

CAPSULES

preliminary notes and applications from Bioanalytical Systems, Inc.

Adsorption of Reduced Glutathione on a Mercury Surface

Key Terms

Adsorption, Glutathione, Mercury Film Electrode, BAS 100, Cyclic Voltammetry, Chronocoulometry

This case study describes the reduction of a 0.2 mM glutathione (oxidized form) solution on an Au/Hg film electrode in 0.15 M monochloroacetate buffer (pH = 3.0). It serves not only to demonstrate the logical sequences of running several experiments, but also to illustrate the ease with which a repertoire of electrochemical techniques can be used to rapidly characterize a redox system. This feature will be highlighted by using cyclic voltammetry and chronocoulometry for the investigation of glutathione adsorption on the Au/Hg surface.

Discussion

The reduction of glutathione on the Au/Hg electrode is a highly irreversible two electron-transfer process with an $E_{pc} = -1.010$ V vs. Ag/AgCl as indicated by the cyclic voltammetric data in Figure 1. Two pre-waves occur at $E_{pc} = -0.150$ V and -0.340 V, respectively, which are far less negative than the potential for the diffusion controlled process. This suggests the ability of Au/Hg surfaces to stabilize the oxidized form of glutathione molecules via strong adsorption. Upon the reversal of potential scan, the reduced products are re-oxidized at $E_{pa} = -0.10$ V.

Once the preliminary cyclic voltammetric experiments are completed, double potential step chronocoulometry can be immediately employed to further characterize the adsorption phenomena of oxidized glutathione on the Au/Hg surface. Figures 2 and 3 show the chronocoulometric, and Q vs. $t^{1/2}$, (Anson plot) data for the reduction for glutathione. The potential of the Au/Hg electrode was stepped from INIT E (MV) = 0 to FINAL E (MV) = -0.450 and -0.240 V respectively. In both cases, the rapid leveling of the Q vs. $t^{1/2}$ curve at short times (10 msec), follow-

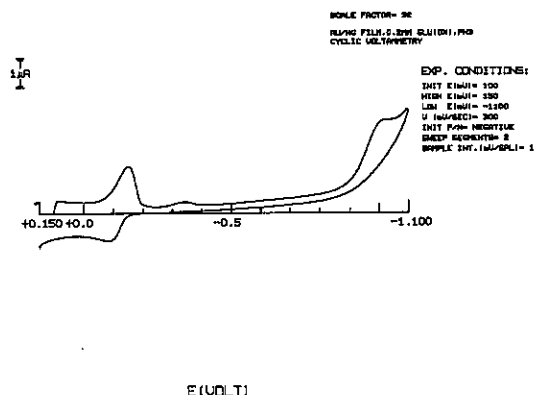


Figure 1. Cyclic Voltammogram of glutathione at an Au/Hg film electrode.

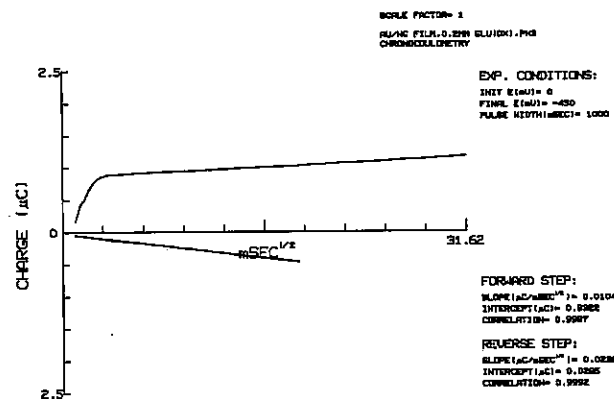


Figure 2. Chronocoulometric response of glutathione, initial E = 0.000 V, final E = -0.450 V.

ing the forward step, indicates the strong adsorption of oxidized glutathione to the Au/Hg surface.

A series of chronocoulometric experiments was quickly conducted with step potential, FINAL E (MV)

Table 1

Double potential step chronocoulometric data for the reduction of 0.2 mM glutathione on the Au/Hg film electrode. INIT E (MV) = 0 volt. PULSE WIDTH = 1000 MSEC.

FINAL E(MV)	QF	QR	Qnet
-0.10	0.0951	0.0746	0.0205
-0.12	0.1405	0.0673	0.0732
-0.14	0.1888	0.0607	0.1280
-0.15	0.1921	0.0598	0.132
-0.17	0.2057	0.0625	0.143
-0.20	0.2560	0.0789	0.177
-0.22	0.2654	0.0944	0.171
-0.23	0.2674	0.1045	0.164
-0.24	0.2682	0.1188	0.149
-0.25	0.2914	0.1219	0.170
-0.26	0.3007	0.1359	0.164
-0.27	0.3294	0.1449	0.185
-0.28	0.3356	0.1536	0.182
-0.29	0.3970	0.1523	0.245
-0.30	0.4250	0.1561	0.267
-0.32	0.4084	0.1470	0.261
-0.33	0.4561	0.1245	0.332
-0.35	0.5901	0.0990	0.491
-0.37	0.8234	0.0903	0.733
-0.39	0.7828	0.1071	0.676
-0.41	0.8439	0.1005	0.744
-0.45	0.8322	0.0285	0.804
-0.47	0.8370	0.0270	0.810
-0.49	0.8265	0.0265	0.800
-0.50	0.8590	0.0290	0.830

varied from -0.100 to -0.500 V in 10 mV increments. For each experiment the charge for the adsorbed species, Q_{net} , was calculated by subtracting Q_r , the intercept of the Anson plot of the reverse step, from Q_f , the intercept for the forward step. These chronocoulometric data were compiled in Table 1 and plotted vs. FINAL E (MV) in Figure 4. The surface coverage of the adsorbed species for the first adsorption wave was calculated to be $\Gamma_1 = 2.2 \times 10^{-10}$ mol/cm² from the Q_{net} corresponding to the plateau at FINAL E (MV) = -0.2 V. In similar manner, the total coverage for both adsorption waves can be calculated from the Q_{net} at second plateau as $\Gamma_T = 5.3 \times 10^{-10}$ mol/cm². The coverage for the second adsorption wave ($\Gamma_2 = 3.1 \times 10^{-10}$ mol/cm²) is calculated by subtracting Γ_1 from Γ_T .

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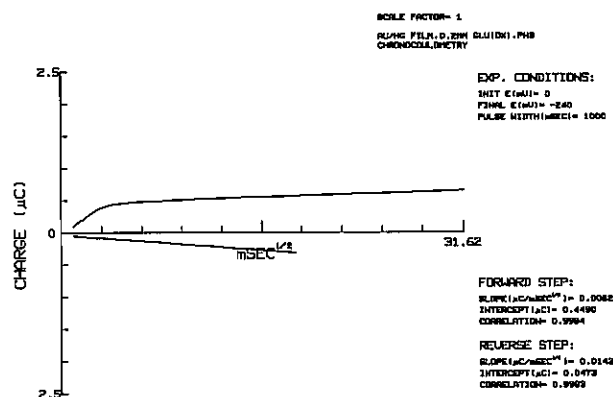


Figure 3. Chronocoulometric response of glutathione, initial E = 0.000 V, final E = -0.240 V.

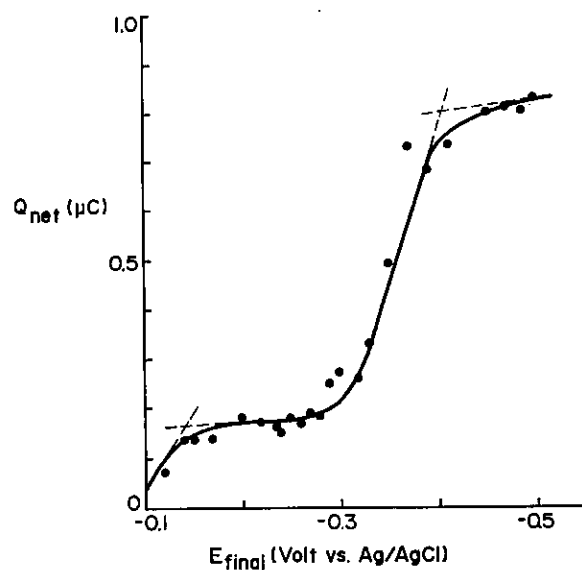


Figure 4. Plot of change of adsorbed glutathione vs. final potential.

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