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# Chronopotentiometry in thin-layer electrochemical cells: a new look at transition–time derivations including multicomponent systems

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## Abstract

A complete derivation is presented for concentration profiles and transition times in a thin layer cell under constant current conditions. Expressions for the concentration across a thin layer cell and the transition time are presented under conditions where the diffusion layer is extremely small (short times) and extremely large (long times) compared to the thickness of the thin layer cell. Excellent agreement with those previously reported in the literature is found. Application to thin layer spectroelectrochemical cells is demonstrated.

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**Keywords:** Thin-layer cell; Chronopotentiometry; Constant current; Multicomponent systems; Transition time

The use of thin-layer electrochemical cells dates back to the early 1960s [1–23]. In these cells, a very small solution volume (a few microliters) is confined to a thin layer (2–100  $\mu\text{m}$ ) between either an electrode and an impermeable boundary or a pair of electrodes. One controls the duration of the experiment so that the cell thickness,  $l$ , is either smaller or larger than the diffusion layer thickness,  $\sqrt{(2Dt)}$ , for a given experimental time  $t$  and diffusion coefficient  $D$ . At long times, the most common situation,  $l \ll \sqrt{(2Dt)}$ , and mass transfer within the cell can be neglected. At shorter times, when  $l \gg \sqrt{(2Dt)}$ , diffusion within the thin solution volume must be considered and at the limit sem infinite behavior obtains. Thin-layer cells have been used in investigations of adsorption, electrodeposition, complex reaction mechanisms, and  $n$ -value determinations [23]. They are also used in spectroelectrochemical studies [24–28].

Thin-layer cell theory can be applied to a wide variety of electrochemical problems [29]. One fundamental thin-

layer problem is the deposition of metals as amalgams into thin films of mercury followed by their subsequent stripping. Another is the electrochemical oxidation or reduction of thin films of oxides, adsorbed layers, or precipitates that have formed on electrode surfaces either intentionally or unintentionally. Electrodes modified synthetically by binding an electroactive species to the surface are described directly by thin-layer concepts. The scanning electrochemical microscopy (SECM) setup [30], where electrochemistry is examined in the gap between an electrode (tip) and a conducting or insulating substrate has been modeled using thin-layer theory.

In chronopotentiometry, a constant current  $I$  is applied to a working electrode and the potential is subsequently determined as a function of time. When the concentration of the electroactive species drops to zero at the electrode surface, the potential of the electrode rapidly shifts toward more negative (for a reduction) values such that a new, second reduction begins so as to satisfy the current demand. The time after application of the constant current when this potential transition occurs is called the transition time,  $\tau$ . For the simple electron-transfer reaction,  $\text{O} + ne^- \rightarrow \text{R}$ , at a planar working electrode under semi-infinite

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diffusion conditions with only species O present at a bulk concentration  $c_o^*$ , an expression for the transition time takes the form of the well-known Sand equation [31]

$$\frac{I\tau^{1/2}}{c_o^*} = \frac{nFAD_o^{1/2}\pi^{1/2}}{2} \quad (1)$$

where the constant  $I\tau^{1/2}/c_o^*$  is known as the transition time constant, which, as Eq. (1) shows, is independent of  $I$  or  $c_o^*$  for a well-behaved system. The parameters  $n$ ,  $F$ ,  $A$ , and  $D_o$  are the number of electrons transferred, Faraday's constant, the electrode area, and the diffusion coefficient of O. A lack of constancy in the transition time constant is an indication of complications due to the electrode reaction from coupled homogeneous chemical reactions, adsorption, or measurement artifacts such as double-layer charging or the onset of convection. Eq. (1) is derived from the surface concentration [32]

$$c_o(0, t) = c_o^* - \frac{2It^{1/2}}{nFAD_o^{1/2}\pi^{1/2}} \quad (2)$$

where the transition time is found when  $c_o(0, t) \rightarrow 0$ . The concentration in space and time is  $c_o(x, t)$  where  $x$  is the spatial coordinate and  $t$  is the time.

Expressions analogous to Eq. (1) and Eq. (2) have been reported in the literature for chronopotentiometry in thin layer cells. The first was reported by Christensen and Anson [1] in 1963, and again by Hubbard [23] in 1973. The cell of thickness  $l'$  is composed of one electrode of area  $A$  and an impermeable boundary such that

$$c_o(0, t) = c_o^* - \frac{Il}{nFAD} \left[ \frac{Dt}{l'^2} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\left\{ \frac{-\pi^2 j^2 Dt}{l'^2} \right\} \right] \quad (3)$$

When  $c_o(0, t) \rightarrow 0$ ,  $t \rightarrow \tau$ , and at long  $t$ , the following can be written

$$\frac{I\tau}{nFAc_o^*l'} + \frac{Il'}{3nFADc_o^*} = 1 \quad (4)$$

In 1970, Hubbard and Anson [20] reported

$$\begin{aligned} c_o(0, t) &= c_o^* - \frac{It}{nFV} - \frac{Il}{nFAD} \\ &\quad \times \left[ \frac{1}{6} - \frac{1}{\pi} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\left\{ \frac{-4j^2\pi^2 Dt}{l^2} \right\} \right] \\ &= c_o^* - \frac{2Il}{nFAD} \left[ \frac{Dt}{l^2} + \frac{1}{12} - \frac{1}{2\pi} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\left\{ \frac{-4j^2\pi^2 Dt}{l^2} \right\} \right] \end{aligned} \quad (5)$$

for a cell of thickness  $l$  composed of two parallel

electrode surfaces, each of area  $A$ . The volume of the thin layer cell,  $V$ , appears to be  $Al/2$ .

When  $c_o(0, t) \rightarrow 0$ ,  $t \rightarrow \tau$ , and at long  $t$ , Eq. (5) reduces to

$$\frac{I\tau}{nFAc_o^*l} + \frac{Il}{6nFADc_o^*} = 1 \quad (6)$$

It is intuitive that a thin layer cell comprised of one electrode and one impermeable boundary will be analogous to one half of a two electrode thin layer cell such that  $l = 2l'$ . Substituting into Eq. (4) leads to Eq. (6), as expected.

At the outset of this investigation we were intrigued by what appeared to be differences in the surface concentrations reported in Eq. (3) and Eq. (5). In searching the literature we were unable to find a thorough derivation for Eq. (5), and the transformation of Eq. (3) from a related application was not apparent. We became interested in understanding these equations while deriving an expression for the second transition time in a chronopotentiometric experiment carried out in a thin layer cell with two electroactive components.

The objectives of this manuscript are fourfold. First, the surface concentration of a single, reversibly reduced species in a chronopotentiometric experiment carried out in a two-electrode thin-layer cell is derived. Second, this derived surface concentration is compared to those reported in Eqs. (3) and (5), and Eq. (6). Third, the expression for the second transition time in a chronopotentiometric experiment in a thin layer cell containing two oxidized species is presented. Fourth, an expression for the time-dependent response of a thin layer spectroelectrochemical cell is presented.

## 1. Derivation of the concentration, current, and transition time expressions

Consider a thin layer cell where there are two working electrodes separated by a distance  $l$ , as shown in Fig. 1. Initially, we consider the reduction of a single reactant, O at both electrodes, where  $O + ne^- \rightleftharpoons R$ . Later we address a two-component system. The boundary and initial conditions for the cell are specified as

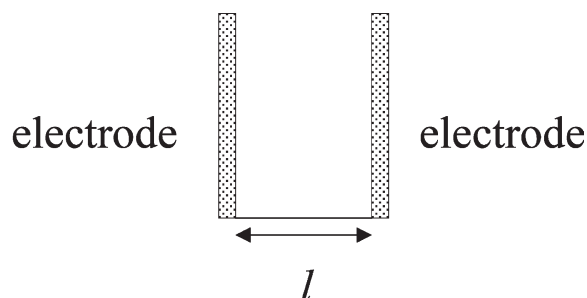


Fig. 1. Diagram of two-electrode thin layer cell.

$$\frac{\partial c_o(x, t)}{\partial t} = D \frac{\partial^2 c_o(x, t)}{\partial x^2} \quad (7)$$

$$c_o(x, t) = c_o^* \quad t = 0; \quad 0 \leq x \leq l \quad (8)$$

$$\left( \frac{\partial c_o(x, t)}{\partial x} \right)_{x=0} = - \left( \frac{\partial c_o(x, t)}{\partial x} \right)_{x=l} = \frac{I}{nFA} \quad (9)$$

where the applied current  $I$  is a constant and  $A$  represents the area of each electrode. The problem is addressed by Laplace Transforms such that the transform of Eq. (7) and substitution of Eq. (8) leads to the following [32]

$$\bar{c}_o(x, s) = \frac{c_o^*}{s} + A' \exp \left\{ -\sqrt{\frac{s}{D}} x \right\} + B' \exp \left\{ \sqrt{\frac{s}{D}} x \right\} \quad (10)$$

The partial derivative in space leads to

$$\frac{\partial \bar{c}_o(x, s)}{\partial x} = -\sqrt{\frac{s}{D}} \left[ A' \exp \left\{ -\sqrt{\frac{s}{D}} x \right\} - B' \exp \left\{ \sqrt{\frac{s}{D}} x \right\} \right] \quad (11)$$

where, from evaluation of Eq. (9),

$$B' = A' \left[ \frac{1 + \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}}{1 + \exp \left\{ \sqrt{\frac{s}{D}} l \right\}} \right] \quad (12)$$

and

$$A' = \frac{I}{nFA\sqrt{Ds^{3/2}}} \left[ \frac{1 + \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}}{\exp \left\{ \sqrt{\frac{s}{D}} l \right\} - \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}} \right] \quad (13)$$

It will transpire that the solutions to Eqs. (7)–(13) will be developed in terms of a series solution (at short times) and hyperbolic functions (at long times) due to ease of convergence at the respective time ranges.

*Series solution: short time.* Eq. (10) at the electrode surface ( $x = 0$ ) becomes

$$\bar{c}_o(0, s) = \frac{c_o^*}{s} - \frac{I}{nFA\sqrt{Ds^{3/2}}} \times \left( \frac{2 + \exp \left\{ \sqrt{\frac{s}{D}} l \right\} + \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}}{\exp \left\{ \sqrt{\frac{s}{D}} l \right\} - \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}} \right) \quad (14)$$

or,

$$\frac{I}{FA s^{3/2}} = n\sqrt{D} \left[ \frac{c_o^*}{s} - \bar{c}_o(0, s) \right] \times \left[ \frac{\exp \left\{ \sqrt{\frac{s}{D}} l \right\} - \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}}{2 + \exp \left\{ \sqrt{\frac{s}{D}} l \right\} + \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}} \right] \quad (15)$$

It is common practice to represent the exponentials inside the second set of square brackets of equation Eq. (15) as an infinite series. The details of this procedure are reported in Appendix A. The result is

$$\frac{I}{FA s^{3/2}} = n\sqrt{D} \left[ \frac{c_o^*}{s} - \bar{c}_o(0, s) \right] \times \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \quad (16)$$

*Transition times.* For a two component, semi-infinite system, the currents for the first and second transition times [32] are specified for  $O_1$  and  $O_2$  as

$$\frac{I_1}{s^{1/2}} = n_1 F A D_1^{1/2} \left[ \frac{c_{o_1}^*}{s} - \bar{c}_{o_1}(0, s) \right] \quad (17)$$

$$\frac{I_2}{s^{1/2}} = n_2 F A D_2^{1/2} \left[ \frac{c_{o_2}^*}{s} - \bar{c}_{o_2}(0, s) \right] \quad (18)$$

By analogy, the following are found from Eq. (16)

$$\frac{I_1}{FA s^{3/2}} = n_1 D_1^{1/2} \left[ \frac{c_{o_1}^*}{s} - \bar{c}_{o_1}(0, s) \right] \times \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \quad (19)$$

$$\frac{I_2}{FA s^{3/2}} = n_2 D_2^{1/2} \left[ \frac{c_{o_1}^*}{s} - \bar{c}_{o_1}(0, s) \right] \times \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \quad (20)$$

The total current,  $I = I_1 + I_2$ , is

$$\frac{I}{FA s^{3/2}} = n_1 D_1^{1/2} \left[ \frac{c_{o_1}^*}{s} - \bar{c}_{o_1}(0, s) \right] \times \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] + n_2 D_2^{1/2} \left[ \frac{c_{o_2}^*}{s} - \bar{c}_{o_2}(0, s) \right] \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \quad (21)$$

The first transition time is specified when  $c_{o_1}(0, s) \rightarrow 0$ . Up until the first transition time, the response is defined

by Eq. (19), leading to

$$\frac{I_1}{FA s^{3/2}} = n_1 D_1^{1/2} \frac{c_{o1}^*}{s} \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \quad (22)$$

For the second transition,  $\bar{c}_{o1}(0, s) = 0$  and  $\bar{c}_{o2}(0, s) \rightarrow 0$ . Eq. (21) leads to

$$\begin{aligned} \frac{I}{FA s^{3/2}} &= n_1 D_1^{1/2} \frac{c_{o1}^*}{s} \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \\ &+ n_2 D_2^{1/2} \frac{c_{o2}^*}{s} \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp \left\{ -j \sqrt{\frac{s}{D}} l \right\} \right] \end{aligned} \quad (23)$$

For the first transition, Laplace inversion of Eq. (22) [32] leads to

$$\frac{2I_1}{n_1 c_{o1}^* FA} \sqrt{\frac{\tau}{\pi D_1}} = 1 + 2 \sum_{j=1}^{\infty} (-1)^j \operatorname{erfc} \left\{ \frac{j l}{2 \sqrt{D_1 \tau}} \right\} \quad (24)$$

For the second transition, where  $\tau = \tau_1 + \tau_2$ , the inversion of Eq. (23) leads to

$$\begin{aligned} \frac{2I}{FA} \sqrt{\frac{\tau}{\pi}} &= n_1 \sqrt{D_1} c_{o1}^* \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \operatorname{erfc} \left\{ \frac{j l}{2 \sqrt{D_1 \tau}} \right\} \right] \\ &+ n_2 \sqrt{D_2} c_{o2}^* \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \operatorname{erfc} \left\{ \frac{j l}{2 \sqrt{D_2 \tau}} \right\} \right] \end{aligned} \quad (25)$$

Eq. (24) and Eq. (25) converge rapidly for large arguments of the erfc function, where the error function complement rapidly approaches zero. This corresponds to large values of  $l/\sqrt{(D\tau)}$ , where the diffusion length at the transition time is small compared to the cell thickness. Thus, the transition time should be the same as it is under semi-infinite conditions. For Eq. (24),

$$\lim_{l/\sqrt{D\tau} \rightarrow \infty} \frac{I_1}{n_1 c_{o1}^* FA} \sqrt{\frac{\tau}{\pi D}} = \frac{1}{2} \quad (26)$$

This is the same as the Sand equation Eq. (1) for the transition time for a single species under semi-infinite conditions. By the same argument, the transition time for two species is determined from Eq. (25). This leads to

$$\frac{2I}{FA} \sqrt{\frac{\tau_1 + \tau_2}{\pi}} = n_1 \sqrt{D_1} c_{o1}^* + n_2 \sqrt{D_2} c_{o2}^* \quad (27)$$

in agreement with that reported for two species in a semi-infinite cell [32].

In principle, Eq. (24) and Eq. (25) can be used to find the behavior of the system at small values of

$l/\sqrt{D\tau}$  where thin layer behavior would be observed. Unfortunately, from summations in a spreadsheet,

$$\lim_{l/\sqrt{D\tau} \rightarrow 0} \sum_{j=1}^{\infty} (-1)^j \operatorname{erfc} \left\{ \frac{j l}{2 \sqrt{D_1 \tau}} \right\} \rightarrow -\frac{1}{2} \quad (28)$$

Because the limit of Eq. (24) and Eq. (25) collapses to zero for small  $l/\sqrt{(D\tau)}$ , an alternative representation of the problem is needed. Such problems are generally represented as hyperbolic trigonometric functions in the Laplace domain.

*Hyperbolic function solution: long times.* The development follows that previously through Eq. (13). Substitution of A' and B' as defined in Eq. (12) and Eq. (13) into Eq. (10) leads to

$$\begin{aligned} \bar{c}_o(x, s) &= \frac{c_o^*}{s} - \frac{I}{nFA \sqrt{Ds^{3/2}}} \\ &\times \left[ \frac{\exp \left\{ -\sqrt{\frac{s}{D}} x \right\} + \exp \left\{ \sqrt{\frac{s}{D}} x \right\}}{\exp \left\{ \sqrt{\frac{s}{D}} l \right\} - \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}} \right. \\ &\left. + \frac{\exp \left\{ \sqrt{\frac{s}{D}} (l-x) \right\} + \exp \left\{ -\sqrt{\frac{s}{D}} (l-x) \right\}}{\exp \left\{ \sqrt{\frac{s}{D}} l \right\} - \exp \left\{ -\sqrt{\frac{s}{D}} l \right\}} \right] \end{aligned} \quad (29)$$

The hyperbolic expression is found by noting that  $\sinh u = (e^u - e^{-u})/2$  and  $\cosh u = (e^u + e^{-u})/2$ . Eq. (29) then becomes

$$\begin{aligned} \bar{c}_o(x, s) &= \frac{c_o^*}{s} - \frac{I}{nFA \sqrt{Ds^{3/2}}} \\ &\times \left[ \frac{\cosh \left\{ \sqrt{\frac{s}{D}} x \right\}}{\sinh \left\{ \sqrt{\frac{s}{D}} l \right\}} + \frac{\cosh \left\{ \sqrt{\frac{s}{D}} (l-x) \right\}}{\sinh \left\{ \sqrt{\frac{s}{D}} l \right\}} \right] \end{aligned} \quad (30)$$

The details of the Laplace inversion are demonstrated in Appendix B, resulting in

$$\begin{aligned} c_o(x, t) &= c_o^* - \frac{I}{nFA l} \\ &\times \left[ 2t - \frac{2l^2}{\pi^2 D} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \left( \exp \left\{ -\frac{j^2 \pi^2 D t}{l^2} \right\} - 1 \right) \right. \\ &\left. \times \left( \cos \left\{ \frac{j \pi x}{l} \right\} + \cos \left\{ \frac{j \pi (l-x)}{l} \right\} \right) \right] \end{aligned} \quad (31)$$

We are interested in the concentration at the electrode

surface, where  $x = 0$ . Noting that  $\cos(n\pi) = (-1)^n$ , Eq. (31) reduces to

$$c_o(0, t) = c_o^* - \frac{2I}{nFAI} \times \left[ t - \frac{l^2}{\pi^2 D} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \left( \exp\left\{ -\frac{j^2 \pi^2 D t}{l^2} \right\} - 1 \right) \times (1 + (-1)^j) \right] \quad (32)$$

The odd terms of the summation will cancel allowing Eq. (32) to be expressed as

$$c_o(0, t) = c_o^* - \frac{2I}{nFAI} \times \left[ t - \frac{l^2}{2\pi^2 D} \sum_{j=1}^{\infty} \frac{1}{j^2} \times \left( \exp\left\{ -\frac{4j^2 \pi^2 D t}{l^2} \right\} - 1 \right) \right] \quad (33)$$

Solving for the current  $I$ , Eq. (33) is rearranged to

$$\frac{2It}{nFAI} = \frac{c_o^* - c_o(0, t)}{1 - \frac{l^2}{2\pi^2 D t} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D t}{l^2} \right\} - 1 \right)} \quad (34)$$

**Transition times.** By analogy to the series solution and Eq. (17) and Eq. (18) for a semi-infinite system,

$$\frac{2I_1 t}{n_1 F A l} = \frac{c_{o_1}^* - c_{o_1}(0, t)}{1 - \frac{l^2}{2\pi^2 D_1 t} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_1 t}{l^2} \right\} - 1 \right)} \quad (35)$$

$$\begin{aligned} \frac{2It}{FAI} &= \frac{2(I_1 + I_2)t}{nFAI} \\ &= \frac{n_1(c_{o_1}^* - c_{o_1}(0, t))}{1 - \frac{l^2}{2\pi^2 D_1 t} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_1 t}{l^2} \right\} - 1 \right)} \\ &\quad + \frac{n_2(c_{o_2}^* - c_{o_2}(0, t))}{1 - \frac{l^2}{2\pi^2 D_2 t} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_2 t}{l^2} \right\} - 1 \right)} \end{aligned} \quad (36)$$

The transition times are defined for  $\tau_1$  when  $c_{o_1}(0, t) \rightarrow 0$  for Eq. (35) and for  $\tau = \tau_1 + \tau_2$  for  $c_{o_1}(0, t) \rightarrow 0$  and  $c_{o_2}(0, t) \rightarrow 0$  for Eq. (36) as follows

$$\frac{2I_1 \tau_1}{n_1 F A l} = \frac{c_{o_1}^*}{1 - \frac{l^2}{2\pi^2 D_1 \tau_1} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_1 \tau_1}{l^2} \right\} - 1 \right)} \quad (37)$$

$$\begin{aligned} \frac{2I(\tau_1 + \tau_2)}{FAI} &= \frac{2(I_1 + I_2)(\tau_1 + \tau_2)}{nFAI} \\ &= \frac{n_1 c_{o_1}^*}{1 - \frac{l^2}{2\pi^2 D_1 (\tau_1 + \tau_2)} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_1 (\tau_1 + \tau_2)}{l^2} \right\} - 1 \right)} \\ &\quad + \frac{n_2 c_{o_2}^*}{1 - \frac{l^2}{2\pi^2 D_2 (\tau_1 + \tau_2)} \sum_{j=1}^{\infty} \frac{1}{j^2} \left( \exp\left\{ -\frac{4j^2 \pi^2 D_2 (\tau_1 + \tau_2)}{l^2} \right\} - 1 \right)} \end{aligned} \quad (38)$$

The objective of the hyperbolic development is to find the behavior of the thin layer cell at small values of  $l/\sqrt{(D\tau)}$  when the cell is well into the thin layer domain. In the thin layer domain, the concentration profiles are flat across the cell. Consider the first transition time, defined by Eq. (37). When  $l/\sqrt{(D_1 \tau_1)}$  is small, the exponential term will tend to vanish and Eq. (37) approaches the limit

$$\lim_{l/\sqrt{D_1 \tau_1} \rightarrow 0} \frac{2I_1 \tau_1}{n_1 F A l} = \frac{c_{o_1}^*}{1 + \frac{l^2}{2\pi^2 D_1 \tau_1} \sum_{j=1}^{\infty} \frac{1}{j^2}} \quad (39)$$

From a sum over a large number of points, it was observed that

$$\sum_{j=1}^{\infty} j^{-2} \rightarrow \pi^2/6.$$

Then, the first transition time for small  $l/\sqrt{(D_1 \tau_1)}$  is specified as

$$\frac{I_1 \tau_1}{n_1 F A c_{o_1}^* l} \left( 1 + \frac{l^2}{12 D_1 \tau_1} \right) = \frac{1}{2} \quad (40)$$

in agreement with Eq. (6). If  $l/\sqrt{(D_1 \tau_1)}$  is extremely small, Eq. (37) and Eq. (40) collapse to

$$\frac{I_1 \tau_1}{n_1 F A c_{o_1}^* l} \rightarrow \frac{1}{2} \quad (41)$$

For the second transition time, in the limit of extremely small  $l/\sqrt{(D_1(\tau_1 + \tau_2))}$  and  $l/\sqrt{(D_2(\tau_1 + \tau_2))}$ , Eq. (38) reduces to

$$\frac{2I(\tau_1 + \tau_2)}{FAI} = n_1 c_{o_1}^* + n_2 c_{o_2}^* \quad (42)$$

The thin layer cell is diffusion coefficient independent and the transition time scales with the concentration and

$n$ -values for the two species as well as the cell thickness. For the semi-infinite case (Eq. (27)), the relationship between the transition time and other system characteristics embeds a square root and the response depends on the concentration,  $n$ -values, and diffusion coefficients for the two species.

## 2. Properties of the reported concentration expressions

*This work.* Rearrangement of Eq. (31) leads to

$$\frac{c_o(x, t)}{c_o^*} = 1 - \frac{2It}{nFAC_o^*l} \left[ 1 - \frac{l^2}{\pi^2 Dt} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \times \left( \exp\left\{-\frac{j^2 \pi^2 Dt}{l^2}\right\} - 1 \right) \left( \cos\left\{\frac{j\pi x}{l}\right\} + \cos\left\{\frac{j\pi(l-x)}{l}\right\} \right) \right] \quad (43)$$

Letting  $f(x, t) = c_o(x, t)/c_o^*$  (fractional concentration),  $Dt/l^2 = a$  (dimensionless time),  $x/l = b$  (dimensionless distance) where  $0 \leq b \leq 1$ , and  $g = Il/nFADc_o^*$  (dimensionless current) allows Eq. (43) to be expressed as

$$f(b, a) = 1 - 2ga \left[ 1 - \frac{1}{\pi^2 a} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \times (\exp\{-j^2 \pi^2 a\} - 1) (\cos\{j\pi b\} + \cos\{j\pi(1-b)\}) \right] \quad (44)$$

The fractional concentration is constrained such that  $0 \leq f(b, a) \leq 1$ . Thus, for a given choice of  $a$  and  $b$ , the value of  $g$  will be constrained. For a given experiment,  $g$  must be the same across all  $b$  and the upper limit on  $g$  is found at  $b = 0$  and  $b = 1$ .

The transition time is defined when  $f(0, a) = f(1, a) \rightarrow 0$ , allowing Eq. (44) to be recast as

$$f(0, a) = f(1, a) = 0$$

$$= 1 - 2ga \left[ 1 + \frac{1}{12a} - \frac{1}{2\pi^2 a} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\{-4j^2 \pi^2 a\} \right] \quad (45)$$

where the series was simplified by noting that

$$\sum_{j=1}^{\infty} j^{-2} = \pi^2/6$$

and, for odd values of  $j$ ,  $1 + (-1)^j = 0$ . The largest allowed value (i.e., where a mass transfer transition time is obtained) of  $g$  for a given  $a$  is then

$$g_{\max}(a) = \frac{1}{2a \left[ 1 + \frac{1}{12a} - \frac{1}{2\pi^2 a} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\{-4j^2 \pi^2 a\} \right]} \quad (46)$$

Values of  $g_{\max}(a)$  are tabulated in Table 1.

The dimensionless time,  $a$ , characterizes the transition between semi-infinite and thin-layer behavior. Because the cell is symmetric, the diffusion profile must be established across approximately half the cell before the response will begin the transition from semi-infinite linear to thin layer. For small  $a$ , the diffusion layers will not be substantially perturbed from the bulk in the middle of the cell and the transition time will be characterized by that appropriate for a semi-infinite solution:  $I\sqrt{(t)/nFA}\sqrt{(\pi D)c_o^*} = g\sqrt{(a/\pi)}$ , consistent with the Sand equation. For larger  $a$ , the diffusion

Table 1

$g_{\max}(a)$ : the maximum allowed values of  $g = Il/nFADc_o^*$  for a given  $a$  according to Eq. (46)

$a = DT/l^2$	$g_{\max}(a) = Il/nFADc_o^*$	$ag_{\max}(a) = It/nFAC_o^*l$ Thin-layer domain	$g_{\max}(a)\sqrt{(a/\pi)} = I\sqrt{(t)/nFA}\sqrt{(\pi D)c_o^*}/(\pi D)$ Semi-infinite domain
0.00562	11.8	0.066	0.500
0.0100	8.86	0.089	0.500
0.0178	6.64	0.118	0.500
0.0316	4.99	0.158	0.500
0.0562	3.73	0.210	0.499
0.100	2.74	0.274	0.489
0.178	1.91	0.341	0.456
0.316	1.25	0.396	0.397
0.562	0.775	0.435	0.328
1.00	0.462	0.462	0.261
1.78	0.268	0.478	0.202
3.16	0.154	0.487	0.155
5.62	0.0877	0.493	0.117
10.0	0.0496	0.496	0.089
17.8	0.0280	0.498	0.067
31.6	0.0158	0.499	0.050
56.2	0.00884	0.500	0.038
100	0.00500	0.500	0.028



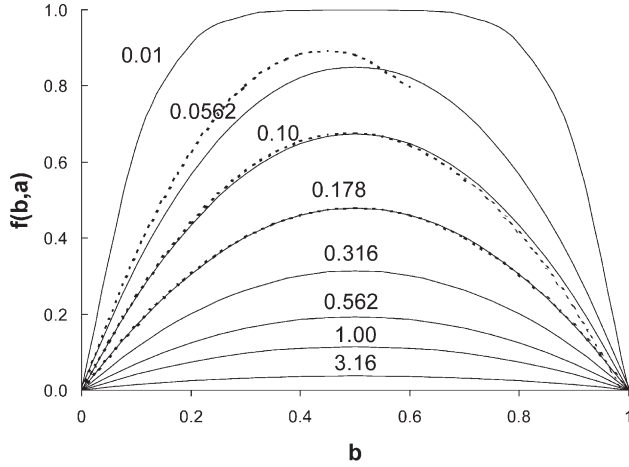


Fig. 2. Fractional concentration profiles across the thin layer cell of thickness  $0 \leq b \leq 1$  for  $0.01 \leq a \leq 3.16$  where  $g = g_{\max}(a)$ . The solid lines were calculated according to Eq. (44) and Eq. (46) derived in this work. The dashed lines were calculated according to Eq. (53) and Eq. (55) from Ref. [20].

profiles will be substantially perturbed from bulk in the middle of the cell and the transition time will be set by the thin layer conditions,  $It \ln Falc_o^* = ga$ . The transition from semi-infinite to thin layer control is reflected in the values of  $g_{\max}(a)\sqrt{(a/\pi)}$  and  $ag_{\max}(a)$  listed in the third and fourth columns of Table 1. As  $a$  decreases,  $g_{\max}(a)\sqrt{(a/\pi)} \rightarrow 0.5$ , consistent with semi-infinite behavior (Eq. (26)); as  $a$  increases,  $ag_{\max}(a) \rightarrow 0.5$ , consistent with thin-layer behavior (Eq. (41)). Note that  $g_{\max}(a)$  is the largest value of  $g$  for a given  $a$ ; a choice of  $g$  smaller than  $g_{\max}(a)$  will tend to move the transition time toward the thin layer domain. For a given  $a$ , thin layer response is ensured for  $ag \rightarrow 0.5$ ; a semi-infinite response requires  $g\sqrt{(a/\pi)} \rightarrow 0.5$ .

Fractional concentration profiles are shown in Fig. 2 where the dimensionless current is taken as  $g_{\max}(a)$ . All profiles were calculated according to Eq. (45). The surface concentrations have been set to zero, consistent with the profiles anticipated for the transition time.

**Reference [33] equation.** A thin-layer system is described by Carslaw and Jaeger [33] with no flux at  $x = 0$  and constant flux at  $x = l'$ . That is, the boundary at  $x = 0$  is impermeable and the electrode is located at  $x = l'$ . The cell thickness is taken as  $l'$  to distinguish it from the thickness of the two electrode cell. Eq. (3) on page 112 in [33] can be expressed in terms of the parameters used in this work as

$$c_o^* - c_o(x, t) = \frac{2Il'}{nFAD} \left[ \frac{Dt}{l'^2} + \frac{3x^2 - l'^2}{6l'^2} - \frac{2}{\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp\left\{-\frac{j^2\pi^2 Dt}{l'^2}\right\} \cos\left\{\frac{j\pi x}{l'}\right\} \right] \quad (47)$$

By redefining the spatial coordinate as  $y = l' - x$ , the electrode surface is shifted to  $y = 0$ , and the imperme-

able boundary to  $y = l'$ , allowing Eq. (47) to be recast as

$$c_o(y, t) = c_o^* - \frac{Il'}{nFAD} \left[ \frac{Dt}{l'^2} + \frac{2l'^2 - 6l'y + 3y^2}{6l'^2} - \frac{2}{\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp\left\{-\frac{j^2\pi^2 Dt}{l'^2}\right\} \cos\left\{\frac{j\pi(l' - y)}{l'}\right\} \right] \quad (48)$$

in agreement with Eq. (66) in [23] [note: there is an  $l$  missing in the numerator of the third term]. The concentration at  $y = 0$  is of interest

$$c_o(0, t) = c_o^* - \frac{Il'}{nFAD} \times \left[ \frac{Dt}{l'^2} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\left\{-\frac{j^2\pi^2 Dt}{l'^2}\right\} \right] \quad (49)$$

**Reference [1] equation.** Eq. (49) is that reported by Christensen and Anson [1] in Eq. (3). This equation is made dimensionless using the following parameters:  $a' = Dt/l'^2$  and  $g' = Il'/nFADc_o^*$

$$f(0, a') = 1 - g'a' \left[ 1 + \frac{1}{3a'} - \frac{2}{\pi^2 a'} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\{-j^2\pi^2 a'\} \right] \quad (50)$$

To compare to Eq. (45), it is necessary to determine the relationships between the dimensionless parameters. The problem developed by Carslaw and Jaeger [33] for one electrode and one impermeable boundary is analogous to one half of the two electrode cell, where the boundary condition  $(\partial c_o(x, t)/\partial x)_{x=l'/2}$  is also applicable. Thus  $l' = l/2$ ,  $a' = 4a$ , and  $g' = g/2$ . Substitution into Eq. (50) leads directly to Eq. (45) and Eq. (46) derived in this work.

**Ref. [20] equation.** Hubbard and Anson [20] reported the concentration in a two-electrode thin-layer cell as [note,  $l^2$  is absent from the denominator of the exponential]

$$c_o(x, t) = c_o^* - \frac{It}{nFV} - \frac{Il}{nFAD} \left[ \frac{6x^2 - 6lx + l^2}{6l^2} - \frac{1}{\pi} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp\left\{-\frac{4j^2\pi^2 Dt}{l^2}\right\} \cos\left(\frac{j\pi(l - x)}{x}\right) \right] \quad (51)$$

$V$  represents the volume of the thin layer cell, and, though not defined in Ref. [20], if it is set to  $Al/2$  then Eq. (51) can be written as

$$c_o(x, t) = c_o^* - \frac{Il}{nFAD} \left[ \frac{2Dt}{l^2} + \frac{6x^2 - 6lx + l^2}{6l^2} - \frac{1}{\pi} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp\left\{-\frac{4j^2\pi^2 Dt}{l^2}\right\} \cos\left(\frac{j\pi(l - x)}{x}\right) \right] \quad (52)$$

Letting  $f(x, t) = c_o(x, t)/c_o^*$ ,  $Dt/l^2 = a$ ,  $x/l = b$  where  $0 \leq b \leq 1$ , and  $g = Il/nFADc_o^*$  allows Eq. (52) to be



expressed as

$$f(b, a) = 1 - 2ga \left[ 1 + \frac{1}{12a} - \frac{b}{2a} + \frac{b^2}{2a} - \frac{1}{2\pi a} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \exp\{-4j^2\pi^2 a\} \cos\{j\pi(1-b)\} \right] \quad (53)$$

Of interest is  $f(0, a)$

$$f(0, a) = 1 - 2ga \left[ 1 + \frac{1}{12a} - \frac{1}{2\pi a} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\{-4j^2\pi^2 a\} \right] \quad (54)$$

which is functionally similar to Eq. (45) but not identical. The difference between the two equations lies in the  $1/\pi$  multiplier (Ref. [20]) and  $1/\pi^2$  multiplier (this work) of the summation. This could be attributed to a typographical error in Ref. [20].

When  $f(0, a) = 0 = f(l, a)$ ,

$$g_{\max}(a) = \frac{1}{2a \left[ 1 + \frac{1}{12a} - \frac{1}{2\pi a} \sum_{j=1}^{\infty} \frac{1}{j^2} \exp\{-4j^2\pi^2 a\} \right]} \quad (55)$$

which is to be compared to Eq. (46). As  $a$  increases,  $ag_{\max} \rightarrow 1/2$ , as the data in the third column of Table 2 demonstrate. As  $a \rightarrow 0$ , Eq. (55) produces results which are unstable as  $a$  decreases to values smaller than 0.0316. The dashed lines in Fig. 1 show the concentration profiles across the thin layer cell. These profiles become identical to those produced by Eq. (44) and Eq. (46) of this work at  $a$  values  $> 0.10$ , at which point, the exponential term contributes  $< 0.2\%$  to the denominator term in Eq. (55) and  $< 0.05\%$  in Eq. (46). That is, the

exponential terms are negligible for  $a \geq 0.10$ . Thus the discrepancies between Eq. (54) and Eq. (45), and Eq. (55) and Eq. (56) then become insignificant.

### 3. Spectroelectrochemistry: the time dependent response

In a spectroelectrochemical experiment, constant current can be established at two optically transparent electrodes, and an electroactive species electrolyzed at both electrodes. The generation of product is monitored spectroscopically by the absorbance. Absorbance is usually measured once all the material in the cell is electrolyzed, but there are conditions where the time dependent response would be of interest. For example, if the product species is not stable or transition to a second species is short, measuring the early time response could simplify experimental protocol.

The absorbance is a measure of product concentration generated across the thickness of the cell. It is characterized by Beer's law,  $A = \varepsilon lc$ , where  $\varepsilon$  is the molar absorptivity and  $c$  is the concentration of the absorbing species. In a time dependent, constant current chronopotentiometry experiment, the concentration varies across the cell and it is the average concentration that is generally of interest in spectroelectrochemical experiments. From the equations developed in this work, expressions are provided for the concentration across the cell as a function of time. The integration of these expressions with respect to distance across the cell thickness and normalizing by the cell thickness will yield the average concentration. Specifically, utilizing Eq. (10), Eq. (12), and Eq. (13), the integration of  $\bar{C}_o(x, s)$  is

Table 2

$g_{\max}(a)$ : the maximum allowed values of  $Il/nFADc_o^*$  for a given  $a$  according to Eq. (55)

$a = Dt/l^2$	$g_{\max}(a) = Il/nFADc_o^*$	$ag_{\max}(a) = It/nFAC_o^*l$ thin-layer domain	$g_{\max}(a)\sqrt{(a/\pi)} = I\sqrt{(t)/nFAC_o^*\sqrt{(\pi D)}}$ semi-infinite domain
0.00562	-8.68	-0.0488	-0.367
0.0100	-22.1	-0.221	-1.25
0.0178	25.1	0.448	1.89
0.0316	7.25	0.229	0.727
0.0562	4.09	0.230	0.547
0.100	2.77	0.277	0.495
0.178	1.91	0.341	0.456
0.316	1.25	0.396	0.397
0.562	0.775	0.435	0.328
1.00	0.462	0.462	0.260
1.78	0.268	0.478	0.202
3.16	0.154	0.487	0.155
5.62	0.0877	0.493	0.117
10.0	0.0496	0.496	0.0885
17.8	0.0280	0.498	0.0666
31.6	0.0158	0.499	0.0501
56.2	0.00884	0.500	0.0376
100	0.00500	0.500	0.0282

$$\begin{aligned}
& \int_0^l \bar{c}_0(x, s) dx \\
&= \int_0^l \left[ \frac{c_o^*}{s} + A' \exp\left\{-\sqrt{\frac{s}{D}}x\right\} + B' \exp\left\{\sqrt{\frac{s}{D}}x\right\} \right] dx \\
&= \frac{lc_o^*}{s} - \frac{2I}{nFA s^2} \quad (56)
\end{aligned}$$

Laplace inversion leads to the average concentration

$$c_{av} = \frac{1}{l} \int_0^l c_o(x, t) dx = c_o^* - \frac{2It}{nFA l} \quad (57)$$

Thus the average concentration is the bulk reactant concentration less the concentration electrolyzed. This expression is applicable until just prior to the transition time.

#### 4. Conclusions

The derivation of the concentration and transition time expressions of a single and two-component, reversibly reduced species in a two-electrode thin layer cell under constant current conditions in the limit of short and long times has been demonstrated. At short times, the diffusion length at the transition time is small compared to the cell thickness and mass transfer occurs by diffusion with a  $\sqrt{(D)}$  dependency as is found in semi-infinite diffusion conditions. At long times, the diffusion length exceeds the cell thickness so that total electrolysis occurs, there is no mass transfer, and subsequently no diffusion coefficient dependency. Agreement was found between the concentration expression of Ref. [1] and this work for the case of a one electrode thin-layer cell. For a two-electrode thin layer cell, a  $1/\pi$  discrepancy in the multiplier of the summation term was found between the concentration expression of Ref. [20] and this work. This could be a typographical error in Ref. [20], but, if not, then this work demonstrates that the summation term becomes insignificant at values of  $Dt/l^2 \geq 0.10$ , which is the usual thin-layer experimental condition. An expression is presented for the time dependent response of a constant current spectroelectrochemical thin layer cell.

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#### Appendix A

The exponentials in the denominator of Eq. (15) are re-expressed by partial fractions. Note that  $2 + e^y + e^{-y} = (1 + e^y)(1 + e^{-y})$ . Thus, a term of the following form is re-expressed as

$$\begin{aligned}
\frac{e^y - e^{-y}}{2 + e^y - e^{-y}} &= \frac{e^y - e^{-y}}{(1 + e^y)(1 + e^{-y})} \\
&= \frac{G}{1 + e^y} + \frac{H}{1 + e^{-y}} \quad (A1)
\end{aligned}$$

$$e^y - e^{-y} = G + H + Ge^{-y} + He^y \quad (A2)$$

By inspection,  $G = -1$  and  $H = 1$ . Eq. (15) becomes

$$\begin{aligned}
\frac{I}{FA s^{3/2}} &= n\sqrt{D} \left[ \frac{c_o^*}{s} - \bar{c}_o(0, s) \right] \left[ \frac{-1}{1 + \exp\left\{\sqrt{\frac{s}{D}}l\right\}} \right. \\
&\quad \left. + \frac{1}{1 + \exp\left\{-\sqrt{\frac{s}{D}}l\right\}} \right] \quad (A3)
\end{aligned}$$

The infinite series is found by noting that for  $a < 1$ ,

$$(1 + a)^{-1} = \sum_{j=1}^{\infty} (-1)^j a^j.$$

To take advantage of this series, the term  $(1 + \exp\{\sqrt{(s/D)l}\})^{-1}$  is multiplied by  $\exp\{-\sqrt{(s/D)l}\}/\exp\{-\sqrt{(s/D)l}\}$  permitting Eq. (A3) to be rewritten as

$$\frac{I}{FA s^{3/2}} = n\sqrt{D} \left[ \frac{c_o^*}{s} - \bar{c}_o(0, s) \right] \frac{1 - \exp\left\{-\sqrt{\frac{s}{D}}l\right\}}{1 + \exp\left\{-\sqrt{\frac{s}{D}}l\right\}} \quad (A4)$$

The series term is introduced

$$\begin{aligned}
\frac{I}{FA s^{3/2}} &= n\sqrt{D} \left[ \frac{c_o^*}{s} - \bar{c}_o(0, s) \right] \left[ 1 - \exp\left\{-\sqrt{\frac{s}{D}}l\right\} \right] \\
&\quad \times \sum_{j=0}^{\infty} (-1)^j \exp\left\{-j\sqrt{\frac{s}{D}}l\right\} \quad (A5)
\end{aligned}$$

which leads to Eq. (16) after simplification.

#### Appendix B

The inverse transform of  $s^{-3/2} \cosh\{y\sqrt{(s)}\}/\sinh\{a\sqrt{(s)}\}$  is not readily available, but other tables of Laplace transforms [34,35] yield the inverse of  $s^{-1/2} \cosh\{y\sqrt{(s)}\}/\sinh\{a\sqrt{(s)}\}$  as follows:

$$\frac{\cosh\{y\sqrt{s}\}}{\sqrt{s}\sinh\{a\sqrt{s}\}} \Leftrightarrow \frac{1}{a} \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp\left\{-\frac{j^2 \pi^2 t}{a^2}\right\} \right] \cos\left\{\frac{j\pi y}{a}\right\} \quad (\text{B1})$$

From one of the basic properties of Laplace transformation,

$$L\left\{\int_0^t F(t)dt\right\} = \frac{1}{s} f(s) \quad (\text{B2})$$

the inverse transform of  $s^{-3/2} \cosh\{y\sqrt{s}\}/\sinh\{a\sqrt{s}\}$  is found by integration in time of the inverse transform of  $s^{-1/2} \cosh\{y\sqrt{s}\}/\sinh\{a\sqrt{s}\}$  as given by Eq. (B1)

$$\frac{\cosh\{y\sqrt{s}\}}{s^{3/2}\sinh\{a\sqrt{s}\}} \Leftrightarrow \int_0^t \frac{1}{a} \left[ 1 + 2 \sum_{j=1}^{\infty} (-1)^j \exp\left\{-\frac{j^2 \pi^2 t}{a^2}\right\} \right] \cos\left\{\frac{j\pi y}{a}\right\} dt$$

$$\Leftrightarrow \frac{1}{a} \left[ t - \frac{2a^2}{\pi^2} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^2} \cos\left\{\frac{j\pi y}{a}\right\} \left( \exp\left\{-\frac{j^2 \pi^2 t}{a^2}\right\} - 1 \right) \right] \quad (\text{B3})$$

Eq. (30) then inverts to Eq. (31).

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