CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Analog Filter Effects on Cyclic Voltammograms

Key Terms
Cyclic Voltammetry, Electronic Filtering

Cyclic Voltammetry is the most common technique used to characterize the electrochemical properties of a system. The potential difference between the anodic and cathodic peak currents (ΔEp) may be used to calculate the heterogeneous electron-transfer rate constant (Capsule #141). Changes in peak potential and peak current may be used for mechanistic studies of chemical reactions coupled to the electron transfer. A low-pass filter is often employed to minimize unwanted noise. However, filtering must be done with caution or distortion of the voltammograms may result. Too large a filter time constant will cause attenuation of the peak potential. The criterion used to relate the maximum time constant (RC, s) of the filter to a given scan rate (v, V s^{-1}) for minimal signal distortion is:

$$2\pi RC \leq \frac{1}{40\,nv} \qquad 1.$$

Following Equation 1 will cause less than 1% distortion as determined by Fourier Transform Analysis (1,2). A qualitative derivation is found in Ref. 3.

The criterion was tested with a BAS CV-27 Voltammograph at time constants of 0.1 s and 0.001 s. According to Equation 1, the maximum scan rate that may be used with a 0.1 s time constant is 40 mV s^{-1}. Superimposed voltammomgrams for the reversible one-electron oxidation of ferrocene at a scan rate of 40 mV s^{-1} obtained with each of the filters are shown in Figure 1. The data show that the peak height is slightly attenuated and the peak potential is shifted a few millivolts with the 0.1 s time constant filter. The distortion is insignificant for most studies.

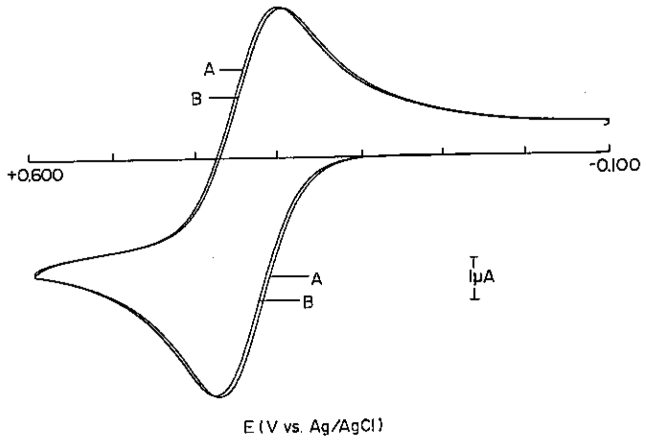

Figure 1. Cyclic voltammogram of 0.92 mM ferrocene in acetonitrile with 0.1 M tetrabutylammonium perchlorate (TBAP), obtained at a scan rate of 40 mV s^{-1}. Filter time constant of: A) 0.001 s; B) 0.1 s.

Voltammograms obtained at scan rates of 100 mV s^{-1} (Figure 2) and 30 mV s^{-1} (Figure 3) with each of the filters are shown for comparison. There are significant differences between the voltammograms at 100 mV s^{-1}, both in the peak current and the peak potential. The voltammograms at 30 mV s^{-1} show very little difference with each filter and are marginally better than those at 40 mV s^{-1}. The data demonstrate that adherence to Equation 1 results in voltammograms with maximum signal-to-noise and minimal distortion. The further the deviation from the condition given by Equation 1, the more pronounced the distortion will be.

The frequency response requirements must also be applied to the recording device. Data acquisition by X-Y recorders is usually restricted to scan rates below 200 mV s^{-1}. A ΔEp of 59/n mV is expected for a reversible electron-transfer reaction. The literature often reports $\Delta Ep > 59$ mV/n for known reversible systems. These large ΔEp values may be due to filter effects, instead of iR effects or kinetic limitations.

References

1. *K. K. Kanazawa, LCEC Symposium 1981, Indianapolis, IN, Abstract No. 14.*

2. *S. G. Weber, Electroanalytical Symposium 1985, Chicago, IL, Abstract No. 27.*

3. *J. O. Howell, W. G. Kuhr, R. E. Ensman, and R. M. Wightman, J. Electroanal. Chem. 209(1986) 77.*

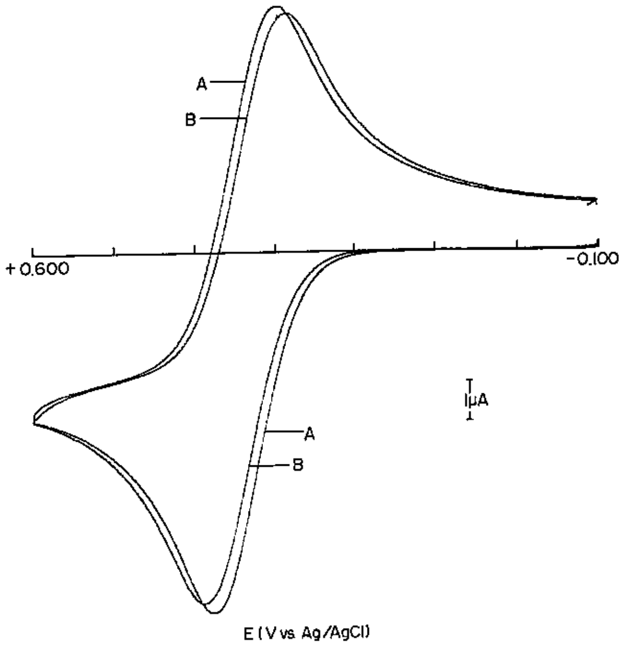

Figure 2. Cyclic voltammogram of 0.92 mM ferrocene in acetonitrile with 0.1 M TBAP, obtained at a scan rate of 100 mV s^{-1}. Filter time constant of: A) 0.001 s; B) 0.1 s.

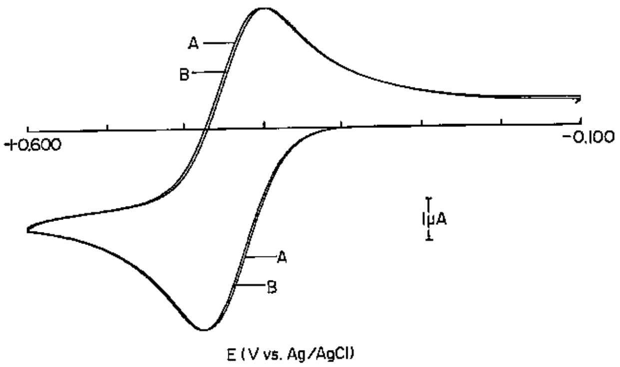

Figure 3. Cyclic voltammogram of 0.92 mM ferrocene in acetonitrile with 0.1 M TBAP, obtained at a scan rate of 30 mV s^{-1}. Filter time constant of: A) 0.001 s; B) 0.1 s.