

Consequently, absolute theoretical predictions of the fundamental and second harmonic ac polarograms were calculable from Equations 1-22 and were compared directly to experimental results without further parameter adjustment. The theory-experiment comparisons obtained on this basis were quite satisfactory. Figure 9 is illustrative. Those theory-experiment disparities evident in Figure 9 are minor, considering the essentially absolute basis for the comparison. Their magnitude is such that further refinement of the rate parameter values to give better agreement would have a negligible influence on the k_c value. The refinement procedure would result only in slight re-estimates of k_s and α to values of approximately 0.22 cm sec^{-1} and 0.48 , respectively. Such exercises in obtaining a "better fit" are not particularly meaningful because the rate parameter adjustments involved are too small to be of consequence for fundamental interpretations of their magnitudes and because one cannot distinguish whether the small original disparities (Figure 9) are due simply to inaccurate k_s and α values, or to minor mechanistic complications such as the follow-up reaction discussed earlier.

In any case, we believe that the results presented here represent a successful correlation between experimental observables and the theoretical rate laws of dc and ac polarography with the catalytic mechanism. This additional contribution to the evidence supporting the fundamental harmonic theory and this initial evidence for the fidelity of the second harmonic rate law provide the basis for greater confidence in applying these electrochemical relaxation techniques to electrode reactions involving the first-order catalytic mechanism.

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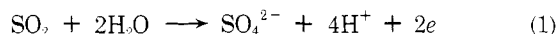
NOTES

Determination of Sulfur Dioxide by Anodic Oxidation on Lead Dioxide Electrodes

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Sulfur dioxide is still a major atmospheric pollutant in industrialized areas. Several methods and instruments are available to measure its concentration and several excellent reviews were recently published describing the commercial instruments (1-4). Every instrument has its own characteristics and limitations, and new approaches to the detection and analysis of SO_2 are needed. We wish to report preliminary experiments that could lead to an instrument measuring the SO_2 in the atmosphere. The method is based on recording the anodic oxidation current of SO_2 on an electrocatalyst held at a controlled potential. Several studies on the anodic oxidation of this molecule were made on noble metals (5, 6), on lead dioxide electrodes (6), and on activated carbon electrodes (7). Lead dioxide (PbO_2) electrodes are particularly attractive since they do not require voltage pretreatment to attain their electroactivity; also it is reported that, in a certain potential range, the main reaction is the anodic oxidation (6):



It is then possible to test a system where a flow of polluted air is passed through a solution and the SO_2 is oxidized in contact with the electrode. For a flow rate of $250 \text{ cm}^3/\text{min}$ of air containing 1.0 ppm of SO_2 , an anodic current of $33 \mu\text{A}$ should be observed for the complete oxidation. This order of current is within the reach of modern electrochemical instrumentation.

One *a priori* advantage of the anodic oxidation at a controlled potential, is the specificity that theoretically can be achieved by the method; by the combination of an appropriate electrocatalyst and the proper potential, selective oxidation can be performed (8), that is oxidation of SO_2 without interference with other pollutants (hydrocarbons, hydrogen sulfide, etc. . .).

EXPERIMENTAL

The electrodes were prepared by the electrodeposition of β - PbO_2 on gold or graphite (9, 10). The gold substrate was given a grid structure so that it occupied 50-75% of the volume of a small Pyrex cell. The compartment of this working electrode had a volume of 10 cm^3 . The graphite-lead dioxide electrode had a cylindrical geometry and occupied a smaller volume (5-10% of total volume). The first type of electrode had this particular geometry to achieve a better contact between the sulfur dioxide and the

- (1) C. D. Hollowell, G. Y. Gee, and R. D. McLaughlin, *Anal. Chem.*, **45**, 63A (1973).
- (2) B. D. Epstein, "Electrochemistry of Cleaner Environments," J. O'M. Bockris, Ed., Plenum Press, New York, N.Y., 1972.
- (3) A. Syty, *Anal. Chem.*, **45**, 1744 (1973).
- (4) I. Melingailis, *IEE Trans. Geosci. Elect.*, **GE10**, 7 (1972).
- (5) E. T. Seo and D. T. Sawyer, *Electrochim. Acta*, **10**, 239 (1965).
- (6) F. Strafeldt and J. Krofta, *Collect. Czech. Chem. Commun.*, **36**, 1634 (1971).
- (7) K. Wiesener, *Electrochim. Acta*, **18**, 185 (1973).

- (8) "Organic Electrochemistry," M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973.
- (9) Y. Shibusaki, *J. Electrochem. Soc.*, **105**, 624 (1958).
- (10) S. Vasundara, K. C. Narasimham, and H. U. K. Udupa, *Electrochim. Acta*, **16**, 1301 (1971).

Table I. Oxidation on Gold Lead Dioxide Electrode^a

[SO ₂], ppm	<i>i</i> _{obsd} , μ A	<i>i</i> _{caled} , μ A	Oxidation, %
0.40	7.7 \pm 0.5	12.7	61
0.32	6.5 \pm 0.4	10.1	64
0.12	2.4 \pm 0.3	3.8	64

^a Flow rate 240 cm³/min; gold lead dioxide electrode; 1N HClO₄ electrolyte.

electrode. Both electrodes had an equivalent apparent area of 2 cm².

A three-electrode potentiostatic system was used: the reference electrode was a Hg/Hg₂SO₄ electrode and a platinum electrode was used as the counter electrode separated from the working lead dioxide electrode by a medium grade sintered disk. A Bi-pad Tacussel potentiostat and a Honeywell recorder (model Electronik 194) were used. An offset and RC filter were used to attenuate the effect of the background current and the noise generated by the air bubbles on the working electrode. The electrolytes used were 1N H₂SO₄ and 1N HClO₄. Better results were obtained from the latter (lower background current drift, smaller air bubbles).

The sulfur dioxide mixtures were prepared by injection with a syringe of known amount of pure SO₂ in 100 l. polyethylene air bags. The exact concentration was determined with a Tracor 250 H analyzer.

RESULTS AND DISCUSSION

For a polarization of +950 mV (w.r.t. Hg/Hg₂SO₄) and a residual current of the order of 20 μ A, the oxidation of the SO₂ on the PbO₂ electrode was completed to 64% of the theoretical value (see Table I). This particular polarization potential was selected as a compromise between an increase in the electrooxidation current (10% increase from 0.9 to 1.0 V) and the increase in the background current (also of the order of 10% for the same potential range). This residual current can be assigned to the oxygen evolution reaction. The signals obtained were reproducible and the time response of the system was of the order of 5 min. The current obtained is linear with the concentration and extrapolate to the origin. The limit in the oxidation efficiency is probably due to the incomplete contact between the electrode and the SO₂. For the graphite lead dioxide electrode, the percentage of oxidation was of the order of 20 to 25% (Table II).

The difference in the electrooxidation efficiency between these two electrodes can be related to the difference in contact between the reacting gas and the electrode surface. For the graphite lead dioxide electrode, the active surface is smaller since it occupies only 5–10% of the vol-

Table II. Oxidation on Graphite Lead Dioxide Electrode^a

[SO ₂], ppm	<i>i</i> _{obsd} , μ A	<i>i</i> _{caled} , μ A	Oxidation, %
10	34.1 \pm 0.7	317	11
5	19.5 \pm 0.4	159	12
1	7.3 \pm 0.1	31.7	23
0.5	4.2 \pm 0.1	15.9	26

^a Flow rate 240 cc/min; Graphite lead dioxide electrode; 1N H₂SO₄ electrolyte.

ume of the cell. To obtain a better contact, a fuel cell porous type electrode should be used where the contact between the three phases is optimized. Such a system would also avoid the bubbling of the air mixture in the solution, thereby reducing the solution depletion (part of the electrolyte being carried away with the air flowing through the solution) and also the electrochemical noise.

For the 10-ppm concentration in Table II, several determinations were carried out and, for 5 consecutive experiments, the standard deviation from the mean was \pm 0.72%. For the other concentrations, the reproducibility was always within 10% for a least three consecutive trials.

With the gold-lead dioxide electrode, a signal for a 0.05-ppm SO₂ mixture was obtained; however, this signal was highly noisy (10% of the signal) but it shows the possibilities of the system.

CONCLUSION

We reported a method to analyze sulfur dioxide in the atmosphere using a lead dioxide electrode as the electrocatalytic oxidizing electrode as reported by Strafelda and Krofta (6). This type of solution seems encouraging since the oxidizing agent is stable, non-consumable and active without any potential pre-treatment. However, further experimental work is needed to assess the full potentiality for this type of system.

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