

Short Communication

Effect of perfluoroalkylsulfonate on the discharge behaviour of PbO₂ electrodes in sulfuric acid solution

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Abstract

Amine perfluoroalkylsulfonate (FC-99) is seen as a prospective additive for lead/acid battery positive plates. Accordingly, its effect on the electrochemical behaviour of PbO₂ electrodes in 5 M H₂SO₄ is studied by cyclic voltammetry, charge/discharge cycling and scanning electron microscopy. For sulfuric acid solution with FC-99, the discharge capacity of the PbO₂ electrode is increased, but the cycle life is reduced. These effects are attributed to adsorption of FC-99 on the electrode surface. The latter changes the morphology of the PbO₂ crystals to enlarge the electrode surface area, but weakens the contact between the positive active material and the substrate metal.

Keywords: Lead dioxide; Sulfuric acid; Perfluoroalkylsulfonate; Discharge behaviour

1. Introduction

The lead/acid battery is commercially the most important rechargeable electrochemical system. Although many other developing high-energy systems, such as nickel/zinc, nickel/metal-hydride and lithium batteries, may challenge this dominance, the high reliability, low cost and excellent operational life of lead/acid batteries put replacement by other secondary batteries well into the future. Nevertheless, there are still many shortcomings of the lead/acid battery that need to be overcome. One of the main disadvantages is the poor utilization of the positive active-material (PAM).

The coefficient of utilization of the PAM could be raised by incorporating some suitable additive(s) that modify the charge/discharge properties of the positive electrode. Most of the additives that have been studied are essentially inorganic compounds [1–8]; only a few organic substances have been investigated [9]. This is because organic substances tend to decompose at the high potential of the positive electrode.

Perfluoroalkylsulfonates (PFAS) possess outstanding chemical and thermal stability; they are more active than their analogous hydrogenated surfactants in lowering the surface tension in aqueous solutions. They are very promising candidate additives for positive electrodes. In fact, the perfluoroalkane sulfonic acid variety has been patented as far back

as 1958 for application in lead/acid batteries as a means to lower the surface tension of the electrolyte solution, and to improve active-material wetting and penetration [10]. Recently, PFAS salts have been used in lead/acid batteries to increase rechargeability after overdischarging and standing [11,12] or to suppress self-discharge [13,14]. The mechanism of their effect has still to be determined.

This communication presents some preliminary results concerning the effect of amine perfluoroalkylsulfonate (FC-99, CF₃(CF₂)_nSO₃⁻NH₄⁺, n ≈ 8) on the electrochemical behaviour of the PbO₂ electrode.

2. Experimental

A single compartment glass cell with five inlets was used for cyclic voltammetric studies. The reference electrode was a saturated calomel electrode (SCE), and a platinum sheet was used as the counter-electrode. The working electrode was either a spec-pure lead disc (Johnson Matthey Chemicals Ltd., Royston, UK) that was embedded in a polytetrafluoroethylene (PTFE) holder and had an exposed area of 0.283 cm², or a lead substrate prepared by galvanostatic electrodeposition on to a gold disc electrode (area: 0.246 cm²) from a 120:30:13.3 solution of Pb(BF₄)₂, HBF₄ and H₂BO₃ with 0.2–1 g l⁻¹ peptone at 10 mA cm² for 10 min. Before each experiment, the pure-lead working electrode was polished mechanically with alumina (particle size: 3–0.05 μm) until

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a mirror surface was obtained, rinsed with double-distilled water, cleaned chemically in a glacial acetic acid/hydrogen peroxide mixture and a methanol solution [15], and then rinsed again thoroughly with double-distilled water. After this procedure, the electrode was immersed immediately in the test solution. The base electrolyte was 5 M H₂SO₄ which was prepared from AR sulfuric acid (Beijing Chemical Factory, Beijing, China) and double-distilled water. The test additive was amine perfluoroalkylsulfonate (FC-99) (3M, St. Paul, MN, USA). The instruments used in the study included a RDE4 bipotentiostat (Pine Instruments, USA) and a Type 3086 x-y recorder (Yokogama Hokushin Electric, Tokyo, Japan).

The charge/discharge cycling experiments were carried out with Planté electrodes. The test 'battery' consisted of a single cell that comprised one positive and two negative plates. The dimensions of the positive and negative plates made from pure lead were 10 mm × 10 mm × 1.5 mm and 20 mm × 20 mm × 1.5 mm, respectively. The formation of active material was conducted in 0.5 M H₂SO₄ without additive as follows: first, the charging process was performed at a constant current of 7 mA for 1 h; then, the cell was discharged at a constant current of 3.5 mA until the potential of the positive electrode dropped to 1.7 V versus a lead electrode. After the first charge/discharge cycle, the same charge/discharge procedure was repeated 21 times (about 24 h). At this stage, the surface of the positive electrode was covered with a porous PbO₂ layer. The electrodes were transferred to cells containing 5 M H₂SO₄ without and with 20 ppm (mg l⁻¹) FC-99, respectively. Charge/discharge cycling experiments were carried out at 2 mA between 1.7 V (end-point of discharge potential of the positive electrode) and 2.3 V (end-point of charge potential) versus a lead electrode. The experiments were conducted with a charge/discharge unit that was controlled by a computer. The charge and discharge processes were also controlled by the charging and discharging time (maximum time was 1.5 h). The surfaces of PbO₂ electrodes after 60 cycles were examined by a scanning electron microscopy (SEM) (Hitachi SEM X-650, Japan).

All the experiments were performed at room temperature.

3. Results and discussion

3.1. Cyclic voltammetric experiments

The cyclic voltammograms for the lead electrode (cathodically electrodeposited on a gold disc) in the 1.2–2.0 V range (versus SCE) in 5 M H₂SO₄ with different concentrations of FC-99 are shown in Fig. 1. The lead electrode was first cycled for about 12 h in sulfuric acid without FC-99 at a scan rate of 5 mV s⁻¹ until there was no further increase in the peak current. The deposited lead was then converted completely into porous lead dioxide. After recording the voltammogram (Fig. 1(a)), 10 ppm of FC-99 was added to the electrolyte.

The PbO₂ electrode was cycled continuously in the same potential range until the shape of the voltammogram did not change. The voltammogram shown in Fig. 1(b) was obtained in 3 h after the addition of the first 10 ppm of FC-99. A further 10 ppm of FC-99 was then added. The concentration of FC-99 was increased in 10 ppm amounts up to 50 ppm. At each concentration, the same procedure was performed and the resulting voltammogram was recorded (Fig. 1(b)–(f)). The cathodic part of each voltammogram corresponds to the reduction of lead dioxide, and the anodic part to the oxidation of lead sulfate. The area under the anodic and cathodic peaks gives, respectively, the charge involved in the anodic (Q_a) and cathodic (Q_c) reactions on the lead dioxide electrode.

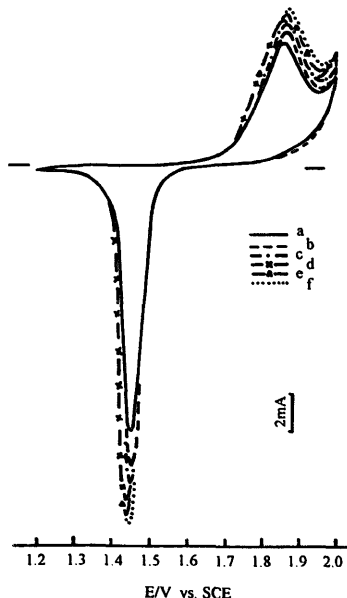


Fig. 1. Cyclic voltammograms for PbO₂ electrode (supported on a gold disc) in 5 M H₂SO₄ with different concentrations of FC-99 (ppm): (a) 0; (b) 10; (c) 20; (d) 30; (e) 40, and (f) 50.

Table 1
Charge involved in anodic (Q_a) and cathodic (Q_c) reactions on PbO₂ electrode in 5 M H₂SO₄ with different concentrations of FC-99

| FC-99 concentration (ppm) | Q_a (mC) | Q_c (mC) |
|---------------------------|------------|------------|
| 0 | 258.64 | 194.73 |
| 10 | 281.95 | 206.39 |
| 20 | 288.72 | 219.34 |
| 30 | 292.75 | 232.29 |
| 40 | 297.73 | 246.11 |
| 50 | 303.54 | 252.16 |

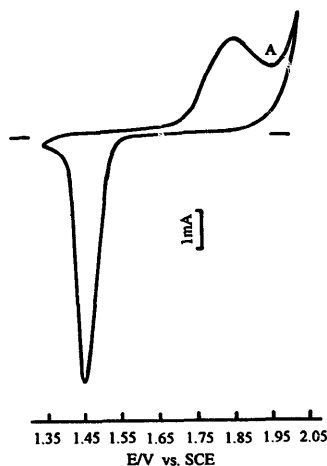


Fig. 2. Typical cyclic voltammogram for PbO_2 electrode in 5 M H_2SO_4 with 20 ppm FC-99 at 50th cycle; scan rate = 5 mV s^{-1} .

Values of Q_a and Q_c , with and without FC-99, are presented in Table 1. It can be seen that both Q_a and Q_c increase steadily with increase in the FC-99 concentration. Also, the anodic and the cathodic peak currents increased as the concentration of FC-99 is raised from 0 to 50 ppm (Fig. 1). The effect of FC-99 on the cyclic voltammograms is related to the adsorption of FC-99 on the electrode. Therefore, FC-99 appears to modify the particle size of the PbSO_4 and/or PbO_2 crystals. The crystal size of the active material is smaller in presence

of FC-99. The morphological characteristics of the cycled PbO_2 electrodes were examined by SEM (see below).

In order to study the long-term stability of FC-99 under such strongly oxidizing conditions, additional cyclic voltammetric studies were conducted with a pure-lead electrode. FC-99 was added to 5 M H_2SO_4 after the electrode was cycled at a scan rate of 5 mV s^{-1} in the potential 1.35–2.05 V range (versus SCE) for 50 cycles in the absence of FC-99, in order to develop a dense PbO_2 layer coating on the electrode surface and to allow the electrode reaction to reach a steady state. The shapes of the voltammograms, with or without 20 ppm of FC-99, are somewhat similar to each other at any given cycle number. (It should be noted that the number of cycles (N) is counted from the first 50 cycles.)

A typical cyclic voltammogram for a lead electrode in 5 M H_2SO_4 with FC-99 after 50 cycles is presented in Fig. 2. The potential of point A is taken to be the initial potential of the oxygen evolution reaction (E_{EO}). The characteristic parameters of the cyclic voltammograms in the absence and the presence of FC-99 at different cycles, are listed in Tables 2 and 3, respectively. Clearly, the presence of FC-99 has negligible influence on the anodic and cathodic peak potentials, but the E_{EO} is shifted to more positive values. The anodic and cathodic peak current, as well as the Q_a and Q_c charges, are increased when FC-99 is added to the electrolyte. Nevertheless, the addition of FC-99 accelerates the rate of PAM shedding and decreases the cycle life of the PbO_2 electrode. The active materials start to become detached from the electrode within less than 175 cycles. By contrast, the cycle life is more than 200 cycles if the PbO_2 electrode is cycled in H_2SO_4 without FC-99. In summary, it is concluded that the long-term stability of FC-99 in the $\text{PbO}_2/\text{PbSO}_4/\text{H}_2\text{SO}_4$ system is excellent, but that FC-99 exerts an adverse effect on the cycle

Table 2
Characteristic parameters of cyclic voltammograms for PbO_2 electrode in 5 M H_2SO_4 at different cycles

| N | E_{pa} (V) | I_{pa} (mA) | E_{pc} (V) | I_{pc} (mA) | E_{EO} (V) | Q_a (mC) | Q_c (mC) |
|-----|---------------------|----------------------|---------------------|----------------------|---------------------|------------|------------|
| 0 | 1.85 | 1.25 | 1.48 | 5.6 | 1.95 | 61.27 | 47.49 |
| 20 | 1.85 | 1.3 | 1.48 | 6.3 | 1.95 | 63.26 | 59.72 |
| 50 | 1.85 | 1.4 | 1.48 | 6.35 | 1.95 | 82.06 | 68.82 |
| 75 | 1.85 | 1.7 | 1.48 | 6.6 | 1.95 | 89.72 | 78.12 |
| 100 | 1.88 | 1.5 | 1.48 | 6.5 | 1.95 | 93.45 | 87.9 |
| 150 | 1.88 | 1.5 | 1.48 | 6.3 | 1.95 | 90.9 | 84.72 |
| 175 | 1.88 | 1.5 | 1.48 | 6.1 | 1.95 | 95.81 | 90.38 |
| 200 | 1.88 | 1.6 | 1.48 | 6.1 | 1.95 | 103.86 | 92.22 |

Table 3
Characteristic values of cyclic voltammograms for PbO_2 electrode in 5M H_2SO_4 with 20 ppm FC-99 at different cycles

| N | E_{pa} (V) | I_{pa} (mA) | E_{pc} (V) | I_{pc} (mA) | E_{EO} (V) | Q_a (mC) | Q_c (mC) |
|-----|---------------------|----------------------|---------------------|----------------------|---------------------|------------|------------|
| 0 | 1.85 | 1.35 | 1.48 | 4.5 | 1.95 | 61.27 | 44.37 |
| 20 | 1.86 | 2.1 | 1.46 | 6 | 1.96 | 87.68 | 64.44 |
| 50 | 1.87 | 2.6 | 1.47 | 6.5 | 1.98 | 106.9 | 83.03 |
| 75 | 1.87 | 2.7 | 1.47 | 9.3 | 1.98 | 114.08 | 87.04 |
| 100 | 1.88 | 2.7 | 1.47 | 9.45 | 1.98 | 119.58 | 88.46 |
| 150 | 1.89 | 2.7 | 1.47 | 9.4 | 1.98 | 113.03 | 88.73 |

life of PbO_2 electrodes. As mentioned above, this influence of FC-99 on cycle life is probably due to a continuous decrease in the particle size of the PbO_2 crystals during successive cycles such that the contact between the substrate metal (lead) and the PAM is weakened or even lost altogether.

3.2. Charge/discharge cycling

The discharge curves for Planté positive electrodes in 5 M H_2SO_4 , with or without 20 ppm FC-99, at the 30th cycle are given in Fig. 3. The discharge potential of the PbO_2 electrode is virtually unaffected when FC-99 is added. On the other hand, the discharge capacity is increased significantly, e.g. the value is about 0.53 mAh (67%) higher in the presence of FC-99 than that in the absence of FC-99 at cycle 10 and about 0.43 mAh (23.6%) higher at cycle 50 (Fig. 4). The beneficial effect of FC-99 is observed for addition at any cycle number. This result is in agreement with that obtained from cyclic voltammetric experiments (Table 3).

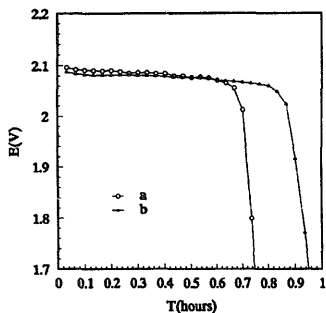


Fig. 3. Discharge curves for Planté positive electrode (a) without or (b) with 20 ppm FC-99 in 5 M H_2SO_4 at 30th cycle; discharge current = 2 mA.

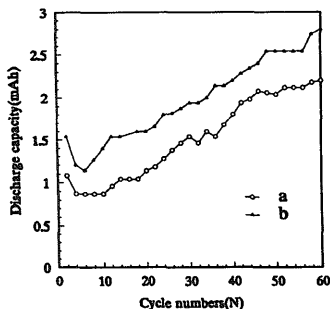


Fig. 4. Capacity changes during first 60 cycles of PbO_2 electrode in 5 M H_2SO_4 (a) without and (b) with 20 ppm FC-99; discharge current = 2 mA, depth-of-charge = 100%.

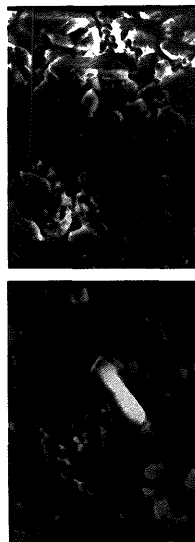


Fig. 5. SEM photographs of PbO_2 electrode after 60 cycles in 5 M H_2SO_4 , (a) without and (b) with 20 ppm FC-99.

After about 60 cycles, the surface morphology of the PbO_2 electrodes, in H_2SO_4 solution with or without FC-99, were examined by SEM. Electron micrographs of the electrode surface in a charged state are presented in Fig. 5. The crystals are PbO_2 and there are marked differences in the morphology of the positive electrode on addition of FC-99. The particle size is smaller, and the electrode surface is more porous, in the presence of FC-99. The smaller particle size of PbO_2 means that the electrode surface area is enlarged, while the higher porosity creates an increased contact area between the active material and the electrolyte. All of these changes give rise to an increase in the discharge capacity of positive electrode, i.e. greater utilization of the PAM. On the other hand, the higher porosity of the electrode decreases the contact between the grid and the PAM.

The effect of FC-99 on the discharge capacity and morphology of the positive electrode may be attributed to the adsorption of the FC-99 on the electrode during cycling. Such adsorption influences the morphology of the PbO_2 and increases the porosity of the electrode. The mechanism of the FC-99 action will be examined in further studies.

4. Conclusions

The addition of FC-99 to 5 M H_2SO_4 solution increases significantly the charges involved in the anodic and cathodic reactions on the PbO_2 electrode, as well as the respective peak

currents at any concentration. The discharge capacity of the PbO_2 electrode is increased, but the cycle life is decreased, when the electrolyte contains FC-99. The crystal size of PbO_2 is reduced and the electrode porosity is increased in the presence of FC-99. Indisputably, in view of the structural characteristics of FC-99 and other PFAS salts, the long-term stability of PFAS salts under strongly oxidizing conditions is excellent, and they are promising organic additives for the positive electrode of the lead/acid battery.

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