



Short communication

Polydivinylferrocene surface modified electrode for measuring state-of-charge of lead–acid battery

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ABSTRACT

This paper outlines an investigation of the electrochemical behaviour of polymeric divinylferrocene (PDVF) produced by direct polymerisation of divinylferrocene (DVF) monomer on a glassy carbon substrate. The findings indicate that PDVF undergoes reversible reduction/oxidation in neutral and acidic aqueous media containing perchlorate (ClO_4^-) and sulfate (SO_4^{2-}). The anodic peak potential of the PDVF shifts linearly to less positive potentials as the sulfuric acid (H_2SO_4) concentration is increased from 1 to 5 M. The polymer film strongly adheres to the glassy carbon surface and is electrochemically stable when subjected to repeated voltammetric cycling in the potential range of -0.2 to $+0.8$ V vs. Ag/AgCl. The potential of the partially oxidized film of PDVF on a glassy carbon substrate against a Ag/AgCl/KCl reference electrode in sulfuric acid solution is stable, reproducible and varies linearly with the acid concentration in the range of 1–5 M. This observation may be suitable for potentiometrically measuring the state-of-charge of lead–acid batteries.

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1. Introduction

The state-of-charge of a lead–acid battery is usually determined by measuring the specific gravity of its electrolyte [1]. Nevertheless, this method is labour intensive and is particularly inappropriate when batteries with large number of cells are involved and where access is difficult. In such cases, remote sensing is highly desirable. Potentiometric measurement of the state-of-charge of a lead–acid battery by a pH-measuring device becomes attractive in this situation. Unfortunately, traditional pH sensors such as the glass electrode cannot be used in the battery electrolyte where H_2SO_4 concentration varies from 1 to 5 M during typical charge–discharge cycles; such a high acid concentration may cause destruction of the glass matrix of the electrode. Accordingly, we are exploring the possibility of using organic redox couples with the view to developing a miniaturised device capable of monitoring H_2SO_4 concentration as a function of state-of-charge of a lead–acid battery. In continuation of our previous work, [2–12], where we investigated several ferrocene derivatives, we report in this paper the results of our findings on polydivinylferrocene (PDVF). In the past, we have examined the following polymeric ferrocenes:

- alkane thiol ferrocenes [4–6,8];
- bridged ferrocene and their alkane thiol derivative [3,12];
- polyvinylferrocene [2,10,11];
- vinylferrocene–propylene sulfide–graft copolymers [7];
- thioether and ferrocene-containing copolymers [9].

The important conclusions from all our previous work are that all of the investigated ferrocenes:

- undergo one-electron reversible oxidation/reduction at the surface of a gold electrode in concentrated H_2SO_4 solutions;
- their anodic and cathodic peaks are dependent on H_2SO_4 concentration;
- the attachment of an alkanethiol group to the ferrocene molecules improves the adherence of the ferrocene molecules to the surface of a gold electrode, which is explained in terms of strong chemisorption of the thiol group;
- bridged ferrocenes are chemically more stable than simple ferrocenes in concentrated H_2SO_4 (1–5 M).

In general, the stability of the investigated ferrocenes was found to be questionable in H_2SO_4 media relevant to the lead–acid battery. In this study, we examine the possibility of determining whether in-situ electro-polymerisation of divinylferrocene (DVF) could form a more stable surface modified electrode (SME).

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2. Experimental

2.1. Organic synthesis

Nuclear magnetic resonance spectra were recorded using Bruker ARX-600 (600.1 MHz for ^1H and 150.9 MHz for ^{13}C), Bruker ARX-300 (300.1 MHz for ^1H and 75.5 MHz for ^{13}C) or Varian Gemini-200 (200.0 MHz for ^1H) spectrometers at ambient temperature. ^1H and ^{13}C chemical shifts were referenced to solvent resonances. Microanalyses were performed. All manipulations of air-sensitive compounds were undertaken under an inert atmosphere using standard Schlenk techniques or in a nitrogen-filled dry-box. All solvents were re-distilled (under the laboratory atmosphere) prior to use. Anhydrous acetonitrile (APS Ajax Finechem) was distilled from phosphorus pentoxide under a nitrogen atmosphere and stored over 0.3 nm molecular sieves. Tetrahydrofuran was dried over potassium and distilled under a nitrogen atmosphere prior to use. Diisopropylamine was distilled from sodium hydroxide under nitrogen and used immediately. Pyridine was distilled from KOH under a nitrogen atmosphere prior to use. Chromatographic separations (flash chromatography) were performed on silica gel (Merck, 4.0×10^{-5} – 6.3×10^{-5} M) using the eluants indicated.

2.2. Electrochemistry

Electrochemical experiments were conducted by means of a MacLab Potentiostat (AD instruments) and controller operated by a Power Macintosh 7100/66AV computer. Analysis of data was performed with MacLab software. Non-aqueous electrolyte solutions were degassed by three freeze/pump/thaw cycles, and then dried overnight with 0.3 nm molecular sieves prior to use. All aqueous solutions were prepared by dissolving commercially available analytical grade chemicals in Millipore purified water. Aqueous electrolyte solutions were degassed by bubbling nitrogen or argon through the solution. All sulfuric and perchloric acid (HClO_4) solutions were prepared by dilution of a calculated mass of the concentrated acid with Millipore water to the required volume. An Ag|AgCl/KCl aqueous reference electrode was used for experiments in aqueous solutions. An Ag|LiCl/acetonitrile non-aqueous reference electrode was used for experiments in non-aqueous solutions. The working electrodes were PEEK-encased disc mini-electrodes of glassy carbon (1.5 mm diameter) or gold (1 mm diameter), from Cypress Systems Inc. The counter electrode was a platinum wire electrode. The working electrode was cleaned by gentle rubbing over aluminum oxide powder (Griffin & George Ltd.) on a soft cloth backing. The electrode was rinsed with de-ionised water, then with acetone, and finally blown dry with a stream of argon. All the chemicals were used as-received unless stated otherwise.

3. Results and discussion

A polymer film of DVF was prepared by electro-polymerisation on the surface of a glassy carbon electrode. The films were produced by applying cyclic voltammetry in the range of -2.8 to $+0.8$ V in 1×10^{-2} M DVF in dry acetonitrile containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. Each experiment was conducted for 20 consecutive cycles, at a scan rate of 100 mV s^{-1} . A typical cyclic voltammogram of the electro-polymerisation is shown in Fig. 1. The cathodic current around -2.0 V decreases quite dramatically with successive cycling and suggests the formation of a polymer film on the electrode surface.

Cyclic voltammograms of the DVF polymer film in 1 M H_2SO_4 and 1 M HClO_4 in the range of -0.2 V to $+0.8$ V at a scan rate of 100 mV s^{-1} are presented in Fig. 2. The DVF polymer films show

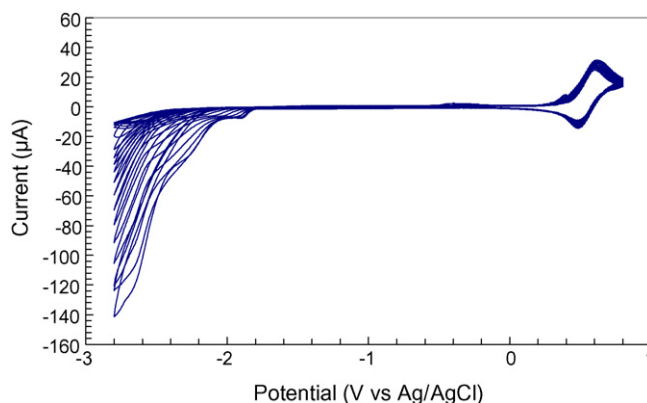


Fig. 1. Cyclic voltammogram for electro-polymerisation of divinylferrocene on a glassy carbon electrode (scan rate of 100 mV s^{-1}).

well-defined reversible oxidation/reduction peaks when tested in neutral and acidic aqueous media containing perchlorate (ClO_4^-) or sulfate (SO_4^{2-}) electrolytes.

Initial stability studies were conducted by subjecting the electrodes to over 30 cycles in the same electrolytes. When tested in both neutral SO_4^{2-} (1 M sodium sulfate (Na_2SO_4)) and ClO_4^- (1 M sodium perchlorate (NaClO_4)) and acidic media (1 M H_2SO_4 and 1 M HClO_4), there was little change in the anodic peak current over 30 cycles. This suggests that the polymer films on the electrode surface are stable in neutral as well as in acidic media.

Encouraged by the above tests, the DVF polymer films were tested further for their stability in H_2SO_4 media as follows. The films were subjected to 100 consecutive cycles in 1 M H_2SO_4 in the potential range of -0.2 to 0.8 V vs. Ag|AgCl. The results show that there is very little change in the height of the oxidation wave during the course of the experiment, as shown in Fig. 3.

The effect of H_2SO_4 concentration on the potentials of the anodic and cathodic peaks for DVF polymer films was investigated. The cyclic voltammetric behaviour of a DVF polymer film prepared as above was investigated by placing it in a series of H_2SO_4 solutions in the concentration range of 1–5 M. It is found that as the concentration is increased from 1 to 5 M the anodic and cathodic peaks shift to less positive potentials. This observation is shown in Fig. 4. The anodic peak potentials (E_{pa}) from Fig. 4 are plotted in Fig. 5. The plot clearly shows that the E_{pa} varies linearly as a function of H_2SO_4 concentration.

The E_{pa} values would normally be expected to be independent of H_2SO_4 concentration because under normal circumstances, protons should not be involved in the oxidation process of the ferrocene polymer. The observed data are therefore interesting, i.e., the E_{pa} is found to be dependent on H_2SO_4 concentration. This suggests that

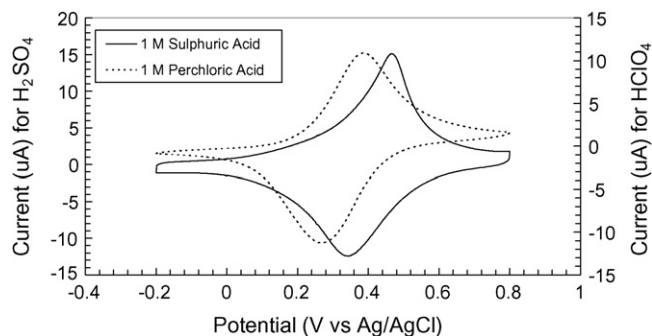


Fig. 2. Cyclic voltammogram for divinylferrocene polymer film on glassy carbon in 1 M sulfuric acid and 1 M perchloric acid (scan rate of 100 mV s^{-1}).

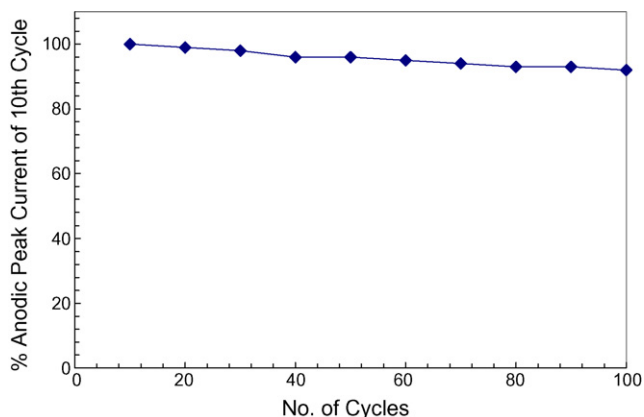


Fig. 3. Stability plot for a divinylferrocene polymer film on glassy carbon electrode in 5 M sulfuric acid.

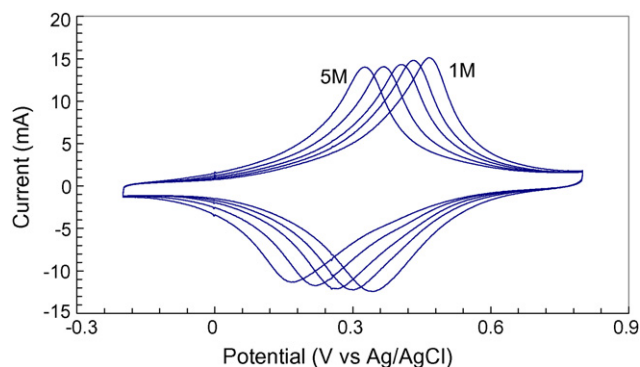


Fig. 4. Effect of sulfuric acid concentration in range of 1–5 M on cyclic voltammogram of divinylferrocene polymer film on glassy carbon electrode (scan rate of 100 mV s^{-1}).

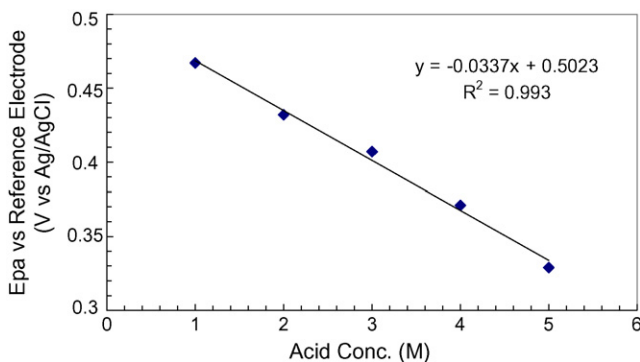


Fig. 5. Variation of anodic peak potential (E_{pa}) as function of sulfuric acid concentration.

some mechanism other than a single-electron transfer is responsible for the behaviour. A similar finding has been reported for other ferrocene polymers [13].

In a further experiment, a freshly prepared DVF polymer film was made by electro-polymerisation on a glassy carbon working electrode. The polymer film was partially oxidized in an aqueous 1 M H_2SO_4 solution by a linear potential sweep between -0.2 and

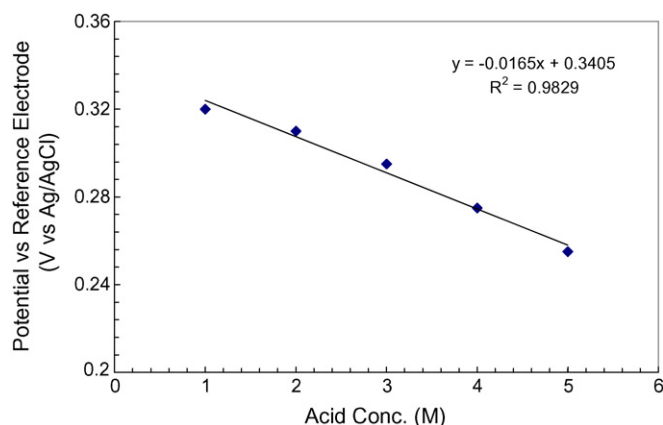


Fig. 6. Divinylferrocene polymer film on glassy carbon electrode. Relationship between electrode potential (vs. Ag/AgCl reference) and sulfuric acid concentration.

$+0.8 \text{ V}$ vs. a Ag|AgCl/KCl aqueous reference electrode, followed by a potential arrest at $+0.8 \text{ V}$ for 30 s. The resulting surface modified electrode was then subjected to potentiometric monitoring in a series of H_2SO_4 solutions in the concentration range of 1–5 M. Ag|AgCl/KCl was again used as the reference electrode. The data in Fig. 6 demonstrate that the electrode potential varies linearly with changing H_2SO_4 concentration, and the results are reproducible over an extended period of 30 days.

4. Conclusion

Divinylferrocene (DVF) directly polymerised on a glassy carbon electrode could be suitable as a potentiometric sensor for measuring the change in sulfuric acid (H_2SO_4) concentration in the range of 1–5 M. The polymer films exhibit excellent chemical stability when tested in H_2SO_4 solutions. The anodic peak potential of a partially oxidized polymer film on a glassy carbon electrode shows a stable value when measured against a Ag|AgCl/KCl reference electrode and varies linearly with H_2SO_4 concentration in the range of 1–5 M. This property could be used to measure the state-of-charge of a lead–acid battery.

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