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AN ELECTROCHEMICAL CELL NOISE STUDY

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AN ELECTROCHEMICAL CELL NOISE STUDY

ABSTRACT

This report describes the noise output of a bubbling electrolytic cell under various conditions of cell operation. The noise spectrum is analyzed and integrated for the purpose of providing a potentiostat noise figure. The report also indicates how a noise spectrum may be used to gain further insight into electrochemical cell mechanisms.

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AN ELECTROCHEMICAL CELL NOISE STUDY

I. INTRODUCTION

A. Purpose of Report

Electrochemical research of the type performed by Dr. J. R. Aylward for CPP Technical required the development of an instrument called a Potentiostat ¹. The Instrument Development Branch provided such an instrument in 1960. At that time a noise figure was not available for an electrochemical cell and could not be obtained because the proper equipment and theoretical capability were not available at the NRTS. Since then, however, the Instrument Development Branch has developed the necessary ingredients to perform such a study. This report is an attempt to rectify the lack of information concerning electrolytic cell noise outputs. Not only will it be useful to any future potentiostat designers, but it also appears that cell noise studies themselves can provide information about electrochemical mechanisms that was hitherto either unavailable or obtainable only with a great deal more difficulty than with a noise study.

B. Technical Background

The type of electrochemical cell that will be considered here is a three-terminal device. It is composed of the usual two electrodes one would expect in any electrochemical device plus a third electrode or measuring electrode. The measuring electrode or "Luggin Capillary" is simply a capillary tube associated very intimately with one or the other of the two usual electrodes. The electrode associated with the Luggin Capillary becomes the working electrode and the other is then the counter electrode. The cell is shown diagrammatically in Figure 1.

Figure 1 - Typical Electrolytic Cell

The potentiostat provides a means of holding the voltage between the Luggin Capillary and the working electrode overvoltage constant by proper manipulation of the total voltage across the cell. The potentiostat, then, is simply a power supply whose output voltage is controlled by another voltage. Figure 2 shows how the cell and the potentiostat are interconnected. It now becomes obvious why the potentiostat may not be considered separately from the cell and vice versa. The two together form a system which has completely different characteristics than either component alone ². Any study involving the noise of the system is also complicated by this fact.

Figure 2 - Potentiostat and Cell Configuration

In such a system as this, there are essentially two sources of noise. One source is generated by the potentiostat and the other by the cell. These are indicated in Figure 3.

Figure 3 - System Noise Sources

In order to compare these noise sources it is convenient to refer them to the same point. Normal servomechanism theory provides the tool required to do this ³. Standard analog computer symbolism is used to describe this situation in Figure 4.

Figure 4 - Equivalent System Noise Sources

One readily sees that if the potentiostat is not to contribute any appreciable noise to the operation of the system, N_p must be considerably smaller than N_c at all frequencies. One might also expect N_c to be minimized if the potentiostat transfer function were developed using optimum filter noise theory⁴. In addition, a study of N_c could very well yield information concerning cell mechanisms.

Since N_p varies between potentiostats and usually can be obtained quite handily, no further discussion of it will be found in this report. Our attention will henceforth be turned to a measurement of N_c .

II. CELL NOISE MEASUREMENT

A. Experimental Apparatus

In order to keep the noise measurement as uncomplicated as possible, the cell was connected directly across a set of storage batteries. The voltage across the cell was varied by changing connections between different types of storage batteries. Figure 5 shows the experimental apparatus with the proper interconnections.

The cell was composed of two platinum electrodes submerged in a 0.1 N sulphuric acid solution and spaced approximately 5.4 cm apart. Each electrode area was one square cm. A saturated calomel reference electrode connected the solution in the Luggin capillary to the pre-amplifier. An offset voltage contained in the pre-amplifier canceled out the D.C. component of the overvoltage. No solution stirrer was used. The Luggin capillary was placed as close to the working electrode as was conveniently possible.

A Sanborn Series 350-1800 stabilized D.C. pre-amplifier performed the function of raising the level of the noise signal high enough for suitable recording on a tape recorder (two volts peak-to-peak). While this pre-amplifier does not represent the ultimate in low-noise amplification, it very closely approaches the state-of-the-art in such matters. Before sufficient voltage was across the cell to cause bubbling, only instrumentation noise was observed. To study mechanisms below this level (bubble formation) would require that very special low-noise amplification techniques be employed. An alternate approach to mechanism study that would embrace this low-level problem would be to cross correlate the output with a suitable "noisy" input.

The tape recorder was an Ampex FR-1300 operating in the FM-60 ips mode.* A 12-minute recording was made for each set of data. The tape was then analyzed according to a scheme described elsewhere⁵ and with the new Instrument Development Branch analyzer. The results from the two methods are within the experimental error as described on the data plot.

*Frequency Modulation Mode - sixty inches per second.

Figure 5 - Diagram of Apparatus

B. Data

The results of three separate measurements of cell output noise are presented graphically in Figures 6, 7 and 8. A chart in Figure 9 indicates the differences between graphs.

Figure No.	Nom. Cell Voltage	Nom. Cell Current	Pre- Amplifier Gain	Nom. Cell Temperature	Total Cell Output (Volts RMS)
6	3.0V	24 ma.	1,000	29°C	0.172×10^{-3}
7	4.2V	53 ma.	100	28°C	4.1×10^{-3}
8	6.3V	131 ma.	50	31.5°C	8.44×10^{-3}

Figure 9 - Chart of Cell Conditions for Each Graph

Bubbling at the electrodes provided the random noise source for the experiment. The modification of this noise by the significant parameters of the electrochemical cell produced the spectrums of Figures 6, 7 and 8. A word of caution; these particular graphs should not be interpreted for their electrochemical significance. They are presented only for the purpose of indicating a possible approach to such studies and to provide a noise figure for potentiostat design. For this reason no special attempt has been made to measure the electrochemically significant parameters with a great deal of precision. The curves will be used, however, as examples for an approach to analysis in Section III. The total cell noise output in Root Mean Square volts was obtained by integrating the voltage density spectrum.

To illustrate how these equations might be used to gain further insight into problems of cell operation, let us assume that they are as exact as it is possible to make them. They appear below:

Figure 6

$$V_1(s) = \frac{2.2 \times 10^{-3} (1+s)(1+.08s)^2}{(1+.7s)(1+.4s)(1+.2s)(1+.01s)(1+.006s)}$$

Figure 7

$$V_2(s) = \frac{4.96 \times 10^{-3} (1+.4s)}{(1+.5s)(1+s)}$$

Figure 8

$$V_3(s) = \frac{1.13 \times 10^{-3} (1+.2s)(1+.02s)}{s(1+.4s)(1+.003s)(1+.002s)^2}$$

(a)

(b)

(c)

where

$$s = j\omega = j2\pi f$$

and

ω = angular frequency

$$j = \sqrt{-1}$$

It is possible by means of modern electrical network theory⁸ to arrive at one or more electrical analogies for each of these equations. For instance, consider the equation of Figure 7. Three possible electrical circuits which will produce the same output noise spectrum appear in Figure 10. By no means do they represent all the possible circuits capable of producing the same spectrum. One can expect an electrochemist to be able to look at a number of such analogs for each equation and select the one which most nearly represents his concept of the particular electrolytic cell involved. Once this has been accomplished, it is a relatively simple matter to make quantitative measurements of electrochemical parameter variations as a function of different cell operating conditions.

A further example will illustrate how this method of cell study may be used to augment or replace the methods presently in use. Consider for a moment the simple cell analog circuit of Figure 11⁹.

Figure 10 - Electrical analog which can produce the same spectrum as Figure 7.

PPCo - A - 5571

Figure 11 - Simple analog of an electrolytic cell

R_1 is the solution resistance, R_2 the interface resistance and C the double layer capacity. One of the ways of measuring C , of course, is to pulse the total cell voltage and measure the overvoltage vs time curve. Another way is to excite the cell with sinc wave voltages at a number of different frequencies and thus measure the cell transfer function which is dependent upon C . These two measurements have the disadvantage of disturbing the cell and disallowing the use of perturbation theory to linearize the basically non-linear differential equations which characterize the cell.

A third method which does not have this disadvantage because its disturbances are only the internal disturbances of the cell itself employs the previously described voltage density spectrum. The measured voltage density curve from Figure 11 would be of the following form.

$$V \text{ overvoltage} = \frac{R_1 R_2 I \text{ noise source}}{\left(\frac{R_1}{R_1 + R_2} \right) \left(\frac{R_1 R_2}{R_1 + R_2} C s + 1 \right)}$$

Once this form is related to the electrochemist's concept of the cell, the determination of the value of C , the double layer capacity, is a simple matter. It, in combination with R_1 and R_2 , forms the coefficient of s in the noise spectrum density equation.

Similarly, one would expect the size of the double layer capacity to be involved in one of the larger coefficients of s in the previous example of Figure 7. The authors feel that with more accurate data and a reasonable electrochemical concept of the cell such as identification would most certainly be possible.

Another interesting feature of the three curves involves their high frequency response. Figure 7 has a completely different high frequency response from Figures 6 and 8, although it had a value of current density between those two. However, Figure 7 was obtained from a cell whose temperature was slightly lower than either of the other two. The authors would not deprive the reader of the pleasure of performing his own speculations at this point.

III. CONCLUSIONS

The mathematical description of the cell noise output spectrum appears to be quite complicated. It should be noted that this mathematical description is by no means the only one capable of fitting the data within the indicated error limits. It is adequate, however, for the purpose of integration to obtain the total RMS noise output of the cell. It quickly becomes obvious, then, that the data must have its error limits reduced by a considerable amount before any electrochemically significant parameters may be studied.

Such reduction can be accomplished in a rather straight forward manner by simply taking data for a longer period of time for each cell condition. Figures 6, 7 and 8 represent data taken for approximately twelve minutes for each cell condition. The time required to obtain a given degree of precision may be readily computed from the following equation: ⁶

$$T = \frac{K}{2\Delta F}$$

T = time in seconds

where ΔF = equivalent rectangular bandwidth of filter in c/s

K = number of degrees of freedom of a chi-squared distribution

The number of degrees of freedom of a chi-squared distribution required to obtain a given degree of precision are available from any standard collection of statistical tables ⁷.

To summarize, a range of values of noise output from a bubbling electrolytic cell have been measured for a number of different current densities. These noise measurements should be of some use to those who design potentiostats. In addition to this, a new method for the investigation of electrochemical phenomena has been explored. It is the belief of the authors that this new method will prove to have much greater significance for the electrochemical world than will the particular values obtained for the total output noise of a cell.

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