



1,1'-Bis(11-mercaptoundecyl)ferrocene for potentiometric sensing of H⁺ ion in sulfuric acid media simulating lead acid battery electrolyte

TOUMA B. ISSA¹, P. SINGH¹, M. BAKER² and B.S. VERMA²

¹Division of Science and Engineering, Department of Chemistry, Murdoch University, WA 6150, Australia

²Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia

Received 24 April 2000; accepted in revised form 8 February 2001

Key words: battery state of charge, ferrocene derivative, hydrogen ion sensor, monolayer electrode, surface modified electrodes

Abstract

The measurement of state of charge of a lead–acid battery by remotely monitoring H⁺ ion concentration of the battery electrolyte potentiometrically is much more attractive than the labour intensive method of measuring specific gravity of the electrolyte. Unfortunately, the traditional H⁺ potentiometric sensors such as the glass electrode cannot be used in the concentrated sulfuric acid battery electrolyte. This paper describes our work on the possibility of using 1,1'-bis(11-mercaptoundecyl)ferrocene Fc(C₁₁SH)₂ for measuring changes in the hydrogen ion concentration with a view to developing a miniaturized battery state of charge determining device. A cyclic voltammetric study of the electrochemical response and chemical stability of the alkanethiol ferrocene derivative redox couple is discussed. It is found that the oxidation peak potential of the investigated ferrocene is independent of pH in the range 2–10. However, in concentrated sulfuric acid media 1–5 M, which is more relevant to the targeted application, the oxidation peak shifts linearly to less positive potentials as a function of the acid concentration. The promise of this observation for determining state of charge of lead–acid batteries is explored.

1. Introduction

Ferrocene (Fc) and its derivatives are important reference compounds for electrochemical studies [1] because they undergo reversible, one electron transfer reactions [2]. This behaviour forms the basis of the ferrocene/ferricenium couple being used as a reference electrode in nonaqueous systems [1, 3]. However, electrochemical potential-sensing electrodes incorporating ferrocenes in aqueous media have, to date, suffered from a short working life due to susceptibility of the ferricenium ion (Fc⁺) to hydrolysis and other decomposition reactions. The decomposition of ferricenium ions in aqueous media has been studied extensively [4–8]. Although the results of these studies are obscure and often contradictory they generally agree that decomposition of the ferricenium ion occurs via displacement of the cyclopentadienyl ligands by nucleophilic groups from the reaction medium [6]. Nevertheless, we have investigated those derivatives of alkanethiol ferrocenes which are expected to be stable in sulfuric acid media. These ferrocenes are known to be strongly chemisorbed on gold [9, 10] to form surface modified electrodes and, hence, investigation of their electrochemistry is relatively straightforward.

2. Experimental details

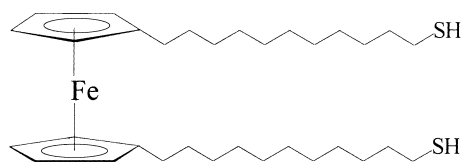
2.1. Materials

All solutions were prepared from analytical reagent grade chemicals and high purity water obtained from a Millipore Milli-Q system. Potassium sulfate and *n*-hexane were supplied by BDH Chemicals. Sulfuric acid and sodium hydroxide were supplied by Ajax Chemicals. Ferrocene was obtained from Aldrich. The solvents used were of commercial grade and were used as received.

A polycrystalline gold electrode (99.99% fine gold; Australian Gold Refineries, Perth) was used as a substrate for all solid electrodes.

1,1'-Bis(11-mercaptoundecyl)ferrocene, Fc(C₁₁SH)₂, was synthesized as follows. Ferrocene was diacylated by treatment with 1-bromoundecanoyl chloride in the presence of AlCl₃ [11]. The resulting 1,1'-bis(11-bromoundecanoyl)ferrocene was reduced to 1,1'-bis(11-bromoundecyl)ferrocene with zinc amalgam [11]. Treatment of bis(11-bromoundecyl)ferrocene with thioacetic acid and sodium methoxide in methanol followed by hydrolysis of the intermediate thioester with methanolic HCl [12] gave Fc(C₁₁SH)₂. After purification by

chromatography (BDH silica gel, 40–63 μm ; 5% ethyl acetate in hexane as eluant), $\text{Fc}(\text{C}_{11}\text{SH})_2$ was obtained as an orange solid. ^1H NMR spectrum (Bruker WP instrument, 80 MHz, CDCl_3): δ 1.2–1.8, m, 38H, $\text{FcCH}_2(\text{CH}_2)_9\text{CH}_2\text{SH}$; 2.2–2.6, 8H, m, $\text{FcCH}_2(\text{CH}_2)_9\text{CH}_2\text{SH}$; 3.9–4.1, 8H, m, Fc-H .



1,1'-bis(11-mercaptoundecyl)ferrocene $\text{Fc}(\text{C}_{11}\text{SH})_2$

2.2. Electrochemistry

For the electrochemical study, the electrodes (surface modified electrodes, SME) bearing a self-assembled monolayer (i.e., chemisorbed films) of $\text{Fc}(\text{C}_{11}\text{SH})_2$ were prepared by dipping gold electrodes in dilute solutions of the ferrocene alkanethiol derivative in hexane [13]. Surface modified electrodes consisting of gold electrodes covered with 'physisorbed' ferrocene were prepared by the drop evaporation method [2]. Prior to dipping, the gold surface was cleaned by polishing with silicon carbide waterproof papers grades 800, 1200, followed by dipping into aqua regia for 1 min. The cleaned electrode was then potentiostated for 5 min at -0.9 V vs SCE in 1.0 M H_2SO_4 where hydrogen gas was evolved vigorously at the electrode surface. The detailed cleaning procedure is described elsewhere [14]. All investigations were carried out under nitrogen atmosphere. The potentials were measured against a saturated calomel electrode (SCE) and are quoted as such.

3. Results and discussion

Figure 1 shows a typical cyclic voltammogram of $\text{Fc}(\text{C}_{11}\text{SH})_2$ chemisorbed on a gold electrode. Symmet-

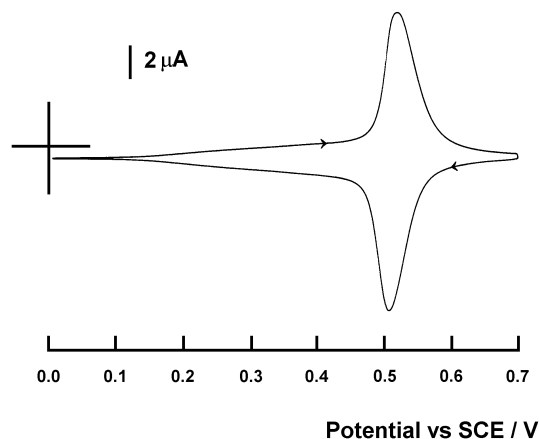


Fig. 1. Cyclic voltammogram of a self-assembled monolayer of $\text{Fc}(\text{C}_{11}\text{SH})_2$ in 1 M H_2SO_4 at a gold electrode. (Sweep rate 100 mV s^{-1}).

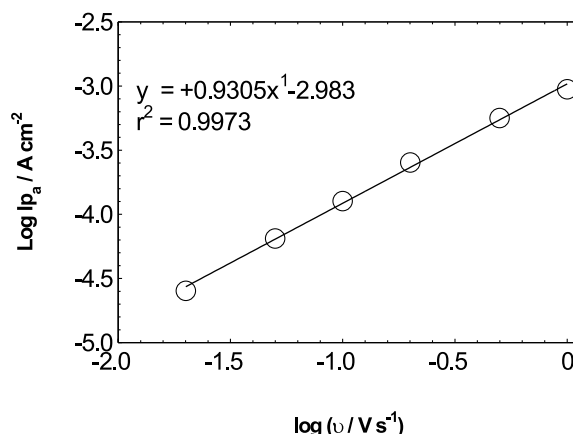


Fig. 2. Log anodic peak current (I_{p_a}) against log scan rate (v) for cyclic voltammogram in 1 M of sulfuric acid for $\text{Fc}(\text{C}_{11}\text{SH})_2$.

rical oxidation–reduction peaks, corresponding to the Fc/Fc^+ one electron transfer are obtained. The plot of log anodic peak current (I_{p_a}) against log scan rate (v) is a straight line with a slope of 0.9305 as is shown in Figure 2. This suggests that the electrode reactions involve surface adsorbed species [15]. The difference in the corresponding anodic and cathodic peak potentials is close to 9 mV. All these observations are consistent with an electron transfer involving surface adsorbed species.

The anodic peak potential (E_{p_a}) of the ferrocene derivative is independent of the solution pH in the range 2 – 10 (Figure 3). This is to be expected because the oxidation process does not involve H^+ ions. However, it is interesting to note that, in the electrolytes containing higher concentrations of sulfuric acid (1 – 5 M), which is the range typically involved in charged/discharged lead acid battery electrolyte, the E_{p_a} varies linearly with acid concentration (Figure 4). This suggests that H^+ ions are somehow involved in the electron transfer mechanism. These observations are similar to those we have reported previously for 11-ferrocenyl-1-undecanethiol FcC_{11}SH [14]. Although the mechanism of this behaviour is still unclear, the observation has important implications in

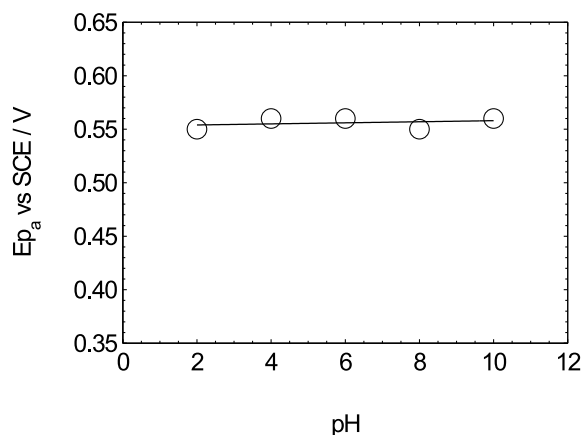


Fig. 3. E_{p_a} against pH for $\text{Fc}(\text{C}_{11}\text{SH})_2$ in 0.1 M K_2SO_4 solution.

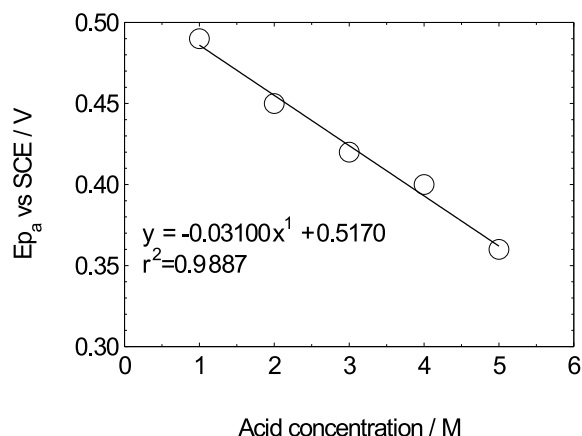


Fig. 4. Anodic peak potential against concentration of sulfuric acid for $\text{Fc}(\text{C}_{11}\text{SH})_2$.

that it could be used to measure the change in H^+ concentration potentiometrically in solutions such as those in lead–acid batteries.

To confirm whether the change in H^+ ion in concentrated sulfuric acid solutions can be monitored by the oxidized/reduced couple of $\text{Fc}(\text{C}_{11}\text{SH})_2$, the following experiments were performed.

A surface modified electrode (SME) was prepared by partially oxidizing a thin layer of $\text{Fc}(\text{C}_{11}\text{SH})_2$ chemisorbed on a gold substrate by way of anodic polarization in a 1.0 M H_2SO_4 solution. The SME was then washed with deionised water, and wiped dry before transferring to a series of sulfuric acid solutions of concentrations varying from 1 to 5 M in each solution the potential of the SME was measured against a saturated calomel electrode for up to 5–10 min before transferring to the next solution. The experiments were conducted starting with the solution of the lowest sulfuric acid concentration (1 M) and increasing the concentration to the highest level (5 M) in steps of 1 M unit, then decreasing the acid concentration in steps of 1 M unit back to 1 M. The experiments were repeated three times. Consistently reproducible potentials corresponding to each of the concentrations of the acid investigated were recorded. Typical experimental data are shown in Figure 5. The results indicate that the SME can be used to potentiometrically determine the concentration of sulfuric acid in the range 1–5 M, which simulates the acid concentration during charge/discharge cycles of lead–acid battery.

If the above SME is to find application in measuring the state of charge of lead–acid batteries, the SME must yield reproducible potential data over long periods of time. The stability of the ferrocene was tested by keeping the SME in contact with a 1.0 M H_2SO_4 solution after the series of experiments described above over varying periods of time, and periodically recording the cyclic voltammetric response of the SME in the potential region where oxidation of $\text{Fc}(\text{C}_{11}\text{SH})_2$ occurs. The peak current, I_{p_a} of the anodic peak was noted for each cyclic voltammetric experiment. It was found that the peak

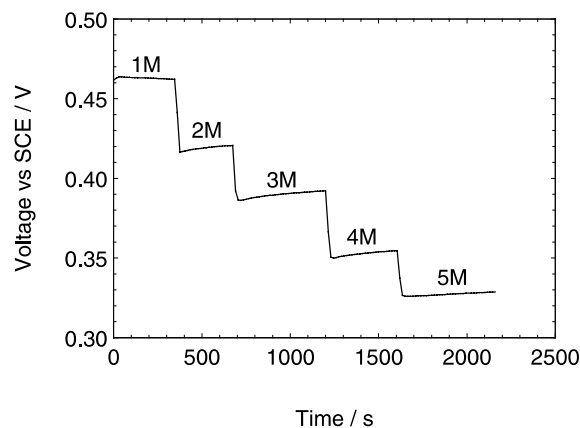


Fig. 5. Anodic peak potential for sulfuric acid concentration (1–5 M) against time for the Fc/Fc^+ couple of $\text{Fc}(\text{C}_{11}\text{SH})_2$.

current was reduced to half of its value in seven days and to zero in fifteen days. This suggests that the active material at the electrode surface is either slowly decomposed or is desorbed from the electrode surface. However, it is important to note that the rate at which the decrease in I_{p_a} occurred was certainly much slower for $\text{Fc}(\text{C}_{11}\text{SH})_2$ than for the simple ferrocene molecule. The electrode modified with simple ferrocene lost its electrochemical reactivity in 1 M H_2SO_4 within the first hour of the experiment.

The stability of $\text{Fc}(\text{C}_{11}\text{SH})_2$ chemisorbed on gold electrodes was further tested by subjecting a freshly prepared SME to repeated voltammetric cycling in the potential range 0 to 0.7 V. The I_{p_a} for each cycle was measured and the data used to calculate $(I_{p_a})_n / (I_{p_a})_1 \times 100$ where n is the cycle number. The function $(I_{p_a})_n / (I_{p_a})_1 \times 100$ defines the percentage of the electroactive material left at the electrode surface at each cycle. These data are plotted in Figure 6. As can be seen from Figure 6, for the thiol substituted ferrocene, the percentage of the residual material on the electrode surface after each voltammetric cycle decreased very slowly. However, for the simple ferrocene, the active material decreased much more rapidly. Almost all the simple ferrocene material was lost from the electrode surface at

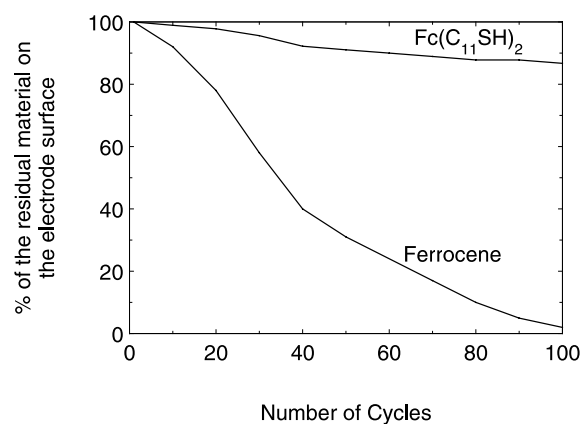


Fig. 6. Percentage residual material on the electrode surface of $\text{Fc}(\text{C}_{11}\text{SH})_2$ and ferrocene against number of cycles.

the 100th cycle where as only 13% of the thiol substituted ferrocene was lost at the same number of cycles. Thus it can be concluded that the presence of thiol groups in ferrocene allows the material to effectively stay on the gold electrode surface and continue to respond to oxidation/reduction cycling much longer than ferrocene itself. Slow degradation of the electrode response in concentrated acid media, however, still occurs. Further work to understand the mechanism through which this degradation occurs would be undertaken in the future.

4. Conclusions

A cyclic voltammetric study of the $\text{Fc}(\text{C}_{11}\text{SH})_2$ in acidic aqueous solutions has shown that the ferrocene derivative undergoes a reversible one electron redox reaction. The anodic and cathodic peak potentials are independent of pH over the range pH 2–10 in K_2SO_4 solutions. However, in concentrated sulfuric acid solutions they vary linearly with the concentration of sulfuric acid in the range 1–5 M. This behaviour of the redox couple of $\text{Fc}(\text{C}_{11}\text{SH})_2$ could be used to monitor changes in H_2SO_4 concentration in the range (1–5 M) which is typical of the change in a lead–acid battery undergoing charge/discharge cycling. However, this application is limited by the chemical solubility and/or stability of the ferrocene material.

References

1. G. Gritzner and J. Kuta, *Pure Appl. Chem.* **56** (1984) 461.
2. R.W. Murray, Chemically Modified Electrodes, in A.J. Bard (Ed.), 'Electroanalytical Chemistry' Vol. 13 (Dekker, New York, 1984), pp. 191–368 and references therein.
3. P.J. Peerce and A.J. Bard, *J. Electroanal. Chem.* **108** (1980) 121.
4. V.D. Matveev and I.G. Poroshenko, *J. Gen. Chem. USSR.* **59** (1989) 533.
5. V.D. Matveev and I.G. Poroshenko, *J. Gen. Chem. USSR.* **59** (1989) 41.
6. J. Holecek, K. Handlir, J. Klikorka and N.D. Bang, *Coll. Czech. Chem. Commun.* **44** (1979) 1379 and references therein.
7. M.M. Aly, *Inorg. Nucl. Chem. Lett.* **9** (1973) 369.
8. R. Prins, A.R. Korswagen and A.G.T.G. Kortbeek, *J. Organomet. Chem.* **39** (1972) 335.
9. R.G. Nuzzo and D.L. Allara, *J. Am. Chem. Soc.* **105** (1983) 4481.
10. A. Ulman, 'An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-assembly' (Academic Press, San Diego, 1991) and references therein.
11. Y. Okahata, G. En-na and K. Takenouchi, *J. Chem. Soc., Perkin Trans. II* (1989) 835.
12. C.D. Bain, E.B. Troughton, Y.T. Tao, J. Evall and G.M. Whitesides, *Langmuir* **4** (1988) 365.
13. J.J. Hickman, D. Ofer, C. Zou, M.S. Wrighton, P. E. Laibinis and G.M. Whitesides, *J. Am. Chem. Soc.* **113** (1991) 1128.
14. Touma B. Issa, P. Singh and M. Baker, Using 11-ferrocenyl-1-undecanethiol surface modified electrode for sensing the hydrogen ion concentration in concentrated sulfuric acid solutions, in N. Akmal and A.M. Usmani (Eds), 'Polymers in Sensors, Theory and Practice' (American Chemical Society, ACS Symposium Series no. 690, 1998), chapter 21.
15. M.E. Gomez and A.E.J. Kaifer, *J. Chem. Ed.* **69** (1992) 501.