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Cyclic Voltammetry

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Cyclic voltammetry (CV) is perhaps the most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with ease of measurement has resulted in extensive use of CV in the fields of electrochemistry, inorganic chemistry, organic chemistry, and biochemistry. Cyclic voltammetry is often the first experiment performed in an electrochemical study of a compound, a biological material, or an electrode surface. The effectiveness of CV results from its capability for rapidly observing the redox behavior over a wide potential range. The resulting voltammogram is analogous to a conventional spectrum in that it conveys information as a function of an energy scan.

In spite of the wide usage enjoyed by CV, this technique is not generally well understood in comparison to other instrumental methods such as spectroscopy and chromatography. It is not uncommon for the experimenter who is performing CV to have a poor understanding of the basic concepts of the technique, such as why the voltammograms have their peculiar shapes. The brief treatment afforded CV in most instrumental analysis textbooks is insufficient to convey an in-depth understanding of this powerful technique.

It is the purpose of this article to provide a description of CV and its capabilities. The authors intend this to be suitable for a supplement to an undergraduate course in instrumental analysis or as an "initial reference" for anyone embarking on a CV experiment for the first time. This article is accompanied by an experiment which has been developed to demonstrate important features of CV.[1]

Fundamentals of Cyclic Voltammetry

CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution, and measuring the resulting current. The potential of this *working electrode* is controlled versus a *reference electrode* such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The controlling potential which is applied across these two electrodes can be considered an *excitation signal*. The excitation signal for CV is a linear potential scan with a triangular waveform as shown in Figure 1. This triangular potential excitation signal sweeps the potential of the electrode between two values, sometimes called the *switching potentials*. The excitation signal in Figure 1 causes the potential first to scan negatively from +0.80 to −0.20 V versus SCE at which point the scan direction is reversed, causing a positive scan back to the original potential of +0.80 V. The scan rate, as reflected by the slope, is 50 mV/s. A second cycle is indicated by the dashed line. Single or multiple cycles can be used. Modern instrumentation enables switching potentials and scan rates to be easily varied.

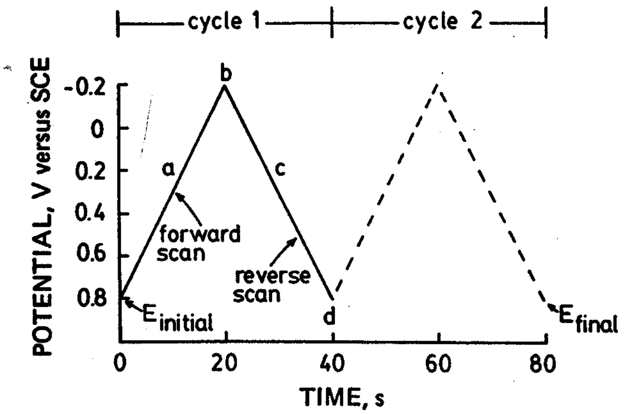

Figure 1. Typical excitation signal for cyclic voltammetry—a triangular potential waveform with switching potentials at 0.8 and −0.2 V versus SCE.

A cyclic voltammogram is obtained by measuring the current at the working electrode during the potential scan. The current can be considered the *response signal* to the potential excitation signal. The voltammogram is a display of current (vertical axis) versus potential (horizontal axis). Because the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. This is helpful in understanding the fundamentals of the technique.

A typical cyclic voltammogram is shown in Figure 2 for a platinum working electrode in a solution containing 6.0 mM $K_3Fe(CN)_6$ as the electroactive species in 1.0 M KNO_3 in water as the supporting electrolyte. The potential excitation signal used to obtain this voltammogram is that shown in Figure 1, but with a negative switching potential of −0.15 V. Thus, the vertical axis in Figure 1 is now the horizontal axis for Figure 2. The *initial potential* (E_i) of 0.80 V applied at (a) is chosen to avoid any electrolysis of $Fe(CN)_6^{3-}$ when the electrode is switched on. The potential is then scanned *negatively*, *forward scan*, as indicated by the arrow. When the potential is sufficiently negative to reduce $Fe^{III}(CN)_6^{3-}$, *cathodic current* is indicated at (b) due to the electrode process

$$Fe^{III}(CN)_6^{3-} + e \rightarrow Fe^{II}(CN)_6^{4-} \qquad (1)$$

The electrode is now a sufficiently strong reductant to reduce $Fe^{III}(CN)_6^{3-}$. The cathodic current increases rapidly (b → d) until the concentration of $Fe^{III}(CN)_6^{3-}$ at the electrode surface is substantially diminished, causing the current to peak (d). The current then decays (d → g) as the solution surrounding

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[1] The experiment to accompany this article appears on page 772 of this issue.