Short communication

Electrochemistry of poly(vinylferrocene) modified electrodes in aqueous acidic media

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Abstract

A cyclic voltammetric study of the electrochemistry and chemical stability of the poly(vinylferrocene) (PVFc) redox couple, coated on a gold substrate, in aqueous solutions of H_2SO_4, $HClO_4$ and HCl was carried out. It was found that the anodic peak potential (E_{pa}) did not depend on the acid concentration in the range (1.0×10^{-2} to 1.0×10^{-7} mol L^{-1}). However, the E_{pa} values shifted linearly to less positive potentials when investigated in more concentrated acid solutions in the range 1–5 mol L^{-1}. The slope of the E_{pa} versus acid concentration graph was found to be in the order $H_2SO_4 > HCl > HClO_4$. In this regard PVFc behaved very similar to 1,1′-bis(11-mercaptoundecyl)ferrocene ($Fc(C_{11}SH)_2$) except for its chemical stability. In H_2SO_4 media the PVFc was found to be much less stable than 1,1′-$Fc(C_{11}SH)_2$. The dependence of E_{pa} on acid concentration could be used to monitor state of charge of lead-acid batteries. However, for this application $Fc(C_{11}SH)_2$ would be a better choice because of its superior chemical stability.
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1. Introduction

The ferrocene/ferricenium redox reaction does not involve any proton, hence the couple is commonly used as a reference electrode in non-aqueous solutions [1–3]. Its use as a reference electrode in aqueous media is also known [4,5]. We have previously reported that the anodic peak potential (E_{pa}) of 1,1′-bis(11-mercaptoundecyl)ferrocene ($Fc(C_{11}SH)_2$) chemisorbed on a gold substrate is independent of the H_2SO_4 concentration when it is $<1.0 \times 10^{-2}$ mol L^{-1}. However, the E_{pa} shows a marked dependence on concentration when the acid is more concentrated (>1 mol L^{-1}) [6]. We proposed that this observation could be used to monitor changes in the acid concentration in lead-acid batteries during charge/discharge cycles. The redox couple could therefore be used as a potentiometric sensor for measuring

state of charge of lead-acid batteries. In this paper we report the results of poly(vinylferrocene) (PVFc) as compared to that of $Fc(C_{11}SH)_2$ reported earlier [6]. PVFc was chosen because its polymeric structure would be expected to render it more stable in concentrated sulfuric acid media and hence potentially more suitable for developing a battery state of charge sensor which monitors changes in the acid concentration during charge/discharge cycles of a lead-acid battery.

2. Experimental

2.1. Materials

All solutions were prepared by dissolving commercially available analytical reagent grade chemicals in high purity water obtained from a Millipore Milli-Q system. All the chemicals were used as-received. The gold electrode was

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made from polycrystalline 99.99% fine gold obtained from Australian Gold Refineries, Perth, Western Australia.

2.2. Electrochemistry

For the cyclic voltammetric study, the ferrocene coated gold electrodes (surface modified electrodes, SME) were prepared by the drop evaporation method [7]. Prior to coating, 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 saturated calomel electrode (SCE) in $1.0 \, mol \, L^{-1} \, H_2SO_4$ where hydrogen gas was evolved vigorously at the electrode surface as described in our earlier publication [8]. A platinum wire was used as a counter electrode. The potentials were measured against a SCE and quoted as such. All investigations were carried out under high purity nitrogen atmosphere.

3. Results and discussion

3.1. Cyclic voltammetry of poly(vinylferrocene)

A typical cyclic voltammogram of PVFc coated on a gold substrate in $1.0 \, mol \, L^{-1} \, H_2SO_4$ is shown in Fig. 1. A well-defined anodic and its corresponding cathodic peak is seen. The potential gap (ΔE_p) between the two peaks is about 45 mV, which is much higher than the ΔE_p value (10 mV) reported earlier for $Fc(C_{11}SH)_2$ [6].

The plot of log anodic peak current (I_{pa}) against log scan rate (ν) is found to be linear with a slope of 0.77 (Fig. 2). The
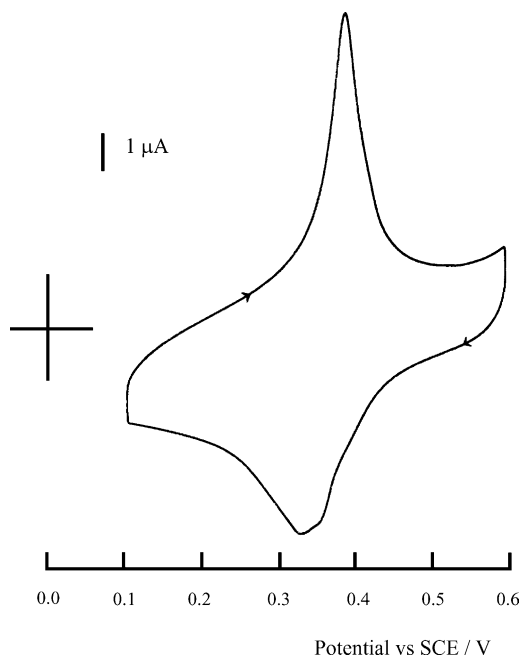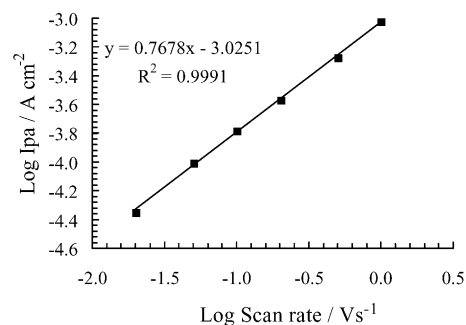

Fig. 2. Log anodic peak current (I_{pa}) against log scan rate (ν) for the cyclic voltammogram in $1.0 \, mol \, L^{-1} \, H_2SO_4$ at a gold for PVFc.

slope of log–log plot for any reaction which involves electron transfer to a surface immobilised species should be 1.0 [9,10]. Similarly, the slope should be 0.5 for a truly diffusion controlled system [9,10]. The fact that the slope for PVFc is found to lie in between these two values, suggests that the electron transfer mechanism for PVFc, immobilized on gold, is a mixture of the two mechanisms. In this respect PVFc resembles $Fc(C_{11}SH)_2$ [6].

3.2. Effect of acid concentration on anodic peak potential of poly(vinylferrocene)

The effect of acid concentration on E_{pa} of PVFc in H_2SO_4 was investigated. As can be seen from Fig. 3 at low concentrations of the acid ($<1.0 \times 10^{-2} \, mol \, L^{-1}$) the E_{pa} is independent of the acid concentration. This is consistent with what would normally be expected of a ferrocene because the electron transfer reaction should not involve a proton. However, the effect of concentrated H_2SO_4 ($1–5 \, mol \, L^{-1}$) on E_{pa} is found to be quite different. In this case the E_{pa} shifts linearly to less positive values as the acid concentration is increased (Fig. 3). The slope of the potential versus concentration is ca. 33 mV per unit molar concentration of the acid (Fig. 3).

This dependence of the E_{pa} of PVFc on sulfuric acid concentration is similar to that reported earlier for $Fc(C_{11}SH)_2$

Fig. 1. Cyclic voltammogram of PVFc in $1.0 \, mol \, L^{-1} \, H_2SO_4$ at a gold electrode (sweep rate = $100 \, mV \, s^{-1}$).
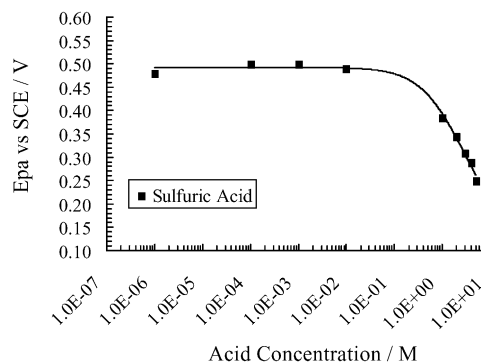

Fig. 3. The anodic peak potential against concentration of sulfuric acid for PVFc.

Table 1
The calculated liquid junction potentials values[a]

Concentration of the acid (mol L^{-1})	H$_2$SO$_4$/saturated KCl (mV)
1	16
2	22
3	26
4	30
5	33

[a] The values calculated as in Senanayake and Muir [11], see text.

Fig. 5. The anodic peak potential against high concentration of sulfuric, perchloric and hydrochloric acid for PVFc.

[6]. As noted earlier the peak potential for any ferrocene/ferricinium couple should be independent of H$^+$ concentration because the electron transfer should not involve H$^+$. One explanation for this unusual observation could be that the measured potential includes high liquid junction potential (LJP) associated with the reference electrode SCE. The LJP was thus calculated using the method described by Senanayake and Muir [11]. The relevant ionic mobility values were taken from the literature [12,13]. The results are shown in Table 1. An examination of the data shows that the calculated LJP values are quite small and cannot explain the magnitude of the variation of E_{pa} of PVFc with the H$_2$SO$_4$ concentration.

In order to establish whether the observed effect of acid concentration on E_{pa} was unique to H$_2$SO$_4$, the effects of HCl, and HClO$_4$ were also investigated. While the individual E_{pa} values for the investigated acids were different, being most positive for HCl and least for HClO$_4$, for each acid it changed linearly to a less positive value as the acid concentration increased (Figs. 4 and 5). The E_{pa} changed by ca. 34 mV for HCl and ca. 44 mV for HClO$_4$ per unit molar concentration of the acid. The E_{pa} is probably related to the salt formation between the anion of the acid and the ferricinium ion (Fc$^+$) generated on oxidation of ferrocene. Such salt formation would change the activity of Fc$^+$ at the surface of the electrode. Similar observations were also made by Inzelt and Szabo [14], and Uosaki et al. [15] for various ferrocenes in aqueous acid media.
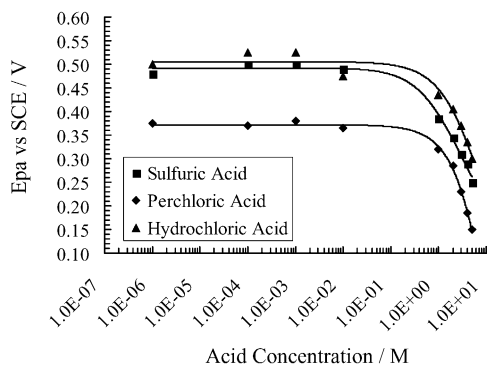
3.3. Stability of PVFc/PVFc$^+$ couple in concentrated acid media

Since a major objective of this work was to determine whether PVFc/PVFc$^+$ couple could be used as a robust chemically stable potentiometric sensor for monitoring state of charge of lead-acid batteries, its stability in concentrated H$_2$SO$_4$ media was evaluated. For this purpose freshly prepared SMEs were subjected to repeat voltammetric cycling in the potential range −0.1 to 0.6 V. The I_{pa} for each cycle was measured and the data recorded as $(I_{pa})_n/(I_{pa})_1 \times 100$ where n is the cycle number. 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. From these results it can be concluded that PVFc is either unstable i.e. it undergoes some irreversible change or is physically shed from the surface of the electrode. When compared to Fc(C$_{11}$SH)$_2$ [6], PVFc is lost much more rapidly. For example at the 100th cycle mark only 31% of the electrochemical response could be detected from the cyclovoltammetric data as compared to 87% for Fc(C$_{11}$SH)$_2$ reported in our earlier publication [6].

A variation in the method of preparing the PVFc SME was investigated. The method used was similar to that of Peerce and Bard [16] which involved deposition of PVFc at the electrode surface by electrodeposition. The SME was then tested for its stability as above. In this regard this SME behaved almost identical to that made by the drop evaporation method.

Fig. 4. The anodic peak potential against concentration of sulfuric, perchloric and hydrochloric acid for PVFc.

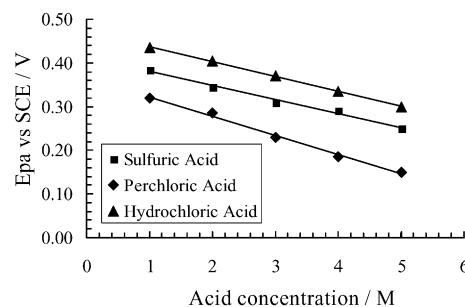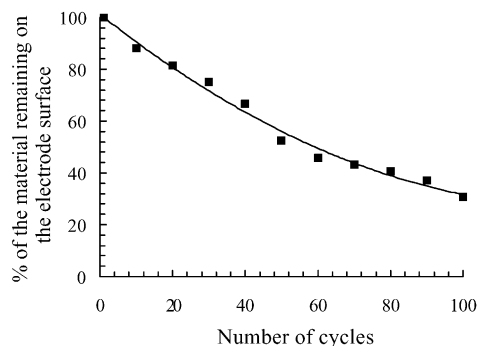Fig. 6. Percent of the residual material on the electrode surface of PVFc against number of cycles in 1 mol L^{-1} H$_2$SO$_4$.

Thus the loss of electroactivity of PVFc from the SME surface must be due to an inherent chemical decomposition.

The above results suggest that in spite of the fact the PVFc has a polymeric structure it is not as stable as $Fc(C_{11}SH)_2$ in concentrated H_2SO_4 media. Thus PVFc is inferior to $Fc(C_{11}SH)_2$ for use as a potentiometric sensor for measuring state of charge of lead-acid batteries.

4. Conclusion

The cyclic voltammetric investigation of poly(vinylferrocene) (PVFc) coated on gold in concentrated H_2SO_4 solutions suggests that its anodic peak potential(E_{pa}) is independent of the acid concentration in the range 1.0×10^{-2} to 1.0×10^{-7} mol L^{-1}. However, in concentrated H_2SO_4 acid (1–5 mol L^{-1}) E_{pa} shifts to less positive values and varies linearly with the acid concentration. Although the individual E_{pa} values are different, they show similar dependence on acid concentration for HCl, $HClO_4$, and H_2SO_4. The individual E_{pa} values are probably related to salt formation between the anion of the acid and ferricinium ion, which is formed on oxidation of PVFc. The dependence of E_{pa} of PVFc on H_2SO_4 concentration could be used as a means of determining state of charge of lead-acid batteries. However, its electrochemical response in concentrated H_2SO_4 tends to deteriorate rapidly. Thus PVFc is not suitable for developing a sensor for lead-acid battery state of charge determination.

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