



On Power-supply as Voltammograph

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Abstract

Electrolytic oxidation of ferrocene in acetonitrile with or without supporting electrolyte in a quiet solution yielded nearly steady-state current-potential response at a platinum semimicro-disk anode. A short platinum wire, immersed in the same solution served as a quasi reference electrode. The investigation suggests that a two electrode configuration utilizing a power-supply unit furnishes results similar to those obtained with three-electrode configuration and a voltammeter.

Keywords: Ferrocene, acetonitrile, platinum-semi-microdisk anode, voltammograph

Introduction

The electrochemical behavior of ferrocene oxidation has been analyzed on a platinum microelectrode (0.28 cm^2) in acetonitrile by means of different transient techniques [1]. It is possible to obtain the same value for the electron transfer rate constant ($k_s = 4.6 \times 10^{-3} \text{ cm/s}$) of the redox couple ferrocene/ferricinium. The existence of a process preceding the electron transfer step was evidenced from chronopotentiometric and chronoamperometric experiments. This process can be substitution of ions in the internal Helmholtz plane by ferrocene molecules and this fact could explain the low values reported for k_s of ferrocene on microelectrodes [1].

The oxidation process of ferrocene has been studied by cyclic voltammetry, rotating disk voltammetry and chronoamperometry in chloroform, at platinum, gold and glassy carbon electrodes using tetra-butylammonium perchlorate as supporting electrolyte. It has been suggested that ferrocene can be used as voltammetric standard in chloroform [2].

Ferrocene was proposed as an effective internal standard for electro-chemical

measurements in aprotic solvents [3]. The oxidation of ferrocene is a model system of an essentially reversible process in acetonitrile or dichloromethane, which can be recommended as a standard for use in electro-analytical voltammetry to assess instrumental and electrode performance at microelectrodes over a wide variety of experimental conditions [4].

Tetramethylorthosilicate matrix embedded with propylene carbonate and sulpholane electrolyte was used for the electrooxidation of ferrocene [5]. Oxidation/reduction of functionally protected ferrocene was used for the mediation of differential conductance switching of planar tunnel junctions [6].

Ferrocene has been widely used to characterize electrochemical set-ups under a wide variety of experimental conditions. This work is related to the use of ferrocene for delineating parameters relevant to recording nearly steady-state current-potential curves obtained with the help of a power-supply unit serving as a voltammeter.

Experimental

The experiments were done using a semimicro-platinum disk electrode as the working anode. This electrode was prepared by sealing a platinum wire with nominal diameter of 1mm into a soft glass tube. Subsequently the end of glass tube was ground flat on silicon carbide paper. Contact to platinum semimicrodisk anode was made via a copper wire touching platinum inside glass tube through mercury. A similar electrode consisting of a short length, ca. 1cm, of platinum extending out from the sealed end of glass tubing was used as the quasi reference electrode. Both electrodes were immersed into the solution of ferrocene in acetonitrile containing sodium perchlorate. Acetonitrile was not dried but was free of water. Similarly no attempt was made to purge the solution free of oxygen. All experiments were done in the quiet solution.

Current potential curves were recorded by point method, i.e. the potential of the semimicro platinum disk anode was enhanced manually in the anodic direction by 0.040 V and the current recorded after an interval of one minute. All current values were multiplied by ten for convenience in making potential vs. log (current) plots. Between successive runs, the platinum electrode was cleaned by dipping into 50% nitric acid followed by copious rinsing with distilled water. The electrode surface was dried by bringing it against a soft tissue paper. Sodium perchlorate was dried before use. A thin layer of hydrous sodium perchlorate was taken in the petri dish and it was placed in an oven at 80°C for overnight, followed by cooling at room temperature. This anhydrous sodium perchloarte was dissolved in the solvent acetonitrile.

Ferricinium solution for experiments in a divided cell was prepared as follows: (a) a saturated solution of ferrocene in acetonitrile containing 1 M sodium perchlorate was electrolyzed at platinum microdisk electrode for ten minutes. This corresponded roughly to generation of less than half micromole of ferricinium. (b) A small tube terminating in a fine porosity frit was filled with this ferricinium solution and a silver wire dipped into it to make up the reference cell compartment for the divided

cell. (c) Subsequently curve 1 was recorded by using the silver wire/ferricinium solution as a reference electrode.

Results and Discussion

The integrity of the glass/platinum seal in the working electrode i.e., platinum microdisk electrode was checked by running cyclic voltammogram of a 3.3 mM ferrocene solution in the three electrode configuration at several sweep rates. As shown in Figure 1, peak current for oxidation of ferrocene varied linearly with the square-root of sweep rate.

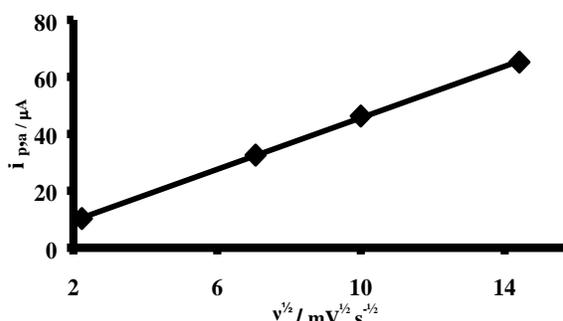


Figure 1. Oxidation peak current for 3.3 mM ferrocene in acetonitrile vs. square root of sweep rate at platinum microdisk electrode.

Figure 2 shows two current potential curves for a saturated ferrocene solution in acetonitrile in a divided, curve 1, and undivided, curve 2, cell. Curve 1 in Figure 2 in which silver-ferricinium ion reference electrode is used, shows that current begins to rise at less than 0.2 V followed by a plateau at 0.4 V extending to 1.6 V, but with a steadily decreasing current. In other words, the plateau has a negative slope, terminating in a dip, signaling the exhaustion of ferricinium ion and beginning of the decomposition of acetonitrile. Curve 2 in Figure 2 indicates that base line current starts at 0.2 V and then it rises with an increase in the potential in an undivided cell.

Figure 3 shows the current potential curves for the oxidation of ferrocene at a number of its concentrations. The lowest curve labeled 1 shows that no current is observed upto 1.4 V so a low concentration of ferrocene shows a plateau for the formation of ferricinium at potentials that are shifted to considerably higher positive values.

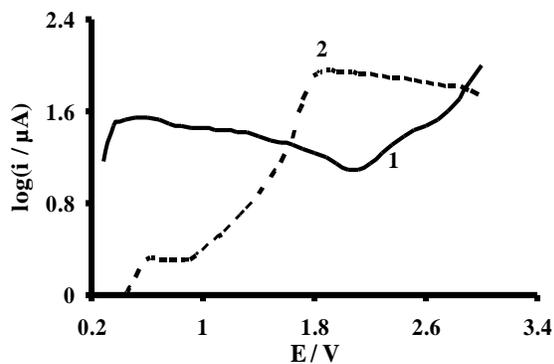


Figure 2. Oxidation currents for saturated ferrocene solution in acetonitrile versus (1) a silver/ ferricinium-ion reference electrode in a separate compartment, and (2) a platinum wire quasi-reference electrode in direct contact with ferrocene solution.

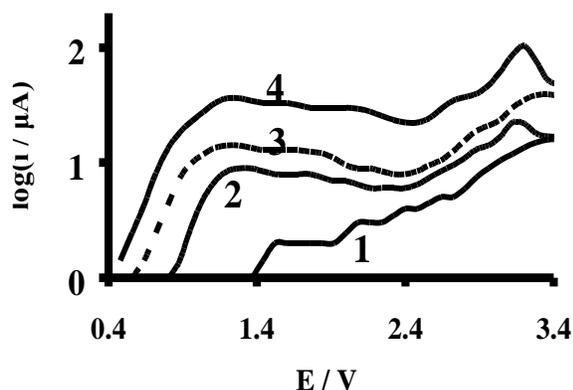


Figure 3. Anodic voltammograms for ferrocene at platinum semimicrodisk electrode in moist acetonitrile containing 0.1 M sodium perchlorate. Potential measured vs. platinum wire quasi-reference electrode in the same solution. Concentrations of ferrocene are (1) 0.1 mM (2) 0.5 mM, (3) 1 mM and (4) 1.5 mM.

Curve 2 in Figure 3 indicates that base line current starts at 0.6 V and then rises with an increase in potential followed by plateau at 1.2 V extending to 1.8 V. Curves 3 and 4 show behavior similar to that of curve 2, but with higher currents due to increased amounts of ferrocene dissolved in the background electrolyte. These curves also show well-formed plateaus.

Figure 4 shows that oxidation current for ferrocene increases linearly with concentration. This curve has a slope of unity. These currents were measured at 1.60 V from the four curves in Figure 3. A slope of one is consistent with an apparent reaction order of one for the formation of ferricinium from ferrocene.

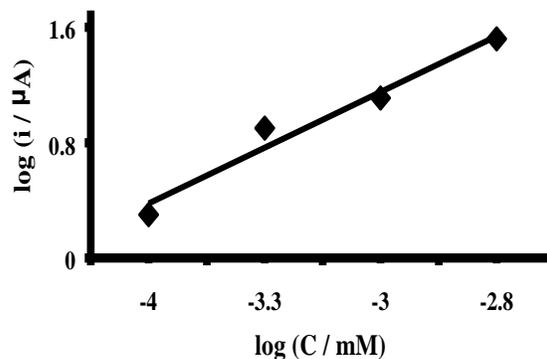


Figure 4: Variation of current with concentration of ferrocene. All currents were noted at 1.60 V from the four curves shown in figure 3.

Conclusion

Our results demonstrate that a two-electrode-configuration with one electrode having semimicro-dimension can be used for manual recording of steady-state polarization curves using an ordinary power supply unit as a voltammeter.

These findings are based on current potential curves obtained at a platinum semimicro disc electrode employing ferrocene as the electroactive substance in acetonitrile containing sodium perchlorate.

The work indicates that a two-electrode configuration gives results similar to those obtained with a three electrode configuration. In other words, a power supply source can be used as a voltammograph with a working electrode, and a quasi-reference electrode in the same solution.

References

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