A Comparison of Cyclic Voltammetry and Cyclic Staircase Voltammetry

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Digital potentiostats use a staircase wave form as an approximation to a linear wave form. It is shown in this article that this approximation is only valid under certain conditions. It is also shown that these conditions are met by BAS digital instruments.

Cyclic voltammetry (CV) is arguably the most widely used technique for the characterization of redox systems. It can provide qualitative information about the number of oxidation states and their stability, as well as the rate of heterogeneous electron transfer reactions. It can also be used in combination with simulation software to calculate rates of homogeneous and heterogeneous reactions. Such studies typically involve varying the scan rate (as well as other conditions) and examining how characteristic features such as the peak currents and peak potentials change in response to these variations (1 - 3) (more sophisticated software also allows fitting of experimental data and simulated data). The wave form used for cyclic voltammetry is a linear ramp (*F1*), the direction of which changes at least once during the experiment. However, digital instruments cannot apply a true linear wave form, and a staircase wave form (*F2*) is used as an approximation. The aim of this article is to determine the conditions under which this approximation is valid and to discuss whether BAS digital instruments (the BAS 100 series and the CV-50W) meet these conditions.

As discussed in the introduction, variation of scan rate is an important element of mechanistic investigations using cyclic voltammetry. Therefore, we must examine how the scan rate is determined in the staircase wave form. Inspection of *F2* shows that there are two parameters that determine the "scan rate": the step potential (ΔE) and the step period (t_p) (i.e., the scan rate = $\Delta E/t_p$). Since there are many combinations of these two parameters that can generate a required scan rate, we need to investigate the effect, if any, of these two parameters on the current response and determine which combinations provide a current response identical to that generated by a true linear wave form. Another complication with the staircase wave form is that the current can be sampled at different points along the potential step. The sampling point is expressed in terms of the sampling parameter α, which is defined by t_s/t_p, where t_s is the time between the application of the pulse and the current sampling; that is, if $\alpha = 1$, the current is sampled at the end of the step (it should be noted that some authors have used the opposite convention).

There have been a number of studies in which the effect of variations of ΔE, t_p and α on the current response have been investigated to see if there are combinations of parameter values that provide the same current response as a linear wave form. These studies have discussed a wide range of different redox mechanisms (4 - 13) (reversible, quasi-reversible, irreversible due to coupled chemical reactions, and adsorptive species). The results of these studies are summarized below.

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F1

Potential wave form for cyclic voltammetry.
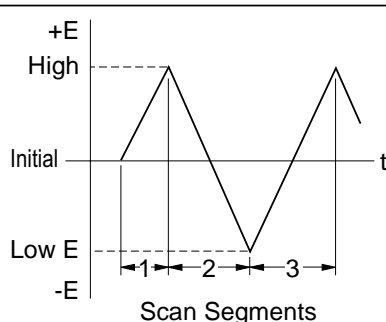
F2

Potential wave form for staircase voltammetry.
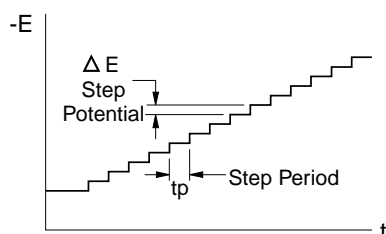
a) Reversible electron transfer

The Fe(III)/Fe(II) oxalate system has been used as an example of a reversible system (7, 10, 12). There is good agreement between the linear and staircase current responses for $\alpha = 0.25$ (9-12) (or 0.3 (7)), both from theory and experiment, for ΔE values up to 8 mV. However, when $\alpha = 1$, ΔE values as small as 2 mV gave a significantly different response for the staircase wave form (9.6% error).

The dependence of the peak current on the scan rate (υ) was also investigated for a reversible process (7,10). The scan rate was varied in 2 ways:

(i) ΔE constant, t_p varied
(ii) ΔE varied, t_p constant

For (i), there was very good agreement for $\Delta E = 2$ mV, $\alpha = 0.25$ for scan rates up to 500 mV/s (differences at higher scan rates were attributed to the contribution of the charging current in CV). The agreement was acceptable up to $n\Delta E \leq 8$ mV, as was predicted from theory (9) (n = number of electrons transferred). The dependence on ΔE was further confirmed by study (ii), which showed poor agreement for $\Delta E > 8$ mV for $\alpha = 0.25$ and for all the selected values of ΔE when $\alpha = 1$ (the smallest value of ΔE used in this second series of experiments

was 3.9 mV). Since the agreement between linear and staircase experiments was dependent on the value of ΔE, it was concluded that the scan rate of the staircase wave form should be varied by changing t_p.

Although the above studies showed that the staircase and linear wave forms generate equivalent current responses for reversible systems under certain conditions, it should be remembered that many redox processes are not reversible. Hence, the staircase wave form must give good agreement for all systems if it is to be considered a viable approximation for the linear potential. Theoretical and experimental results have been reported for the following systems (5, 11, 12): quasi-reversible (slow electron transfer kinetics), amalgam formation, CE, EC, EC' (catalytic) and ECE (E = electron transfer reaction, C = chemical reaction). For all these examples, the parameter values DE = 5 mV, tp = 0.05s (this corresponds to a scan rate of 100 mV/s) were used unless otherwise indicated.
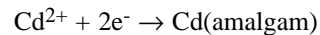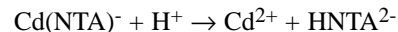
b) Quasi-reversible electron transfer

Theory predicted that there should be good agreement for $\alpha = 0.5$ (11), and this was shown to be the case for the Eu(III)/Eu(II) and Cr(III)/Cr(II) systems for small values of ΔE (e.g., 5 mV) (12).

c) Amalgamation

The well known $Cd^{2+} + 2e^- \rightarrow Cd(Hg)$ reaction was used as the example. Since the reduction (deposition) and oxidation (stripping) scans are controlled by different physical processes, good agreement for both steps could not be obtained with one unique value of α. Good agreement was obtained for $\alpha = 0.25$ for the cathodic current, and $\alpha = 0.5$ for the anodic current (12).

d) CE

The system that was used as an example of a CE mechanism was

$$Cd(NTA)^- + H^+ \rightarrow Cd^{2+} + HNTA^{2-}$$

$$Cd^{2+} + 2e^- \rightarrow Cd(amalgam)$$

The voltammograms showed a reversible process for Cd^{2+} and an irreversible reduction for the NTA complex (irreversible due to slow electron transfer kinetics); that is, there are in fact two processes to consider. Theory predicts that $\alpha = 0.5$ should provide the best agreement for both oxidations (11). However, experiments showed that the best agreement for the peak of the reversible oxidation of the Cd^{2+} was obtained with $\alpha = 0.25$, whereas $\alpha = 0.5$ provided the best agreement for the irreversible oxidation (12).

e) EC

The oxidation of ascorbic acid showed good agreement for $\alpha = 0.5$ (12), as predicted by theory (11).

f) EC'

The example studies for this type of reaction were the reduction of Ti(IV) to Ti(III), followed by the reaction of Ti(III) with hydroxylamine to regenerate Ti(IV). The best agreement was obtained for $\alpha = 0.25$ (12) (as predicted theoretically (11)); however, at sufficiently high hydroxylamine conditions, a steady-state current response was obtained, the magnitude of which was shown to be independent of the value selected for α.

g) ECE

The reduction of p-nitrosophenol was used as the example of an ECE process. For $\Delta E = 5$ mV, no one value of α gave good agreement over the whole voltammogram. The closest match was obtained by lowering ΔE to 2 mV for $\alpha = 0.5$ (12).

h) Adsorption

Since adsorbed redox-active molecules are already present at the electrode surface, the application of a potential pulse of the appropriate magnitude will cause the instantaneous electrolysis of the adsorbed

molecules, which leads to a current "spike" with no diffusional tailing. The current response for the staircase potential for adsorbed redox systems is therefore more sensitive to variations in ΔE and α than solution redox systems. For example, a study of the adsorption of mercury bromide ion at a mercury electrode has been reported (13). When $\Delta E = 1$ mV, the peak currents due to the adsorbed mercury bromide vary considerably with α (by a factor of 2). As ΔE was increased, these current peaks decreased sharply (to zero for $\Delta E = 6$ mV).

It can be seen from the above examples that a staircase wave form cannot be guaranteed to provide the same current response as a linear wave form if ΔE is on the order of millivolts. In addition to the dependence on α shown in the above examples, there are a number of other points to remember:

1) As noted above, the optimum value for α can depend on the reversibility of the redox process. However, reversibility depends on the time scale of the experiment; that is, the scan rate (for cyclic voltammetry). Therefore, a redox process can be changed from reversible to, for example, quasi-reversible by increasing the scan rate. The study of such a redox process would require a change in the value of α used.

2) The examples discussed above were relatively simple, in that there was only one factor that caused irreversibility; for example, if there was a chemical reaction, the electron transfer kinetics were assumed to be rapid. However, many redox systems have slow electron transfer kinetics in addition to a coupled chemical reaction, and it is not clear whether such systems could be assigned a unique value of α.

3) Another study (14) showed that exact equivalence between the current responses of the staircase and linear wave form requires different values of α for different parts of the curve.

Therefore, the above examples show that data obtained using such a staircase wave form should be examined with care. However, it should be noted that the value of ΔE of at least 1 mV was used for all these examples. It has been shown (9) that the difference between the current responses for staircase and linear wave forms decreases as ΔE decreases, and that, at least for solution redox species, the current response for a staircase wave form is essentially identical to that for a linear wave form for all values of α if $\Delta E \leq 0.26$ mV (i.e., ΔE is at least one order of magnitude smaller than that used in the above studies). Therefore, a small value of ΔE (0.1 - 0.2 mV) is desirable in the staircase wave form used by a digital instrument. However, it has been argued (9,13) that using such a small value for ΔE would lead to an unacceptably large number of data points or would restrict the size of the potential window (since the number of potential steps available on a digital instrument is fixed by the resolution of the Digital-to-Analog (DA) converter, increasing the number of steps per mV (by decreasing ΔE) decreases the available potential range).

These two problems can be diminished by decreasing the rate of current sampling (i.e., the current is not sampled on each potential step) and by using a high-resolution DA converter. For example, on BAS digital instruments, the minimum value of ΔE is 0.1 mV (i.e., it is small enough that the current response for the staircase wave form used for cyclic voltammetry is identical to the current response for a true linear wave form, at least for solution species). However, even at slow scan rates, the current is only sampled at 1 mV intervals (the size of the interval increases with increasing scan rate). A 16 bit DA converter is used, and hence the potential range is ± 3.276 V, which is quite adequate for many redox systems.
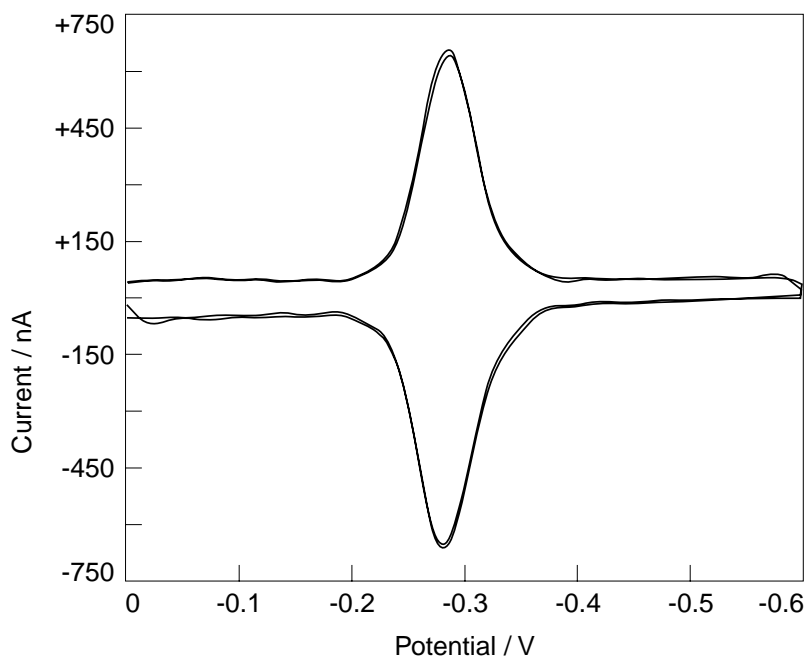
More recent work on the current responses of adsorbed species has suggested that the current responses for a linear wave form and a staircase wave form for adsorbed species can be made equivalent by analog filtering of either the applied potential wave form or the current response (15). It was proposed that analog filtering available on BAS digital instruments is sufficient to achieve this equivalency. To test this proposal, cyclic voltammograms were recorded on a solution of 0.5×10^{-5} M alizarin complexone hydrate (which adsorbs readily at a mercury electrode) using both a BAS 100B/W and CV-27 (which uses a true analog linear wave form for CV).

In the first set of experiments, the default analog filtering provided by the BAS 100B/W was used, and the cyclic voltammograms measured using the BAS 100B/W and the CV-27 were found to be essentially equivalent (there was less than 2% difference between the peak currents) at scan rates between 10 mV/s and 500mV/s (the maximum scan rate was limited by the response of the XY recorder used for the CV-27). The effect of the analog filtering of the BAS 100B/W was then examined. At scan rates faster than 30 mV/s, it was found that there was little difference between the unfiltered and filtered current responses (for example, there was about 2% difference between the filtered and unfiltered currents at a scan rate of 100 mV/s (**F3**)). However, at scan rates less than 30 mV/s, the unfiltered current response was not satisfactory.

The magnitude of ΔE on the BAS 100B/W depends on the units used for the scan rate. For mV/s, ΔE is 0.1 mV (as discussed above), whereas for V/s, it is 1.6 mV. This difference in the step height does have a significant effect on the magnitude of the current response, as is shown in **F4**. The three voltammograms in this figure were

Comparison of cyclic voltammograms recorded using a BAS 100B/W for 5 µM alizarin complexone in 0.05 M HAc-NaAc solution (pH = 4.7) at a BAS CGME, scan rate = 100 mV/s using a) default analog filter values and b) no analog filtering.

for a linear wave form for both solution species and adsorbed species, provided that a small value is used for ΔE (≤ 0.26 mV) and that appropriate analog current filtering is used (both of these conditions are met by BAS digital instruments). If larger values of ΔE are used, the current response becomes dependent on the value of the current sampling parameter, α, and equivalence between the current responses for staircase and linear wave forms can only be obtained for certain values of α (the appropriate value of α depends on the redox mechanism exhibited by the system).

References

1. R.S. Nicholson, Anal. Chem. 37 (1965) 1351.

2. J. Heinze, Agnew. Chem., Int. Ed. Engl. 23 (1984) 831.

3. R.S. Nicholson and I. Shain, Anal. Chem. 36 (1964) 706.

4. J.H. Christie and P.J. Lingane, J. Electroanal. Chem. 10 (1965) 176.

5. D.R. Ferrier, D.H. Chidester and R.R. Schroeder, J. Electroanal. Chem. 45 (1973) 361.

6. J.J. Zipper and S.P. Perone, Anal. Chem. 45 (1973) 452.

7. L-H.L. Miaw, P.A. Boudreau, M.A. Pichler and S.P. Perone, Anal. Chem. 50 (1978) 1988.

8. S. Stefani and R. Seeber, Anal. Chem. 54 (1982) 2524.

9. M. Seralthan, R.A. Osteryoung and J.G. Osteryoung, J. Electroanal. Chem. 214 (1986) 141.

10. R. Bilewicz, R.A. Osteryoung and J. Osteryoung, Anal. Chem. 58 (1986) 2761.

11. M. Seralathan, R.A. Osteryoung and J.G. Osteryoung, J. Electroanal. Chem. 222 (1987) 69.

12. R. Bilewicz, K. Wikiel, R. Osteryoung and J. Osteryoung, Anal. Chem. 61 (1989) 965.

13. Z. Stojek and J. Osteryoung, Anal. Chem. 63 (1991) 839.

14. M. Penczek, Z. Stojek and J. Buffle, J. Electroanal. Chem. 270 (1989) 1.

15. P. He, Anal. Chem. Anal. Chem. 67 (1995) 986.

Cyclic voltammograms recorded using a BAS 100B/W for 5 µM alizarin complexone in 0.05 M HAc-NaAc solution (pH = 4.7) at a BAS CGME, a) scan rate = 1000 mV/s with default current filtering, b) scan rate = 1 V/s with default current filtering c) scan rate = 1 V/s without current filtering.
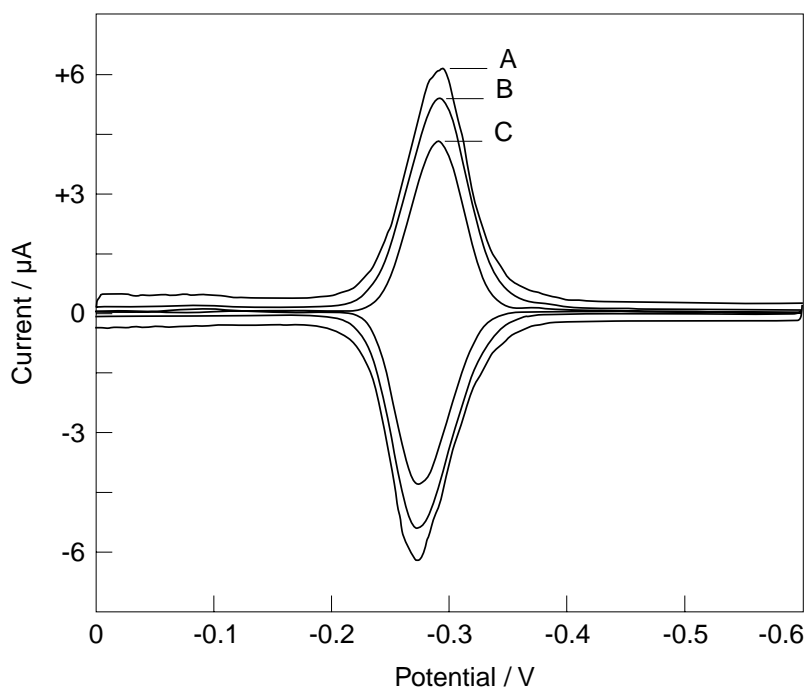
measured at scan rates of 1000 mV/s (with current filtering) (a) and 1 V/s (with (b) and without (c) current filtering). It can be seen that the peak current and charging current both decrease when the larger potential step height is used. However, the extent of these decreases are lessened by using analog current filtering.

Conclusions

The above discussion shows that the current response for a staircase wave form is equivalent to that