

## POTENTIAL STEP-CURRENT STEP TECHNIQUES

KEY WORDS: electrochemistry, chronopotentiometry, potential step

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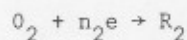
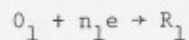
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ABSTRACT

A technique involving the application of a constant potential step before chronopotentiometric examination of multicomponent systems is shown to be useful in reducing the effect of more easily electrolyzed components on the following waves. A mathematical treatment of the technique and experimental results are given. A technique involving a constant potential step before reversal chronopotentiometry of a single component system is also discussed.

INTRODUCTION

Chronopotentiometric determinations of multicomponent systems suffer the disadvantage of involving transition times for the second and succeeding components enhanced by all preceding components. For a two component system



the relationship between  $\tau_1$  and  $\tau_2$  is

$$(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} = \frac{\pi^{1/2} n_2 F D_2^{1/2} C_2^0}{2i} \quad (1)$$

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For the simple case where  $n_1 D_1^{1/2} C_1^0 = n_2 D_2^{1/2} C_2^0$ ,  $\tau_2 = 3\tau_1$  as shown in Figure 1. One way of eliminating or decreasing the effect of preceding waves is to impose a potential  $E_2$  between the two waves (where only  $O_1$  is reduced) as shown in Figure 1. As the current decays (Fig. 1), a diffusion layer of reduced species  $R_1$  is formed. At time  $T_c$  a constant cathodic current is imposed on the system. Since much of  $O_1$  has been reduced in the vicinity of the electrode, the transition time observed for reduction of species  $O_2$  will be smaller (Fig. 1).

#### THEORETICAL

The current during the potential step at  $E_2$  is given by:<sup>2</sup>

$$i(t)_1 = \frac{n_1 F A D_1^{1/2} C_1^0}{\pi^{1/2} t^{1/2}} \quad (2)$$

The current during the current step portion is simply  $i(t)_2 = i$ . The entire process can be considered as a programmed current experiment, with a current  $i(t) = n_1 F A D_1^{1/2} C_1^0 / \pi^{1/2} t^{1/2}$  applied for time  $T_c$ , followed by a current step to a value of  $i$  by the addition of a component  $i - n_1 F A D_1^{1/2} C_1^0 / \pi^{1/2} (t+T_c)^{1/2}$ . The value of  $i\tau^{1/2}$  obtained by solving this problem using Laplace transform techniques, is

$$i\tau^{1/2} = \frac{FA\pi^{1/2}}{2} [n_2 D_2^{1/2} C_2^0 + n_1 D_1^{1/2} C_1^0 \left( \frac{2}{\pi} \tan^{-1}(\sqrt{\tau/T_c}) \right)] \quad (3)$$

where  $n_2 F A D_2^{1/2} C_2^0 / 2$  and  $n_1 F A D_1^{1/2} C_1^0 / 2$  are the values of  $i\tau_2^{1/2}$  and  $i\tau_1^{1/2}$  respectively for chronopotentiometry of each component in the absence of the other. If  $\frac{2}{\pi} \tan^{-1}(\sqrt{\tau/T_c})$  is replaced by  $X$ , equation 3 can be written

$$i\tau^{1/2} = i\tau_2^{1/2} + i\tau_1^{1/2} X \quad (4)$$

Equation 4 suggests two approaches for obtaining  $\tau_2$  in mixtures. One involves using ratios of  $\tau/T_c$  which are sufficiently small that  $i\tau_1^{1/2} X$  is small compared to  $i\tau_2^{1/2}$ . An alternate approach is to measure

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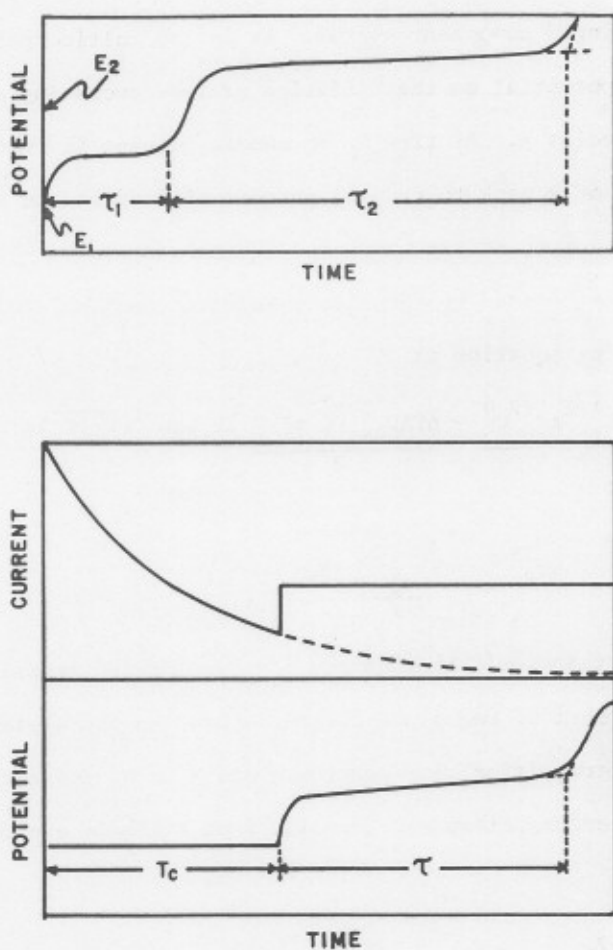


FIG. 1

Potential step-current step responses for a two component system.

Top: Conventional chronopotentiometry of a two component system.

Bottom: Current time and potential time behavior for potential step-current step on a two component system.

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$\tau$  for various values of  $T_c$ , and calculate  $i\tau^{1/2}$  and  $X$ . If  $i\tau^{1/2}$  is plotted against  $X$ , a straight line of slope  $i\tau_1^{1/2}$  and intercept  $i\tau_2^{1/2}$  is obtained.

An extension of this technique involves current reversal after the potential step in a single component system. As in the multicomponent system one imposes a potential on the diffusion plateau producing a diffusion layer of species R. At time  $T_c$  an anodic current is imposed causing the oxidation of R back to O. The current-time curve and potential-time curve for this experiment are shown in Figure 2.

This system can be treated by the Murray-Reilley<sup>3</sup> response function technique; the resulting equation is

$$i\tau_b^{1/2} = \frac{nFAD_0^{1/2} \pi^{1/2} C^0}{2} - \frac{nFAD_0^{1/2} C^0 \pi^{1/2}}{2} \left( \frac{2}{\pi} \tan^{-1}(\sqrt{\tau/T_c}) \right) \quad (5)$$

This can be simplified to

$$i\tau_f^{1/2} = \frac{i\tau_b^{1/2}}{1-X} \quad (6)$$

where  $\tau_f$  is the value that would be obtained for the forward transition time if a cathodic current of magnitude  $i$  were imposed on the system,  $\tau_b$  is the actual reverse transition time observed, and  $X$  is as defined previously. The value for  $i\tau_f^{1/2}$  can be determined directly from a single experiment.

#### RESULTS AND DISCUSSION

A solution of  $10^{-2}M$  iron(III),  $10^{-2}M$  cerium(IV), and  $1.5M$   $H_2SO_4$  was chosen as a representative multicomponent system. Cerium(IV) was reduced with a potential step (+0.70 V. vs. SCE) for a time  $T_c$ , after which a cathodic current  $i$  of 0.296 ma was imposed. The results of a series of transition time measurements for the multicomponent system is shown in Table 1. A plot of  $i\tau^{1/2}$  against  $X$  yields an intercept,  $i\tau_2^{1/2}$ , of 13.23

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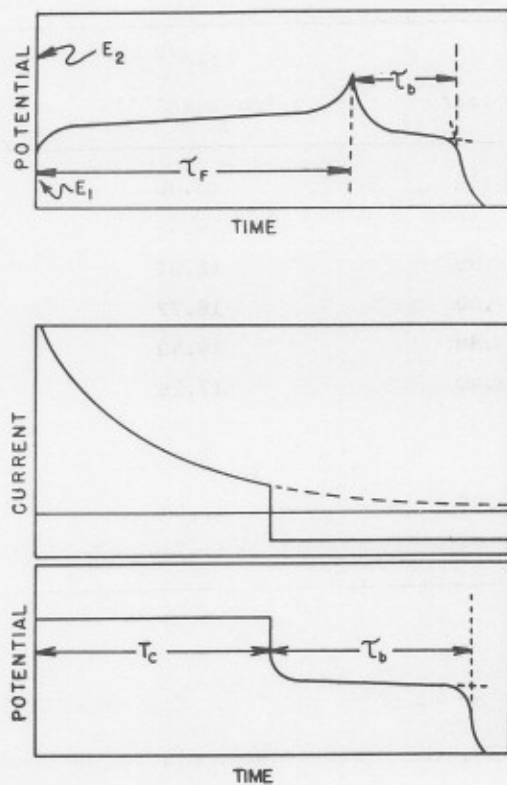


FIG. 2

Potential step-current reversal responses for a single component system.

Top: Conventional chronopotentiometry with current reversal of a single component system.

Bottom: Current time and potential time behavior for potential step-current reversal on a single component system.

TABLE 1

Potential Step-Current Step Results for Iron(III)-Cerium(IV) System. The system contained  $10^{-2}$  M iron(III),  $10^{-2}$  M cerium(IV), and 1.5 M  $H_2SO_4$ . A potential of + 0.70 V vs. SCE was imposed for a time  $T_c$ , at which time a cathodic current of 0.296 ma was applied.

$T_c$ (secs)	$\tau$ (secs)	$i_{\tau}^{1/2}$ (ma-msec <sup>1/2</sup> )	X
1.24	4.73	20.36	0.699
1.99	4.38	19.59	0.622
2.50	4.09	18.92	0.578
3.03	4.00	18.72	0.544
4.06	3.88	18.43	0.492
6.10	3.40	17.26	0.408
7.45	3.30	17.00	0.374
9.00	3.11	16.51	0.338
10.03	3.05	16.35	0.321
20.11	2.84	15.77	0.229

ma-msec<sup>1/2</sup>, and a slope of 10.12 ma-msec<sup>1/2</sup>. The value of  $i_{\tau_2}^{1/2}$  obtained with a solution iron(III), the second component, in the absence of cerium(IV) was 13.35 ma-msec<sup>1/2</sup>.

The iron(III) system was also used to test the reversal equation. Table 2 shows the results of several reversal experiments at each of three different currents. The average value of  $i_{\tau_b}^{1/2}/(1-X)$  was 12.1 ma-msec<sup>1/2</sup>. The average of several direct determinations of  $i_{\tau_f}^{1/2}$  was 12.4 ma-msec<sup>1/2</sup>.

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TABLE 2

Potential Step-Current Reversal Results for Iron(III) System. The system contained  $10^{-2}$  M iron(III) and 1.5 M  $H_2SO_4$ . A potential of +0.166 v. vs. SCE was imposed for a time  $T_c$ , at which time an anodic current was applied.

$i$ (ma)	$T_c$ (sec)	$\tau_b$ (sec)	$i\tau_b^{1/2}$ (ma-msec <sup>1/2</sup> )	X	$i\tau_b^{1/2}/(1-X)$
0.460	0.800	0.30	7.96	0.35	12.3
	2.93	0.412	9.35	0.229	12.1
	4.36	0.445	9.71	0.197	12.1
	8.10	0.470	9.97	0.151	11.7
	11.43	0.500	10.3	0.132	11.9
0.661	1.02	0.200	9.33	0.266	12.7
	2.45	0.235	10.13	0.191	12.6
	4.50	0.260	10.6	0.151	12.5
	6.10	0.262	10.54	0.131	12.1
0.294	1.00	0.575	7.06	0.413	12.0
	2.03	0.700	7.80	0.338	11.8
	3.95	0.850	8.60	0.277	11.9
	8.48	1.00	9.33	0.211	11.8

CONCLUSIONS

The technique when applied to multicomponent systems seems to be effective in decreasing the interference of preceeding waves and in conventional chronopotentiometry of eliminating small prewaves. The reversal technique may be useful when the reduction of the species of interest takes place at or beyond the potential where electrolysis of solvent or supporting electrolyte occurs. If the background electrolysis is irreversible, and oxidation of the species resulting from the electrolysis of species of interest can be observed at potentials before background, the potential could be held

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in the background region. The value of  $\tau_b$  obtained upon passage of the reversal current can be used to calculate  $i\tau_f^{1/2}$ .

These methods obviously suffer from the usual disadvantages inherent in chronopotentiometry; related double potential step and potential scan techniques have been described. Details of the theoretical derivations, experimental apparatus, and extension to cases involving kinetic complications will be discussed elsewhere.

#### ACKNOWLEDGEMENTS

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