

Determining Electrode Reaction Mechanisms with Cyclic Square Wave Voltammetry

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Cyclic voltammetry has been the electrochemical method of choice for the evaluation of the mechanism of charge transfer for three decades. The advantages of this method include the low cost instrumentation required and the extensive theory available to guide the experimentalist in the interpretation of empirical results. These advantages have contributed to its widespread popularity especially among those who are not specialists in electrochemistry. Numerous applications of this method are in the current literature. However, this method has two shortcomings. First, the determination of the mechanism of the second of two or more closely spaced charge transfer reactions (along the potential axis) is often difficult. This poor resolution is a result of the current voltage peak asymmetry. Second, for non surface confined electroactive materials, the concentration of the analyte must be at least 10 μM for the attainment of reliable mechanistic information. This lower concentration limit is not a reflection of the poor sensitivity of the method, but rather the result of the high capacitance current that results from sweeping the potential linearly with time.

Square wave voltammetry is an important electroanalytical method. Compared to both linear sweep and cyclic voltammetry, square wave voltammetry has a much broader dynamic range and lower limit of detection because of its efficient discrimination of capacitance current. Analytical determinations can be made at concentrations as low as 10 nM. Theory to guide in the evaluation of charge transfer mechanisms has been developed.

Cyclic square wave voltammetry is a composite waveform that is ideal for the evaluation and identification of electron transfer mechanisms. This waveform utilizes a square wave which steps through the region of the formal potential of the electroactive species under study in two directions. The use of this waveform for mechanistic determinations merits consideration for several reasons. First, the utilization of the square wave potential waveform and the discrete current sampling regimen will permit mechanistic evaluations at trace levels. Second, the reverse potential sweep functions as a probe of the stability of the product generated on the forward potential sweep. Third, the method is readily adaptable to existing instrumentation capable of both square wave and cyclic voltammetry. Fourth, the data display format is familiar to nonelectrochemists who currently make extensive use of cyclic voltammetry for compound characterization. The aim of this paper is to critically examine the strengths and weaknesses of this waveform for determining electrode reaction mechanisms.