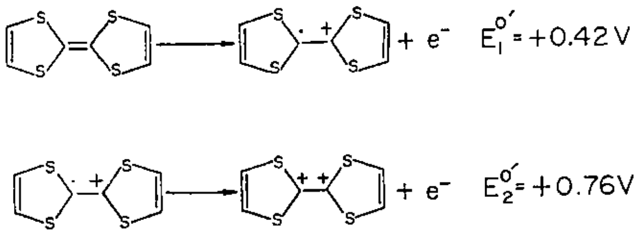
CAPSULES
notes and applications from Bioanalytical Systems, Inc.

Cyclic Voltammetry, BAS-100A

Key Terms
Cyclic Voltammetry, Tetrathiafulvalene, Non-aqueous medium, BAS-100A

Cyclic voltammetry is the electrochemistry equivalent of spectroscopy. It is a useful tool for the characterization of redox systems and has been enjoying growing popularity among chemists in many disciplines. Not only is thermodynamics information available but also the kinetics and mechanism of electrochemical systems can be obtained. The experimental data can be acquired in a wide range of scan rates (e.g., from less than 1 mV/s to many V/s).

The BAS-100A Electrochemical Analyzer is capable of running fast electrochemical experiments. For example, in conjunction with the iR compensation package, cyclic voltammetric experiments can be operated at scan rates up to 300 V/s depending on the concentration of the redox species and the size of the working electrode (please see comments at end of capsule). This feature is illustrated with the voltammetry of tetrathiafulvalene (TTF) on a Pt electrode (PTE), in CH$_3$CN with 0.1 M Et$_4$NClO$_4$ as supporting electrolyte. This system is chosen for demonstration because (1) it gives two well-formed, consecutive, one-electron oxidation waves, and (2) it does not require nitrogen purging.



Reagents
1 mM TTF in 0.1 M Et$_4$NClO$_4$/CH$_3$CN solution:
Dissolve 0.0051 g TTF (Aldrich) and 0.57 tetraethylammonium perchlorate in 25 mL CH$_3$CN (Burdick and Jackson).

Equipment
BAS-100A Electrochemical Analyzer
C-1A Cell Stand with Platinum working (PTE) electrode and RE-1 reference electrode (Ag/AgCl).

Procedures
1. Assemble cell by placing the working electrode, platinum wire auxiliary electrode, and RE-1 in the 1 mM TTF solution.

2. Respond to the CRT prompts as indicated below. This will generate the voltammograms shown below.

Prompt	Response
POWER ON	Press Any key
DATE=##-XXX-##	®
TIME=##:##:##	®
OPERATING MODE=	CV®
INIT E(MV)=#	0®
HIGH E(MV)=#	900®
LOW E(MV)=#	®
V (MV/SEC)=#	200®
SWEEP SEGMENTS=#	®
SENSITIVITY (A/V) = 1.0 E-#	4®
*	IR®
TEST E(MV)=#	0®
COMPENSATION EXTENT (%)=100	®
OVERSHOOT (%)=10	®
RESISTANCE (OHM)=###	
CELL RC CONSTANT (uS)=##	
R TO BE COMPENSATED (%)=###	
UNCOMPENSATED R(OHM)=#	
*	R®
RUN IN PROGRESS	
IR COMPENSATED	

((Data displayed on screen) ® = Return

When the * prompt reappears label and generate a plotted output via the LABEL and PB star commands. When the plotting is finished the star prompt returns.

3. Repeat the cyclic voltammetric experiments at other scan rates by issuing the CG command to change the scan rate (MV/SEC) to 10,000, 20,000 and 30,000. The units of scan rate can be changed via the command SCAN to V/s or µV/s.

Repeat the iR compensation after each parameter change.

Comments

1. The frequency response of the BAS 100A will not significantly distort the voltammograms at scan rates up to 300V/s (sensitivity at 10^{-6} to 10^{-1}). However, the potential resolution at the faster scan rates is limited by the 20 kHz sampling rate of the analog-to-digital converter (see Table 1).

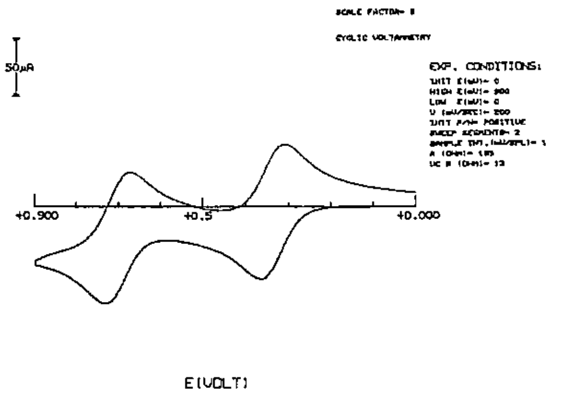
Table 1.

V	Sample interval
≤15753 mV/s	1 mV
51200 mV/s	5 mV
50 V/s	3 mV
102 V/s	8 mV
204 V/s	14 mV
297 V/s	19 mV

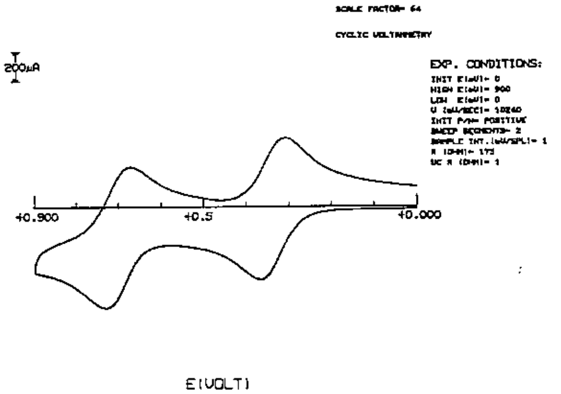
2. Figure 4 shows the cyclic voltammograms of TTF oxidation at V = 34,000 mV/sec with and without the implementation of iR compensation. As you can see, the voltammogram without iR compensation is completely distorted and gives no significant information at all. In contrast, the incorporation of iR compensation displays a "text-book" example of two consecutive one-electron oxidation waves. Such a sharp difference can be further substantiated by issuing the command "XX", to display peak potentials and peak currents of both segments on the CRT.

3. When scan rates above 50 V/s are employed, the data should not be smoothed by the moving average method. The point density is low and significant distortion would occur. Either disable the smoothing routine via the NA star command, or select Fourier Transform smooth via the SMTH star command.

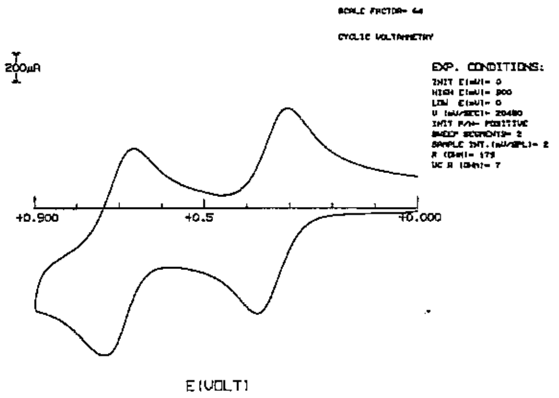
1)



2)



3)



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