

**CIHM
Microfiche
Series
(Monographs)**

**ICMH
Collection de
microfiches
(monographies)**



Canadian Institute for Historical Microreproductions / Institut canadien de microreproductions historiques

© 1995

Technical and Bibliographic Notes / Notes techniques et bibliographiques

The Institute has attempted to obtain the best original copy available for filming. Features of this copy which may be bibliographically unique, which may alter any of the images in the reproduction, or which may significantly change the usual method of filming, are checked below.

L'Institut a microfilmé le meilleur exemplaire qu'il lui a été possible de se procurer. Les détails de cet exemplaire qui sont peut-être uniques du point de vue bibliographique, qui peuvent modifier une image reproduite, ou qui peuvent exiger une modification dans la méthode normale de filmage sont indiqués ci-dessous.

- Coloured covers/
Couverture de couleur
- Covers damaged/
Couverture endommagée
- Covers restored and/or laminated/
Couverture restaurée et/ou pelliculée
- Cover title missing/
Le titre de couverture manque
- Coloured maps/
Cartes géographiques en couleur
- Coloured ink (i.e. other than blue or black)/
Encre de couleur (i.e. autre que bleue ou noire)
- Coloured plates and/or illustrations/
Planches et/ou illustrations en couleur
- Bound with other material/
Relié avec d'autres documents
- Tight binding may cause shadows or distortion along interior margin/
La reliure serrée peut causer de l'ombre ou de la distorsion le long de la marge intérieure
- Blank leaves added during restoration may appear within the text. Whenever possible, these have been omitted from filming/
Il se peut que certaines pages blanches ajoutées lors d'une restauration apparaissent dans le texte, mais, lorsque cela était possible, ces pages n'ont pas été filmées.

- Coloured pages/
Pages de couleur
 - Pages damaged/
Pages endommagées
 - Pages restored and/or laminated/
Pages restaurées et/ou pelliculées
 - Pages discoloured, stained or foxed/
Pages décolorées, tachetées ou piquées
 - Pages detached/
Pages détachées
 - Showthrough/
Transparence
 - Quality of print varies/
Qualité inégale de l'impression
 - Continuous pagination/
Pagination continue
 - Includes index(es)/
Comprend un (des) index
- Title on header taken from:/
Le titre de l'en-tête provient:
- Title page of issue/
Page de titre de la livraison
 - Caption of issue/
Titre de départ de la livraison
 - Masthead/
Générique (périodiques) de la livraison

Additional comments:/
Commentaires supplémentaires:

This item is filmed at the reduction ratio checked below/
Ce document est filmé au taux de réduction indiqué ci-dessous.

10X	12X	14X	16X	18X	20X	22X	24X	26X	28X	30X	32X
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

The copy filmed here has been reproduced thanks to the generosity of:

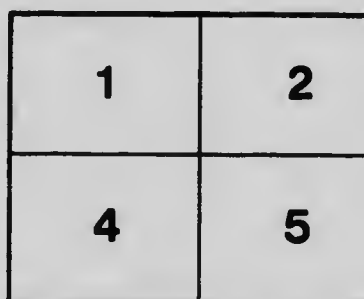
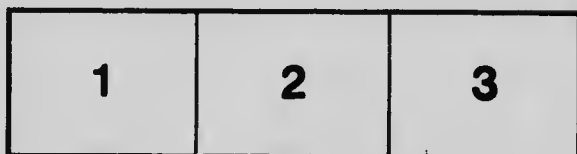
University of Toronto Archives

The images appearing here are the best quality possible considering the condition and availability of the original copy and in keeping with the filming contract specifications.

Original copies in printed paper covers are filmed beginning with the front cover and ending on the last page with a printed or illustrated impression, or the back cover when appropriate. All other original copies are filmed beginning on the first page with a printed or illustrated impression, and ending on the last page with a printed or illustrated impression.

The last recorded frame on each microfiche sheet contain the symbol \rightarrow (meaning "CONTINUED"), or the symbol ∇ (meaning "END"), whichever applies.

Maps, plates, charts, etc., may be filmed at different reduction ratios. Those too large to be entirely included in one exposure are filmed beginning in the upper left hand corner, left to right and top to bottom, as many frames as required. The following diagrams illustrate the method:



L'exemplaire filmé fut reproduit grâce à la générosité de:

University of Toronto Archives

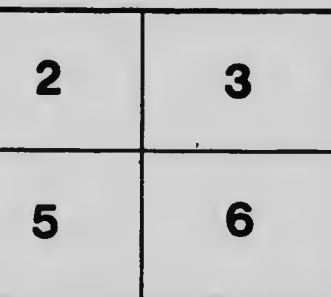
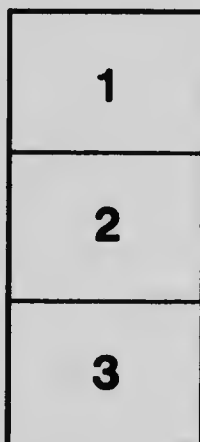
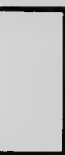
Les images suivantes ont été reproduites avec le plus grand soin, compte tenu de la condition et de la netteté de l'exemplaire filmé, et en conformité avec les conditions du contrat de filmage.

Les exemplaires originaux dont la couverture en papier est imprimée sont filmés en commençant par le premier feuillet et en terminant soit par le dernier feuillet qui comporte une empreinte d'impression ou d'illustration, soit par le second feuillet, selon le cas. Tous les autres exemplaires originaux sont filmés en commençant par le premier feuillet qui comporte une empreinte d'impression ou d'illustration et en terminant par le dernier feuillet qui comporte une telle empreinte.

Un des symboles suivants apparaîtra sur la dernière image de chaque microfiche, selon le cas: le symbole \rightarrow signifie "A SUIVRE", le symbole ∇ signifie "FIN".

Les cartes, planches, tableaux, etc., peuvent être filmés à des taux de réduction différents.

Lorsque le document est trop grand pour être reproduit en un seul cliché, il est filmé à partir de l'angle supérieur gauche, de gauche à droite, et de haut en bas, en prenant le nombre d'images nécessaire. Les diagrammes suivants illustrent la méthode.



MICROCOPY RESOLUTION TEST CHART

(ANSI and ISO TEST CHART No. 2)



4.5

5.0

5.6

6.3

7.1

8.0

9.0

10

11.2

12.5

14.3

16.0

18.0

20

22.5

25

28.2

31.5

35

39.6

45

50

56

2.8

3.2

3.6

4.0

2.5

2.2

2.0

1.8

1.6



APPLIED IMAGE Inc

1653 East Main Street
Rochester, New York 14609 USA
(716) 482 - 0300 - Phone
(716) 288 - 5954 - Fax

UNIVERSITY OF TORONTO
STUDIES

PAPERS FROM THE CHEMICAL
LABORATORIES

No. 100: ELECTRODEPOSITION OF METALS, BY W. LASH
MILLER

(REPRINTED FROM THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY,
VOL. XXIII)

THE UNIVERSITY LIBRARY: PUBLISHED BY
THE LIBRARIAN, 1913



University of Toronto Studies
COMMITTEE OF MANAGEMENT

Chairman: ROBERT ALEXANDER FALCONER, M.A., Lit . D.D.
President of th v

PROFESSOR W. J. ALEXANDER, PH.D.

PROFESSOR W. H. ELLIS, M.A., M.B.

PROFESSOR J. J. MACKENZIE, B.A.

PROFESSOR J. P. McMURRICH, PH.D.

PROFESSOR G. H. NEEDLER, PH.D.

PROFESSOR GEORGE M. WRONG, M.A.

General Editor: H. H. LANGTON, M.A.
Librarian of the University



The Presidential Address, introducing the Symposium on Electrodeposition of Metals, at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913.

THE ELECTRODEPOSITION OF METALS

By W. LASH MILLER.

In opening this symposium, I wish first of all to convey the hearty thanks of the Society to our members, Messrs. Bancroft, Bennett, Frary, Kern, Mathers and Watts, who have carried through the laborious task of collecting the data that are in our hands today. To make this collection it was necessary to go through the patent literature, and to search monographs, abstract journals and text-books of inorganic chemistry, electrochemistry, electroanalysis, electroplating and electrorefining for sources of information, and then to consult the original articles in dozens of scientific and technical journals. No attempt has been made to give only the "good" recipes; in photochemistry, as is well known, the art of photography has far outstripped the science, and here too it may be found that some "obviously silly addition to the bath, recommended by a technical man, may in practice have a beneficial effect for reasons unsuspected and unexplained.

The compilers, of course, accept no responsibility except for the correctness of their abstracts. Their work has furnished us with a summary of permanent value and a basis for today's discussions. Our thanks are due them, and are hereby tendered, for all the trouble they have taken.

Our subject of today was brought before this Society nine years ago at one of its joint meetings with the Fifth International Electrical Congress at the St. Louis Exposition, in a paper by Bancroft¹ on "The Chemistry of Electroplating." In this paper the author, among other matters, compared the structure of metals deposited electrolytically by heavy currents with the structure of precipitates produced rapidly by purely chemical means, and in this analogy found the only explanation we yet

¹ Bancroft, *These Transactions*, 6, 27-43 (1904).



have of the direct effect of current density on the structure of the deposit.

Now, nine years later, this parallelism between "electrochemical" and purely chemical processes,² which Bancroft was one of the first to emphasize, is generally recognized; and some striking new instances have been found by Skrabal³ in his study of the reduction of the chromates; it is, moreover, at the bottom of all the explanations recently put forward to account for certain puzzling voltages observed at the electrodes during electrolysis, which is the subject I have chosen to speak on today.

If the electromotive force needed to send a heavy current through a given electrolytic cell is greater than that required to send a light current by more than the product of the current-difference into the resistance of electrolyte and wiring, the cell is said to be "polarized" by the current. The same word is frequently made use of when it is found that a higher voltage is needed to bring about a given reaction—say, the liberation of hydrogen—at an electrode of one material, say mercury, than when another material, say platinum, is employed. Two causes for such polarization have long been recognized. The first is the formation of a precipitate or film which may shut off the current altogether, as with anodes of aluminum or tantalum,⁴ or which may cut down the current and so permit the precipitate to dissolve, giving rise to periodic phenomena, as in the electrolysis of sodium sulphide⁵ or of some nickel salts,⁶ or which finally, while letting the current pass, may protect the metal from solution and so render it "passive," as with anodes of lead⁷ and tin⁸ in solutions of caustic soda. The second long-recognized cause of polarization is the electromotive force due to concentration changes set up at the electrodes by the current.

Other causes, of course, have been suggested; but, until recently, acting on what Mach calls the principle of "economy" in

² See also, Luther, *Zeit. f. Elektrochem.*, 8, 646 (1902), and Bancroft, *These Transactions*, 8, 33 (1905).

³ Skrabal, *Zeit. f. Elektrochem.*, 14, 529 (1908).

⁴ v. Bolton, *Zeit. f. Elektrochem.*, 11, 49 (1905).

⁵ Kuessner, *Zeit. f. Elektrochem.*, 10, 769 (1910).

⁶ Koelichen, *Zeit. f. Elektrochem.*, 7, 62 (1901).

⁷ Küster, *Zeit. anorg. Chem.*, 46, 113 (1905).

⁸ Thiel u. Windelschmidt, *Zeit. f. Elektrochem.*, 12, 737 (1906), and 13, 317 (1907).

⁹ Elbs u. Forsell, *Zeit. f. Elektrochem.*, 8, 760 (1902).

¹⁰ Foerster u. Dolch, *Zeit. f. Elektrochem.*, 16, 599 (1910).

science,⁹ electrochemists have endeavored to refer all cases of polarization to one or the other of the two classes just defined. It was not always easy. Experiments with anodic mirrors,¹⁰ for instance, have discredited the oxide-film theory of the passivity of iron, while the concentration-cell explanation loses plausibility when it assumes such concentrations as ten tons of hydrogen per liter to "explain" the polarization of mercury in normal sulphuric acid.¹¹ Still, it is always possible to assume "invisible films" and endow them with any properties desired; and equation which lead to impossibly high concentrations awake in some minds a feeling of reverence rather than criticism; so that the necessity for new explanations was recognized only when it appeared that concentration changes at the electrodes may be calculated from the laws of diffusion, and that in certain instances they are wholly insufficient to account for the polarization observed.

The first to make such calculations was Weber;¹² his results, like those of his successors, Warburg¹³ and Sand,¹⁴ were based on the assumption that in the experimental work all convection—whether due to stirring, vibration, heating, evolution of gases, or change of specific gravity in the solutions—was strictly excluded. The great advance in the theory of diffusion which has freed experimenters from such difficult conditions was made in Noyes and Whitney's¹⁵ paper on the rate of solution of solids; and their theory of diffusion through an adherent liquid film,¹⁶ applied by Nernst,¹⁷ Brunner¹⁸ and Merriam,¹⁹ has led to quick and reliable laboratory methods of determining the concentrations sought.²⁰

⁹ Mach, Popular scientific lectures, Chicago, Open Court Publishing Co. (1895).
¹⁰ Müller u. Königsberger, Physik. Ztschr., **5**, 413, 797 (1904); Zeit. f. Elektrochem., **13**, 659 (1907).

¹¹ 0.42 volt, according to Müller, Zeit. anorg. Chem., **26**, 1 (1900); higher according to Coehn u. Danneberg, Zeit. phys. Chem., **38**, 609 (1901), and Caspari, Zeit. phys. Chem., **30**, 80 (1899).

¹² Weber, Wied. Ann., **7**, 536 (1879).

¹³ Warburg, Wied. Ann., **67**, 493 (1899).

¹⁴ Sand, Zeit. phys. Chem., **35**, 641 (1900); Phil. Mag., [6] **1**, 45 (1901).

¹⁵ Noyes and Whitney, Zeit. phys. Chem., **23**, 689 (1897).

¹⁶ A similar hypothesis has just been introduced into the theory of the conduction of heat in gases, and promises to be equally fruitful. See Langmuir, this vol., p. 290.

¹⁷ Nernst, Zeit. phys. Chem., **47**, 52 (1904).

¹⁸ Brunner, Zeit. phys. Chem., **47**, 56 (1904).

¹⁹ Nernst u. Merriam, Zeit. phys. Chem., **53**, 235 (1905).

²⁰ A full treatment of the mathematical theory of the concentration changes at the electrodes brought by direct, interrupted, or alternating current, which includes the case of non-instantaneous reactions between the primary products of electrolysis and the other constituents of the solution, is given by T. R. Rosbrugh and W. Lash Miller, Jour. Phys. Chem., **14**, 816-884 (1910).

The inadequacy of the film and concentration explanations once recognized, what is the nature of the new explanations now advanced? Again the parallelism between electrolytic and purely chemical reactions is appealed to: The growth of copper at the cathode is compared with that of crystals in an undercooled solution; reactions at the electrode hitherto supposed instantaneous are seen to take their time like others; hypothetical hydrated ions are introduced, requiring time to give up their water; "intermediate" compounds of all kinds are assumed—in short, the whole collection of viewpoints and hypotheses built up by the study of chemical kinetics is transferred bodily to electrochemistry. One thing at least is gained: The old, undue simplicity is gone; while Faraday's and Hittorf's laws, of course, remain, and the principles of thermodynamics are as valid as ever, it is now recognized, never again to be forgotten, that electrochemical processes like those of pure chemistry are subject to the Bancroft-Ostwald law as well, according to which the thermodynamically "most probable" reaction is in practice perhaps the least likely to occur.²¹

Smale²² thought years ago, and all thought with him, that he had determined the electromotive force of the reversible oxygen-hydrogen cell to be 1.075 volt; Haber²³ shows that 1.23 volt is nearer the truth. Much work²⁴ was done to clear the matter up, and now it seems that the electrodes—even "unattackable" platinum and iridium—are converted during electrolysis into oxides or hydrides, by whose subsequent decomposition oxygen and hydrogen are formed.²⁵ At all events, such substances have been prepared,²⁶ and prove to have the properties required. The assumption that these oxides are only slowly formed explains the need for waiting several days²⁷ before the "chromic acid electrode" attains its final electromotive force, while the observation often made that platinum or iridium serves "better" than gold²⁸

²¹ Bancroft, *Jour. Phys. Chem.*, **1**, 137 (1896); see also Wald, *Zeit. phys. Chem.*, **24**, 509 (1897); Ostwald, *Zeit. phys. Chem.*, **22**, 306 (1897).

²² Smale, *Zeit. phys. Chem.*, **14**, 577 (1894); **16**, 562 (1895).

²³ Haber, *Thermodynamik technischer Gasreaktionen*, p. 161 (1905).

²⁴ Luther, *Zeit. f. Elektrochem.*, **13**, 290 (1907).

²⁵ Lorenz, *Zeit. f. Elektrochem.*, **14**, 78 (1908).

²⁶ Wöhler, *Zeit. f. Elektrochem.*, **17**, 98 (1911).

²⁷ Scobai, *Zeit. f. Elektrochem.*, **9**, 879 (1903).

²⁸ Crotono, *Zeit. anorgan. Chem.*, **24**, 245 (1900).

for oxidation cells may be due to the lack of a suitable series of gold oxides or to the slower rate at which they may be formed.

The conception of the electrode process thus has changed. No longer does the H^+ sign simply lose its *plus*—or the ion its charge, if that form of symbolism be preferred—and then uniting two by two leave the electrode with the exact potential most convenient for thermodynamical computations, all over in an instant. Now we must think of purely chemical reactions, of series of indefinite hydrides, or oxides, as the case may be, slowly reaching equilibrium with the solution.

The only reliable test of a conception is its fruitfulness, and Mills'²⁹ criterion of a good scientific hypothesis is that it may be tested. The point of view just set out suggested and offers a satisfactory explanation of some experiments carried out by students in the Toronto laboratory, to which I shall now refer.

If sulphuric acid, potassium bichromate and potassium iodide are dissolved in the right proportions in water, iodine is slowly liberated.³⁰ It must be obvious that in such a solution the electromotive force thermodynamically "necessary" to reduce the chromic acid is less than that required to reduce the iodine. In point of fact, however, if a cathode be introduced, it is the iodine, and not the chromic acid, that reacts. The "oxide theory" of the chromic acid electrode, taken together with Merriam's observation that the electrolytic reduction of iodine is practically instantaneous, gives the explanation. A gold electrode is most convenient, because platinum catalyses the reaction between chromic acid and iodide; the "oxide" explanation of this difference between the two metals has just been gone into, and it is hoped that measurements of the rate of catalysis may furnish a check.

Arsenic acid behaves just like chromic; in this case, moreover, conditions under which the reverse reaction can conveniently be studied are known,³¹ and a few experiments served to show that an anode oxidized iodide instead of arsenious acid, in solutions where all the while iodide was being formed and arsenious

²⁹ "The hypothesis, by suggesting observations and experiments, puts us on the road to that independent evidence, if it be really attainable; and till it be attained, the hypothesis ought only to count for a more or less plausible conjecture." J. S. Mills, *System of Logic*, Book III, Chap. 14.

³⁰ De Lury, *Jour. Phys. Chem.*, **7**, 239 (1903).

³¹ Roebuck, *Jour. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905).

acid destroyed by the "purely chemical" reaction. Particularly sharp results can be obtained with solutions where the two reactions are in equilibrium, working with low concentration of free iodine, as described by Roebuck,³² but I shall not take up time with these details.

Perhaps the most interesting are the results obtained with iron.³³ Four years ago Mr. D. A. Welsh found that in solutions where iodide was slowly undergoing oxidation by a ferric salt, platinum accelerated the reaction, and a gold cathode reduced the iodine. The ferric salt thus behaves exactly like chromic acid. If the explanation is to be the same, a new formula for the electrolytic reduction must be used; $Fe^{+++} \rightarrow Fe^{++}$ will not serve any longer; intermediate steps have been left out.

More closely connected with our subject of today is the cathodic polarization observed by LeBlanc³⁴ with the oscillograph during electrolysis of the sulphates or nitrates of copper, nickel and silver. The study of these and similar cases has been continued by Reichinstein, who, working with direct current,³⁵ observed polarizations as high as 0.7 volt during the deposition of copper on a copper cathode in slightly acid solutions of copper sulphate, and has elaborated a theory to account for these results, based on the assumed primary formation of a hydrogen-copper alloy.

With apparatus constructed after Reichinstein's description,³⁶ Mr. Burt-Gerrans and Mr. Brant were able to reach polarizations of the same order as his, the deposit being pure copper and no hydrogen being evolved; in order to check the theoretical explanations offered, they repeated the experiments, adding a nickel salt to the solution. As the decomposition voltage of nickel sulphate is less than 0.6 volt higher than that of copper sulphate, it is hard to see how a deposit of alloy on the electrode, or delay in the dehydration of copper ions, or a deficiency of cuprous salt at the cathode, could interfere with the deposition of nickel if the electromotive force between solution and cathode were kept 0.7 to 0.8 volt higher than that needed (with low currents) to deposit

³² Roebuck, *loc. cit.*, p. 392.

³³ See also Maitland, *Zeit. f. Elektrochem.*, 12, 264 (1906), and Nernst u. Merriam, *loc. cit.*

³⁴ LeBlanc, *Abh. d. Deutschen Bunsen Ges.*, No. III (1910).

³⁵ Reichinstein, *Zeit. f. Elektrochem.*, 18, 850 (1912).

³⁶ Reichinstein, *loc. cit.*, p. 855.

copper. The wished-for voltage was maintained for fifteen minutes with a current of 0.44 ampere, but the deposit contained no trace of nickel. Similar experiments with the chlorides of copper and tin, and with the nitrates of silver and copper, likewise gave negative results.

Another explanation of the polarization must therefore be sought. Reichinstein's cathode consisted of a plate of copper covered with paraffin except for five square centimeters of one of its surfaces, in front of which—*i. e.*, directly between cathode and anode—and "extremely close to the paraffin-free surface," rotated a Witt's stirrer of glass. The siphon leading to the hydrogen electrode and the potentiometer circuit with which the polarization was measured entered the cell behind the cathode plate. It is obvious that, in order to find the true polarization with such an arrangement, the potentiometer readings must be corrected by subtracting something for the drop of potential along the (curved) path of the electrolyzing current; the order of magnitude of this correction, however, cannot be estimated without knowledge of the dimensions of the apparatus. This correction will depend, for instance, on the distance between anode and cathode, and it will be the greater the larger the stirrer and the nearer it is to the cathode, the larger the anode surface, and the larger the paraffined margin around the cathode surface.

In the absence of such data the curves³⁷ themselves give a hint. Above 0.1 volt they are almost straight lines, voltage rising with current; and in Fig. 532³⁸ (which records a number of measurements with different solutions, made without disturbing the apparatus) their slopes are proportional to the specific resistances of the solutions used. These curves, then, suggest very strongly that the higher "polarizations" recorded would be substantially cut down by a suitable correction for the potential drop in the electrolyte, and, provisionally at least, may be regarded as confirming the negative result obtained in the nickel experiments.

If this turns out to be the case it would seem that there is still room for a very old-fashioned explanation of some cases of polarization side by side with the most modern developments of the chemical analogy!

³⁷ The ordinates record the uncorrected "polarization," and the abscissae the electrolyzing current.

³⁸ *Loc. cit.*, p. 860.



