F}{\Delta t} \quad (4)$$

where  $\Delta N_{\text{SO}_2}$  are the gram equivalent of  $\text{SO}_2$ , oxidized over the time period,  $\Delta t$ . These measurements were performed several times during the experiment and yielded constant values within the limits of the error inherent in the iodometric titration method, which in our case was  $\pm 2\%$ . This comparatively small error was achieved in the electrochemical cell with a  $200\text{ cm}^2$  g.d.e. as mentioned in the experimental details.

(ii) by the difference of the  $\text{H}_2\text{SO}_4$  concentration in the electrolyte at the start and the end of the experiment at a constant volume,  $400\text{ ml}$ . This difference was interpreted as a current using Equation 4.

The data from the two methods agree well as shown in Table 1.

The juxtaposition of the two curves in Fig. 5 shows that they differ significantly. A considerable amount of  $\text{SO}_2$  is oxidized without the aid of the externally applied current. This is particularly obvious for the point where  $I = 0$ , that is, no-external current is

Table 1. Comparison of the amounts of oxidized  $\text{SO}_2$

$I_{\text{far}}$ /mA	Initial $C_{\text{SO}_2}$ /vol %	Final $C_{\text{SO}_2}$ /vol %	$\Delta N_{\text{SO}_2}$ for 5 h /g equiv.	Current ( $\text{SO}_2$ ) /mA	$\Delta N_{\text{H}_2\text{SO}_4}$ for 5 h /g equiv*	Current ( $\text{H}_2\text{SO}_4$ ) /mA
0	1.050	0.705	0.077	412	0.0774	414
100	1.050	0.701	0.078	418	0.0785	419
440	1.050	0.638	0.092	498	0.0917	498

\* The initial concentration of  $\text{H}_2\text{SO}_4$  was between 3 and  $8\text{ g equiv. dm}^{-3}$ .

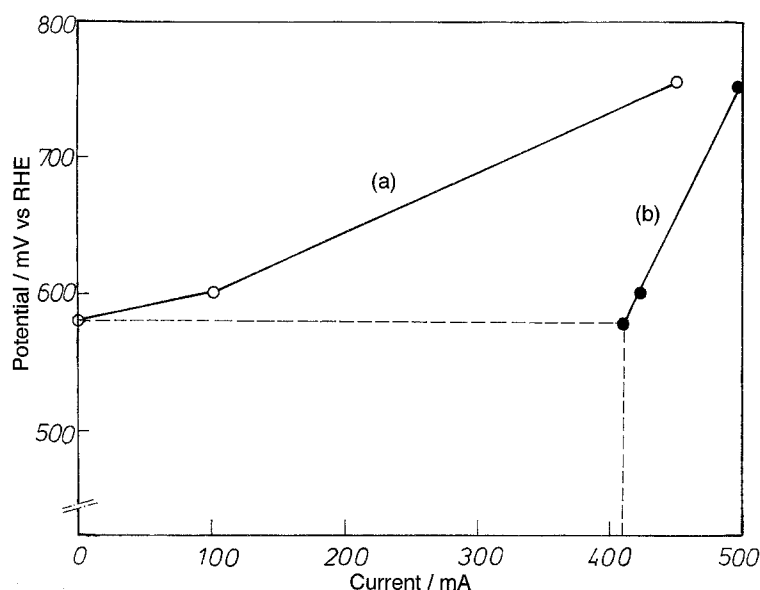
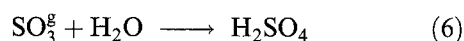
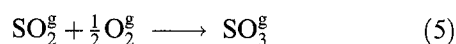


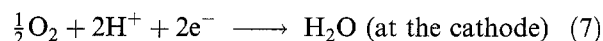
Fig. 5. Polarization and calculated curves of gas diffusion electrodes operating with  $\text{SO}_2$  + air mixtures;  $t = 25^\circ\text{C}$ ;  $4.5\text{N H}_2\text{SO}_4$ ; g.d.e.:  $S = 200\text{ cm}^2$ ; gas flow rate  $50\text{ dm}^3\text{ h}^{-1}$ ; 1 vol %  $\text{SO}_2$  in air; Norit-NK; curve (a): (○), externally applied constant current; curve (b): (●), total amount of  $\text{SO}_2$  converted into  $\text{H}_2\text{SO}_4$  at the g.d.e.

flowing through the electrode. In this case the  $\text{SO}_2$  oxidation rate, presented as current density, is comparatively high,  $i = 2\text{ mA cm}^{-2}$  or  $I_{\text{calc}} = 412\text{ mA}$ . The application of lower polarization does not substantially increase the amount of oxidized  $\text{SO}_2$ . At polarization higher than 100 mV  $\text{SO}_2$  is oxidized predominantly by the external current applied.

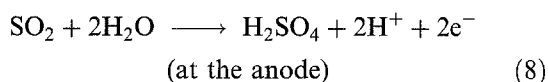
Questions arise concerning the oxidation mechanism without external current. One possible route is chemical oxidation in the gas phase [1]:



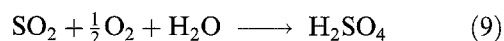
The second route is electrochemical oxidation in short-circuited microgalvanic cells in the catalytic layer of the g.d.e. In this case the reactions are [6]



and



or, overall



The oxidation in the gas phase at the catalyst surface is ruled out by the experimental fact that at room temperature  $\text{SO}_2$  does not oxidize to  $\text{SO}_3$ . The feasibility of the electrochemical oxidation mechanism of  $\text{SO}_2$  is illustrated in Fig. 6, presenting the cathodic (with oxygen as reagent) and anodic (with  $\text{SO}_2$  as reagent) polarization curves on a g.d.e. catalysed with Norit-NK + CoPc having the optimum composition with respect to oxygen reduction [12] and  $\text{SO}_2$  oxidation [9]. It is seen that the cathodic potential for oxygen reduction is more positive with respect to the anodic potential of the  $\text{SO}_2$  oxidation, whereby the  $\text{SO}_2$  oxidation reaction can proceed spontaneously with release of energy. The intercept of the two curves determines the value of the mixed

potential and the short circuit current. The shape of the curves and the coordinates of the intercept depend on the catalytic activity and the structure of the g.d.e. It is seen that the catalyst developed in this laboratory is highly active with respect to both reactions (i.e., the catalyst is bifunctional).

It may thus be postulated that the oxidation of  $\text{SO}_2$  at the g.d.e. without external current is due to numerous dispersed micro galvanic short-circuited cells (i.e., the process is electrocatalytic). This assumption was checked by plotting the partial polarization curves (anodic and cathodic), under the same conditions as those applied in plotting the polarization curve of the electrode shown in Fig. 5. The gas flow rate in this case was reduced to  $2.5\text{ dm}^3\text{ h}^{-1}$  since the geometric area of the electrode was only  $10\text{ cm}^2$ . Figure 7 presents the cathodic polarization curve (reagent air) and the anodic (reagent Ar + 1%  $\text{SO}_2$ ). The mixed potential,  $E_{\text{mix}}$  (reagent air + 1%  $\text{SO}_2$ ) when the external current is zero is denoted by  $\Delta$ .

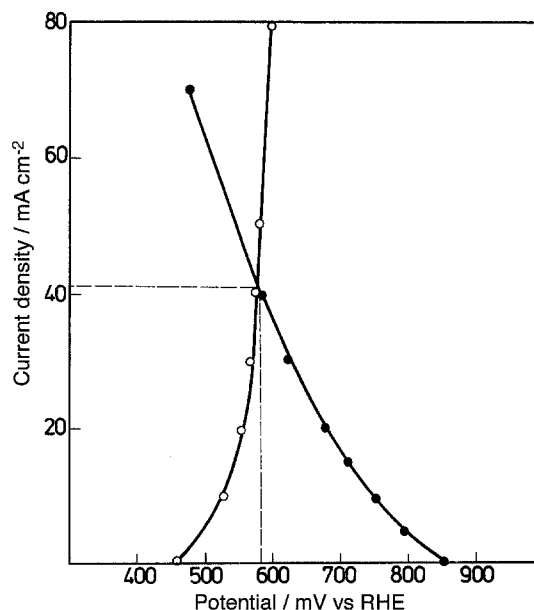


Fig. 6. Cathodic and anodic polarization curves at a gas diffusion electrode; (●) oxygen reduction; (○)  $\text{SO}_2$  oxidation;  $t = 25^\circ\text{C}$ ;  $4.5\text{N H}_2\text{SO}_4$ ; Norit-NK + CoPc.

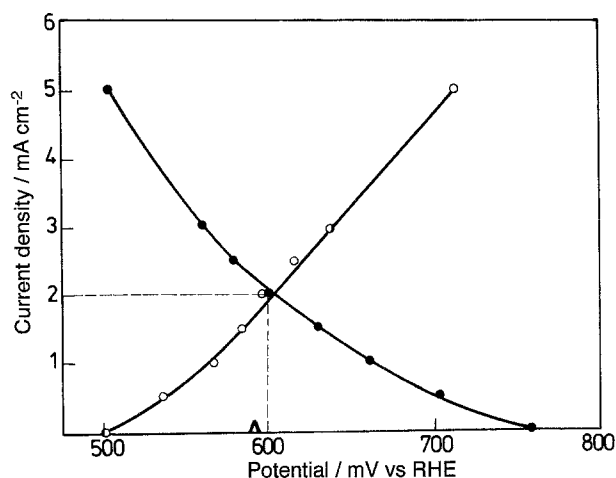


Fig. 7. Partial polarization curves of a gas diffusion electrode;  $t = 25^\circ\text{C}$ ;  $4.5\text{ N H}_2\text{SO}_4$ ; gas flow rate:  $2.5\text{ dm}^3\text{ h}^{-1}$ ; Norit-NK; (●) cathodic (reagent-air); (○) anodic (reagent Ar + 1 vol%  $\text{SO}_2$ ); ( $\Delta$ ) value of  $E_{\text{mix}}$  at  $i = 0$ .

From the intercept of the partial curves we can determine the value of the short-circuit current,  $i = 2\text{ mA cm}^{-2}$ , which is exactly the same as that calculated from the amount of oxidized  $\text{SO}_2$  for the case where no external current flows (Fig. 5). There is also a very good agreement between the potentials  $E_{\text{oc}}$  at zero current for the gas mixture air + 1%  $\text{SO}_2$  shown in Figs 5 and 7, and  $E_{\text{mix}}$ , corresponding to the intercept of the anodic and cathodic curves in Fig. 7,  $E_{\text{oc}} = E_{\text{mix}} = 590\text{--}600\text{ mV}$ .

The above findings corroborate the electrochemical mechanism of the oxidation of  $\text{SO}_2$  by atmospheric oxygen when no external current is applied.

Additional information for the mechanism of the  $\text{SO}_2$  oxidation at the bifunctional catalyst Norit-NK/CoPc can be obtained from the potential dependence of the overall current of the galvanic short-circuited cells. The shift of the potential with respect to the mixed potential in the anodic or cathodic direction increases the rate of the respective partial reaction and, consequently, the value of the overall current according to

$$i = i_a - i_k \quad (10a)$$

or, in the case of the gas mixture air +  $\text{SO}_2$ ,

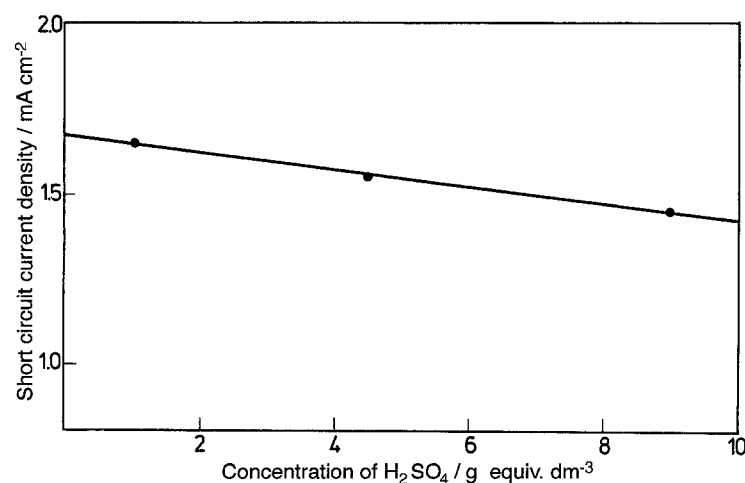


Fig. 9. Effect of the  $C_{\text{H}_2\text{SO}_4}$  on the short circuit current in the range 1 to  $10\text{ N H}_2\text{SO}_4$ ;  $C_{\text{SO}_2} = 0.24\text{ vol\%} = \text{const.}$ ;  $t = 25^\circ\text{C}$ ;  $4.5\text{ N H}_2\text{SO}_4$ ; Norit-NK + CoPc.

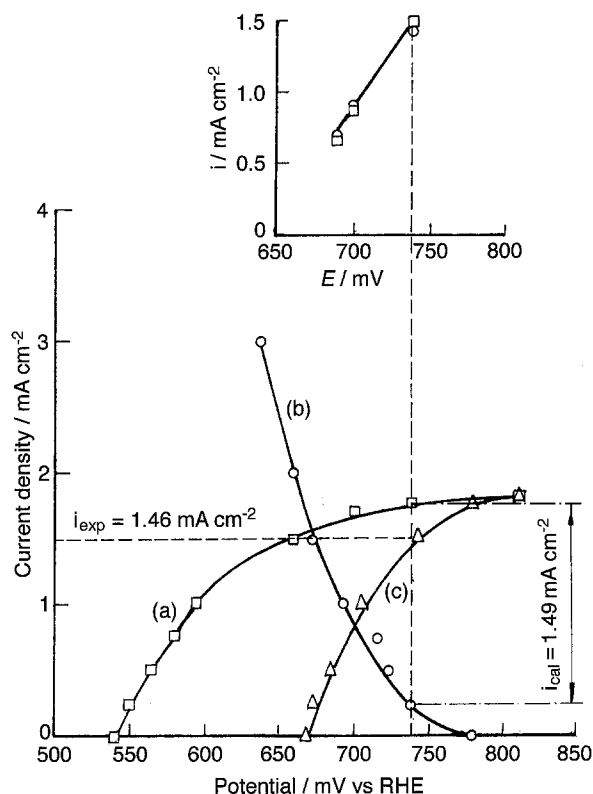


Fig. 8. (lower) Partial polarization curves of a gas diffusion electrode;  $t = 25^\circ\text{C}$ ;  $4.5\text{ N H}_2\text{SO}_4$ ; Norit-NK + CoPc; (○) cathodic (reagent-air); (□) anodic (reagent Ar + 0.24 vol%  $\text{SO}_2$ ); ( $\Delta$ ) mixed curve (reagent-air + 0.24 vol%  $\text{SO}_2$ ). (Upper) Juxtaposition of the values of (○)  $i_{(\text{air}+\text{SO}_2)}$  and (□)  $i_{(\text{Ar}+\text{SO}_2)} - i_{(\text{air})}$  calculated from the data in the upper  $i/E$  plot.

$$i_{(\text{air}+\text{SO}_2)} = i_{(\text{Ar}+\text{SO}_2)} - i_{(\text{air})} \quad (10b)$$

The  $i/E$  plots at an electrode catalysed with Norit-NK/CoPc, using Ar +  $\text{SO}_2$  (curve (a)), air (curve (b)), and air +  $\text{SO}_2$  (curve (c)) are shown in Fig. 8 (lower). The  $i/E$  plot for the gas mixture air +  $\text{SO}_2$  is calculated from the partial currents at the respective potentials (from the difference  $i_{(\text{Ar}+\text{SO}_2)} - i_{(\text{air})}$ , as shown for  $E = 740\text{ mV}$ ) which is juxtaposed with the experimental ( $i_{(\text{air}+\text{SO}_2)}$ ) in Fig. 8 (upper). The good agreement between these two plots confirms the validity of the electrochemical mechanism of the oxidation of  $\text{SO}_2$  in the potential range studied.

Finally, an attempt was made to study the influence of the basic parameters on the rate of the process.

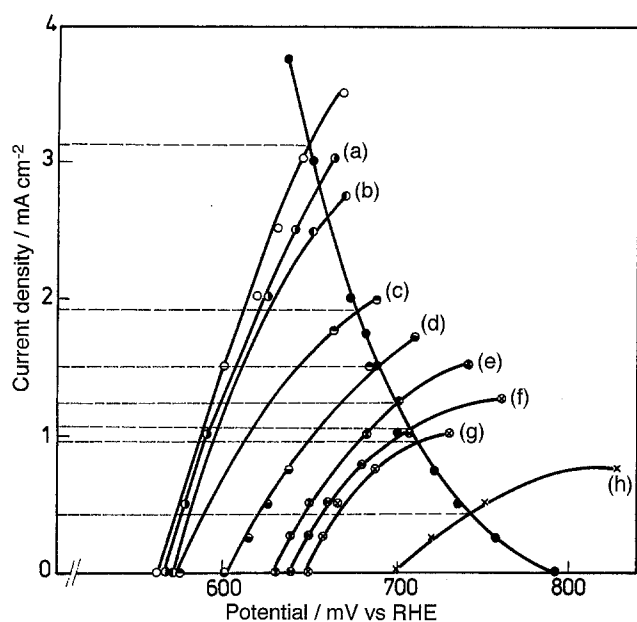


Fig. 10. Partial polarization curves of a gas diffusion electrode;  $t = 25^\circ\text{C}$ ;  $4.5\text{ N H}_2\text{SO}_4$ ; Norit-NK + CoPc; (●) cathodic (reagent-air); (○) anodic (reagent Ar + 1.0 vol %  $\text{SO}_2$ ). Key: (a) anodic with 0.8%  $\text{SO}_2$ ; (b) anodic with 0.6%  $\text{SO}_2$ ; (c) anodic with 0.3%  $\text{SO}_2$ ; (d) anodic with 0.24%  $\text{SO}_2$ ; (e) anodic with 0.20%  $\text{SO}_2$ ; (f) anodic with 0.16%  $\text{SO}_2$ ; (g) anodic with 0.13%  $\text{SO}_2$ ; (h) anodic with 0.06%  $\text{SO}_2$ .

According to Appleby [16] and Tarasevich [8] these are the  $\text{SO}_2$  concentrations (we studied concentrations lower than 1.0 vol %, as in waste gases) and the concentration of  $\text{H}_2\text{SO}_4$ . The effect of  $C_{\text{SO}_2}$  and  $C_{\text{H}_2\text{SO}_4}$  was studied by measuring the 'short circuit' current, determined by the intercept of the anodic (reagent Ar +  $\text{SO}_2$  at various concentrations) and cathodic (reagent air) polarization curves at constant  $C_{\text{H}_2\text{SO}_4}$  and  $C_{\text{SO}_2}$ , respectively. As expected [6, 16] the experiment showed (Fig. 9) that the influence of  $C_{\text{H}_2\text{SO}_4}$  at constant  $C_{\text{SO}_2} < 1$  vol %, in the 1–10 N  $\text{H}_2\text{SO}_4$  range is very slight.

Figure 10 presents the partial polarization curves at various  $C_{\text{SO}_2}$ . It is seen that the intercepts of the anodic ( $\text{SO}_2$ ) and cathodic (air) partial curves are in the region of the transition from activation to transport control, whereby limiting currents are not attained. This is illustrated by the Tafel plots in Fig. 11 of part of the anodic partial polarization curves from Fig. 10. They do not exhibit a linear region, which is indicative of mixed kinetic control of the anodic oxidation of  $\text{SO}_2$ . The values of the short circuit currents from Fig. 10 are presented as a function

of the  $\text{SO}_2$  concentration in Fig. 12. The curve has an exponential character. The theoretical analysis of the  $i/C_{\text{SO}_2}$  and  $i/C_{\text{H}_2\text{SO}_4}$  relationships requires the knowledge of the functions  $C_{s,j} = f(i)$ , where  $C_{s,j}$  is the surface concentration of  $\text{SO}_2$  or  $\text{H}_2\text{SO}_4$  [17]. The analytical expressions for porous systems are complex [18] and lie beyond the scope of this paper.

For up to 0.3% by volume of  $\text{SO}_2$ , the dependence is linear; this means that the relationship between the rate of  $\text{SO}_2$  oxidation and its concentration in the gas mixture, at room temperature on active carbon plus CoPc without external current source, can be expressed by the simple equation:

$$v = kC_{\text{SO}_2} \quad (11)$$

where  $v = i_{\text{SC}}/F$  is the number of gram equivalents.  $\text{SO}_2$  is oxidized for the period of time  $\Delta t$  ( $v = \Delta N_{\text{SO}_2}/\Delta t$ , see Equation 4).

The simple relation (Equation 11) is conveniently employed in the evaluation of the performance characteristics of devices for purification of waste gases containing up to 0.3% by volume of  $\text{SO}_2$  in air, operating on the present principle [15].

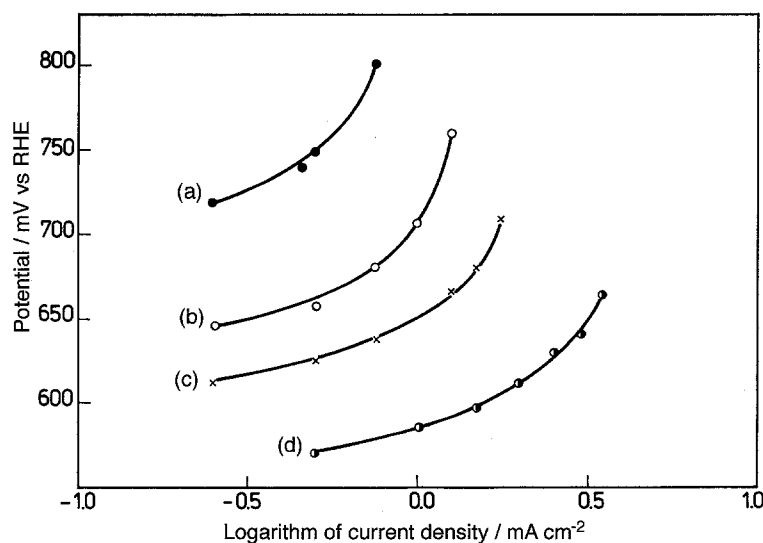


Fig. 11. Tafel plots of part of the polarization curves in Fig. 10;  $t = 25^\circ\text{C}$ ;  $4.5\text{ N H}_2\text{SO}_4$ ; Norit-NK + CoPc; (a) anodic with 0.06%  $\text{SO}_2$ ; (b) anodic with 0.16%  $\text{SO}_2$ ; (c) anodic with 0.24%  $\text{SO}_2$ ; (d) anodic (reagent Ar + 1.0 vol %  $\text{SO}_2$ ).

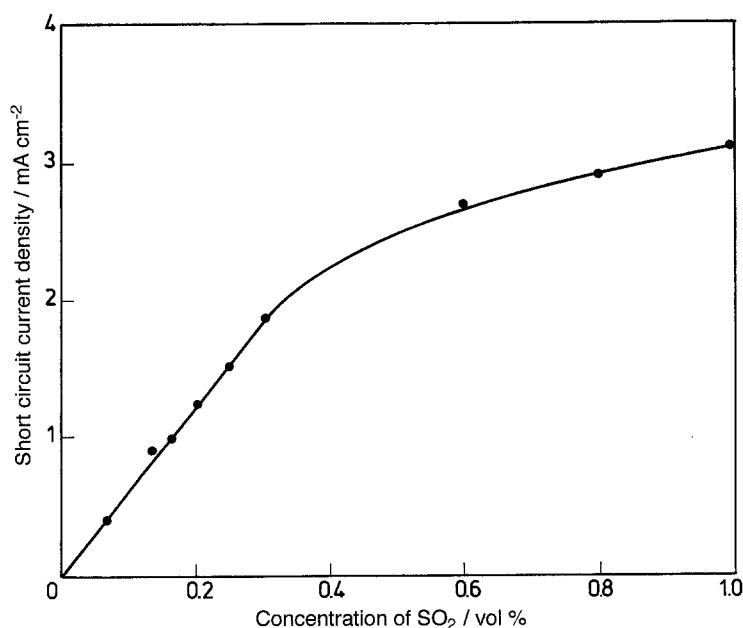


Fig. 12. Dependence of the oxidation rates (the short circuit current from Fig. 10) on the SO<sub>2</sub> concentration in the gas mixture:  $t = 25^\circ\text{C}$ ; 4.5N H<sub>2</sub>SO<sub>4</sub>; Norit-NK + CoPc.

#### 4. Conclusions

A process for oxidation of SO<sub>2</sub> in mixtures with air at gas diffusion electrodes has been studied. It is found that 100% oxidation can be achieved at SO<sub>2</sub> concentrations up to 20% by volume of SO<sub>2</sub> oxidation, at low concentrations in air on the catalyst active carbon + CoPc, without the application of external current. The mechanism of the process has been elucidated and its electrocatalytic character revealed. The dependence of the rate of oxidation on the concentration of SO<sub>2</sub> has also been determined. A linear relationship between the rate of oxidation and SO<sub>2</sub> concentration up to 0.3% by volume SO<sub>2</sub> in air was found. Thus, based on these results, a novel method for the purification of SO<sub>2</sub> from waste gases is proposed.

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