# Application of Cyclic Chronopotentiometry to the Study of Electrode Reaction Mechanisms*

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## ABSTRACT

Cyclic chronopotentiometry is a technique in which the current applied to an electrode in an unstirred solution is successively reversed at each transition. The use of this technique in distinguishing possible mechanisms of electrode reactions, including charge transfer with preceding and following chemical reactions and reactions leading to the formation of an electroactive species, is described. Theoretical calculations for the various cases are given and compared with experiment for the electrooxidation of $p$-aminophenol at a platinum electrode and for the electroreduction of $p$-nitrosophenol at a mercury electrode.

Cyclic chronopotentiometry (CC) is a technique in which the applied current is successively reversed at each transition. The result is a series of potential–time curves for reductions and oxidations; each wave in the chronopotentiogram has a characteristic transition time. Electrode reactions, especially those involving organic substances, are usually complex and often involve preceding or following chemical reactions, some of which may form electroactive species. This paper describes how the relative magnitudes of the transition times in a cyclic chronopotentiogram can be used to distinguish between various possible mechanisms of reactions at an electrode, especially when these transitions are compared to those expected from purely diffusion-controlled behavior. The basic theory and instrumentation of diffusion-controlled CC in single and multi-component systems has been presented,[1,2] and will only be briefly outlined.
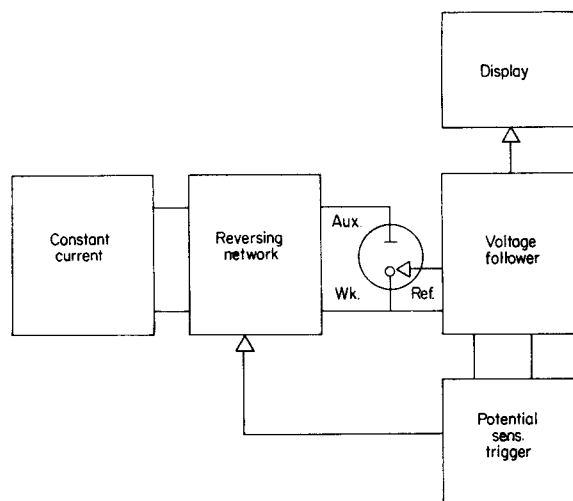
Fig. 1. Block diagram of apparatus used for cyclic chronopotentiometry.

EXPERIMENTAL

The apparatus and procedure for cyclic chronopotentiometry is similar to that for conventional chronopotentiometry (fig. 1). In the simplest case the current can be manually reversed by an observer monitoring the display. Simple trigger circuits for automatic reversal are somewhat more convenient, especially for short transition times.[1] The display may be either a strip-chart recorder[1] or an electronic counter and digital printer.[3] A typical cyclic chronopotentiogram is shown in fig. 2.
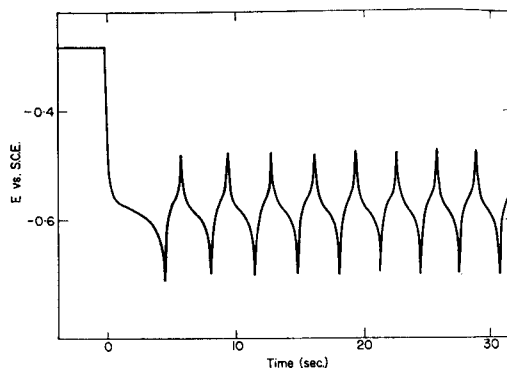


Fig. 2. Typical cyclic chronopotentiogram for reduction of cadmium(II). Solution contained 0.58 m$M$ cadmium(II) in 0.2 $M$ potassium nitrate. Current density was 0.174 mA cm$^{-2}$ at a mercury pool electrode.

## THEORETICAL TREATMENT

The following overall electrode reaction schemes have been treated. In general O, R, O′, and R′ represent electroactive species; Y and Z are not electroactive.

*Case 1.* Simple diffusion-controlled reaction.

$$O + n\,e \rightleftharpoons R$$
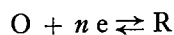
Neither O nor R are involved in any chemical reactions. The double arrow only implies that O is reduced to R during cathodization and R is oxidized to O during anodization; thermodynamic reversibility of the electrode reaction is not necessary.

*Case 2.* Kinetic case; following chemical reaction leading to non-electroactive products.
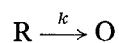
(a) Irreversible reaction

$$R \xrightarrow{k} Z$$

(b) Reversible reaction

$$R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z$$
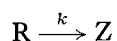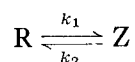
*Case 3.* Catalytic case; following chemical reaction leading to re-generation of O.

(a) Irreversible reaction

$$R \xrightarrow{k} O$$

(b) Reversible reaction

$$R \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O$$
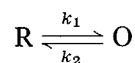
*Case 4.* Kinetic–catalytic case; following simultaneous kinetic and catalytic reactions.

$$R \xrightarrow{k_1} O$$

$$R \xrightarrow{k_2} Z$$
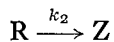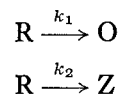
*Case 5.* ECE case; following chemical reaction generating a species more easily reduced than O.

$$O + n_1\,e \rightleftharpoons R$$

$$R \xrightarrow{k} O'$$

$$O' + n_2\,e \rightarrow R'$$
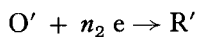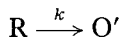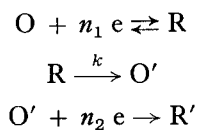
*Case 6.* Preceding case; preceding reaction producing O.

$$Y \underset{k_2}{\overset{k_1}{\rightleftarrows}} O$$
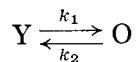
*Case 7.* Simultaneous preceding and following reactions.

(a) Preceding–kinetic reactions

$$Y \underset{k_2}{\overset{k_1}{\rightleftarrows}} O + n\,e \rightleftarrows R \overset{k}{\longrightarrow} Z$$
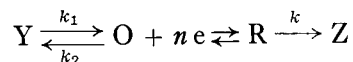
(b) Preceding–catalytic reactions

$$Y \underset{k_2}{\overset{k_1}{\rightleftarrows}} O + n\,e \rightleftarrows R \overset{k}{\longrightarrow} O$$
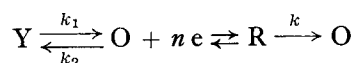
These cases have been treated mathematically with the following assumptions. All substances involved are soluble and not adsorbed on the electrode. The transition times and concentrations are such that double layer capacity and oxide film effects are negligible. In some cases the diffusion coefficients of the species are assumed to be equal. All chemical reactions are pseudo-first or first order; the effect of higher-order reactions will be discussed later. Although all cases can be treated for different cathodic and anodic current densities, in the discussion that follows these are assumed to be equal. Except for case 3(b), R will be assumed to be absent initially. The following treatment also assumes reversals about a single chronopotentiometric wave, although expansion of the potential axis to regions where Y and Z are electroactive may frequently be used. The following discussion is for an initial reduction followed by reversals of current, although the results apply equally well to an initial oxidation.

The mathematical treatment of CC for the various cases is relatively simple compared to an analogous treatment for cyclic voltammetry. In general, use is made of the "response function additivity principle" of Murray and Reilley[4]

$$\sum_m n_m F D_m^{\frac{1}{2}} [C_m^0 - C_m(0, t)] = \sum_p Z_p(0, t - t_p)$$

where $Z_p(0, t - t_p)$ is the current impulse response function, and the other symbols have their usual meanings. The mathematical treatment involves obtaining expressions for $Z_p$ based on a solution of Fick's equation for the first reduction and extension to the case of $n$ transitions arising from $n$ current reversals by successively allowing $C_O(0, t)$ and $C_R(0, t)$ to be zero. Solutions to Fick's equation for the first transition for many cases of interest are available.[5,6] The resulting series of equations are solved successively for the transition times $\tau_1, \tau_2, \ldots$ using standard

numerical methods or more easily, with the aid of a digital computer.[1-3] The results are conveniently represented as relative transition times, $a'_n s (a_n = \tau_n/\tau_1)$, as functions of the dimensionless parameter $k\tau_1$. Under these conditions the relative transition times in a series are independent of concentration and diffusion coefficient (for first-order chemical reactions).

## RESULTS

The final results of the mathematical treatment are tables of $a_n$ for each case for various values of $k\tau_1$. Typical results for various cases for $k\tau_1 = 1$ (for $k$'s of all reactions involved in the case) are shown in Table 1.

TABLE 1

Relative transition time values for cyclic chronopotentiometry for various reaction schemes for $k\tau_1$ of one.

| Case 1 | 2(a) | 2(b) | 3(a) | 3(b) | 4 | 5 | 6 | 7(a) | 7(b) |
|---|---|---|---|---|---|---|---|---|---|
| Diff. | Kinetic | | Catalytic | | Kin.-Cat. | ECE | Prec. | Prec. kin. | With cat. |
| $n$ | Irrev. | Rev. | Irrev. | Rev. | | | | | |
| 1 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 2 0.333 | 0.167 | 0.207 | 0.167 | 1.413 | 0.104 | 0.093 | 0.333 | 0.167 | 0.167 |
| 3 0.588 | 0.384 | 0.438 | 0.673 | 1.407 | 0.367 | 0.362 | 0.665 | 0.468 | 0.867 |
| 4 0.355 | 0.138 | 0.201 | 0.169 | 1.408 | 0.090 | 0.076 | 0.385 | 0.149 | 0.182 |
| 5 0.546 | 0.292 | 0.373 | 0.658 | 1.408 | 0.282 | 0.269 | 0.631 | 0.373 | 0.888 |
| 6 0.366 | 0.120 | 0.198 | 0.169 | 1.408 | 0.081 | 0.066 | 0.410 | 0.135 | 0.186 |

Although these relative transition times are different for different values of $k\tau_1$, the trends shown and the direction of deviation with respect to the diffusion case (with the exception of cases 3(b) and 4) remain the same for any value of $k\tau_1$. Longer tables or computer programs for the calculation of $a_n$ values for other values of $k\tau_1$, including the possibility of nonequal forward and reverse current densities and some R initially present, are either available[1,2] or are being prepared. For the present discussion only the trends are important for qualitatively identifying the overall reaction scheme.

To apply CC to the study of an electrode reaction, the following experiments may be performed:

(1) Record a cyclic chronopotentiogram starting with a reduction.
(2) Repeat, changing the current density by a factor of about 3 or 4.

13*

(3) Try an initial oxidation to find if any R is initially present.

(4) Vary the initial concentration of O and obtain a cyclic chrono-potentiogram with the same $\tau_1$ as in (1) or (2).

(5) Widen the limits of reversal potential to see if any new waves appear.

The results of these experiments and Table 1 can be used to classify the reaction under consideration according to the cases described.

## Relative transition times

$\tau_2/\tau_1$ (1) $\tau_2 = 0.333\tau_1$, cases 1 (diffusion) and 6 (preceding).

  (2) $\tau_2 < 0.333\tau_1$, cases 2 (kinetic), 3 (catalytic), 4 (kinetic-catalytic), 5 (ECE) and 7.

  (3) $\tau_2 > 0.333\tau_1$, only for case 3(b), when some R is initially present. Also occurs if adsorption of R is significant.

$\tau_3/\tau_1$ (1) $\tau_3 = 0.588\tau_1$ only for case 1, although a fortuitous combination of $k_1$, $k_2$, and $\tau_1$ could also lead to this result (case 4).

  (2) $\tau_3 < 0.588\tau_1$, for any mechanism involving a kinetic reaction, i.e. cases 2, 4, and 7(a), as well as case 5.

  (3) $\tau_3 > 0.588\tau_1$, for any mechanism involving a catalytic reaction, i.e. cases 3, 4, and 7(b), and for case 6.

From the above considerations an initial separation between the various cases can be made. Reinforcement of this choice can be accomplished by comparison of $\tau_4$, $\tau_5$, ... with diffusion values, assuming convection does not interfere with the measurements. Differentiation of reversible and irreversible following reactions, such as cases 2(a) and 2(b) or 3(a) and 3(b), can be made by observing the trends in the successive transition times. A reversible following reaction tends to cause a leveling-off or a constancy for later transition times, while a slow variation is observed with irreversible reactions.

*Effect of variation of i.* Only for case 1 are the relative transition times independent of the value of $\tau_1$ (and therefore of $i$). In all other cases increasing $i$ will decrease $\tau_1$ and simultaneously cause a variation in the relative transition times; the effect on the relative transition time is generally the same as an effective decrease in the various values of $k$. For example for case 2 increasing $i$ will cause $a_2(\tau_2/\tau_1)$ and $a_3$ to become larger. For case 3 an increase in $i$ will cause $a_2$ to become larger and $a_3$ smaller. For case 6, $a_2$ is independent of $i$, but $a_3$ becomes smaller with increasing $i$.

*Initial oxidation.* An initial oxidation sweep provides evidence that R is initially absent. If R is initially present, and is not the result of purposeful

introduction, case 3(b) may be indicated. For this case CC starting with an oxidation scan should also follow the scheme of case 3(b).

*Effect of increasing reversal potential limits.* Increasing the reversal potential limits will often lead to additional waves which can provide evidence in favor of a particular reaction mechanism. For example in case 2(a), increasing the potential range may allow Z to become electro-active (i.e. oxidizable) and the overall transition times, for reduction of O and the oxidation product of Z, and the oxidation of R and Z should follow the diffusion case (case 1), since all species are electroactive in the potential range now under consideration. For the ECE mechanism (case 5) an expanded potential scale may yield a wave for the oxidation of R' to O'.

*Effect of varying initial concentration of O.* For all of the cases discussed above, involving only pseudo-first or first-order reactions, for a given value of $\tau_1$, the relative transition times are independent of the initial concentration of O. For higher-order reactions one would expect that an increase in the initial concentration of O would change the relative transition times (for a given value of $\tau_1$) in general tending towards the same effect as an increase in the value of $k$ for the higher-order chemical reactions. Therefore variation of the $a$-values with initial concentration can provide evidence of higher-order reactions in the reaction scheme.

*Quantitative fitting of data.* Once a reaction scheme is selected, the experimental data can be compared to sets of theoretical relative transition times calculated for different values of $k\tau_1$. A good fit should be obtained and $k$-values can then be calculated. If the general trend is correct but a good quantitative correspondence between experimental and theoretical values cannot be obtained, perturbation of the electrode reaction by adsorption, oxide film effects, or additional parallel complicating reactions is suggested. Some cases corresponding to both of these conditions will be discussed below.

## EXAMPLES

*Oxidation of p-aminophenol.* The oxidation of $p$-aminophenol (PAP) in dilute $H_2SO_4$ at a platinum electrode has been shown to occur as follows [see references (3) and (7) and the references contained therein]

$$HO—C_6H_4—NH_2—2e \rightleftarrows O=C_6H_4=NH + 2H^+$$

$$O=C_6H_4=NH + H_2O \xrightarrow{k} O=C_6H_4=O + NH_3$$
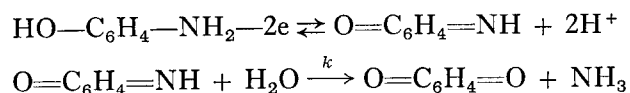
so that the CC should follow case 2(a), when the potential limits are set so that only the oxidation of PAP and the reduction of the imine occur.

Typical experimental results for the CC of PAP compared to theoretical results are shown in Table 2. The agreement of the experimental and

TABLE 2

Theoretical and experimental relative transition times for the cyclic chronopotentiometry of $p$-aminophenol solution contained 1.14 m$M$ $p$-aminophenol in 0.1 $M$ $H_2SO_4$. Current density was 0.271 mA cm$^{-2}$ at a platinum disc electrode.
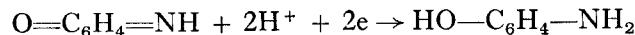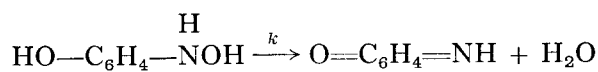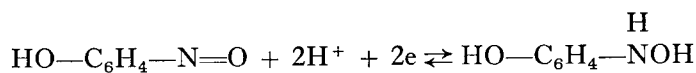
| $n$ | $a_n$ | |
|---|---|---|
| | Experimental | Calculated for $k\tau_1 = 0.75$ |
| 1 | 1.000 | 1.000 |
| 2 | 0.193 | 0.193 |
| 3 | 0.418 | 0.420 |
| 4 | 0.177 | 0.164 |
| 5 | 0.325 | 0.326 |
| 6 | 0.141 | 0.144 |

theoretical values is very good and the calculated rate constant, 0.086 and 0.115 sec$^{-1}$ at 24.5° and 30°C respectively, is in good agreement with results of previous workers. When the cathodic potential limit is set at a more negative potential, the reduction of benzoquinone can occur during the even-numbered transitions,

$$O=C_6H_4=O + 2H^+ + 2e \rightleftarrows HO-C_6H_4-OH$$
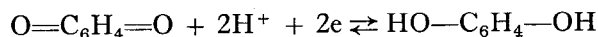
following the reduction of the benzoquinoneimine, and the oxidation of hydroquinone occurs during the odd-numbered transitions (except for $\tau_1$) along with the oxidation of PAP. The overall oxidation and reduction transition times under these conditions then follow the diffusion-controlled case.

*Reduction of p-nitrosophenol.* Alberts and Shain[8] suggest that the reduction of $p$-nitrosophenol (PNP) in an acetate medium at a mercury pool electrode occurs as follows

$$HO-C_6H_4-N=O + 2H^+ + 2e \rightleftarrows HO-C_6H_4-\overset{H}{N}OH$$

$$HO-C_6H_4-\overset{H}{N}OH \xrightarrow{k} O=C_6H_4=NH + H_2O$$

$$O=C_6H_4=NH + 2H^+ + 2e \rightarrow HO-C_6H_4-NH_2$$

On reversal, for a narrow potential range, only the oxidation of $p$-hydroxylamine phenol occurs. Typical experimental results for the reaction compared to theoretical values of $k\tau_1$ for case 5 are given in Table 3. In

TABLE 3

Theoretical and experimental relative transition times for the cyclic chronopotentiometry of $p$-nitrosophenol.

Solution contained 1.57 m$M$ $p$-nitrosophenol in a buffer containing 0.1 $M$ acetic acid, 0.1 $M$ potassium acetate and 0.2 $M$ potassium nitrate. Cathodic current density was $0.34$ mA cm$^{-2}$ and anodic current density was $0.063$ mA cm$^{-2}$ at a mercury pool electrode.[a]

| $n$ | $a_n$ | | |
| --- | Experimental | Calculated for $k\tau_1 = 6.0$ | Calculated for $k\tau_1 = 2.3$ |
| 1 | 1.000 | 1.000 | 1.000 |
| 2 | 0.137 | 0.040 | 0.134 |
| 3 | 0.218 | 0.115 | 0.254 |
| 4 | 0.137 | 0.038 | 0.115 |
| 5 | 0.162 | 0.087 | 0.182 |
| 6 | 0.133 | 0.037 | 0.106 |

[a] Because of the rapidity of the intermediate chemical reaction, a decreased anodic current density was needed to give a measureable transition time.

this case, although the overall trends in the experimental data follow case 5, a quantitative agreement between theoretical and experimental values could not be obtained for any value of $k$. This suggests that perhaps adsorption of one of the species is perturbing the reaction. For example, if the $p$-hydroxylaminephenol was adsorbed, the even-numbered transitions would tend to be increased over those expected in the absence of adsorption. An alternate explanation is that the reaction mechanism is not the assumed ECE mechanism, but that it involves other parallel reactions or a different, similar, scheme, such as the disproportionation of the $p$-hydroxylaminephenol to PNP and PAP. Further work on this and related systems using CC and other techniques is in progress.

## CONCLUSIONS

CC is in many ways similar to cyclic voltammetry. Cyclic chronopotentiometry has the advantage of requiring relatively simple apparatus and being amenable to direct and rigorous mathematical analysis, even for complex reaction schemes. Of course the complete elucidation of a reaction mechanism requires the use of other electrochemical techniques,

such as polarography and coulometry, as well as analysis of reaction products and intermediates using such techniques as spectrophotometry and electron spin resonance spectroscopy. It must be pointed out that the cases discussed here are representative but not inclusive, and that even a good quantitative fit between theoretical calculations and experimental data is no guarantee that the proposed mechanism is the correct one. Moreover, all of the reaction schemes degenerate to diffusion-controlled behavior at very high or very low current densities, so that conformation of the measured values to those of case 1 may merely indicate that all chemical reaction times are either very slow or very fast compared to the transition times.

Chronopotentiometric data can be applied in other ways in the elucidation of electrode reaction mechanisms. Reinmuth[9] has described the use of potential–time curves for distinguishing between mechanisms. For example, the variation of $E_{\frac{1}{4}}$ with current density and concentration can be used as a diagnostic tool for distinguishing among various reversible and irreversible charge transfer reactions, with or without following chemical reactions. Using only transition time measurements in CC has the advantage of not being dependent upon precise potential measurements, so that slight changes in the reversibility of the charge-transfer itself, for example because of changes in the electrode surface, do not effect the method. On the other hand this procedure provides no information about the rate of the charge-transfer step itself. However, simultaneous potential measurements on the CC curves is possible and can yield information about the reversibility of the electrode reaction[2].

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