Electrochimica Acta, 1963, Vol. 8, pp. 313 to 322. Pergamon Press Ltd. Printed in Northern Ireland

A COMPARISON OF DIFFERENT EXPERIMENTAL METHODS APPLIED TO THE STUDY OF INDIUM CATHODE PROCESSES*

G. SERRAVALLE and B. MAZZA
Institute for Electrochemistry, Physical Chemistry and Metallurgy,
Milan Polytechnic, Milan, Italy
Laboratorio del gruppo di ricerca "Elettroliti e processi elettrochimici" del C.N.R.

Abstract—To compare the different methods of investigation of the kinetics of electrode processes, the cathodic phenomena at indium electrodes in chloride and sulphate baths have been studied by the amperostatic pulse method, the tensiostatic method, the methods of the train of current rectangular and triangular pulses, and the faradaic impedance method. The information obtainable by these different methods is discussed.

Résumé—Comparaison, sur l'exemple expérimental du comportement cathodique des électrodes d'indium en bains de chlorures ou sulfates, de différentes méthodes de recherche du processus cinétique d'une réaction électrochimique. L'on met successivement en oeuvre la méthode d'impulsion ampèrostatique, la méthode tensiostatique, les méthodes d'impulsions rectangulaires ou triangulaires et la méthode d'impédance faradique. L'on discute l'ensemble des résultats obtenus.

Zusammenfassung—Verschiedene Methoden zur Untersuchung der Elektrodenkinetik wurden anhand des Beispiels einer Indiumelektrode in Chlorid- und Sulfatlösungen miteinander verglichen. Der Kathodenprozess wurde mittels der folgenden Methoden untersucht: amperostatische Impulse; tensiostatische Methode; aufeinanderfolgende viereckige und dreieckige Stromimpulse; Messung der faradayischen Impedanz. Die Aufschlüsse, welche durch diese verschiedenen Methoden erhalten werden können, werden diskutiert.

THE present research follows others[1] where the electrochemical behaviour of indium was studied by the traditional methods of investigation of the kinetics of electrode processes.

The preceding measurements were performed by the amperostatic pulse method. Although they proved the "normal"[2] electrochemical behaviour of indium, they showed also the appearance of important anomalies of the cathodic behaviour under particular experimental conditions.

In this research the amperostatic pulse method has been resumed to complete the phenomenological picture and also other new methods have been applied, especially to investigate the above mentioned anomalies. The main purposes were the following:

(a) To investigate the phenomenological aspects of the cathodic phenomena at indium electrodes by different methods.

(b) To confirm if the occurrence of the anomalies is influenced by the method of investigation.

(c) To attempt a measurement of the electrical parameters which refer to the electrode system.

Among the new methods we have chosen those that can be reasonably applied when the electrode process is not simple, the departure from equilibrium conditions is not small, and when solid electrodes are used.

* Presented at the 13th meeting of CITCE, Rome, 1962.

EXPERIMENTAL TECHNIQUE

The cells used have been already described elsewhere.[3] The electrodes (cathodes) to be investigated were prepared by indium deposition on copper disks, from 0·6 N chloride solutions (pH $\simeq$ 1·5; current density $\simeq$ 200 A/m^2; electrolysis time $\simeq$ 30 min).

The reference electrodes were obtained by indium deposition on copper wires, under the same conditions. Side-channel capillaries were used. Solutions were prepared by dissolution of very pure metal in the acids. pH was adjusted to the desired value by adding a little amount of freshly precipitated indium hydroxide, or acid. Chemicals used were of analytical reagent grade.

The apparatus comprised the following units:

(a) Amperostatic pulse method—an electronically regulated d.c. supply; a set of variable resistors; an electronic (10^{-5} s) or electronically operated mechanical switch (10^{-3} s); a Leeds and Northrup Speedomax recorder (30 s/in.) or a Tektronix cathode-ray oscilloscope (0·5–300 ms/cm) with a Robot camera. A high-input impedance valve amplifier assured the de-coupling between the tensiometric cell (PT) and the recorder.

(b) Tensiostatic method—a Wenking potentiostat and a Leeds and Northrup recorder.

(c) Method of the train of rectangular current pulses—an Electro-Pulse general purpose pulse generator and a Tektronix dual-beam cathode-ray oscilloscope, to record both the cell current and the PT voltage output.

(d) Method of the train of triangular current pulses—a versatile triangular pulse generator, manufactured in our Institute, and a Tektronix dual-beam cathode-ray oscilloscope.

(e) Faradaic impedance method—an ESI universal impedance bridge with a.c. generator and detector (electron-ray null indicator).

A Hartmann and Braun oscillographic null-indicator or a Tektronix cathode-ray oscilloscope were also used as detectors.

EXPERIMENTAL RESULTS

The experimental results generally show that the reaction resistance is time dependent. This follows from the voltage or current/time recordings obtained by the different methods.

The results concerning the measurements performed by the amperostatic pulse method are depicted in Fig. 1, where the different types of curves observed are shown. They represent both the voltage output of the PT and the integral reaction-resistance.

When the voltage of the PT is fixed at any constant value and the current flowing through the cell is recorded, the current/time curves are as shown in Fig. 2. They can be assumed to represent also the reciprocal of the integral reaction resistance.

It follows from these graphs that the electrode processes are influenced by the method of current supply to the cell.

In the measurements performed by the amperostatic pulse method, in fact, the reaction resistance changes abruptly from quasi-reversible conditions to high dissipation ones. Oscillatory phenomena sometimes appear. Steady or quasi-steady conditions can be reached only for very low or very high overvoltage (i.e. reaction resistance) values. There is a wide range of overvoltage values which cannot correspond to any steady condition.

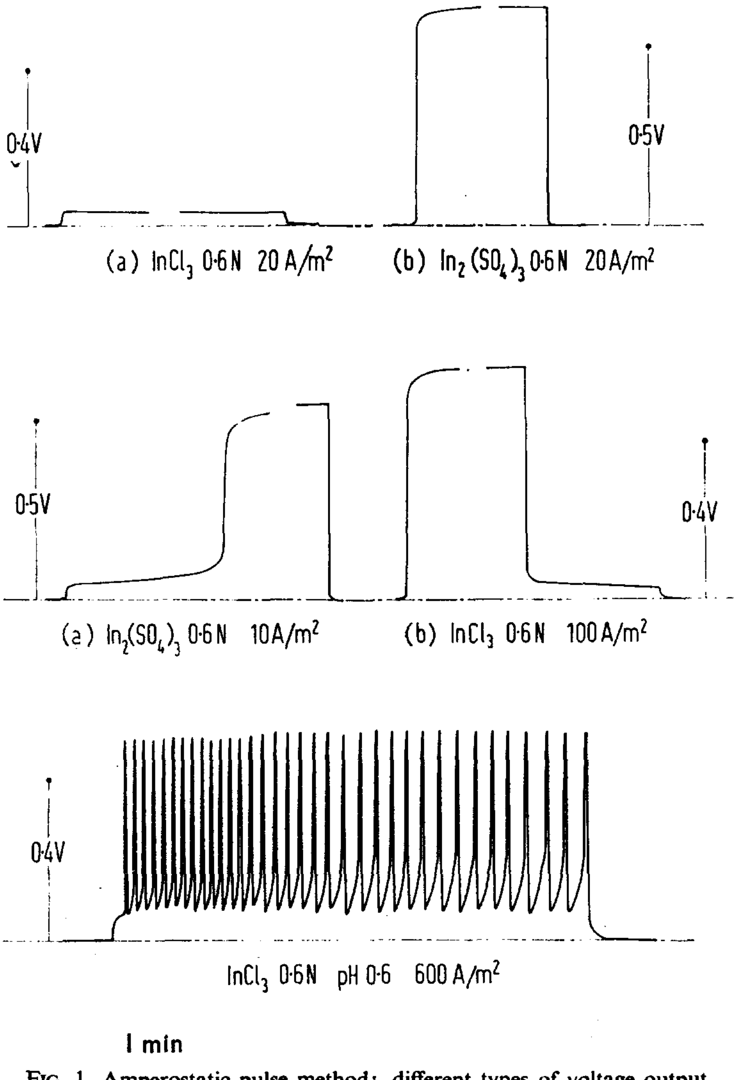

FIG. 1. Amperostatic pulse method: different types of voltage output of the tensiometric cell.

When the tentiostatic method is used, on the contrary, the reaction–resistance changes generally in a continuous way, except some little irregularities and some irregular oscillatory phenomena for the highest values of the voltage input.

Voltage/current characteristics can be plotted only when steady conditions are reached.

The appearance of the "voltage jump" observed by the amperostatic pulse method depends, other conditions being equal, upon the following:

(1) The composition of the solution, particularly as regards the presence of Cl^- and pH value. The presence of Cl^- added both as KCl and as HCl holds back the appearance of the voltage jump. The same occurs when pH is increased. The case in which HCl is added is very peculiar, since two contrary actions exist.[1]

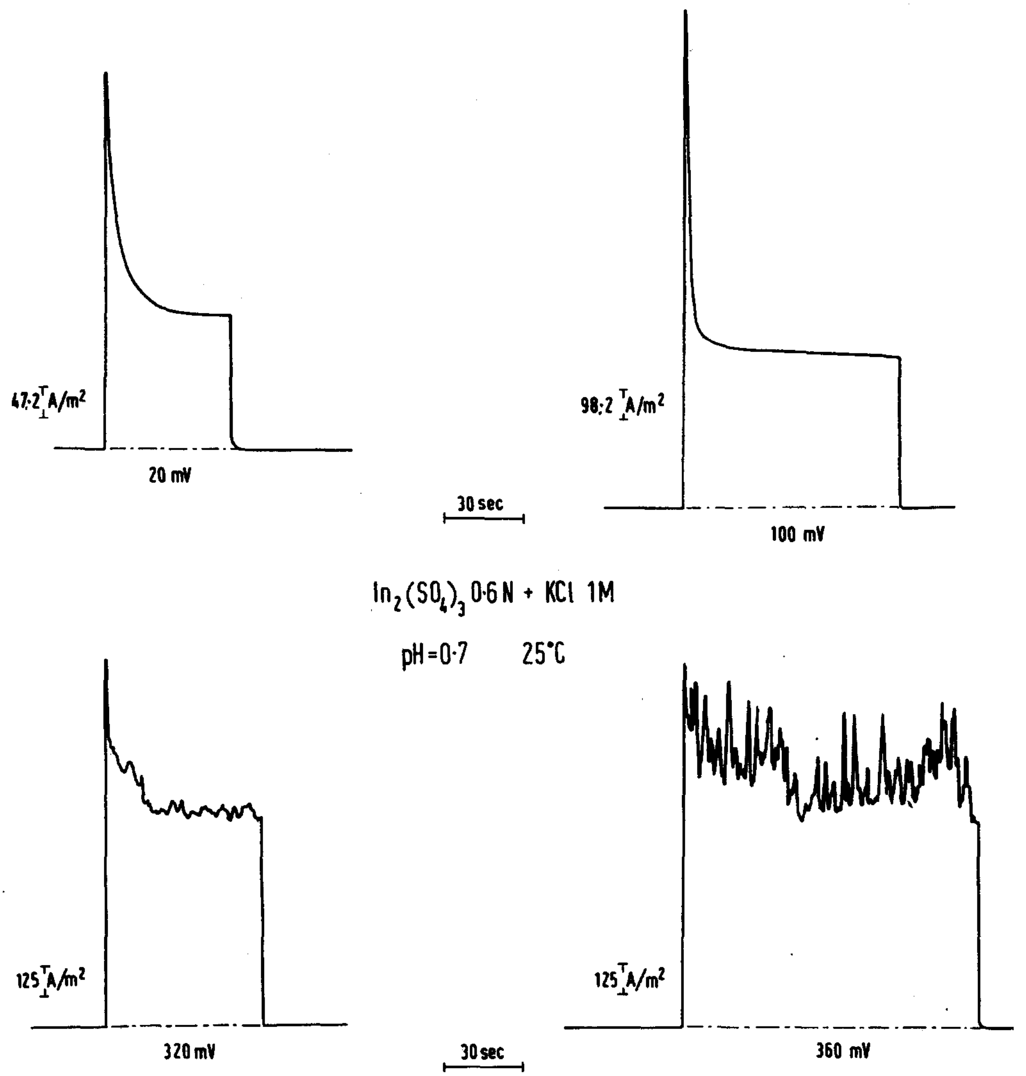

FIG. 2. Tensiostatic method: different types of current/time recordings.

(2) The history of the electrode, particularly as regards the current pulse width and frequency. The appearance of the voltage jump is enhanced by current circulation.

To investigate the latter point some measurements have been performed by the method of the train of current rectangular pulses, the pulse width and frequency being variable in a wide range. The different types of overvoltage output are represented in Fig. 3.

The cathodic phenomena at indium electrodes have been also studied by the method of the train of current triangular pulses.

This method enables the plotting of the dynamic characteristics of the system for different rates of current change. The overvoltage/time curves, which also represent the dynamic voltage/current characteristics, are shown in Fig. 4.

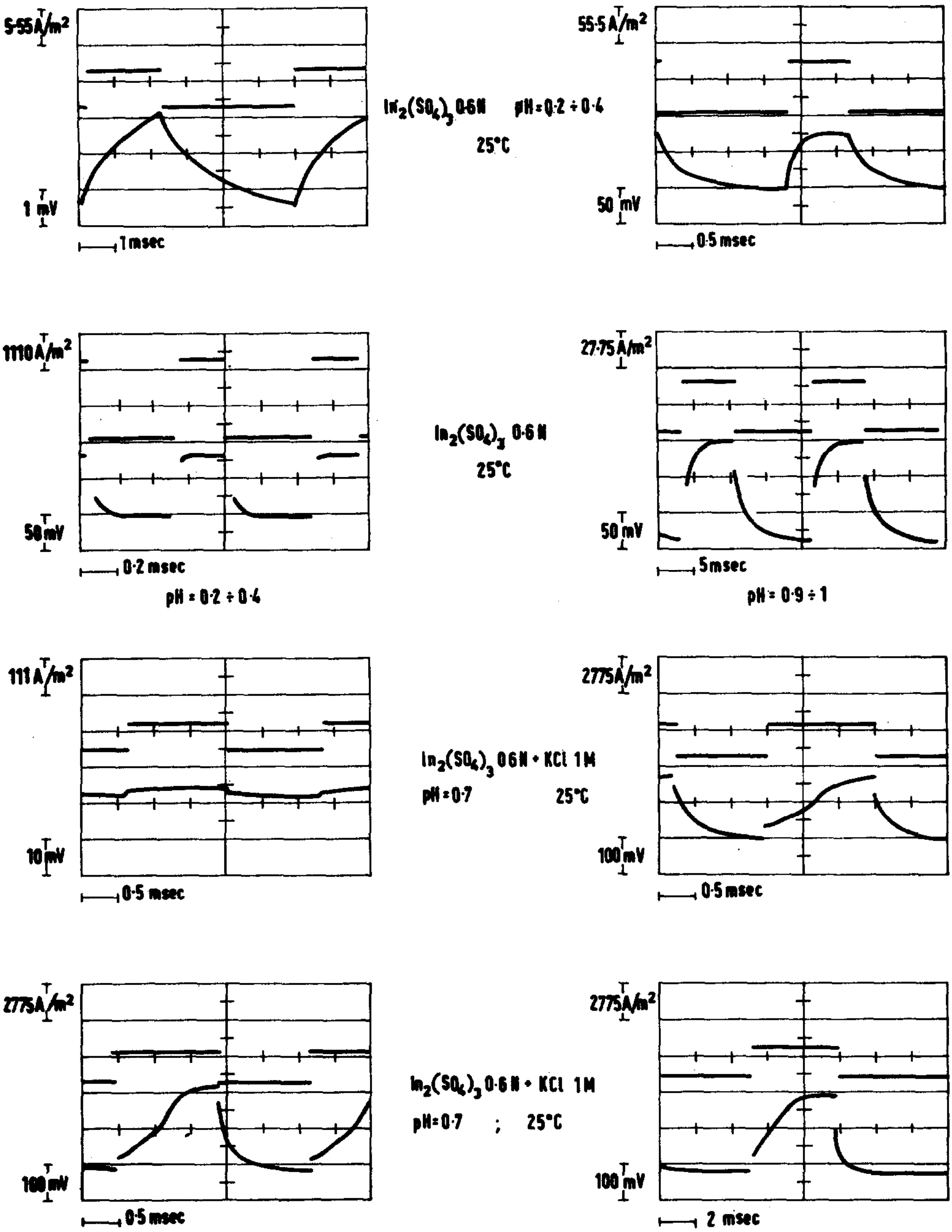

FIG. 3. Method of the train of current rectangular pulses: different types of voltage output of the tensiometric cell.

The faradaic impedance method was tried, a direct current being superimposed. The purpose was to verify if any change in the electrode impedance parameters occurred when the voltage jump appeared. As regards the capacitance, meaningless results were obtained. Fig. 5(a) refers to the resistance component and represents

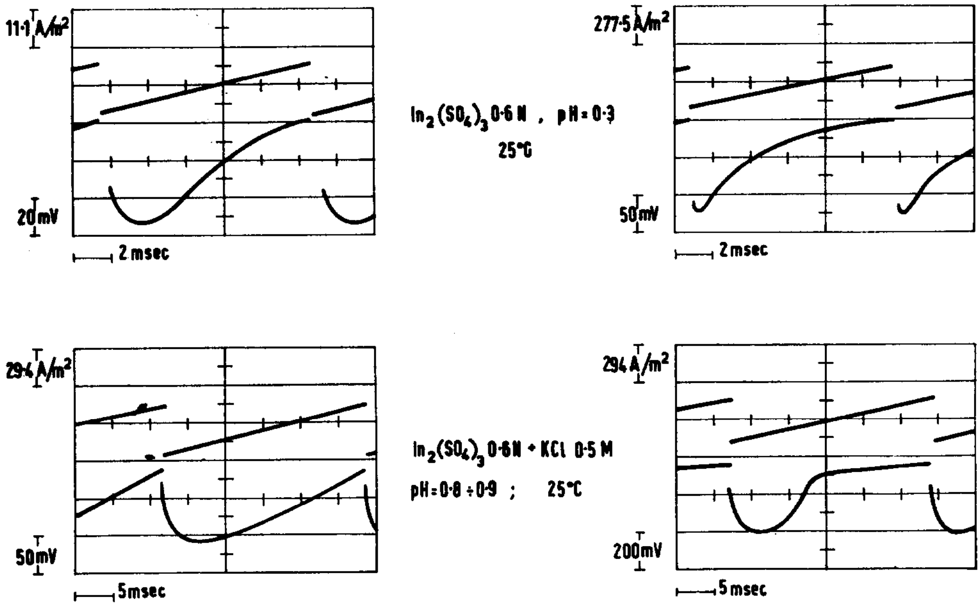

FIG. 4. Method of the train of current triangular pulses: overvoltage/time curves.

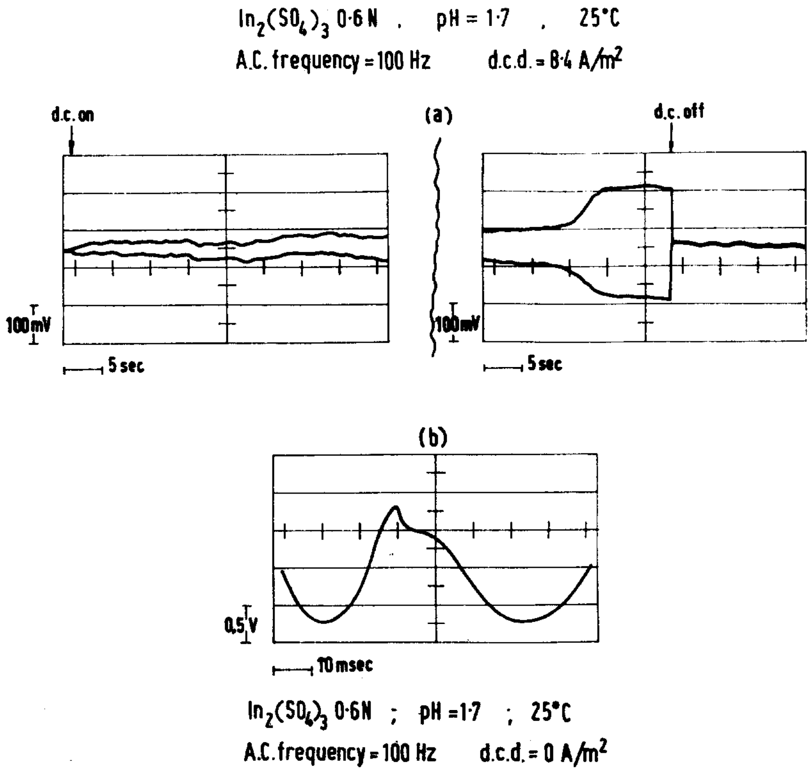

FIG. 5. Faradaic impedance method. (a) Bridge unbalance as a time function: before during and after direct current flowing; only the resistance component is referred to. (b) Distorted waves observed in the highest a.c. voltage range.

the bridge unbalance as a time function, before, during and after direct current flowing. Distorted waves were also observed in the highest a.c. voltage range (Fig. 5(b)).

DISCUSSION

In the electrode systems that have been studied, there is a simultaneous occurrence of indium and hydrogen discharge processes. We shall refer especially to the amperostatic pulse method. Three fields are distinguishable in the voltage/current graphs (Fig. 6). In the range on the left of i_I, the overvoltage values are very low and a quasi-steady condition is reached immediately. The current efficiency is nearly unity for indium deposition.

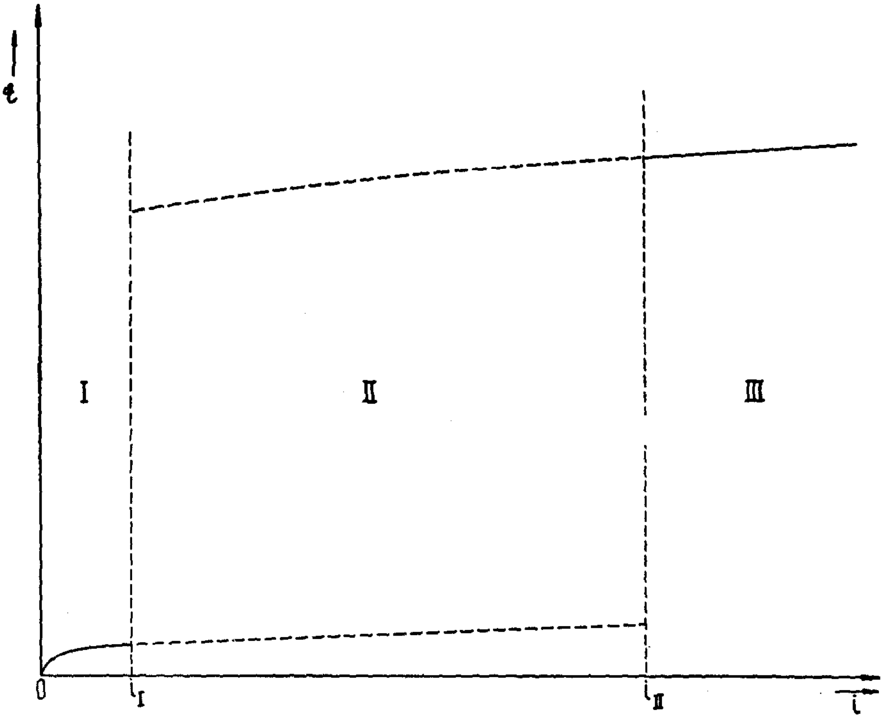

FIG. 6. Amperostatic pulse method: voltage/current schematic diagram.

In the range between i_I and i_{II}, the voltage jump or oscillatory phenomena occur. The steady conditions sometimes attained correspond to the high overvoltages of the III field. The current efficiency values are neither reproducible nor meaningful, since they depend on the charge ratio between the charges involved in the low-dissipation or high-dissipation process.

In the range on the right of i_{II}, the process occurs with very high overvoltages since the beginning, and steady conditions are reached immediately. Indium-discharge current efficiency is then low, generally $< 0{\cdot}2$, except for the case of chloride solutions.

Thus there are only two fields in which the relation between voltage and current is unequivocal. In the intermediate range both indium and hydrogen discharge occur, depending on the experimental conditions, particularly on the pulse amplitude and width.

The most important characteristics to be determined are:

(1) The value of i_I and its variation with solution composition, pH, temperature and electrode surface condition.

(2) The width of the range between i_I and i_{II} and its changes.

The main results are summarized in Table 1; the values are merely indicative, since the measurements are scarcely reproducible.

TABLE 1*. VALUES OF i_I AND WIDTH OF THE RANGE BETWEEN i_I AND i_{II}

Solution		i_I (A/m²)	$i_I \div i_{II}$ range (A/m²)
$InCl_3$ 0·6N;	pH = 1·5	50	50 ÷ 80
$InCl_3$ 0·6N + KCl 0·6N;	pH = 1·5	100	100 ÷ 300
$In_2(SO_4)_3$ 0·6N;	pH = 2·1	20	20 ÷ 50
$In_2(SO_4)_3$ 0·6N;	pH = 0·4	10	10 ÷ 50
$In_2(SO_4)_3$ 0·6N + KCl 0·6N;	pH = 1·5	50	50 ÷ 100
$In_2(SO_4)_3$ 0·6N + KCl 1·2N;	pH = 1·5	80	80 ÷ 300

* The measurements have been performed at 25°C.

The method of the train of current rectangular pulses has completed the picture by showing that both the value of i_I and the width of the range between i_I and i_{II} depend on the duration and the frequency of the amperostatic pulses. In fact, the shorter the current pulses, the higher is the value of i_I. The longer is the pulse spacing and the shorter was the time portion of the preceding pulse in which high overvoltages appeared, the more i_{II} increases. Under particular conditions the values of i_I and i_{II} can be the same. This occurs, for example, when the amplitude of the amperostatic pulse is decreased.

Useful information on the details of the transient conditions corresponding to the voltage jump can be obtained by integrating the data given by the amperostatic pulse method with those given by the others. The results obtained by the tensiostatic method show that the reaction resistance is slowly time-dependent and steady conditions are often reached. Therefore steady condition current/voltage characteristics can be plotted, even in the range that appears to be unsteady by the amperostatic pulse method (Fig. 7).

By the method of the train of current triangular pulses the appearance of the voltage jump is peculiar, since it occurs while the current is increasing. The dynamic characteristics show that a single correspondence between voltage and current exists for every given rate of current change. By varying the current change rate, the dynamic characteristics may be spread over the unsteady range of the voltage/current graphs plotted by the amperostatic measurements.

The results of these measurements enable us to advance the following interpretation. The resistance changes can be caused by inhibition phenomena at the electrode surface due to hydrogen. Hence the processes of indium and hydrogen discharge are not only in competition, but they even interfere with each other.

In the amperostatic pulse method the total current is fixed at a constant value and the motor work can be made available to any extent. Therefore the inhibition phenomena, after they have started, increase with regenerative action, until a condition of complete inhibition is reached. If the changes occurring in the solution near the electrode exert an influence in the sense of making the inhibition unstable, oscillatory phenomena can be observed. In the tensiostatic method, on the contrary, the current decrease which follows the beginning of the inhibition phenomena acts as a moderating factor upon the reaction resistance increase. Therefore the inhibition rate is smaller and the reaction resistance can attain steady intermediate values. The methods of the train of current rectangular or triangular pulses are comparable with the amperostatic pulse method, since the current is controlled.

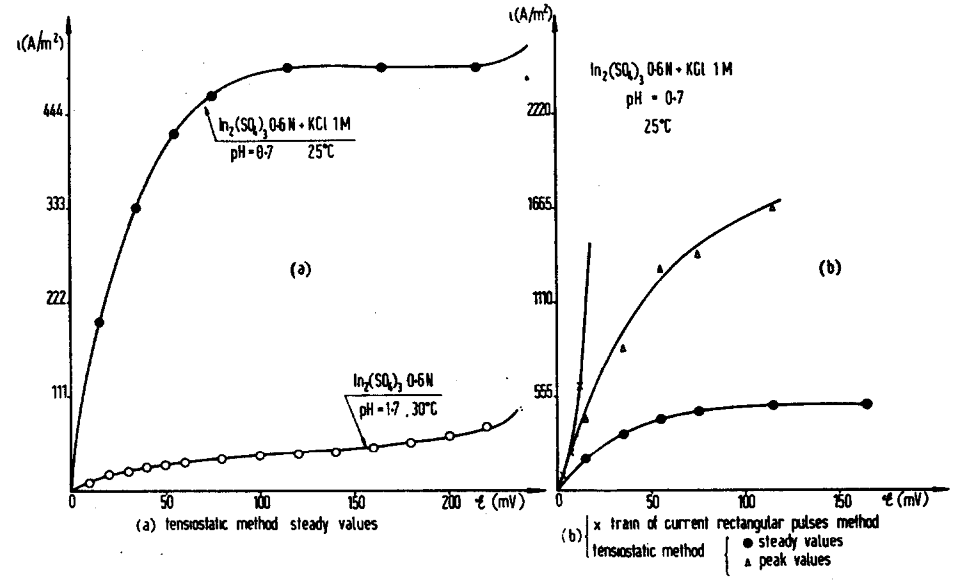

FIG. 7. $i/\mathscr{E}$ diagrams plotted by different methods.

As regards the inhibiting action of hydrogen, we can suggest the following causes (see Ref. 1 for details):

(1) Formation of a hydride film, which acts as a double layer, opposing indium discharge.

(2) Formation of a gaseous film, which acts as a material obstacle to indium discharge.

These mechanisms are not mutually exclusive ; on the contrary we can suppose that the former precedes the latter. In other words, the formation of a hydride film would imply an inhibiting action (like a passivation due to coating layers) on indium discharge. The beginning of the formation of a hydrogen film, increasing the overvoltage of indium discharge, would lead to a progressive hydrogen saturation of the electrode surface, thus giving rise to an unstable but relatively permanent "cathodic passivation".

Notice that this phenomenological picture rejects the hypothesis of the formation of a hydroxide layer.[4]

CONCLUSIONS

The present research confirms the results already obtained in our laboratory as regards the processes that occur at indium cathodes, and particularly the inhibition of the electrode surface for indium discharge due to hydrogen discharge.

The different methods of investigation have revealed new phenomenological aspects which complete the picture of the electrochemical behaviour of indium. Besides they have shown that the results depend on the method of supply of cell current.

For example, the reaction resistance varies gradually in the tensiostatic measurements, but abruptly in the amperostatic ones. This means that the inhibition phenomena increase, with regenerative action, if the current density is fixed at any constant value.

On the contrary, the inhibition phenomena proceed slowly when the current density decreases owing to their appearence, the voltage input of the PT being constant.

By the methods of the train of rectangular or triangular current pulses it has been possible to study the changes of i_I corresponding to:

(a) Different values of the pulse width/frequency ratio;

(b) Different current change rates.

When the electrode processes are not simple and particularly when the reaction resistance is strongly time-dependent, great difficulties are met in obtaining quantitative results independent of the measuring method. Each method can give a set of different aspects that are often complementary. Nevertheless we think that the amperostatic pulse method is still the most fruitful, in giving general information.

As a matter of fact, this method:

(1) Is realizable in a simpler way, and less liable to systematic errors than the others.

(2) Is susceptible of an easier interpretation, since the total current, i.e. the total reaction rate, is fixed.

As far as the alternating current methods are concerned, serious difficulties arise when solid electrodes are used. The need of operating near to equilibrium conditions restricts:

(1) The field of the systems that can be studied.

(2) The number of the phenomena that can be observed.

This is a weakness of all the relaxation methods. Therefore the traditional methods are still valid, provided they are realized by the means offered by the modern techniques.

Acknowledgements—Thanks are due to the company "Oronzio de Nora, Impianti Electrochimici" for a grant awarded to B. M.

REFERENCES

1. R. PIONTELLI and M. SIMONETTA, *Gazz. Chim. Ital.* **79,** 716 (1949); R. PIONTELLI and G. POLI, *C. R. 2me Réun. CITCE, Milan* 1950 p. 136. *Tamburini, Milan* (1951); R. PIONTELLI, G. POLI and G. SERRAVALLE, *Rend. Ist. Lomb. Sci. Lett.* (A) **93,** 301 (1959); G. SERRAVALLE, *Rend. Ist. Lomb. Sci. Lett.* (A) **93,** 653 (1959); W. KANGRO and Fr. WEINGARTNER, *Z. Elektrochem.* **58,** 505 (1954).
2. R. PIONTELLI, *J. Chem. Phys.* **45,** 115 (1948); *Z. Elektrochem.* **59,** 778 (1955).
3. R. PIONTELLI, U. BERTOCCI, G. BIANCHI, C. GUERCI and G. POLI, *Z. Elektrochem.* **58,** 86 (1954).
4. H. FISCHER, *Elektrolytische Abscheidung und Elektrokristallisation von Metallen* S. 248. Springer-Verlag, Berlin (1954).