

Short communication

# Potentiometric measurement of state-of-charge of lead-acid battery by using a bridged ferrocene surface modified electrode

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## Abstract

Alkanethiol bridged, 3-(11-mercaptoundecyl)[3](1,1') ferrocenophane and 3-(11-mercaptoundecyl)[5](1,1') ferrocenophane were synthesized and their electrochemical behaviour in aqueous sulphuric acid electrolyte investigated. It is found that these compounds, chemisorbed on a gold substrate, undergo reversible electrochemical oxidation/reduction. The anodic and cathodic peak potentials are independent of the acid concentration in the range  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-7}$  M but change linearly with the acid concentration in the range 1–5 M. While this behaviour is similar to that for other ferrocenes like [3](1,1') ferrocenophane and [5](1,1') ferrocenophane the materials are much more chemically stable in aqueous sulphuric acid media. The presence of thiol group enhances the retainability of the bridged ferrocene while maintaining its chemical stability. The possibility of applying this observation for determining state-of-charge of lead-acid battery is discussed.

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## 1. Introduction

The use of lead-acid batteries is usually a fundamental component of any power supply system utilising renewable energy sources. For a long battery life and efficient energy management, it is necessary that the state-of-charge of the battery be monitored during operation [1]. The concentration of the battery electrolyte, sulphuric acid, decreases on charge and increases on discharge, which provides means of indicating the state-of-charge of the lead-acid battery. Generally the state-of-charge estimation is achieved by examining any property of the electrolyte, which changes as a function of sulphuric acid concentration during the charge/discharge cycle. For example, variation of properties of the electrolyte such as conductivity, refractivity, heat capacity, impedance of the quartz crystal oscillatory, optical absorption, magnetic permeability, equilibrium vapour pressure and ionic activities have been considered [1–7]. However, specific gravity measurement by hydrometer is the most frequently used method at the present [1]. This is a good reliable method, however it is messy, time wasting and labour intensive. It is especially unsuitable when banks of batteries

are considered and when they are located in isolated areas. In such conditions remote monitoring is extremely practical. Determination of the state-of-charge of lead-acid batteries by using potentiometric methods becomes very attractive in these cases.

The potentiometric measurement of the change in hydrogen ion concentration  $[H^+]$  in the lead-acid battery electrolyte would provide a simple route to the state-of-charge determination. Unfortunately, the  $H^+$  ion sensors such as the glass electrode and the antimony oxide electrode cannot be used because the battery electrolyte contains a high concentration (1–5 M) of sulphuric acid.

One of the major aims of this paper is to explore the possibility of exploiting surface modified electrode (SME) chemistry in developing an inexpensive, rugged, miniaturised probe for measuring  $[H^+]$  in the battery electrolyte as a means of monitoring the battery state-of-charge. The use of SMEs in measuring hydrogen ion concentration is not new. For example, a Nernstian response to  $[H^+]$  has been reported for poly(1,2-diaminobenzene) films on platinum and glassy carbon [8,9]. Similarly, Rubinstein [10] could measure the pH of solutions by measuring the reduction peak potential values of surface-bound poly(1,2-diaminobenzene) with respect to surface-bound  $Ru(bipy)_3^{3+/2+}$  (in nafion) reference SME. However, study of SMEs directed towards measuring  $[H^+]$  in concentrated

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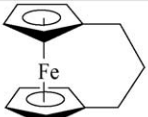
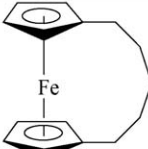
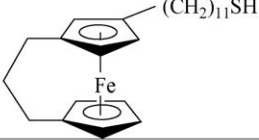
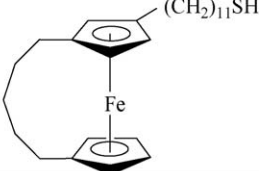
BF (I)		<b>[3](1,1')ferrocenophane</b>
BF (II)		<b>[5](1,1')ferrocenophane</b>
BF (III)		<b>3-(11-mercaptoundecyl)[3](1,1')ferrocenophane</b>
BF (IV)		<b>3-(11-mercaptoundecyl)[5](1,1')ferrocenophane</b>

Fig. 1. Structural formulas of the investigated ferrocenes.

sulphuric acid solutions similar to that in the lead-acid battery electrolyte has not been hitherto reported.

This paper examines the use of SMEs made from various ferrocene compounds for monitoring change in  $[H^+]$  in lead-acid batteries as a function of the state-of-charge of the battery.

Ferrocene is one of the most stable organometallic compounds. The one-electron oxidation of ferrocene to ferricenium ion proceeds in a straightforward manner. Consequently, the ferrocene/ferricenium ion system is routinely used by electrochemists as a model redox system [11]. Ferrocene and its derivatives have found numerous applications in electrochemistry. These include use as electroactive material for batteries [12], electron transfer agents for enzyme-based glucose sensors [13,14], and as reference materials for electrochemical pH sensors [15]. Electrochemical reference electrodes based on the ferrocene/ferricenium redox couple in non-aqueous media have been investigated extensively [11]. In aqueous media, this couple tends to undergo hydrolysis and hence its chemical stability limits its use in electrochemical devices for aqueous systems.

This paper examines the use of various bridged ferrocene derivatives, which are more stable than ferrocene [16–18]. These include ferrocenes whose cyclopentadienyl groups are linked by  $(-CH_2-)_n$  groups. In particular, this paper focuses on the bridged ferrocenes with  $n = 3$  and 5.

With a view to improving the retainability of the bridged ferrocene at the electrode surface, we have investigated the insertion of alkanethiol  $[(CH_2)_{11}SH]$  groups into the bridged ferrocene molecules. The attachment of thiol group to ferrocene provides a mechanism through which ferrocene/ferricenium couple can be attached to a gold surface [19]. The ferrocenes investigated in this work are shown in Fig. 1.

The underlying objective of the work was to investigate whether the  $BF^+/BF$  couple could be used as SME's for moni-

toring changes in  $H_2SO_4$  concentration which in turn could be used for determining state-of-charge of lead-acid batteries.

## 2. Experimental

All solutions were prepared by dissolving commercially available analytical grade chemicals in high purity water obtained from a Millipore Milli-Q system. All the chemicals were used as received. The ferrocenes were synthesized in our laboratory by using standard techniques as reported in the literature [20–23]. A polycrystalline gold electrode (99.99% fine gold; Australian Gold Refineries, Perth) was used as a substrate. BF(I) and BF(II) coated on gold SME's were prepared by the drop evaporation method [24]. BF(III) and BF(IV) coated on gold SME's were prepared by adopting a procedure similar to that reported in the literature [15]. 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 versus SCE in  $1.0 \text{ mol L}^{-1} H_2SO_4$  where hydrogen gas evolved vigorously at the electrode surface. A platinum wire was used as a counter electrode. The potentials were measured against a saturated calomel electrode (SCE) and quoted as such. All investigations were carried out under nitrogen atmosphere.

### 2.1. Results and discussion

The cyclic voltammograms (CV) for BF(I) and BF(II) are shown in Fig. 2(a and b), respectively. As can be seen, for both the ferrocenes symmetrical oxidation/reduction peaks corresponding to one electron transfer were obtained. The corresponding CV's for BF(III) and BF(IV) are shown in Fig. 3(a and b)

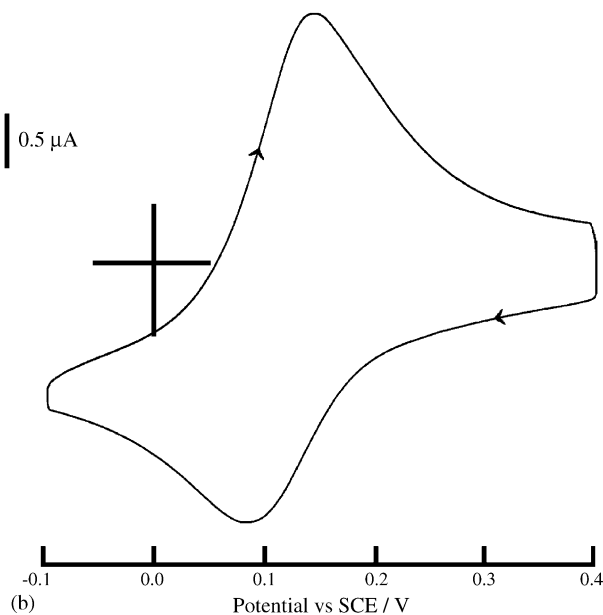
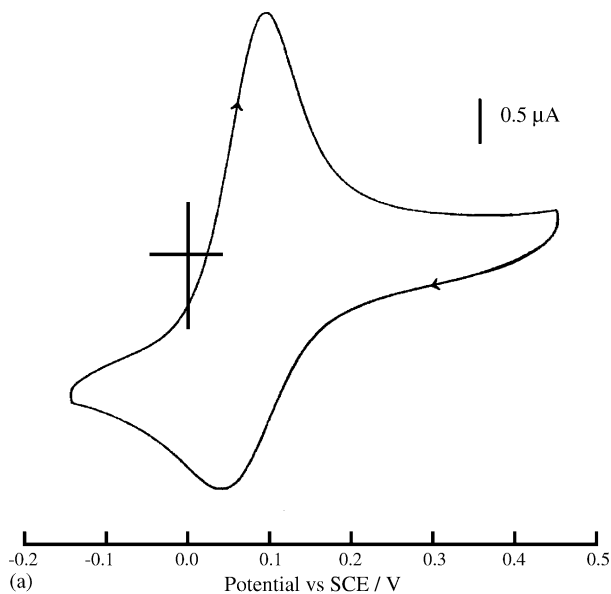


Fig. 2. (a) Cyclic voltammogram of [3](1,1')ferrocenophane, BF(I) in 1.0 M  $\text{H}_2\text{SO}_4$  on a gold electrode (sweep rate  $100 \text{ mV s}^{-1}$ ). (b) Cyclic voltammogram of [5](1,1')ferrocenophane, BF(II) in 1.0 M  $\text{H}_2\text{SO}_4$  on a gold electrode (sweep rate  $100 \text{ mV s}^{-1}$ ).

which show that the bridged ferrocenes with attached  $-\text{SH}$  group behaved similarly. The experimental anodic and the cathodic peak potential values of the investigated ferrocenes are noted in Table 1 which show that the anodic and the corresponding

Table 1  
Cyclic voltammetry parameters for bridged ferrocenes (BF) in 1.0 M  $\text{H}_2\text{SO}_4$

Ferrocene	$E_{\text{pa}}$ (mV)	$E_{\text{pc}}$ (mV)	$\Delta E_{\text{p}}$ (mV)
BF(I)	90	40	50
BF(II)	120	55	65
BF(III)	415	400	15
BF(IV)	380	365	15

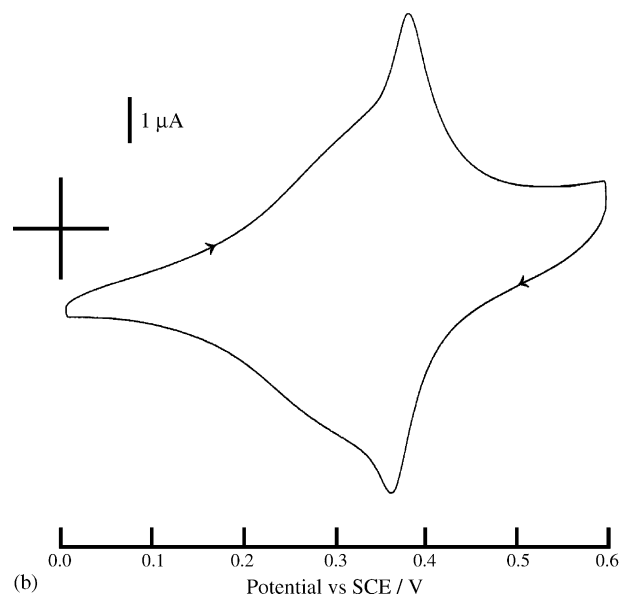
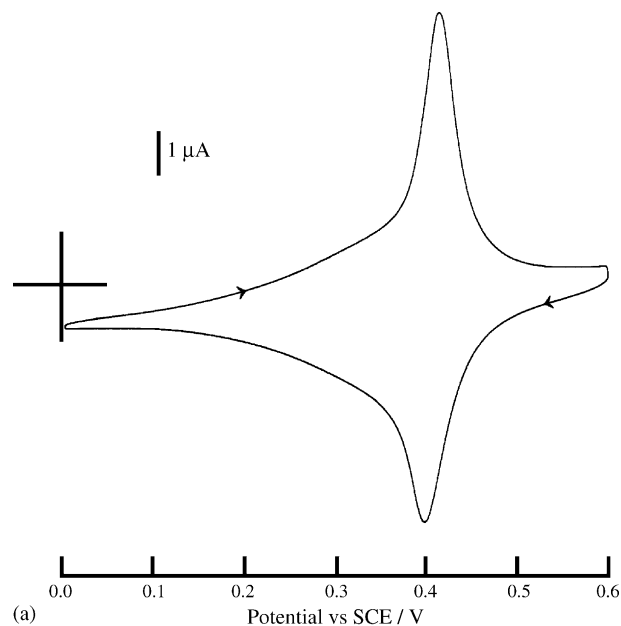


Fig. 3. (a) Cyclic voltammogram of 2-(11-mercaptoundecyl)[3](1,1')ferrocenophane, BF(III) in 1.0 M  $\text{H}_2\text{SO}_4$  on a gold electrode (sweep rate  $100 \text{ mV s}^{-1}$ ). (b) Cyclic voltammogram of 3-(11-mercaptoundecyl)[5](1,1')ferrocenophane, BF(IV) in 1.0 M  $\text{H}_2\text{SO}_4$  on a gold electrode (sweep rate  $100 \text{ mV s}^{-1}$ ).

cathodic peak potentials shifted to more positive values when  $-\text{SH}$  group was attached to the ferrocene (Table 1). The  $\Delta E_{\text{p}}$  ( $E_{\text{pa}} - E_{\text{pc}}$ ) values approached zero suggesting that the  $-\text{SH}$  group improved the adhesion of the ferrocene to the substrate so that the electrode behaved more like a truly reversible surface modified electrode.

The log anodic current ( $\log I_{\text{pa}}$ ) versus log scan rate ( $\log \nu$ ) plots for all the bridged ferrocenes were found to be linear. In particular the slope for the bridged ferrocenes with the  $-\text{SH}$  group was found to be close to the theoretical value of 1.0, indicative of a reversible redox process involving a species immobilised at the surface of an electrode [25,26] (Fig. 4).

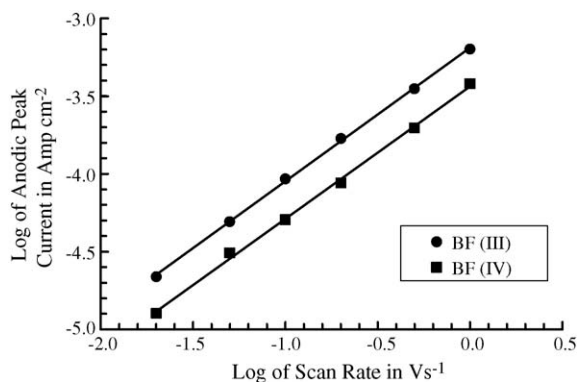
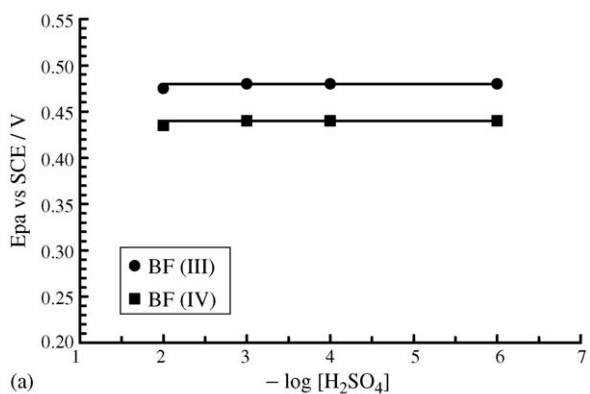


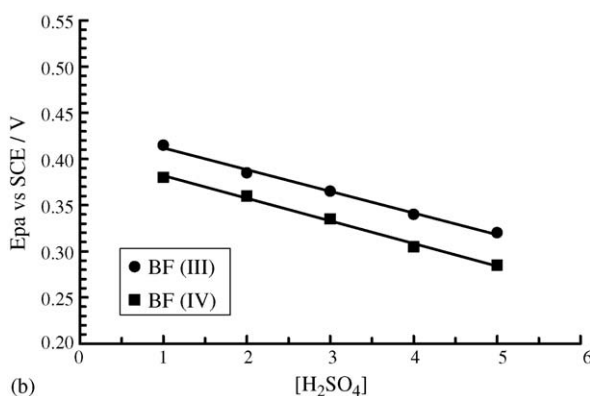
Fig. 4. Log anodic peak current ( $\log I_{pa}$ ) vs. log scan rate ( $\log \nu$ ) for the cyclic voltammogram in  $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at a gold for BF(III) and BF(IV).

The  $E_{pa}$  values of all the investigated ferrocenes were found to be independent of the  $\text{H}_2\text{SO}_4$  concentration in the range  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-7} \text{ M}$ . Surprisingly the peak potential values shifted linearly to less positive potentials as the acid concentration increased from 1 to 5 M (Fig. 5(a and b)). The slopes of the graph  $E_{pa}$  versus  $[\text{H}_2\text{SO}_4]$  for each of the ferrocenes was 24 mV per unit molar concentration of the acid. The data for BF(III) and BF(IV) are shown in Fig. 5(a and b).

As noted earlier, a major objective of this study was to establish whether the bridged ferrocene molecules coated on



(a)



(b)

Fig. 5. (a) The anodic peak potential vs. concentration ( $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-7} \text{ M}$ ) of sulphuric acid for BF(III) and BF(IV). (b) The anodic peak potential vs. concentration (1–5 M) of sulphuric acid for BF(III) and BF(IV).

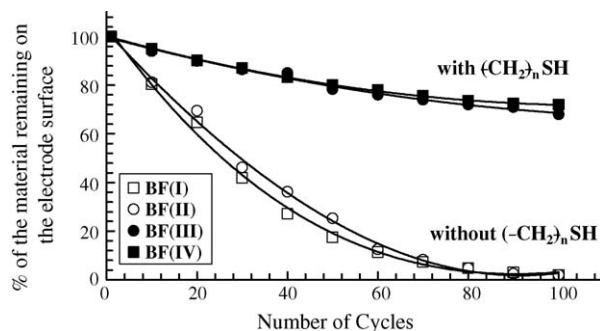


Fig. 6. Percent residual the bridged ferrocenes on the electrode surface vs. cycle number in  $1.0 \text{ M H}_2\text{SO}_4$ .

a gold substrate were stable to be used as potentiometric sensors in concentrated  $\text{H}_2\text{SO}_4$  media. This was, investigated by subjecting each of the ferrocenes coated on gold, to repeated voltammetric cycling in the potential range  $-0.2$  to  $0.6 \text{ V}$  in  $1.0 \text{ M H}_2\text{SO}_4$ . The  $I_{pa}$  for each cycle was measured and the  $(I_{pa})_n / (I_{pa})_1 \times 100$ , where  $n$  is the cycle number, calculated. The function  $(I_{pa})_n / (I_{pa})_1 \times 100$  defines the percentage of the electroactive material left at the electrode surface at each cycle. These data are plotted in Fig. 6. As can be seen only 2% of BF(I) and BF(II) were left on the electrode surface at the 100th cycle. This suggest that neither BF(I) nor BF(II) molecule was chemically stable or retained at the electrode surface to be used as a SME for the desired application. On the other hand the thiol derivatives (i.e. BF(III) and BF(IV)) seem to be stable and/or retained on the electrode surface better than BF(I) and BF(II). For example the data in Fig. 6 shows that 68% of the BF(III) and 72% of BF(IV) were available at the electrode surface at the 100th cycle. Clearly the attached  $-\text{SH}$  groups increases the retainability of the active ferrocene molecules on the surface of gold. Thus, the BF(III) and BF(IV) both have the potential for being used as stable electroactive couples in concentrated  $\text{H}_2\text{SO}_4$  media and being used for monitoring state-of-charge of lead-acid batteries potentiometrically. This characteristic was investigated by partially electro oxidising BF(III) and BF(IV) on the gold electrode surface and measuring the potential of the corresponding  $\text{BF}^+/\text{BF}$  couple against SCE in a series of beakers containing solutions of different  $\text{H}_2\text{SO}_4$  concentrations in the range 1–5 M. The data is given in Table 2. Clearly the measured potential directly relates to the acid concentration. The values were found to be reproducible. Thus the  $\text{BF}^+/\text{BF}$  couple could be used to sense the acid concentration in the range 1–5 M.

Table 2

The potential of  $\text{BF}^+/\text{BF}$  couple vs. SCE in  $\text{H}_2\text{SO}_4$

Acid concentration (M)	$\text{BF}^+/\text{BF}$ potential vs. SCE (mV)	
	BF(III)	BF(IV)
1	394	358
2	363	337
3	345	311
4	317	280
5	294	259

### 3. Conclusion

The cyclic voltammetric investigation of bridged ferrocenes BF(I), BF(II), BF(III) and BF(IV) coated on a gold substrate shows that these molecules behave as reversible surface immobilised redox couples in H<sub>2</sub>SO<sub>4</sub> acid media. For each of these molecules the  $E_{pa}$  values were independent of the acid concentration in the range  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-7}$  mol L<sup>-1</sup>. However, the potentials shifted linearly to less positive values as the acid concentration increased in the range 1–5 M. The BF(I) and BF(II) do not have the required chemical stability and or retainability on gold substrate for being used as SMEs in concentrated H<sub>2</sub>SO<sub>4</sub> media. Their thiol derivatives, BF(III) and BF(IV) are more acceptable. For these ferrocenes molecules the potential of BF<sup>+</sup>/BF couple is directly related to H<sub>2</sub>SO<sub>4</sub> concentration in the range 1–5 M. The values are reproducible. The BF(III)<sup>+</sup>/BF(III) and BF(IV)<sup>+</sup>/BF(IV) redox couples have the potential of being used as sensors for monitoring change in H<sub>2</sub>SO<sub>4</sub> concentration in lead-acid battery electrolyte during charge/discharge cycles.

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