Potentiometric Measurement of State-of-Charge of Lead-Acid Batteries Using Polymeric Ferrocene and Quinones Derivatives

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Abstract

Measurement of state-of-charge of lead-acid batteries using potentiometric sensors would be convenient; however, most of the electrochemical couples are either soluble or are unstable in the battery electrolyte. This paper describes the results of an investigation of poly (divinylferrocene) (PDVF) and Poly(diethylnlanthaquinone) (PAQ) couples in sulfuric acid with the view to developing a potentiometric sensor for lead-acid batteries. These compounds were both found to be quite stable and undergo reversible reduction/oxidation in sulfuric acid media. Their redox potential difference varied linearly with sulfuric acid concentration in the range of 1 M - 5 M (i.e. simulated lead-acid electrolyte during battery charge/discharge cycles). A sensor based on these compounds has been investigated.

Keywords

Surface Modified Electrodes, Ferrocene, Quinone, State-of-Charge, Lead-Acid Battery

1. Introduction

Lead-acid batteries are currently an essential component of any power supply based on renewable energy systems including solar, wind, diesel, and hybrid resources. The life of the battery plays an important role in the reliability and economies of such systems and therefore it is essential that the state-of-charge of the battery is pre-
cisely monitored throughout the operation of the system in order to achieve longer battery life and efficient energy management.

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, sulfuric acid, decreases on discharge and increases on charge, as explained in the electrochemical reactions (1-4), thus provides means of indicating the state-of-charge of the lead-acid battery.

During charge:

\[\text{Anode} (+): \text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + \text{H}_2\text{SO}_4 + 3\text{H}^+ + 2\text{e}^- \quad (1)\]
\[\text{Cathode} (-): \text{PbSO}_4 + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_4 + \text{Pb} \quad (2)\]

During discharge:

\[\text{Anode} (+): \text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \quad (3)\]
\[\text{Cathode} (-): \text{PbO}_2 + \text{H}_2\text{SO}_4 + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \quad (4)\]

Generally the state-of-charge estimation is achieved by examining any property of the electrolyte, which changes as a function of sulfuric 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 vapor pressure, and ionic activities have been considered [1]-[17]. Currently, the most widely used and successful method for measuring the state-of-charge of lead-acid batteries is the measurement of the battery electrolyte specific gravity during the charge/discharge cycle [1]. However, this method is messy, time consuming, labor intensive and particularly undesirable when batteries with a large number of cells are involved and located in inaccessible locations such as those in Remote Area Power Supply (RAPS) applications. Clearly, it is more practical to monitor remotely the state-of-charge of lead-acid batteries by potentiometric methods, which relate to the change in hydrogen ion concentration in the battery electrolyte. Hydrogen ion concentration can be measured using traditional pH sensors such as the glass electrode. Unfortunately, such electrodes do not work in concentrated acid in the battery electrolyte; this high acid concentration may cause destruction of the glass matrix of the electrode.

In this paper we will discuss the possibility of exploiting surface modified electrode (SME) chemistry in developing an inexpensive, rugged, miniaturized probe for determining the state-of-charge of lead-acid batteries. A SME is an inert conducting substrate (metal or carbon) which has been chemically or physically coated with an electrochemically active or inactive material, known as the modifier. The aim, with respect to modification, is to impart some of the properties of the modifier upon the electrode [18] [19]. Hence, the electrode can be modified to exhibit predictable properties that are desirable for the target application. It is known in the literature that SMEs may be used to measure hydrogen ion concentration. For example, a Nernstian response to [H⁺] has been reported for poly(1,2-diaminobenzene) films on platinum and glassy carbon [20] [21]. Similarly, Rubinstein [22] could measure the pH of solutions by measuring the reduction peak potential value for surface bound poly(1,2-diaminobenzene) with respect to surface bound \(\text{Ru(bipy)}^3/2^+\) (in Nafion) reference SME.

Rubinstein [22] was the first to report a voltammetric procedure for the measurement of pH. He used an electrode that had been dip-coated with chloranil as a pH-sensitive electrode. This pH sensitive electrode was not durable, however, as the chloranil slowly dissolved from the electrode surface. Hickman et al. [23] work with voltammetric pH-sensors improved on Rubinstein’s efforts by chemically binding quinone groups to the electrode surface. Righton’s group used gold electrodes, and modified those electrodes with quinones and ferrocenes containing thiol groups, which bind to gold strongly. Cyclic voltammetry demonstrated that the redox behavior of the quinone groups varied as a function of pH, as expected, but the long-term durability of these electrodes was not adequate.

We envisage that SMEs consisting of polymer films containing ferrocene derivatives (as a pH-insensitive electrode) and quinone derivatives (as a pH-sensitive electrode) will prove to be more stable and hence more reliable as potentiometric sensors.

Attachment of redox-active polymers to the electrode surface has become a popular method for preparing SMEs in recent years. Albagli et al. [24] have reported the surface attachment of polymers via the covalent attachment of the polymer end group to the electrode surface. Polymerization directly to the electrode surface may
prove a more suitable method for preparing polymer film SMEs. It is known that poly (styrene) “brush-type” layers can be prepared using a self-assembled monolayer of biphenyllithium on gold substrates to initiate anionic polymerization of styrene [25]. Electrochemical polymerization utilizes the electrode as initiator of the polymerization process. In this process radical intermediates are formed in the vicinity of the electrode via oxidation or reduction of the monomer in solution where the radicals react with other monomer molecules to form a polymer film directly on the electrode surface [19]. Funf and Gray [26] described the electropolymerization of phenyl-substituted ethylenes by cyclic voltammetry. Indeed, Ju and Leech [27] have demonstrated that highly stable electroactive thin films of poly (vinylferrocene) can be prepared by reductive electropolymerization of the vinylferrocene monomer in solution using cyclic voltammetry.

In this paper, we propose to use a polymer containing quinone units to form a SME that is sensitive to pH. Etori et al. [28] has reported the preparation of various polymers containing recurring quinone units via the dehalogenation polycondensation of dichloroquinones. The redox behavior of these polymers was investigated by cyclic voltammetry using a cast film on platinum substrate.

This paper describes the results of the systematic study of the electrochemistry, and chemical stability of PAQ in concentrated aqueous sulfuric acid media. The electrochemical studies of PDVF were presented in our previous publication [29].

The underlying objective of the work was to development a robust, cheap, miniaturized sensor for measuring the state-of-charge of lead-acid batteries in-situ or on-line. The target sensor includes two key components: a PDVF-SME, to be used as a pH-insensitive reference material; a PAQ-SME, to be used as pH-sensitive material.

2. Experimental

2.1. Organic Synthesis

The synthesis of 2,6-Diethynylantraquinone is shown in the reaction scheme below in Figure 1. This compound was prepared in order to provide an anthraquinone monomer suitable for polymerization by chemical means.

Figure 2 outlines the reaction sequence for the polymerization of diethynylanthaquinone. The polymerization was initially approached as a two-step reaction where diethynylanthaquinone was obtained and purified prior to attempting the oxidative polymerization reaction.

2.2. Electrochemistry

Electrochemical experiments were conducted using a MacLabPotentiostat (AD Instruments) and controlled by a computer. Non-aqueous electrolyte solutions were degassed by three freeze/pump/thaw cycles and dried overnight using 0.3 nm molecular sieves prior to use. All aqueous solutions were made 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 acid solutions were prepared by dilution of a calculated mass of the concentrated acid with Millipore water to the required volume. A Ag/AgCl/KCl aqueous reference electrode was used for experiments in aqueous solutions. A Ag/LiCl/acetonitrile non-aqueous reference
electrode was used for experiments in non-aqueous solutions. The working electrodes were PEEK-encased disk 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 aluminium oxide powder (Griffin & George Ltd.) on a soft cloth backing. The cleaned electrode was then potentiostated for 5 min at −0.9 V versus saturated calomel electrode (SCE) in 1.0 M H₂SO₄ where hydrogen gas was evolved vigorously at the electrode surface as described in our earlier publication [30].

The electrode was rinsed with Millipore water, then acetone and blown dry using a stream of argon across the electrode surface. All the chemicals were used as received unless noted.

3. Results and Discussion

3.1. Cyclic Voltammetry of Poly(Diethynylanthraquinone)

A drop-coated electrode was prepared on glassy carbon by applying a single drop of a PAQ/dimethyl formamide (DMF) solution onto the surface of the electrode and allowing it to dry. A typical cyclic voltammogram of PAQ coated on a glassy carbon substrate in 1.0 M H₂SO₄ is shown in Figure 3. A well-defined anodic and its corresponding cathodic peak is seen in the potential range between −0.5 V and +0.5 V vs Ag/AgCl/KCl aqueous reference electrode that correspond to a reversible redox response for the PAQ in 1.0 M H₂SO₄. The potential gap (ΔEp) between the two peaks is about 160 mV, which is much higher than the ΔEp value (10 mV) reported earlier for Fc (C₁₁SH)₂ [31].

3.2. Stability of Poly(Diethynylanthraquinone) Film in Concentrated Acid Media

Initial stability tests for the polymer on glassy carbon were conducted in 1.0 M H₂SO₄ cycling between −0.3 V and +0.3 V over 100 - 200 cycles. These tests showed that after 100 continuous cycles the anodic peak current (Ipa) had only decreased to 80% of its original value. Obviously this was very encouraging and a study of the stability of the polymer on glassy carbon was investigated over an extended period of continued cycling.

A fresh PAQ drop-coated electrode was prepared and subjected to repeated cycling between −0.3 V and +0.3 V for 4600 cycles. The Ipa was noted for every 100th cycle and expressed as a percentage of the second cycle as shown in the stability plot in Figure 4. During the first 1000 cycles, the anodic peak current tended to decrease, but following this initial period, the current remains approximately constant at 40% of its original value.

3.3. The Potentiometric Sensor

A simple potentiometric sensor incorporating a PDVF electrode and a PAQ electrode was prepared and used to conduct potentiometric studies in sulfuric acid solutions varying in concentration from 0.1 M to 5 M in order to replicate the concentration range associated with a charge-discharge cycle in a lead-acid battery. The sensor is shown below in Figure 5. It consists of two glassy carbon electrodes containing polymer films of PDVF or PAQ.
Figure 3. Cyclic voltammogram of a PAQ drop-coated electrode in 1 M H₂SO₄ at a glassy carbon electrode, (Sweep rate 100 mV s⁻¹).

Figure 4. Percentage residual material on the electrode surface of PAQ against number of cycles.

Figure 5. The potentiometric sensor.

prepared by drop-coating method. The two surface modified electrodes were simply suspended in the sulfuric acid solution and connected via alligator clip to the potentiostat. The potential between the two electrodes was monitored at zero current.

3.4. Response to Different Sulfuric Acid Concentrations

This potentiometric sensor was used in experiments to determine whether the measured potential between the two electrodes responds to changes in H₂SO₄ concentration. The two electrodes were immersed in a solution of 5 M H₂SO₄ and the potential between the electrodes was monitored over a five minute period. Following this,
both electrodes were removed from solution and transferred to a 4 M H₂SO₄ solution, again monitoring the potential for a five minute period.

This procedure was followed in a stepwise manner, gradually decreasing the acid concentration to 0.1 M in 1 M steps. Then the procedure was reversed, starting with 0.1 M and increasing the concentration back to 5 M. The experiment was repeated a number of times in order to observe whether the recorded potentials were reproducible for each particular concentration of H₂SO₄. Figure 6 shows typical results for this experiment. These results clearly show that changing concentrations of H₂SO₄ influence the potential for the device.

Figure 7 give an idea on how the measured potential for a particular concentration of sulfuric acid varies with successive measurements for the experiment described above. The recorded potentials are significantly different and the general trend for the data is the same for each concentration of sulfuric acid.

3.5. Changing Concentration of Sulfuric Acid In-Situ

The potentiometric device was used in similar experiments where the H₂SO₄ concentration was altered in-situ and potentials recorded at different acid concentrations. The procedure was as follows: The potentiometric sensor was suspended in a beaker containing 5 M H₂SO₄ (20 mL) and a magnetic stirrer bar. The system was covered with foil and the cell was kept oxygen-free by a flow of argon during the experiment. The potential between the two electrodes was monitored for five minutes. Following this, a calculated volume of degassed Millipore water was added to the beaker to dilute the concentration to 4 M. The solution was allowed to stir for approximately 1 min and then the potential was monitored at the new concentration for five minutes. This procedure was repeated using calculated dilutions to change the concentration in 1 M steps until a final concentration of 1 M was reached. A typical set of results is shown below in Figure 8.

This plot clearly shows that the potential of the sensor responds to changing H₂SO₄ concentration in which, the effect of concentrated H₂SO₄ (5 - 1 M) on the potential is found to be shifting linearly to higher positive values as the acid concentration is increased (Figure 9). The slope of the potential versus concentration is ca. 40 mV per unit molar concentration of the acid (Figure 9).
4. Conclusion

The PAQ studied showed desirable properties to be used as the pH-sensitive material in the target potentiometric sensor. The material showed excellent chemical stability when tested in sulfuric acid solution. The potentiometric response for the PAQ was found to vary linearly with changing sulfuric acid concentration in the range 1 M - 5 M. A basic potentiometric sensor consisting of two surface modified electrodes based on PDVF and the PAQ was prepared. An investigation was conducted to determine whether the potentiometric response of the device varies with changing sulfuric acid concentration in the range 1 M - 5 M. The potential of the device was found to vary as a function of sulfuric acid concentration in a linear fashion. The polymer film exhibit excellent chemical stability when tested in H2SO4 solutions. Clearly, more detailed studies are required to determine the long term reproducibility of the basic sensor; however, initial results for such a device are extremely encouraging in term of using such a device to monitor the state-of-charge of lead-acid batteries.

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