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ELECTROCHEMISTRY OF FUMING SULPHURIC ACIDS—III. MECHANISM OF THE CATHODIC REACTIONS ON PLATINUM*

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Abstract—The cathodic potential-decay process on platinum electrodes in oleums has been investigated by means of a rotating disk. The non-steady parameters are compared with those already reported under steady-state conditions. Both results are discussed in terms of a general reaction mechanism comprising various consecutive as well as alternative steps, considering that the main cathodic product is sulphur dioxide. The SO_3-containing species acts as a depolarizer by reacting with hydrogen atoms adsorbed on the electrode surface.

Résumé—Le processus cathodique de décroissance du potentiel de l'électrode de platine dans les oleums a été étudié au moyen d'un disque tournant. Les paramètres non-stationnaires sont comparés avec ceux qui furent obtenus dans conditions stationnaires. Les deux résultats sont discutés avec un mécanisme de réaction général comprenant plusieurs étapes consécutives et alternatives, considérant que le produit cathodique principal est l'anhydride sulfureux. L'espèce contenant du SO_3 agit comme dépolarisateur en réagissant avec les atomes d'hydrogène adsorbés sur la surface de l'électrode.

Zusammenfassung—Es wurde der kathodische Verfallprozesse der Elektrodenspannung in Oleum an einer sich drehenden Platin scheiben Elektrode untersucht. Die nicht-stationnären Parameter werden mit den im stationnären Zustand erhaltenen verglichen. Beide Ergebnisse werden in Rahmen ein allgemeiner Reaktionsmechanismus welcher verschiedene aufeinanderfolgende sowie auch abwechselnde Schritte besprochen, wobei berücksichtigt wird, dass das Hauptprodukt Schwefeldioxyd ist. Die SO_3-enthaltende Verbindung wirkt als Depolarisator indem sie mit den auf der Elektrodenoberfläche absorbierte Wasserstoffatomen reagiert.

INTRODUCTION

In previous publications[1–3] the different processes occurring in the electrolysis of oleums at platinum electrodes were described. It was shown that the main cathodic process comprising the reduction of the SO_3-containing species to sulphur dioxide was an activated process involving a large overvoltage. The mechanism of the activated electrode process however, could not be definitely established and only the potential region where the reaction is controlled by a convective–diffusion process could be analysed in detail. Thus an interpretation of the limiting current, directly proportional to the "free" sulphur trioxide content in the fuming acid, could be presented.

The reaction occurring at potentials where no appreciable interference by the convective–diffusion process occurs, deserves further study to determine the cathodic reaction mechanism.

Steady cathodic current/voltage measurements on a platinum rotating disk[3] have shown that Tafel regions exist which are nearly independent of the speed of rotation of the working electrode, but from the corresponding Tafel slopes no straightforward interpretation of the reaction, in terms of some possible reaction mechanism, could be advanced. Therefore, in order to get a better knowledge of the cathodic process, some experiments were envisaged employing a rotating platinum disk electrode under

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non-steady conditions, to measure in particular the cathodic overvoltage decay under different experimental conditions. These results complement those obtained under steady-state conditions, making it possible to apply mechanistic criteria for all the processes occurring at the cathode during the electrolysis of the fuming sulphuric acids on platinum electrodes.

EXPERIMENTAL TECHNIQUE

The experimental arrangement to determine overvoltage decay was the same as that already described.[4] However, the working electrode was a bright platinum rotating disk mounted and operated as mentioned elsewhere.[5] Its geometrical area was $7{\cdot}06 \times 10^{-2}$ cm^2. Fuming sulphuric acid (C. Erba) was used. The SO_3 concentration was varied between 7·7–27%, although most of the experiments were made with acid of 27% SO_3 content in order to get the highest limiting cd and to avoid the interference of the convective–diffusion process. Experiments were performed at 25°C and rotation speeds from *ca* 600 to 2000 rev/min.

RESULTS

Steady cathodic current/voltage curves were measured before a set of build-up and decay curves was recorded in order to compare them directly. Semilogarithmic plots of current/voltage characteristics are shown in Fig. 1, where the electrode potential E is corrected for the pseudo-ohmic drop, IR. The latter was obtained from the initial instantaneous drop read on the potential/time oscilloscope traces.

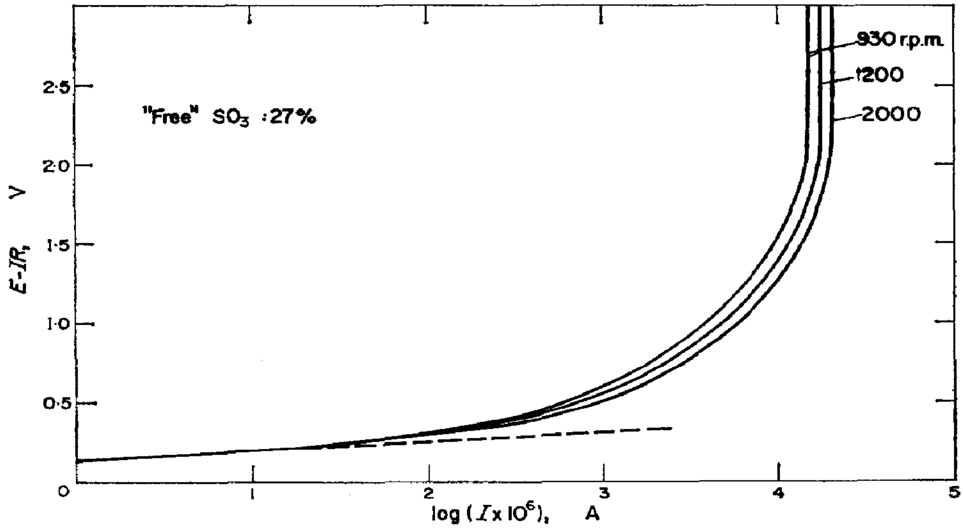

FIG. 1. Semilogarithmic plot of current/voltage curves at different rotation speeds. 25°C. Dotted line corresponds to a slope of 2·3(RT/F) V.

At low electrode potential there is a Tafel slope very close to 2·3 (RT/F) but in the intermediate electrode potential region no definite Tafel slope could be obtained, the slope increasing continuously until the limiting cd was reached. As the electrode potential increases, the effect of the rotation speed of the working electrode becomes appreciable. The parameters deduced from the current/voltage characteristics coincide with those already reported.[3] The Tafel region shifts along the log I co-ordinate when the SO_3 concentration increases, as shown in Fig. 2. The order of reaction with

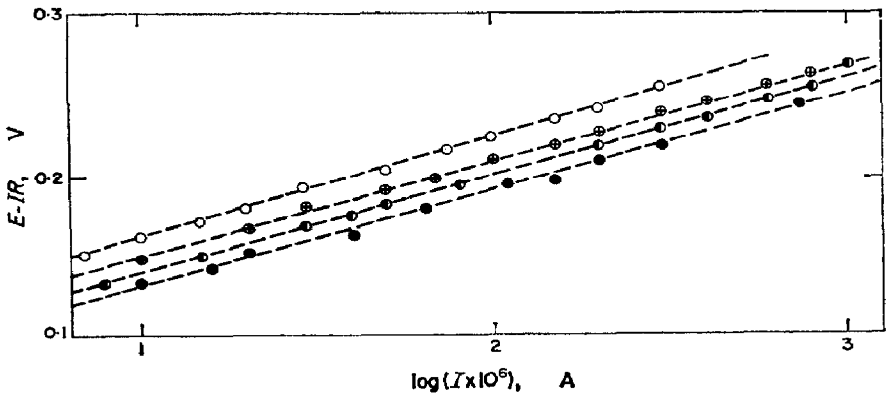

FIG. 2. Semilogarithmic plots of current/voltage curves at different SO_3 concentrations. 25°C. ○, 7·7%; ⊕, 14%; ◐, 19%; ●; 27%.

respect to the SO_3 concentration, derived from these plots at constant $E - IR$, is very close to 1.

Potential-decay curves are semilogarithmically plotted as shown in Figs. 3–6 for four different rotation speeds. Three regions are distinguishable in these plots. Initially the slope $\partial E/\partial(\log t)$ is very small; it approaches zero when t approaches zero. The extent of this first region depends on the cd at interruption; it diminishes as the latter increases. The middle region shows a linear dependence between electrode potential and log t, and a decay slope $b_d = \partial E/\partial(\log t)$ can be definitely established. Finally as t approaches infinity the electrode potential becomes again time-independent.

The final electrode potentials obtained after interrupting the electrolysis current increase as the cd increases. This is an indication of a residual polarization at the cathode, which causes the marked increase of the Tafel slope obtained from the steady current/voltage curves at high cds. This may be due to reduction by atomic hydrogen of some sulphur-containing species present in the electrolyte to sulphur.

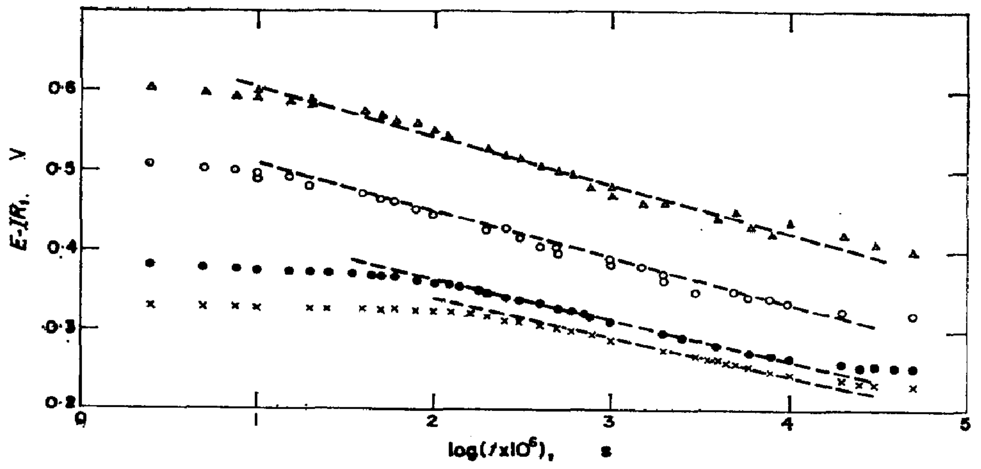

FIG. 3. Semilogarithmic plot of cathodic overvoltage decay after interrupting electrolysis current. 666 rev/min. 25°C. ×, 0·20 mA; ●, 0·5 mA; ○, 2·0 mA; △, 5·0 mA.

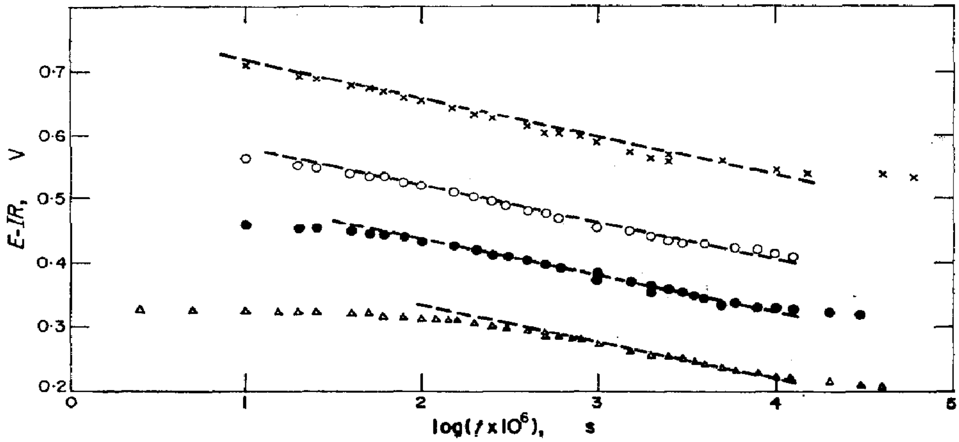

FIG. 4. Semilogarithmic plot of cathodic overvoltage decay after interrupting electrolysis current. 930 rev/min. 25°C. △, 0·25 mA; ×, 4·0 mA; ●, 1·0 mA; ○, 2·0 mA.

This residual polarization dissappears quite slowly, depending on the sulphur dissolution rate in the oleums. If only the linear $E/\log t$ region of slope RT/F is supposed to be actually related to the electrochemical reduction of the SO_3-containing species, it is possible to reconstruct a steady Tafel plot having a slope close to RT/F over a larger cd range than those shown in Fig. 1. These features of cathodic electrode potential decay were repeatedly obtained at the various rotation speeds employed.

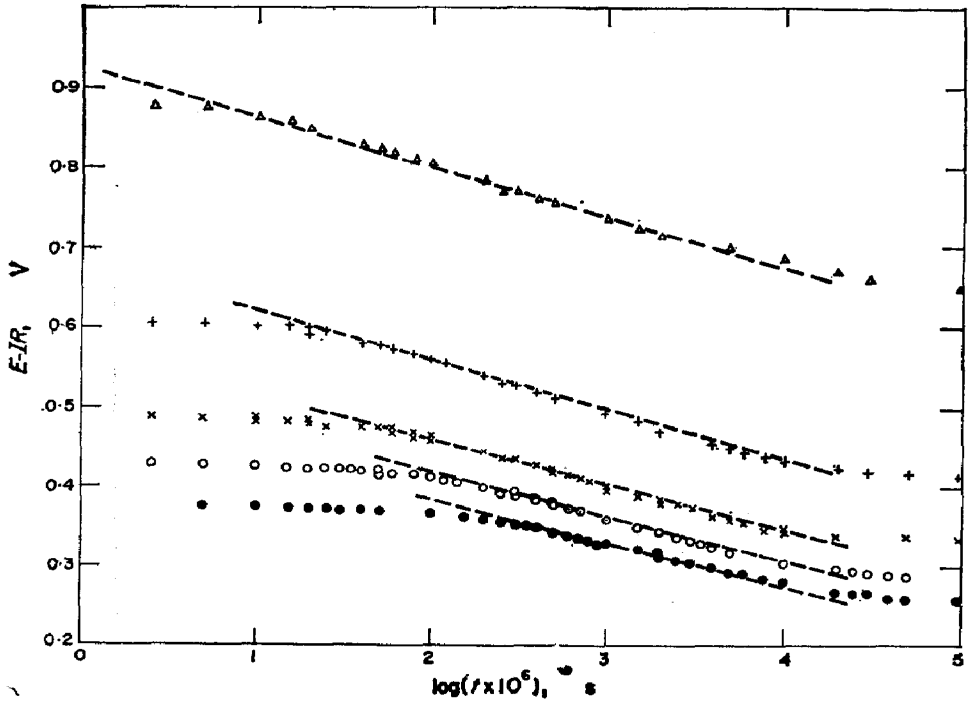

FIG. 5. Semilogarithmic plot of cathodic overvoltage decay after interrupting electrolysis current. 1200 rev/min. 25°C. ●, 0·25 mA; ○, 0·50 mA; ×, 1·0 mA; □, 2·0 mA; △, 5·0 mA.

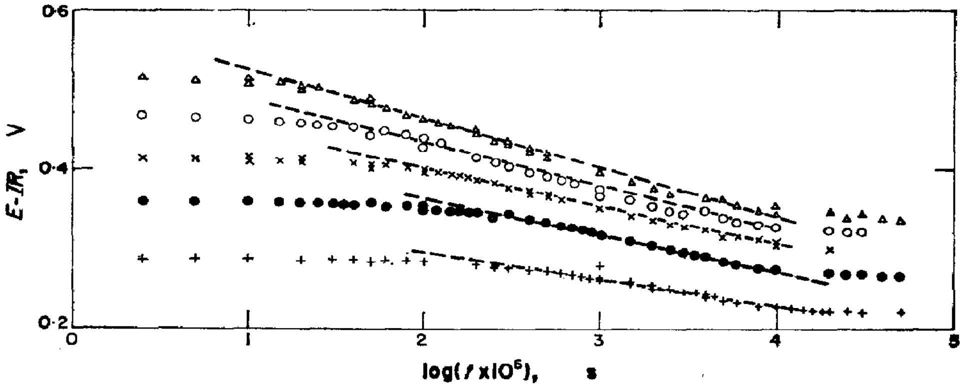

Fig. 6. Semilogarithmic plot of cathodic overvoltage decay after interrupting electrolysis current. 1600 rev/min. 25°C. +, 0·1 mA; ●, 0·25 mA; ×, 0·50 mA; ○, 1·0 mA; △, 2·0 mA.

Parameters deduced from decay curves are shown in Table 1. The initial current, I, the electrode potential corrected for the pseudo-ohmic drop, $E - IR$, the time t' corresponding to the extrapolation of the line with slope b_a, at the initial electrode potential, and the experimental differential electrode capacitance, C, are assembled in Table 1. In the range of electrode potential investigated, C is practically potential-independent. The decay slope at high electrode potential is close to $2{\cdot}3(RT/F)$ V.

Table 1

$I \times 10^3$ A	$(E - IR)$ V	$t' \times 10^6$ s	b_a V	C μF/cm^2
		660 rev/min		
0·20	0·330	120	0·050	15·6
0·50	0·380	51·0	0·051	16·3
2·00	0·505	12·0	0·058	13·5
5·00	0·635	5·9	0·059	13·9
		930 rev/min		
0·25	0·327	100	0·053	15·4
1·00	0·465	25·5	0·055	15·1
2·00	0·565	12·5	0·060	13·6
4·00	0·730	7·1	0·065	14·3
		1200 rev/min		
0·25	0·377	100	0·055	15·0
0·50	0·430	47·9	0·058	13·5
1·00	0·490	25·4	0·060	14·0
2·00	0·610	12·6	0·060	13·7
5·00	0·880	5·0	0·060	13·2
		1600 rev/min		
0·10	0·290	140	0·034	13·5
0·25	0·365	97·0	0·048	12·0
0·50	0·420	40·0	0·050	13·1
1·00	0·470	22·9	0·056	13·3
2·00	0·520	12·6	0·062	13·3
5·00	0·685	5·7	0·062	15·0

The electrode differential capacitance obtained from the initial slope of galvanostatic build-up curves is about 3 $\mu F/cm^2$, a figure lower than those already reported at the various cathode potentials.

DISCUSSION

As already reported,[2] the main product of the cathodic reaction is sulphur dioxide, which dissolves in the oleums without chemical interaction.[6] Sulphur and hydrogen gas are also formed as minor products. Their relative yields increase at high negative potentials. Sulphur dissolves in the oleums producing a blue colour in the catholyte. The mechanism of the electrode reaction should comprise the possibility of the formation of all these substances.

The results obtained from the cathode potential decay indicate that the decay process is independent of any convective–diffusion polarization in the potential region preceding the establishment of the limiting cd, and the decay slope which is likely to be related to the cathodic reaction is RT/F. This coincides with the Tafel slope at low cathodic polarization. Therefore, the electrochemical double-layer discharge process is probably governed by the same mechanism prevailing during the steady electrode process.

To postulate a reaction scheme on the basis of the kinetic results reported above, the following additional fact must be emphasized. There is a first-order dependence of cd on the concentration of the sulphur trioxide containing species in the region of activated overvoltage. Then, there are two simple possibilities to consider, namely either a reaction scheme involving a simultaneous 2-electron transfer process as rate-determining, or one where the reaction proceeds *via* an intermediate species, such as a hydrogen adatom, under Temkin adsorption conditions. The first possibility must be discarded, because a rate-determining step involving the straightforward electrochemical reduction of any SO_3-containing ion is unlikely. The second possibility is more reasonable and involves only one electron-transfer process with the participation of a solvated proton under any of the existing forms in the oleums. The final reactions of the hydrogen adatoms yielded by the primary step would be responsible of the final products formed. Thus the following reaction scheme can be postulated,

$$(H^+)_{solv} + Pt(e) = Pt(H), \tag{1}$$

$$2Pt(H) + (SO_3)_{solv} = SO_2 + H_2O + 2Pt, \tag{2}$$

$$Pt(H) + Pt(H) = H_2 + 2Pt, \tag{2a}$$

$$4Pt(H) + SO_2 \rightarrow S + 2H_2O, \tag{2b}$$

$$S + H_2S_2O_7 \rightarrow \text{Blue-tinged solution}, \tag{3}$$

$$H_2O + H_2S_2O_7 = 2H_2SO_4. \tag{4}$$

From the hydrogen-electrode studies in aqueous solutions and in ionic melts with hydrogen-containing ions[7–10] it can be assumed that reaction (1) is a fast process on platinum and that the surface coverage by hydrogen adatoms is already appreciable at low overvoltages. Therefore, step (1) must be discarded as the rate-determining step. On the other hand, there is no easy explanation for the slope RT/F if step (1) is rate-determining.

Steps (2), (2a) and (2b) correspond to alternative reactions involving hydrogen adatoms. However reaction (2b) can occur only if either sulfur dioxide is initially present in the solution or if reaction (2) has occurred. Reaction (2b) may be neglected as far as the electrode process occurring at low cathode potentials is concerned. Therefore, following reaction (1) only two important steps are left; these are reactions (2) and (2a) and as they are alternative steps the fastest reaction path prevails. As a matter of fact cathodic efficiencies[3] show that step (2) predominates over step (2a).

The occurrence of step (2) as rate-determining step at low cathodic potentials does not necessarily mean that it occurs as a three-particle reaction. It may also comprise two partial reactions as follows:

$$\mathrm{Pt(H)} + (\mathrm{SO_3})_{\mathrm{solv}} = \mathrm{Pt(HSO_3)} \tag{2-I}$$

and

$$\mathrm{Pt(HSO_3)} + \mathrm{Pt(H)} = \mathrm{SO_2} + \mathrm{H_2O} + 2\ \mathrm{Pt}. \tag{2-II}$$

Steps (2-I) and (2-II) involves the participation of the intermediate $(\mathrm{SO_3H})\mathrm{Pt}$. Let us then consider the possible mechanisms of reactions where reactions (2), (2-I) and (2-II) may become rate-determining, yielding the kinetic parameters obtained for the cathodic reaction at low potentials.

In reaction (2) the $\mathrm{SO_3}$-containing species acts as a depolarizer. If this reaction is rate-determining, the reaction rate v_2 is

$$v_2 = k_2 X_{\mathrm{H}}^2 c_{\mathrm{SO_3}} \tag{5}$$

where k_2 is the formal rate constant for the forward reaction, X_{H} the degree of surface coverage by hydrogen adatoms and $c_{\mathrm{SO_3}}$ the concentration of the $\mathrm{SO_3}$-containing species at the electrical double layer. Assuming a Temkin isotherm prevails for adatoms and neglecting any double layer effect, as the electrolyte may be considered as an ionic melt, the following equation in terms of current density, i, is for an activated adsorption process,

$$i = 2Fk_2' X_{\mathrm{H}}^2 c_{\mathrm{SO_3}} \exp\,(2\alpha\eta F/RT), \tag{6}$$

where k_2' contains all constant terms independent of the overvoltage η and X_{H}. α is the transfer coefficient assisting the reaction in the forward direction. Therefore, the dependence on overvoltage of the adatom concentration determines the dependence of the rate of the over-all reaction on potential. Taking $\alpha = 0{\cdot}5$, the Tafel slope derived from (6) is equal to RT/F. Equation (6) comprises also, at constant overvoltage, a first-order dependence on the concentration of the $\mathrm{SO_3}$-containing species.

As a second possibility, let us assume that reaction (2) is split in steps (2-I) and (2-II), the former being rate determining. The rate equation for reaction (2-I), $v_{2-\mathrm{I}}$, is:

$$v_{2-\mathrm{I}} = k_{2-\mathrm{I}} X_{\mathrm{H}} c_{\mathrm{SO_3}}. \tag{7}$$

If the surface coverage is low, approaching the conditions of a Langmuir isotherm, then reaction (1) is under a quasi-equilibrium and the following expression for X_H in terms of overvoltage is immediately derived,

$$X_{\mathrm{H}} \approx K_1 \exp\,(\eta F/RT), \tag{8}$$

where K_1 is the equilibrium constant of the primary step (1). From (7) and (8) the rate of the over-all reaction is

$$i = 2Fk_{2-\text{I}}K_1c_{\text{SO}_3} \exp (\eta F/RT). \tag{9}$$

Equation (9) involves again a first order dependence on c_{SO_3} and a Tafel slope equal to RT/F.

If reaction (2-I) is rate-determining under a Temkin isotherm, although the first-order kinetics with respect to the SO_3-containing species is also derived, the theoretical Tafel slope differs from the experimental one.

Finally, let us consider reaction (2-II) as rate determining. Under Temkin conditions, after considering an activated adsorption process for hydrogen adatoms, the following rate equation for the over-all reaction results:

$$i = 2Fk_2{}'_{-\text{II}}X_{\text{H}}{}^2c_{\text{SO}_3} \exp (2\alpha\eta F/RT), \tag{10}$$

which is similar to (6). The theoretical analysis of this mechanism in terms of a Langmuir isotherm yields kinetic parameters which differ from those experimentally obtained.

Therefore the already mentioned reaction schemes under reaction control either by step (2) or (2-II) under Temkin conditions, for the hydrogen adatoms are the more likely reaction paths yielding SO_2 formation.

Therefore, by adding up steps (1) and (2), the over-all reaction comprising sulphur dioxide formation is

$$2\,(\text{H}^+)_{\text{solv}} + (\text{SO}_3)_{\text{solv}} + 2\,\text{Pt(e)} = \text{SO}_2 + \text{H}_2\text{O} + 2\,\text{Pt}. \tag{11}$$

According to this reaction, if the SO_3-containing species is exhausted at the electrochemical interface, a convective–diffusion limiting cd appears, as shown also in Fig. 1. This convective–diffusion process has been discussed in a previous publication.[3] But when the cathodic potential increases and the $(SO_3)_{solv}$ diminishes, the rate of SO_2 formation also decreases, and reactions (2a) and (2b) compete in the cathodic process, yielding respectively hydrogen gas and sulphur at the electrode surface. The latter dissolves in the oleums to produce the blue-tinged solutions already described.[1] Previous studies on the current efficiency[2] indicate that the hydrogen and the blue compound yields actually increase after reaching the limiting cd related to the reduction of the SO_3-containing species. The formation of sulphur on the platinum surface at high cathodic potentials was clearly detected on the rotating disk electrode.[3] Reactions (3) and (4) are chemical reactions which are included to complete the scheme of the cathodic process.

The postulated reaction mechanism is congruent with the kinetic parameters earlier reported. Thus, the cd at the rest potential related to sulphur trioxide reduction according to the total reaction represented by (11), is on the average $10^{-4\cdot5}$ A/cm^2 at 25°C.[3] This figure is higher than that obtained for concentrated sulphuric acid, $10^{-5\cdot4}$ A/cm^2 at 25°C. The latter may be assigned to a reaction scheme involving only step (1) followed by (2a) exclusively.

Consequently in the cathodic process occurring with the oleums under no concentration gradient of the SO_3-containing species, steps (2) and (2a) being alternative steps, the latter occurs preferentially after the primary reaction. Hydrogen adatoms and SO_3-containing species must contribute also to some extent to increase the cathodic Tafel slope by blocking partially the electrode surface and also provoking a continuous change of the actual free energy of adsorption, which is dependent on the degree of surface coverage.

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REFERENCES

1. A. J. Arvia and J. S. W. Carrozza, *Electrochim. Acta* **11**, 1641 (1966).
2. H. A. Garrera, J. S. W. Carrozza and A. J. Arvia, *Electrochim. Acta* **13**, 771 (1968).
3. J. S. W. Carrozza, H. A. Garrera and A. J. Arvia, *Electrochim. Acta* **14**, 205 (1969).
4. W. E. Triaca and A. J. Arvia, *Electrochim. Acta* **10**, 409 (1965).
5. A. J. Calandra, M. E. Martins, G. Paus and A. J. Arvia, *An. de Asoc. Quim. Argent.* **57**, 91 (1969)
6. A. V. Gladkii, E. I. Surkov and I. N. Shokin, *Trudés mosk. khim-tekhnol. Inst.* **56**, 195 (1967); C.A. **70**, 7017 (1969).
7. K. J. Vetter, *Elektrochemische Kinetik*, p. 410. Springer, Berlin (1961).
8. A. J. Arvia, A. J. Calandra and H. A. Videla, *Electrochim. Acta* **10**, 21 (1965); **10**, 33 (1965).
9. B. E. Conway, *Theory and Practice of Electrode Processes*, p. 138. Ronald Press, New York (1965).
10. R. Parsons, *Trans. Faraday Soc.* **54**, 1053 (1958).