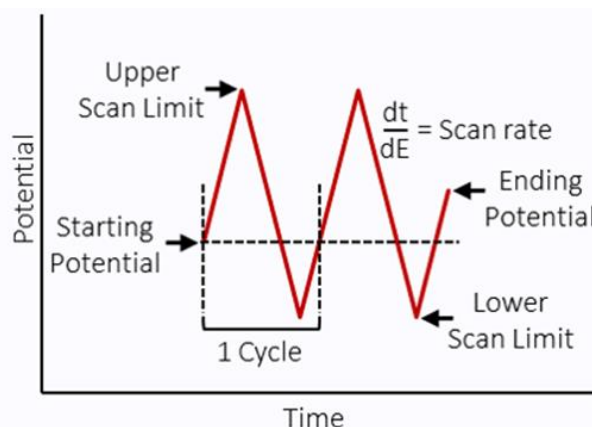




Using Cyclic Voltammetry To Study Redox Reactions

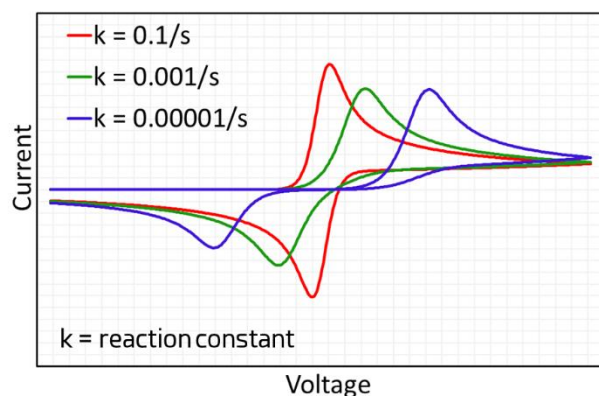
Cyclic Voltammetry is the defining test method potentiostats are designed to perform. There are several key considerations to understand when running CVs on samples.

Cyclic Voltammetry (CV) is the most popular method in analytical electrochemistry for studying redox reactions. The applied voltage signal looks like one or more triangles when graphed with time on the x-axis. The parameters to control during CV experiments are starting/ending voltage, voltage window (upper and lower voltage limit of the scan), scan rate, and the number of cycles. A wide variety of mechanistic information about the sample being scanned can be obtained from CV experiments. Examples include the number of redox reactions, types of redox reactions, reaction mechanisms, and diffusion coefficients.



Categorizing Redox Reaction Reversibility

One of the first pieces of information someone may want to know from a cyclic voltammogram (Current vs Voltage plot) is the reversibility of the reaction. In the simulated CV shown below, only the reaction rate is varied. As the reaction rate decreases, the separation between the reduction peak position (E_p^R) and the oxidation peaks position (E_p^O) widens. For a truly reversible reaction, the separation between cathodic and anodic peaks should be 59 mV/n, where n is the number of electrons. Also, the reduction peak height (i_p^R) is equal to the oxidation peak height (i_p^O) for a reversible reaction. However, peak height is difficult to determine for a real cyclic voltammogram. Another indicator of reversibility of reaction is that the peak position is independent of the scan rate.



Requirements for True Reversibility

$$\Delta E = E_p^R - E_p^O = \frac{59\text{mV}}{n}$$

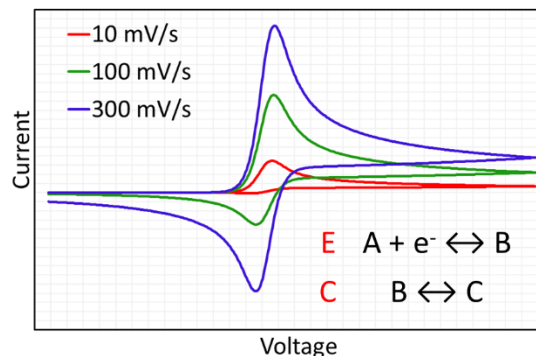
$$|i_p^R| = |i_p^O|$$

The peak position is independent of the scan rate

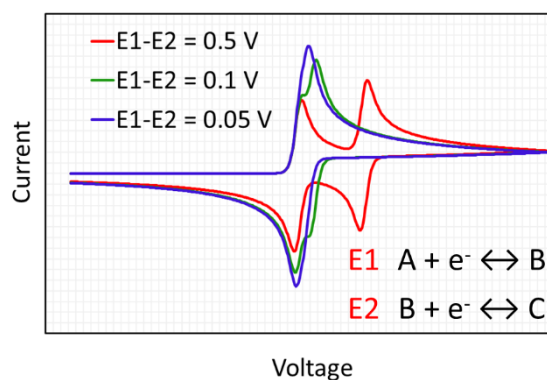
By studying peak separations, reactions can be categorized into reversible (all the products can be changed back to the substrate by changing the direction of voltage), quasi-reversible (some product can be changed back to the substrate), and irreversible (product cannot be changed back to the substrate) reaction.

Revealing Redox Reaction Mechanisms

CVs can also help to elucidate reaction mechanisms. Different redox reaction mechanisms result in different CV profiles. For example, the CV on the right shows an electrochemical reaction (E) is followed by a chemical reaction (C). At low scan rates, the cyclic voltammogram is that of an irreversible reaction. As the scan rate increases, the CV is that of a quasi-reversible reaction. This is because the chemical reaction cannot keep up with the electrochemical reaction. In this example, 'B' is produced at a faster rate than it can be turned to 'C' such that some of the 'B' turns to 'A' during the reverse scan at higher scan rates.



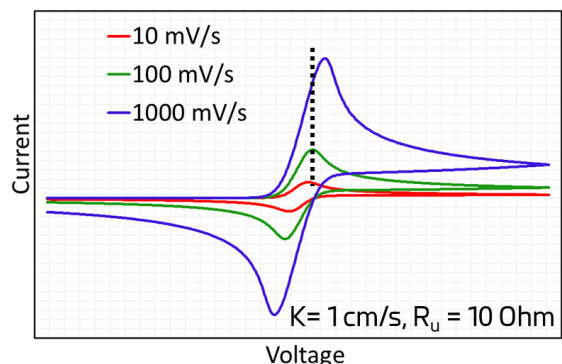
Let's consider a different scenario in which there are two electrochemical reactions taking place. In the E1E2 reaction to the right, two electrochemical reactions are taking place. The separation between the peaks of the same type (reduction or oxidation) depends on the difference in their standard reduction potential. As the difference decreases, peaks merge to resemble a single redox process. CV curves can be modeled to calculate reaction mechanisms and important parameters such as reaction constants, diffusion constants, capacitance, etc.



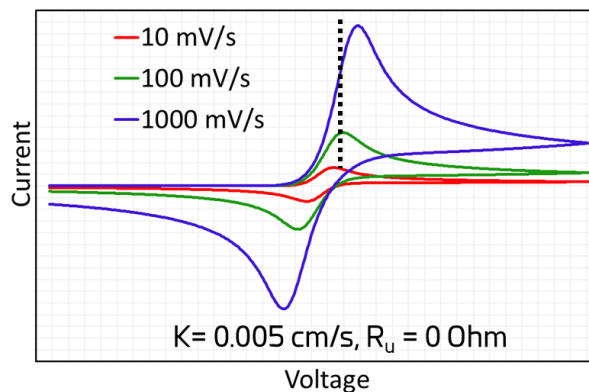
Accounting For Uncompensated Resistance

When running CVs, one must be aware of the possible effects from uncompensated resistance that can lead to erroneous measurements unless properly compensated for. Uncompensated resistance (R_u) is the resistance between the RE and the WE. Due to the R_u , the WE does not experience all of the voltage applied by the potentiostat. The loss of applied voltage depends on the R_u and the magnitude of the current given by Ohm's law ($V = iR_u$).

Theoretically, the peak position should be independent of the scan rate for a reversible reaction. However, because of the R_u , a systematic shift in peak position can be observed when the scan rate is increased. This is illustrated in the figure to the right. This occurs because the peak current increases with the scan rate, which means the voltage loss also increases.

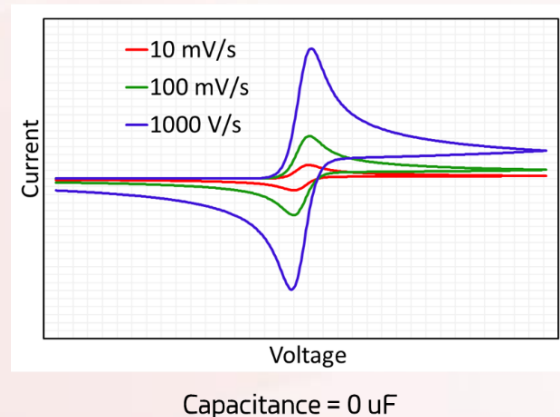


This behavior is similar to that of a quasi-reversible reaction devoid of R_u . This is illustrated in the figure to the right. Applying IR compensation in situations like this is very important for accurate qualitative and quantitative analysis of CV. Most potentiostats, including our family of Squidstats from Admiral Instruments, have IR compensation capabilities selectable in the potentiostat control software.

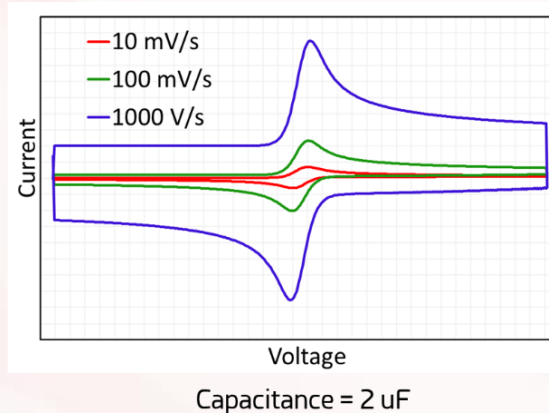


Accounting For Effects From Capacitance

Another possible source of error when running and analyzing CV data is the effect of capacitance. Redox peak current from a reversible reaction is proportional to the square root of the scan rate. By contrast, the capacitive current is linearly proportional to the scan rate.



$$\text{Redox Peak Current} \propto (\text{Scan rate})^{1/2}$$



$$\text{Capacitive Current} = \text{Scan rate} \times \text{Double-Layer Capacitance}$$

Thus, capacitive current can completely dominate the redox peak current at a high scan rate, thereby adding uncertainty about how to properly interpret the peak. The capacitive effect might cause an error in the determination of peak height and area. To avoid this issue, one should try different scan rates to determine the optimal scan rate for their purpose.

Summary

Cyclic Voltammetry is the most often used electrochemical measurement method to study reduction-oxidation reactions. The plot generated by a CV scan, called a cyclic voltammogram, differs from one redox reaction to another. There are several factors to keep in mind when running CVs and analyzing the resulting data:

- 1) The scan rate should be optimized. Insights into the nature of the system can be obtained by varying the scan rates.
- 2) Uncompensated resistance should be accounted for using the IR compensation feature common to research-grade potentiostats.
- 3) The capacitive effect should be normalized for the proper analysis of peaks.
- 4) Modeling and fitting should be applied to gain mechanistic insights.

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