Ouachita Baptist University

Scholarly Commons @ Ouachita

Honors Theses

Carl Goodson Honors Program

1967

Chronopotentiometry of Metals

Lana Sue LeGrand

Ouachita Baptist University

Follow this and additional works at: https://scholarlycommons.obu.edu/honors_theses

Part of the Materials Chemistry Commons

Recommended Citation

LeGrand, Lana Sue, "Chronopotentiometry of Metals" (1967). *Honors Theses*. 424.
https://scholarlycommons.obu.edu/honors_theses/424

This Thesis is brought to you for free and open access by the Carl Goodson Honors Program at Scholarly Commons @ Ouachita. It has been accepted for inclusion in Honors Theses by an authorized administrator of Scholarly Commons @ Ouachita. For more information, please contact mortensona@obu.edu.

CHRONOPOTENTIOMETRY OF METALS

by

Lana LeGrand

Special Studies
Spring Semester 1967
Instructor: Dr. Alex Nisbet

"Chronopotentiometry is the name given to electrolysis experiments in which the time-dependent variations of the potential of an electrode caused by the passage of current through it are measured." Usually the current is kept constant but it can be taken as a function of time.[1]

For a long time now the general characteristics of potential-time curves in constant current electrolysis have been known and studied. In 1901 Sand derived his equation giving a relationship for the transition time τ(sec.), providing that the solution is unstirred and linear diffusion is the controlling factor. The Sand equation is as follows:

$$\tau^{1/2} = \frac{\pi^{1/2} n F A D^{1/2} C}{2i}$$

where C is concentration (moles/cm^3) of the electroactive species in solution, i is constant electrolysis current (amp.), D is the diffusion coefficient of the reacting species (cm.^{2}/sec.), F is the faraday (96,500 coulombs), A is the electrode area (cm.^{2}), n is the number of faradays per molar unit of reaction.[2]

Verification of the diffusion control can be made by measuring various currents and transition times, keeping all other values constant. These should give a constant value for $i\tau^{\frac{1}{2}}$.[3]

---

[1] Fred C. Anson, "Chronopotentiometry," The Encyclopedia of Electrochemistry, ed. Clifford A. Hampel, (New York, Reinhold Publishing Company, 1964), pp. 204-205.

[2] James J. Lingane, Electroanalytical Chemistry (New York, Interscience Publishers, Inc., 1958), p. 620.

[3] Lingane, p. 620.

There are usually three electrodes in the electrolysis cell. These are the working electrode where the reaction prodeeds; a reference electrode, which is usually saturated calomel, against which the potential of the working eledtrode is measured; and the auxiliary electrode to complete the electrolysis circuit.[4]

The auxiliary electrode is isolated by placing it in a compartment which makes contact with the test solution by a sintered glass disk. A simple glass tube with a sintered glass bottom immersed in the solution is sufficient. Also, the tip of the salt bridge on the reference electrode should be placed as close as possible to the surface of the working electrode to minimize the iR drop included in the apparent potential of the working electrode.[5]

It is important that the solution be kept undistubbed so that the transition time is due to the diffusion of the reactant. Therefore, the cell should be mounted so that there will be the minimum of vibration or disturbance. Also, there should be a large concentration of a supporting electrolyte to help carry the current and to cut down the resistance of the solution. If several measurements are being made with the same solution the solution should be stirred after each trial to destroy the diffusion layer at the electrode from the previous trial. Then it should be allowed to settle for about a minute.[6]

---

[4] Anson, pp. 204-205.

[5] Lingane, p. 627.

[6] Lingane, p. 628.

When the electroylsis current is flowing, what actually happens is that the reactant is consumed and its concentration at the surface of the electrode is decreased, causing a concentration gradient. This concentration gradient causes reactant from the body of the solution to diffuse toward the electrode. The supply of reactant due to diffusion is not sufficient to maintain the constant current which is flowing; therefore, a second electrode reaction must commence in order to keep the current constant. Most often in solutions of one component this second reaction is the decomposition of the solvent. This reaction takes place at an electrode potential quite different from that at which the primary reactant is consumed, ordinarily, so that a sharp change in the potential results. The time that passes between the initiation of the current through the cell and this sharp change, signifying the consumption of essentially all of the reactant at the electrode surface, is called the transition time τ.[7]

The relationship between the transition time and the other given conditions is given by the Sand equation as stated above. The constant current used in the acquired data of this paper was furnished by a 360 volt power supply with an adjustable number of resistors in series.

---

[7] Anson, pp. 204-205.

Diffusion Equation: Calculations for reduction.

$V = A\Delta X$ concentration $= \frac{N}{V} = \frac{N}{A\Delta X}$

$$\frac{\partial N}{\partial t} = AD\frac{\partial c}{\partial x}$$

$$\lim_{\Delta X\to 0}\frac{1}{A\Delta X}\left(\frac{\partial N}{\partial t}(X+\Delta X) - \frac{\partial N(X)}{\partial t}\right) = \lim_{\Delta X\to 0}\frac{D}{\Delta X}\left(\frac{\partial c}{\partial X}(X+\Delta X,t) - \frac{\partial c}{\partial X}(X,t)\right)$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial X^2}$$

$$s\bar{c}(X,s) - c(X,0) = D\frac{\partial^2 \bar{c}}{\partial X^2}$$ where $\bar{c}(X,s) = L\{c(X,t)\}$

$$\frac{s}{D}\bar{c}(X,s) - \frac{c}{D}(X,0) = \frac{d^2\bar{c}}{dX^2}$$

$$\frac{d^2\bar{c}}{dx^2} - \frac{s}{D}\bar{c}(X,s) = -\frac{c}{D}(X,0)$$

$$\bar{c}(X,s) = P(s)e^{X\sqrt{s/D}} + Q(s)e^{-X\sqrt{s/D}} + \frac{c^b}{s}$$

where P, Q are constants.

Initial conditions and boundary conditions

1. $c(X,0) = c^b$ — c^b equals the bulk concentration.
2. $\lim_{X\to\infty} c(X,t) = c^b$

i amp = coul/sec.
1 mole of e^- = 96,500 coul. = 1 F
n = moles of elections
per mole of ions in reaction

$$\frac{\partial N}{\partial t} = AD\frac{\partial c}{\partial X}$$

$$\left.\frac{\partial N}{\partial t}\right)_{X=0} = \frac{i}{nF}$$

$$AD\frac{\partial c}{\partial x} = \frac{i}{nF}$$

3. $$\left.\frac{\partial c}{\partial x}\right)_{X=0} = \frac{i}{nFAD}$$

$\lim_{x \to \infty} \bar{c}(x,s) = \frac{c^b}{s}$ $\quad \therefore P = 0$

$\frac{\partial \bar{c}}{\partial x}(0,s) = \frac{i}{nFADs}$ $\quad \frac{\partial \bar{c}}{\partial x} = -Q\sqrt{\frac{s}{D}}\, e^{-x\sqrt{s/D}}$

$$\frac{i}{nFADs} = -Q\sqrt{s/D}$$

$$Q = \frac{-i}{nFAD^{\frac{1}{2}} s^{3/2}}$$

$$\therefore \bar{c}(x,s) = \frac{c^b}{s} - \frac{i e^{-x\sqrt{s/D}}}{nFAD^{1/2} s^{3/2}}$$

$$\bar{C}(0,s) = \frac{c^b}{s} - \frac{i}{nFAD^{\frac{1}{2}} s^{3/2}}$$

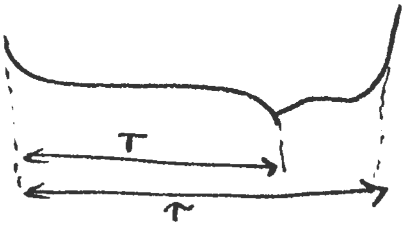
$$c(0,t) = c^b - \frac{2i\sqrt{t}}{nFA\sqrt{D\pi}}$$

This is the concentration at the surface any time t after the current is switched on.

$$C(0,\tau) = c^b - \frac{2i\sqrt{\tau}}{nFA\sqrt{D\pi}} = 0$$

$$\frac{i\sqrt{\tau}}{C^b} = \frac{nFA\sqrt{D\pi}}{2}$$

Calculations for reversal:



$C_R(0,\tau) = 0$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$$

Boundary and initial conditions

1. $C_R(X,0) = 0$
2. $\lim_{x \to 0} C_r(x,t) = 0$

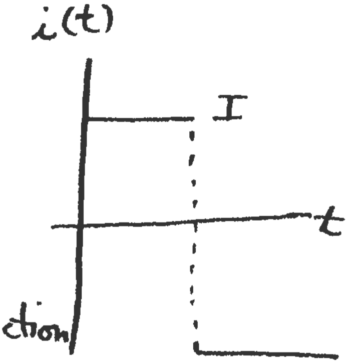
$$\left.\frac{\partial C_{ox}}{\partial x}\right)_{x=0} = \frac{+i(t)}{nFAD_{ox}}$$

$i(t) = I(1 - 2S_T(t))$

where S_T is the step function

$S_T = 0 \quad t < T$

$S_T = 1 \quad t > T$



$$\frac{\partial N}{\partial t} = AD\frac{\partial c}{\partial x}$$

$Ox \longrightarrow Red + e^-$

$$-\left.\frac{\partial N_R}{\partial t}\right)_{x=0} = \left.\frac{\partial N_{ox}}{\partial t}\right)_{x=0}$$

$$-AD_R \frac{\partial C_R}{\partial x}(0,t) = AD_{ox}\frac{\partial C_{ox}}{\partial x}(0,t)$$

$$-D_R \frac{\partial C_R(0,t)}{\partial x} = \frac{i(t)}{nFA}$$

3. $$\frac{\partial C_R(0,t)}{\partial x} = -\frac{i(t)}{nFAD_R}$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$$

$$s\,\bar{c}_R(x,s) - C_R(x,0) = D_R \frac{\partial^2 C_R}{\partial x^2} \qquad \text{where } \bar{c}_R(x,s) = L\left\{c_R(x,t)\right\}$$

$$\frac{s\,\bar{C}_R(x,s)}{D_R} - \frac{C_R(x,0)}{D_R} = \frac{\partial^2 C_R}{\partial x^2}$$

$$\frac{d^2 C_R}{d x^2} - \frac{s\,\bar{c}_R(x,s)}{D_R} = -\frac{C_R(x,0)}{D_R}$$

$$\bar{c}_R(x,s) = P(s)e^{x\sqrt{s/D_R}} + Q(s)\,e^{-x\sqrt{s/D_R}} + \frac{C_R}{s}(x,0)$$

where P, Q are constants and functions of s.

$\bar{C}_R(x,s) = Q(s)\,e^{-x\sqrt{s/D_R}}$ because of boundary condition number two: $\lim_{x\to 0} C_R(x,t) = 0$

$$\frac{\partial C_R}{\partial x}(0,t) = \frac{-i(t)}{nFAD_R} = \frac{-I[1-2S_T(t)]}{nFAD_R}$$

$$\frac{\partial \bar{C}_R}{\partial x}(0,s) = -Q\sqrt{s/D_R}$$

$$L\left\{\frac{-I[1-2S_T(t)]}{nFAD_R}\right\} = L\left\{\frac{-I}{nFAD_R} + \frac{2S_T(t)}{nFAD_R}\right\}$$

$$= \frac{-I}{mFAD_R s} + \frac{2Ie^{-Ts}}{s\,mFAD_R}$$

$$\therefore -Q\sqrt{s/D_R} = \frac{-I}{mFAD_R s} + \frac{2Ie^{-Ts}}{s\,mFAD_R}$$

$$Q = \frac{I}{mFAD_R^{1/2} s^{3/2}} - \frac{2Ie^{-Ts}}{s^{3/2} mFAD_R^{1/2}}$$

$$\bar{c}_R(0,s) = \frac{I}{mFAD_R^{\frac{1}{2}}\, s^{\frac{3}{2}}} - \frac{2Ie^{-Ts}}{s^{3/2}\, mFAD_R^{\frac{1}{2}}}$$

$$c_R(0,t) = \frac{2It^{\frac{1}{2}}}{mFA(D_R\pi)^{\frac{1}{2}}} - \frac{4I\sqrt{t-T}\;\; S_T(t)}{mFA(D_R\pi)^{\frac{1}{2}}}$$

$$c_R(0,\tau) = 0 = \frac{2I\sqrt{t}}{mFA(D_R\pi)^{\frac{1}{2}}} - \frac{4I\sqrt{t-T}}{mFA(D_R\pi)^{\frac{1}{2}}}\,(S_T(t))$$

$$\sqrt{\tau} - 2\sqrt{\tau - T} = 0$$

$$\sqrt{\tau} = 2\sqrt{\tau - T}$$

$$\tau = 4\tau - 4T$$

$$\tau = \frac{4}{3}T$$

Data

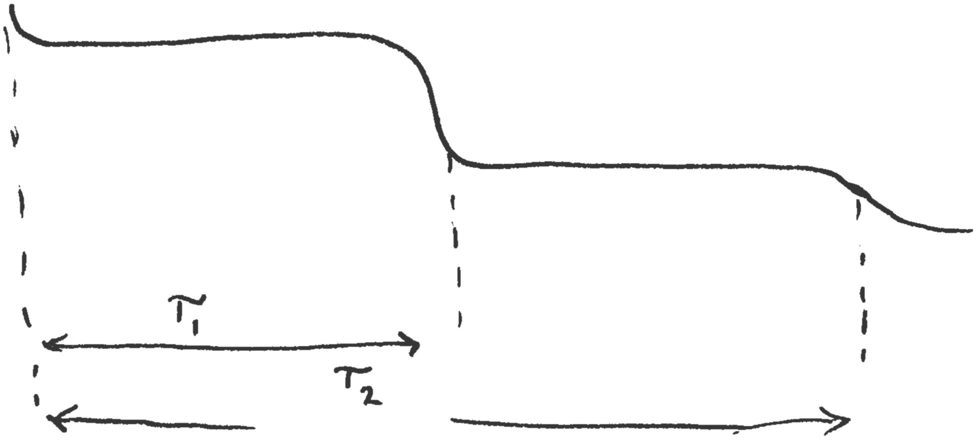
solution: .01 F $CuCl_2$
.1 HCl

Date data was acquired: 2-17-67

$i\tau_1^{\frac{1}{2}} =$	$i\tau_2^{\frac{1}{2}} =$
.508	1.14
.575	1.25
.624	1.33
.623	1.29

Date: 3-20-67

$i\tau_1^{\frac{1}{2}} =$	$i\tau_2^{\frac{1}{2}} =$
.635	1.46
.716	1.41
.732	1.45
.732	1.45
.738	1.43



Laplace Transforms - Problems

1. $$L\{\sqrt{2}\} = \int_0^{\infty} e^{-st}\sqrt{2}\,dt = -\frac{\sqrt{2}}{s}e^{-st}\Big]_0^{\infty} = \frac{\sqrt{2}}{s}$$

2. $$L\{e^t t\} = \int_0^{\infty} e^{-(s-1)t}\,t\,dt = \left[\frac{e^{-(s-1)t}}{(s-1)^2}\left(-(s-1)t-1\right)\right]_0^{\infty} = \frac{1}{(s-1)^2}$$

3. $$L\{\sin t\} = \int_0^{\infty} e^{-st}\sin t\,dt = \frac{e^{-st}(-s\sin t-\cos t)}{s^2+1}\Big]_0^{\infty} = \frac{1}{s^2+1}$$

4. $$L\{e^{\alpha t}\sin mt\} = \int_0^{\infty} e^{-(s-\alpha)t}\sin mt\,dt = e^{-(s-\alpha)t}\left[\frac{(\alpha-s)\sin mt - m\cos mt}{(s-\alpha)^2+m^2}\right]_0^{\infty}$$

$$= \frac{m}{(s-\alpha)^2+m^2}$$

5. $$L\{a+bt\} = \int_0^{\infty} e^{-st}(a+bt)\,dt = -\frac{ae^{-st}}{s} + \frac{be^{-st}}{s^2}(-st-1)\Big]_0^{\infty}$$

$$= \frac{a}{s} + \frac{b}{s^2} = \frac{as+b}{s^2}$$

6. $$L\{a+bt+ct^2\} = \int_0^{\infty} e^{-st}(a+bt+ct^2)\,dt$$

$$= -\frac{ae^{-st}}{s} + \frac{be^{-st}}{s^2}(-st-1) + \frac{ct^2e^{-st}}{-s} + \frac{2c}{s}\left(\frac{e^{-st}(-st-1)}{s^2}\right)\Big]_0^{\infty}$$

$$= \frac{a}{s} + \frac{b}{s^2} + \frac{2b}{s^3} = \frac{as^2+bs+2c}{s^3}$$

$$F(t) = \sin t + 2\cos t$$

7. $$L\{F(t)\} = \int_0^{\infty} e^{-st}(\sin t + 2\cos t)\,dt$$

$$= \int_0^{\infty} e^{-st}\sin t\,dt + \int_0^{\infty} e^{-st}\,2\cos t\,dt$$

$$= \frac{e^{-st}(s\sin t - \cos t)}{1+s^2} + \frac{2e^{-st}(\sin t - s\cos t)}{1+s^2}\Big]_0^{\infty}$$

$$= \frac{1}{1+s^2} + \frac{2s}{1+s^2} = \frac{2s+1}{s^2+1}$$

$F(t) = \sin t \cos t$

8. $$L\{F(t)\} = \int_0^\infty e^{-st} \sin t \cos t \, dt = \frac{e^{-st}(-s \sin 2t - 2\cos 2t)}{2(s^2+4)}\bigg]_0^\infty$$

$$= \frac{2}{2(s^2+4)} = \frac{1}{s^2+4}$$

$F(t) = \cos^2 t$

9. $$L\{F(t)\} = \int_0^\infty e^{-st}\cos^2 t \, dt = \frac{e^{-st}\cos t(2\sin t - s\cos t)}{4+s^2} - \frac{2e^{-st}}{s(4+s^2)}\bigg]_0^\infty$$

$$= \frac{s}{(4+s^2)} + \frac{2}{s(4+s^2)} = \frac{s^2+2}{s(s^2+4)}$$

10. $L^{-1}\left\{\frac{a}{s(s+a)}\right\}$ $\quad \frac{A}{s} + \frac{B}{s+a} = \frac{a}{s(s+a)}$ $\quad a+B=0$

$a=1 \quad B=-1$

$$L^{-1}\left\{\frac{1}{s} - \frac{1}{s+a}\right\} = 1 - e^{-at}$$

11. $y''(t) - K^2 y(t) = 0 \quad K \neq 0$ $\quad$ Let $c_1 = y(0)$

$c_2 = y'(0)$

$$L\{y''(t)\} - K^2 L\{y(t)\} = 0$$

$$s^2 y(s) - s c_1 - c_2 - K^2 y(s) = 0 \quad \text{where } y(s) = L\{y(t)\}$$

$$y(s) = \frac{sc_1}{s^2-K^2} + \frac{c_2}{s^2-K^2}$$

$$y(t) = c_1 \cosh Kt + \frac{1}{K} c_2 \sinh Kt$$

12. $y''(t) + K^2 y(t) = a \quad K \neq 0$

Let $c_1 = y(0) \quad c_2 = y'(0)$

$$L\{y''(t)\} + K^2 L\{y(t)\} = L\{a\}$$

$$s^2 y(s) - sc_1 - c_2 + K_2 y(s) = \frac{a}{s} \quad \text{where } y(s) = L\{y(t)\}$$

$$y(s) = \frac{sc_1}{s^2+K^2} + \frac{c_2}{s^2+K^2} + \frac{a}{s(s^2+K^2)}$$

$$y(t) = c_1 \cos Kt + \frac{c_2}{K}\sin Kt + \frac{a}{K^2}(1 - \cos Kt)$$

13. $y''(t) + 2Ky'(t) + K^2 y(t) = 0$ Let $C_1 = y(0)$ $C_2 = y'(0)$

$$s^2 y(s) - C_1 s - C_2 + 2K[sy(s) - C_1] + K^2 y(s) = 0$$

$$(s^2 + 2Ks + K^2)\,y(s) = C_1 s + C_2 + C_1 2K$$

$$y(s) = \frac{C_1 s}{(s+K)^2} + \frac{C_2 + C_1 2k}{(s+K)^2}$$

$$y(t) = C_1\left[e^{-Kt} + Kte^{-Kt}\right] + (2KC_1 + C_2)te^{-Kt} = e^{-Kt}(C_2 + tC_3)$$

14. $y''(t) - 2ay'(t) + (a^2+b^2)y(t) = 0$ $y(0) = 0$ $y'(0) = 1$

$$s^2 y(s) - 1 - sy(s) + (a^2+b^2)y(s) = 0$$

$$y(s) = \frac{1}{(s^2 - 2s + a^2) + b^2} = \frac{1}{(s-a)^2 + b^2}$$

$$y(t) = \frac{1}{b} e^{at} \sin bt$$

15. $y''(t) + 4y(t) = \sin t$ $y(0) = y'(0) = 0$

$$s^2 y(s) + 4y(s) = \frac{1}{s^2+1}$$

$$y(s) = \frac{1}{s^2+1} \cdot \frac{1}{s^2+4} = \int_0^t \frac{\cos t - \cos 2t}{3}$$

$$y(t) = \frac{1}{3}\left[\sin t - \frac{1}{2}\sin 2t\right]$$

16. $y'''(t) + y'(t) = e^{2t}$ $y(0) = y'(0) = y''(0) = 0$

$$y(s) = L\{y(t)\}$$

$$s^3 y(s) + sy(s) = \frac{1}{s-2}$$

$$y(s) = \frac{1}{(s-2)(s^3+s)} = -\frac{1}{2s} + \frac{1}{10}\frac{1}{(s-2)} + \frac{2}{5}\frac{s}{(s^2+1)} - \frac{1}{5}\frac{1}{(s^2+1)}$$

$$y(t) = -\frac{1}{2} + \frac{1}{10}e^{2t} + \frac{2}{5}\cos t - \frac{1}{5}\sin t$$

BIBLIOGRAPHY

Anson, Fred C., "Chronopotentiometry, The Encyclopedia of Electrochemistry, ed. Clifford A. Hampel. New York: Reinhold Publishing Company, 1964.

Lingane, Electroanalytical Chemistry. New York: Interscience Publishers, Inc., 1958.