REDUCTION PROCESSES AT THE DROPPING MERCURY ELECTRODE IN PULSATING FIELDS : THE LEAD ION

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INTRODUCTION

DOSS AND AGARWAL[1] have studied the discharge of the lead ions at the dropping mercury electrode by extending Breyer and Gutman's[2] technique to different frequencies of the A.C. field ranging from 12·5 to 600 cycles per second using the oscillograph for measuring the alternating current. Doss and Kalyanasundaram[3] have studied the discharge of the nickel ions by a modified technique. The present paper deals with the application of this technique to study the behaviour of lead ions.

EXPERIMENTAL

The circuit diagram is given in Fig. 1. The source of A.C. is a B.S.R. oscillator capable of giving frequencies ranging from 0–16,000 cycles per second. 10 Volts from the oscillator is fed on to a potentiometric arrangement consisting of resistances R, R_1, R_2, and R_3. This arrangement serves to give 45 mv. across R_2 which is superimposed on the dropping mercury electrode along with a D.C. voltage obtained from a Cambridge pH potentiometer (with the galvanometer shorted off) used as a potential divider. The A.C. component of the pulsating current is obtained after filtering off the D.C. across a condenser. This is measured by means of a two-stage amplification system consisting of 1 LD 5 valves.[3] R_5 is adjusted such that the potential drop across this gives the same deflection as that of the potential drop across R_3. Thus the A.C. current passing through the dropping electrode can be calculated from a knowledge of the resistance R_5. The frequency of the oscillator is maintained constant at the desired value making use of the Du Mont 208 B oscillograph.

The dropping mercury electrodes have the following characteristics:—

	Dropping electrode I (Fig. 3)	Dropping electrode II (Fig. 4)
m. (mg./sec.)	0·69	0·33
t in sec. in M KCl-aq; Open circuit	5·3	3·6

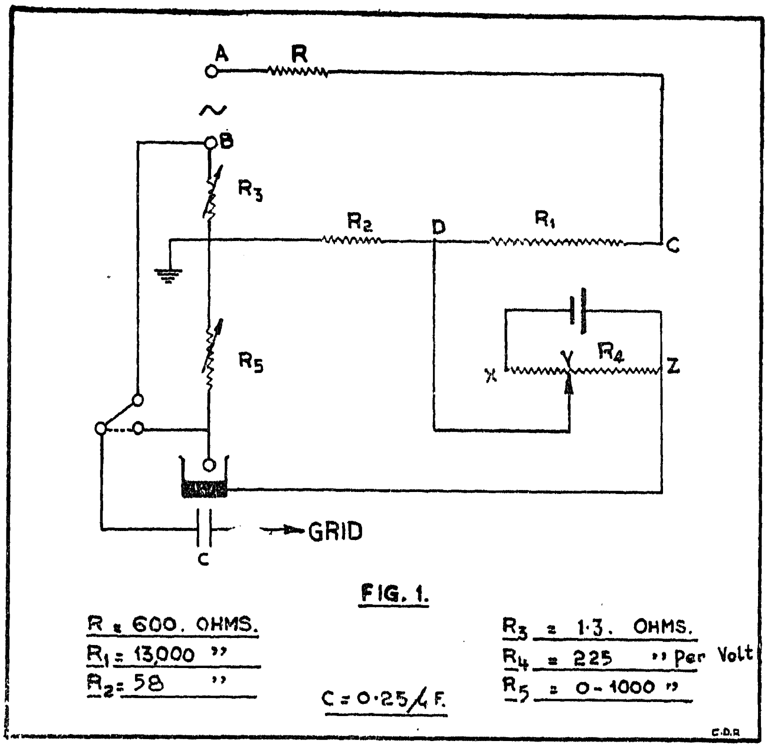
A
R
~
B
R₃
R₂
D
R₁
C
R₄
X
Y
Z
R₅
C
GRID
FIG. 1.
R = 600. OHMS.
R₁ = 13,000 ”
R₂ = 58 ”
C = 0·25 μF.
R₃ = 1·3. OHMS.
R₄ = 225 ” Per Volt
R₅ = 0 - 1000 ”
C.D.R.

FIG. 1

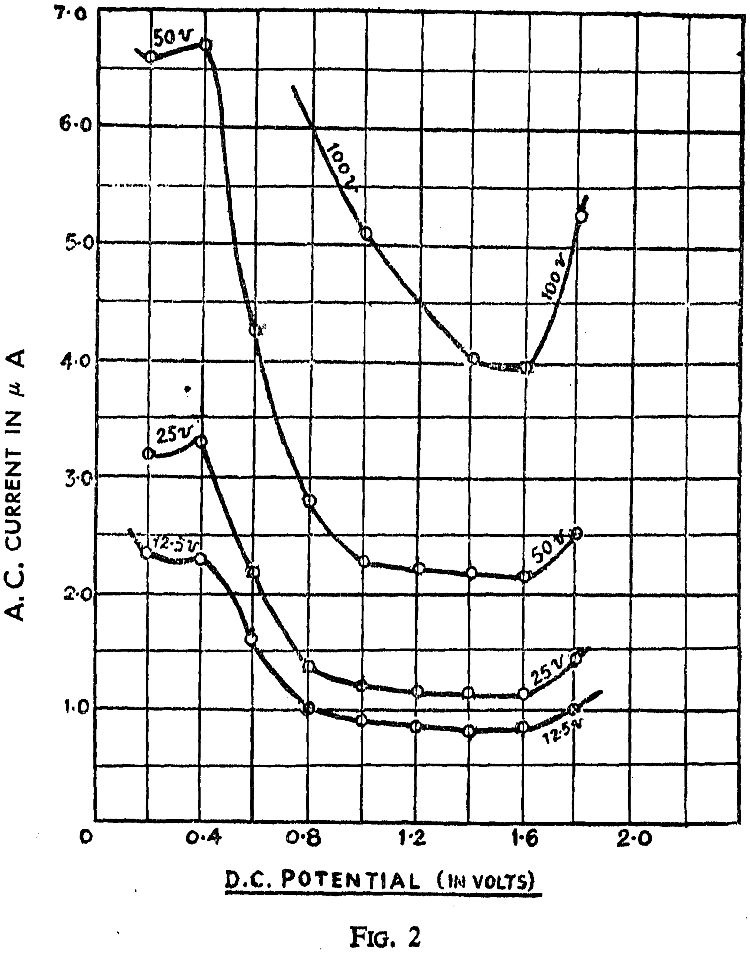
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
0·4
0·8
1·2
1·6
2·0
A. C. CURRENT IN μ A
D.C. POTENTIAL (IN VOLTS)
50 V
100 V
100 V
50 V
25 V
25 V
12·5 V
12·5 V

FIG. 2

The experiment is first performed with 1 M KCl containing no other dischargeable ions. Hydrogen of high purity is obtained electrolytically in the usual manner but with an auxiliary cathode helping in 'cleaning up' the residual oxygen diffusion.[4] This is passed into the solution for about fifteen minutes to remove the traces of oxygen present. The A.C. passing through the dropping electrode at the different D.C. potentials are measured. The experiments are carried out at different frequencies of A.C. and are represented in Fig. 2.

Figs. 3 and 4 represent the results obtained with 1 M KCl containing 2×10^{-3} M lead ions (in the form of lead nitrate).

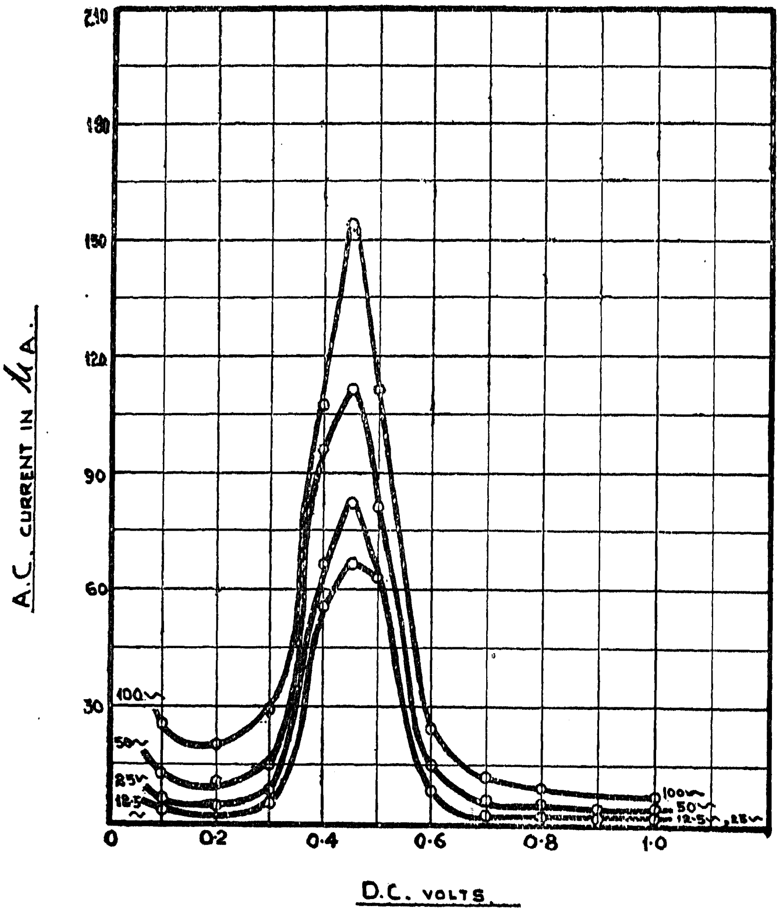

FIG. 3. Behaviour of lead ion in pulsating fields

Fig. 5 represents the polarographic curve of lead obtained with dropping electrode I.

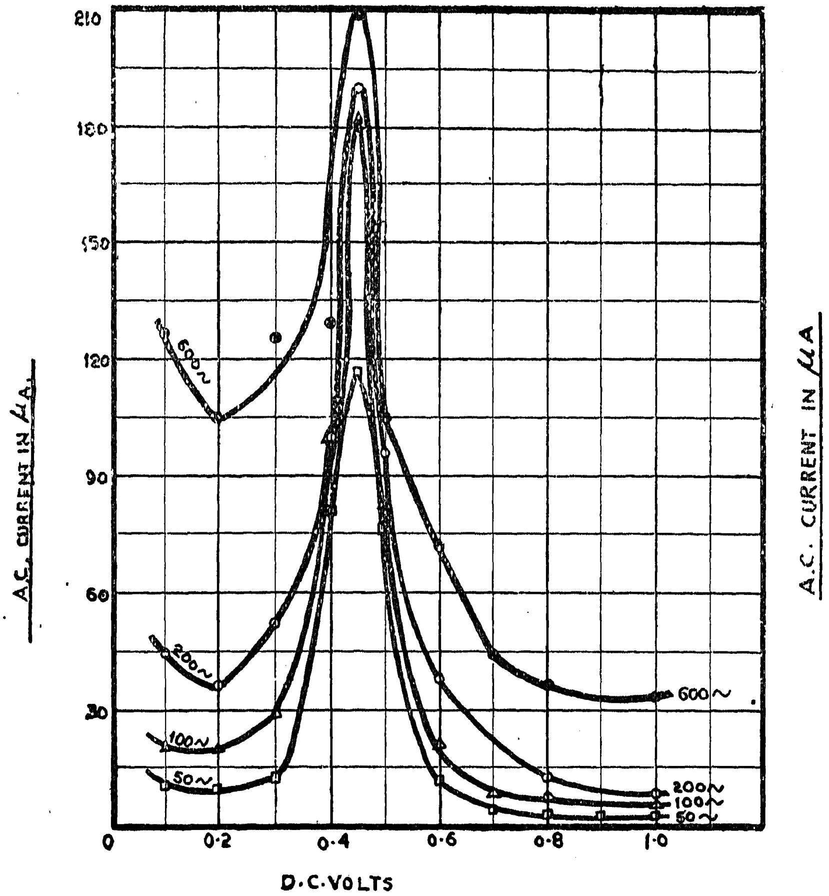

FIG. 4. Behaviour of lead ion in pulsating field

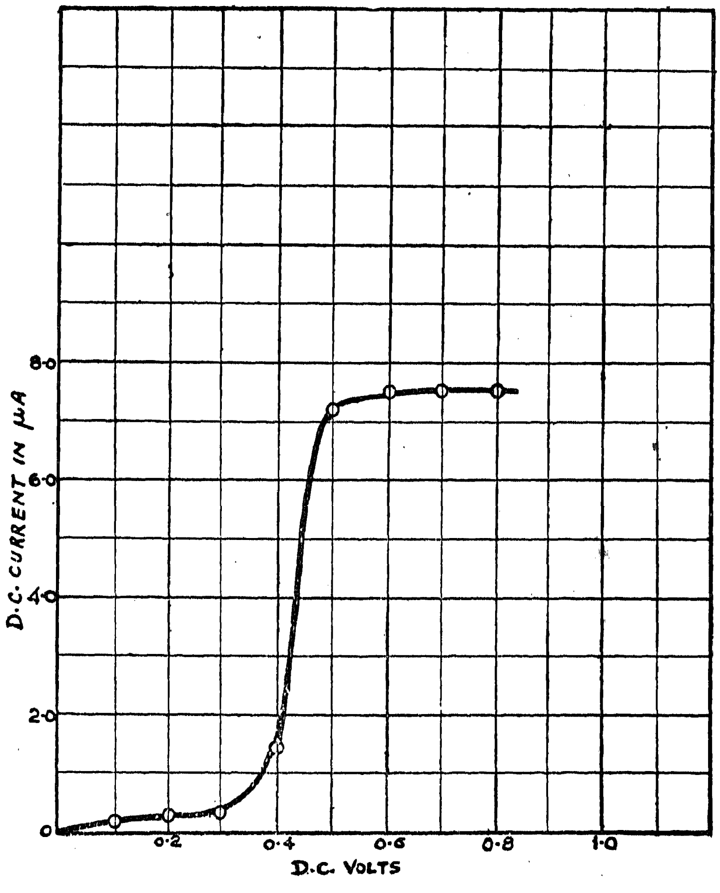

FIG. 5. Polarographic curve for lead

DISCUSSION

The A.C. current–D.C. potential curves in the system containing the indifferent electrolyte only.—

An examination of Fig. 2 shows that the A.C. current starts with a high value at 0·4 V, falls rapidly upto 0·8 V, remains more or less constant upto 1·6 V and thereafter begins to rise. The first fall of A.C. current in the D.C. voltage interval of 0·4 V to 0·8 V coincides approximately with the region in which the electrocapillary maximum occurs. It is well known that the capacity of the electric double layer on the positive side of the electrocapillary maximum is much higher than on the negative side. From this point of view, it is of interest to calculate the capacity of the electric double layer from the observed alternating current values. There are complications arising out of the facts that an average current is measured and also that the size of the drop itself is changing with time. The relationship between the observed average alternating current and the capacity of the electric double layer can be formulated as follows:—The capacitative impedance due to the electric double layer at the mercury drop can be put as equal to K_1ct, where c represents the capacity of the electric double layer in farads/sq.cm. and $K_1 t$ is the area of the mercury drop at time t. If R is the external resistance in ohms, the average current as registered in the measuring equipment will be

$$i_{av} = \frac{\displaystyle\int_0^{t_{\text{max.}}} \frac{\mathrm{E}}{\left[\mathrm{R}^2 + \dfrac{1}{(k_1 c t^{2/3})^2}\right]^{\frac{1}{2}}}\, dt}{t}.$$

Making rough calculations, on the basis of the above formula, taking R to be negligible we get for the capacities of electric double layer at 0·4 V and 1·2 V (with reference to N.C.E.) at 50 cycles/sec., the values of 67 and 26/μF respectively. These values are high as compared with the values of 49/μF and 22/μF per sq.cm. respectively as given by Philpot.[5] These high values may be partly due to the fact that the mercury drop is growing all the time during the measurement or it may be an artefact of some sort. The results however generally indicate the large changes in the capacities of the electric double layer near the electrocapillary maximum. The difference cannot be due to the fact that the effect of resistive impedance is neglected. For, the fact that the current gets nearly doubled as one passes from 25 to 50 cycles both at 0·8 V and 1·2 V shows that the existing impedance is mainly capacitative in character and the resistive part is comparatively negligible. The later rise in the curves beyond 1·6 V is perhaps to be connected with some reductive process coming into play.

The A.C. current-D.C. potential curves in the system containing 0·002 *M lead in MKCl.—*

The observations of Breyer and Gutman that A.C. current maximum occurs at nearly the half-wave potential is confirmed by the present system as well. It is to be seen that the magnitude of the maximum goes on increasing with the frequency of A.C. even upto 600 cycles/second. This behaviour is different from that of nickel reported earlier[3] as well as from even that of lead itself as measured by Doss and Agarwal[2] using the oscillograph. With nickel, even at a frequency of 100 cycles/second, the maximum has disappeared. With lead, in the oscillographic mode of measurement, at 600 cycles/second, the maximum is of a negligible magnitude. Further, the magnitude of the A.C. by this method is much lower than that obtained in the present work.

The above facts can be understood by a detailed consideration of the phenomenon. This can be discussed from two points of view, *viz.*, the molecular kinetic and secondly, the electrical equivalent of the dropping mercury electrode. The molecular kinetic point of view may first be taken up. At low D.C. voltages, say, of the order of 0·2 V there is no discharge of lead ions and hence the system is behaving like a perfectly polarizable electrode. The capacity of the dropping electrode is small, its impedance large and hence the resultant A.C. current is small. As the half-wave potential is reached, the system becomes imperfectly polarizable due to the reduction of the lead ions. There are three important factors to be considered in this connection: the electrode process, *viz.*, the discharge of lead ions and dissolution of lead from the lead amalgam at the surface of the mercury drop, the diffusion processes building up the diffusion layers both on the solution side and in the mercury drop and thirdly, the external resistance of the system. It may be pointed out that the diffusion processes are more or less similar in all the systems studied, as the diffusion coefficients are oft he same order of magnitude. This would not therefore, bring about material differences in the behaviour of the different systems. The main cause of the differences in behaviour appears to be the rate of the electrode processes which may vary several thousand fold in the different systems. For instance, thallium has a rate constant of 1·5 units (moles per sq.cm. per second per mol. per c.c.) whereas zinc, with KNO_3 as indifferent electrolyte, has the value of $4 \cdot 3 \times 10^{-3}$.[6] Apart from the Randles technique which gives an elegant way of determining the rate constants, a qualitative idea of the same can be had from the slope of the polarographic curves taken under similar conditions. A high slope indicates a fast reaction. When the A.C. is incident at the half wave potential, there will be a tendency for the electrode process to keep in pace with the pulsating field. The result will be a pulsating current. As has already been pointed out,[3] the A.C. component of the current cannot be predicted quantitatively from the polarographic curve. This is seen clearly from Fig. 6 wherein the theoretical A.C. current-D.C. voltage curve (Curve I, Fig. 6) worked out from the polarographic curve (Fig. 5) and the experimental curve at 12·5 cycles (Curve II, Fig. 6) are given. The observed A.C. current at the half-wave potential is much higher than that predicted on the basis of the polarographic curve. Further, this difference is much more at higher frequencies of A.C. The magnitude of the fluctuations in the current due to the fluctuating field would depend on the rapidity with which the electrode process would respond to the fluctuations. With a rapid electrode reaction as in the case of lead, the electrode reaction follows easily the fluctuations in the potential and hence large maxima are observed even at as high frequencies as 600 cycles/second.

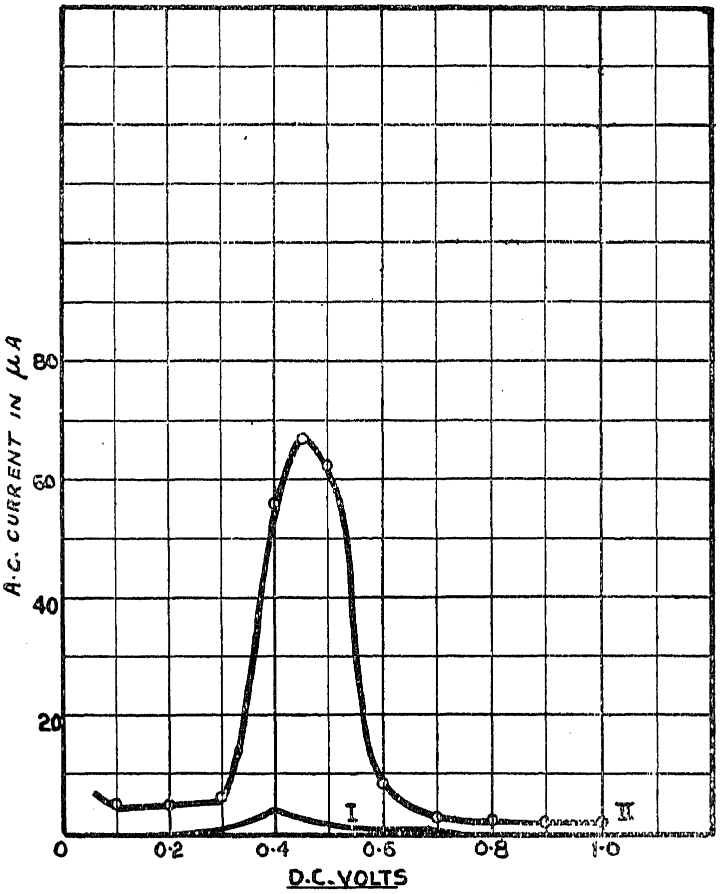

Fig. 6. Theoretical and experimental curve

Nickel, on the other hand, represents a slow electrode process. The Randles' technique has not yet been applied to a system involving nickel. But the rate of electrode process can be judged from the slope of the polarographic curve at the half-wave potential. According to the theory of absolute reaction rates,[7] the rate of the cathodic electrode process should fall exponentially with the fall in the cathodic potentials. This explains the quick rise of the polarographic wave near the half-wave potential. But the actual slope should depend on the free energy of activation for the particular electrode reaction. The slope would therefore be smaller for slow reactions and larger for fast reactions. The low slope of the polarographic wave for nickel indicates that it is a slow reaction. With nickel, therefore, the A.C. maximum disappears at a much lower frequency of the A.C., *viz.*, 100 cycles/second, at which the system behaves as if the nickel ions are absent and the solution contains only the indifferent electrolyte.

It is to be noted, however, that the response of the electrode reaction is dependent on the resistive impedance of the system as it would affect the movement of electrons taking part in the electrode processes. A high external resistance would bring down the maximum of the A.C. current and would lower the frequency at which the A.C. maximum would disappear. This phenomenon has perhaps a correspondence with the lowering of the slope of the polarographic curve at the half-wave potential with the increase in the external resistance. With slow reactions as the external resistance would have a greater effect, a pronounced A.C. maximum can be obtained only by having very low external resistances. With nickel (a slow electrode reaction), for instance, even at a circuit resistance of 600 ohms, the maximum has disappeared at 100 cycles per second whereas with lead with over 1,000 ohms[1] as circuit resistance the maximum is perceptible even at 600 cycles per second. In the present work, the persistance of a large maximum with lead even at 600 cycles is due to the very low circuit resistance (200 ohms) used in the present mode of measurement. A detailed investigation of the effect of external resistance will be published shortly.

It is to be pointed out that the difference between the current at the A.C. maximum and the corresponding current for the indifferent electrolyte at the same D.C. potential (Figs. 2 and 3) is a semi-quantitative measure of the amount of electrode process in which the lead ions are involved. It is to be seen that this difference is small at low frequencies, increases at higher frequencies, reaches a maximum and again becomes small at higher frequencies. The frequency at which the maximum difference is observed appears to be a measure of the rapidity of the electrode reaction if the resistance of the circuit is constant. It is of interest to consider the possibility of determining the rate constant by these measurements suitably modified so as to avoid the complications arising from the changes due to the growing drop, the large amplitude of the applied A.C. potential as well as the average nature of the A.C. current measured.

Whatever has been discussed above can be pictured in terms of the electrical equivalent. The large rise in the A.C. current at the half-wave potential is a result of diminution in the impedance of the dropping electrode system. This can be pictured as brought about by two parallel shunts, *i.e.*, a resistance and a capacity to the electric double layer at the mercury-solution interface. The capacity shunt would have a high impedance for a slow reaction as in the case of nickel whereas it would have a low impedance in the case of lead. This would completely explain the observed frequency dependance. It is of interest to examine how the capacity shunt corresponding to the electrode reaction would get affected by changes in frequency.

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SUMMARY

The discharge of the lead ions at the dropping mercury electrode has been studied by the Breyer and Gutman technique at different frequencies. This system has revealed interesting features which are different from the systems investigated by others. The results have been interpreted taking into account the kinetics of discharge of the lead ion at the electrode.

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