CAPSULES
notes and applications from Bioanalytical Systems, Inc.
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Determination of Electrode Area with Chronocoulometry

Key Terms
Chronocoulometry, Diffusion coefficient determination, Anson Plot, BAS 100 Series

Accurate knowledge of electrode area is necessary for many electrochemical experiments. Chroncoulometry is a technique commonly employed for the determination of electrode area. Ferricyanide is a well-characterized anion and will be used in this determination. The potential waveform for chronocoulometry is shown in Figure 1. The initial potential (where no electrolysis of ferricyanide occurs) and final potential (where complete reduction occurs) can be obtained from a cyclic votammogram (Figure 2). The chronocoulometric response (Figure 3) is the total charge passed (Q) vs. time (t) from initiation of the step.

The response is described by:

$$Q_t = \frac{2nFACD_0^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_0$$

where Q_{dl} is the capacative charge. Γ_0 is the surface excess of reactant, and the other terms have their usual meaning. The diffusion coefficient (D) of ferricyanide is 7.6×10^{-6} cm^2 s^{-1} (1). A plot of Q vs. $t^{1/2}$ (Anson plot, Figure 4) transforms the data into a linear relationship whose slope is $2nFACD_0^{1/2}/\pi^{1/2}$. Note: Be sure to convert to appropriate units. The slope is reported as $\mu c/ms^{1/2}$.

The active area of the electrode determined from the presented data is 7.78×10^{-2} cm^2. The calculated radius of 0.157 cm is more accurate than the measured geometric radius of 0.15 cm.

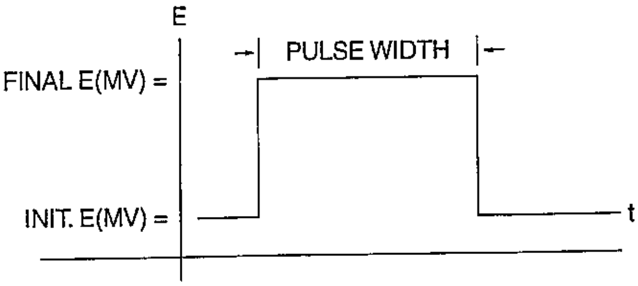


Figure 1. Potential excitation for chronocoulometry.

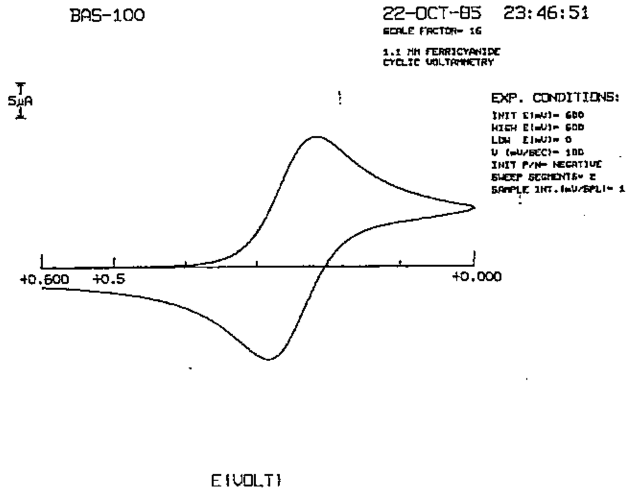
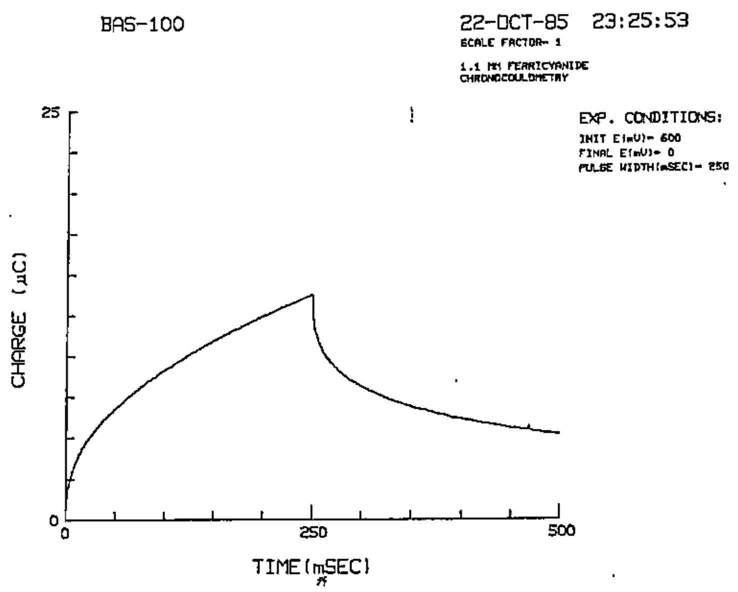


Figure 2. Cyclic voltammogram for the reduction of 1.1 mM ferricyanide in 0.1 M KCl pH 3 obtained at a glassy carbon electrode.

References

1. *R.N. Adams, "Electrochemisty at Solid Electrodes," Marcel Dekker, New York, 1969, p. 219 (and references therein).*

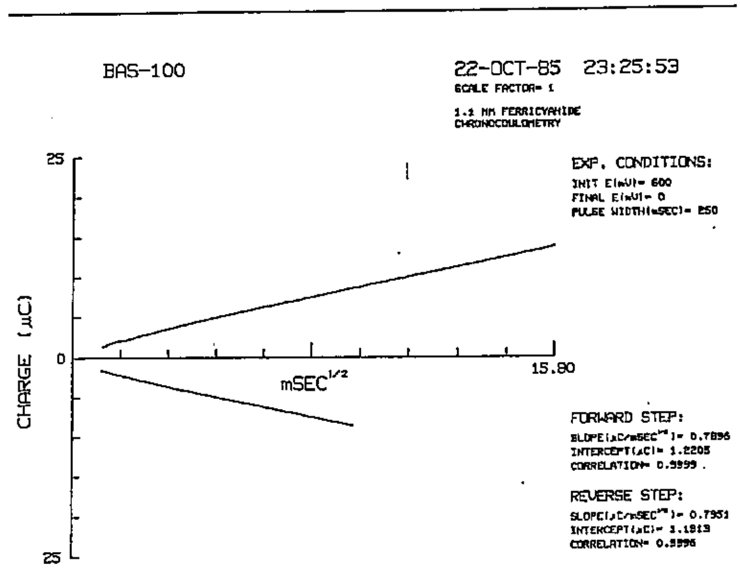


22-OCT-85 23:25:53
SCALE FACTOR= 1

1.1 MM FERRICYANIDE
CHRONOCOULOMETRY

EXP. CONDITIONS:
INIT E(mV)= 600
FINAL E(mV)= 0
PULSE WIDTH(mSEC)= 250

Figure 3. Chronocoulometric response for 1.1 mM ferricyanide.



22-OCT-85 23:25:53
SCALE FACTOR= 1

1.1 MM FERRICYANIDE
CHRONOCOULOMETRY

EXP. CONDITIONS:
INIT E(mV)= 600
FINAL E(mV)= 0
PULSE WIDTH(mSEC)= 250

FORWARD STEP:
SLOPE(µC/mSEC$^{1/2}$)= 0.7896
INTERCEPT(µC)= 1.2205
CORRELATION= 0.9999

REVERSE STEP:
SLOPE(µC/mSEC$^{1/2}$)= 0.7951
INTERCEPT(µC)= 1.1813
CORRELATION= 0.9996

Figure 4. Anson Plot of data shown in Figure 3.