Influence of perfluorinated surfactants on the positive active-material of lead/acid batteries

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Abstract

The influence of perfluorinated anionic (FC-99), cationic (FC-135), and non-ionic (FSN) surfactants on the discharge capacities and cycle live of Planté positive electrodes in sulfuric acid are studied by cyclic voltammetry, charge/discharge cycling, X-ray diffraction, and scanning electron microscopy. The discharge capacities of PbO_2 electrodes, i.e., the utilization of the positive active-material, are increased for the electrolytes with FC-99 or FC-135, but the cycle live both surfactants are reduced. On the other hand, the presence of FSN has negligible influence on the discharge capacity and the cycle life of the PbO_2 electrode. The differences in the effects of the various types of perfluorinated surfactants are discussed with respect to the adsorption of perfluorinated surfactant molecules on the PbO_2 electrode surface during the charge and/or the discharge process. © 1998 Elsevier Science S.A.

Keywords: Positive active-material; Perfluorinated surfactants; Lead/acid batteries; Charge/discharge behaviour; Cycle life

1. Introduction

The lead/acid battery exhibits a low specific energy, both with respect to other secondary battery systems and to its own theoretical value. One of the main reasons for the low specific energy of a practical lead/acid battery is the poor utilization of the positive active-material (PAM). In commercial practice, lead/acid batteries are usually designed with an excess of negative active-material so that the capacity and the cycle life are strongly dependent on the active material in the positive plate. Thus, it is very important to improve the utilization of PAM in order to raise the performance of commercial lead/acid batteries. This objective has attracted the attention of scientists and engineers for a long time.

It has been found that the low utilization of the PAM is due to blockage of the pores by the discharge product of the cell, namely, lead sulfate. This hinders diffusion in the pores and leads to a lack of electrolyte [1]. Perfluorinated surfactants (PFSAS) possess excellent surface activity in aqueous solutions which enhances the diffusion of elec-

trolyte in the pores. Also, PFSAS can absorb on the surface of the $PbSO_4$ and/or PbO_2 crystals and cause a change in morphology of the PbO_2 crystals so as to enlarge the electrode surface area. Hence, PFSAS would be very suitable additives for the positive electrode, provided they are stable at the high potential experienced at this electrode. In fact, perfluoroalkylsulfonates have been patented for use as additives for positive electrodes [2–6]. We have also found that the addition of amine perfluoroalkylsulfonnate (FC-99) to sulfuric acid electrolyte is beneficial to the utilization of PAM, though the cycle life of the positive electrode is shortened [7]. The mechanism of the FC-99 action is still to be elucidated.

The present work is devoted to understanding the mechanism of the influence of the different types of PFSAS on the electrochemical behaviour of PbO_2 electrodes as positive plates in lead/acid batteries.

2. Experimental

The experimental details of the working electrode, electrolyte concentration, equipment and temperature of cyclic voltammetry, as well as the details of the 'test battery' construction, formation of the Planté electrode and cycling method, have been described elsewhere [7].

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Table 1
Properties of the PFSAS used in this work [8,9]

Surfactant	Molecular formula	Ionic type	Surface tension (dyne cm^{-1})	Remarks
FC-99	$C_nF_{2n+1}SO_3^-NH_4^+$ ($n \sim 8$)	anionic	$73^a \to 40(0.004\%)^b \to 23(0.04\%)^b$ (19%H$_2$SO$_4$)^c	Outstanding surface activity in acidic and oxidizing systems. Chemically stable with excellent water solubility.
FC-135	$C_nF_{2n+1}SO_2NHC_3H_6N^+(CH_3)_3I^-$ ($n \sim 8$)	cationic	$73^a \to 23(0.002\%)^b$ 17(0.02%)^b (10%H$_2$SO$_4$)^c	Outstanding activity in acid solutions. Excellent in basic and neutral solutions.
FC-170C	$C_nF_{2n+1}SO_2N(C_2H_5)(CH_2CH_2O)_xH$ ($n \sim 8$)	nonionic	$73^a \to 49(0.001\%)^b$ 22(0.01%)^b (10%H$_2$SO$_4$)^c	Excellent activity in neutral and acid solutions.
FC-129	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2COO^-K^+$ ($n \sim 8$)	anionic	$73^a \to 42(0.002\%)^b \to 27(0.02\%)^b$ (19%H$_2$SO$_4$)^c	Excellent leveling agent in alkaline systems. Good foamer.
FSN	$F(CF_2CF_2)_{3-8}H_2CH_2O(CH_2CH_2O)_xH$	nonionic	$76^a \to 29(0.001\%)^b \to 25(0.01\%)^b$ (25%H$_2$SO$_4$)^c	Excellent activity in alkaline, neutral and acid systems. Stable in heat, acids and alkalines, unstable in oxidizing agents.

[a] Surface tension of bulk solution without surfactant
[b] Concentration of surfactant (wt.%).
[c] Concentration of bulk solution.

The morphological aspects of the PbO_2 electrodes after about 60 charge/discharge cycles in 5 M H_2SO_4 without or with different PFSAS, were characterized by scanning electron microscopy (SEM) (Hitachi SEM X-650, Japan). The X-ray analysis of the crystal structure of the PbO_2 electrode after 60 cycles was performed by means of a Rigaku Rotafies diffractometer using the K α ray of copper ($\lambda_{K\alpha,Cu} = 1.5418$ Å).

The ionic types, molecular formula, and other properties of the PFSAS used in this work are given in Table 1 [8,9]. Since the commercial PFSAS all contain organic solvents and/or water, all PFSAS were subjected to prolonged heating at about 80 °C to remove volatile solvents before use. The treated PFSAS were then dissolved in double-distilled water. The surfactant with a hydrocarbon-based hydrophobic group (CHSAS), viz., cetyltrimethyl ammonium bromide (CTAB) was purchased from the BDH Company (Pool, UK).

3. Results

3.1. Cyclic voltammetric experiments

The cyclic voltammograms for lead electrodes (cathodically electrodeposited on a gold disc) in the 1.2 to 2.0 V (versus satuurated calomel electrode (SCE)) range in 5 M H_2SO_4 with 30 ppm (mg l^{-1}) of various PFSAS are shown in Figs. 1–3. The solid lines are the voltammo-
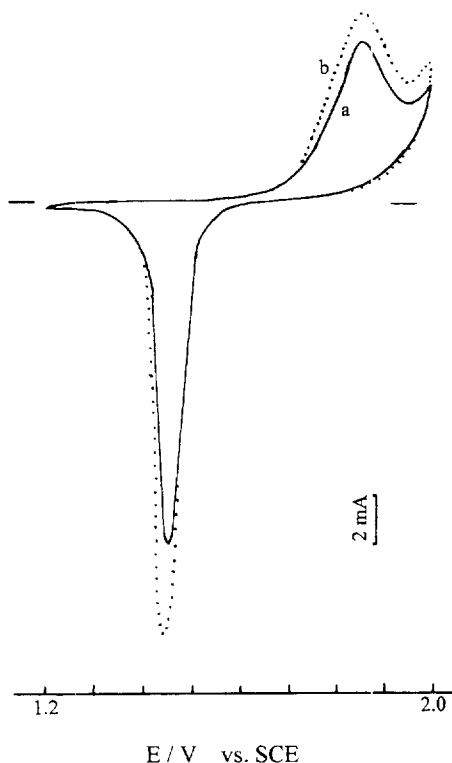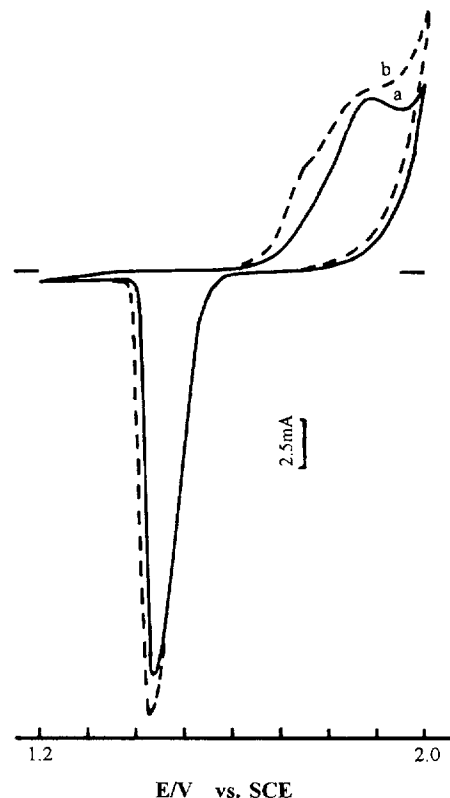

Fig. 2. Cyclic voltammograms for PbO_2 electrode (supported on a gold disc) in 5 M H_2SO_4: (a) without, and (b) with 30 ppm FC-135.

grams obtained after the lead electrodes were cycled for about 12 h in H_2SO_4 without PFSAS at a scan rate of 5 mV s^{-1} until there was no further increase in the peak current, i.e., when the deposited lead was converted completely to porous lead dioxide. Then, 30 ppm samples of various types of PFSAS were added individually to the H_2SO_4 electrolyte, respectively. The PbO_2 electrode was cycled continuously over the same potential range until the shape of the voltammogram did not change. The effects of these PFSAS after several hours of continuous cycling are represented by the dashed lines in Figs. 1–3. Obviously, the shapes of voltammograms did not change before and after the addition of FC-99 and FSN. With the addition of FC-135, however, a new anodic peak appears at 1.77 V in addition to that at 1.86 V which corresponds to the oxidation of $PbSO_4$ to PbO_2.

The molecular formula of FC-135 is $C_nF_{2n+1}SO_2NHC_3H_6N^+(CH_3)_3I^-$ ($n \sim 8$), so the new peak may result from either the oxidation of the hydrophobic chain $(C_nF_{2n+1}SO_2NHC_3H_6-)$ and/or I^- ions, or from the adsorption of hydrophilic groups $-N^+(CH_3)_3$ or hydrophobic chains on the electrode surface. To determine the exact cause of this new peak, the electrochemical behaviour of a pure lead was studied in H_2SO_4 with two other types of PFSAS (i.e., FC-170C and FC-129) whose hydrophobic chains are the same as that of FC-135, and one type of CHSAS (CTAB) whose hydrophilic group is

Fig. 1. Cyclic voltammograms for PbO_2 electrode (supported on a gold disc) in 5 M H_2SO_4: (a) without, and (b) with 30 ppm FC-99.

the same as that of FC-135 but the negative ions are Br⁻ ions, together with FC-135 (Fig. 4). As before, the anodic peak at 1.77 V appeared when the electrolyte contained FC-135. By contrast, this peak was not present when the H_2SO_4 electrolyte contained FC-170C, FC-129, or CTAB. Clearly, the new anodic peak in the voltammogram for PbO_2 in H_2SO_4 with FC-135 is due to the oxidation of I⁻ ions.

Since the concentration of FC-135 in the electrolyte is very low, the charge corresponding to the oxidation of I⁻ ions in FC-135 can be ignored. Therefore, the area under the anodic and cathodic peaks in Figs. 1–3 gives the charge involved in anodic (Q_a) and cathodic (Q_c) reactions on the positive electrode, respectively. Values of Q_a and Q_c, with and without various PFSAS, are tabulated in Table 2. Q_a^0, Q_c^0 and Q_a', Q_c' represent the charge before and after the addition of various PFSAS, respectively. Both Q_a and Q_c are increased at the presence of FC-99 and FC-135, compared with those in H_2SO_4 without additive. The addition of FSN, however, has negligible effect on the Q_a and Q_c charges.

To study the long-term stability of various PFSAS under strongly oxidizing conditions, cyclic voltammetric studies were carried out with a pure-lead electrode. Preparation of this electrode has been reported previously [7]. The various types of PFSAS were respectively added to 5 M H_2SO_4 after the electrode was cycled over the potential
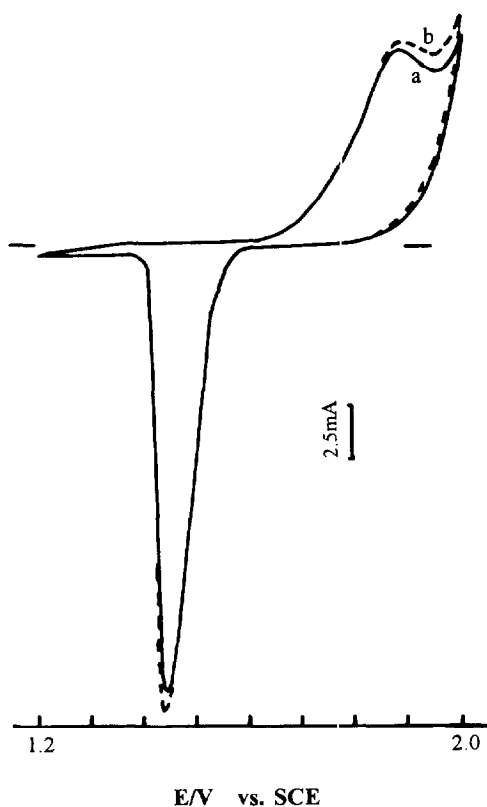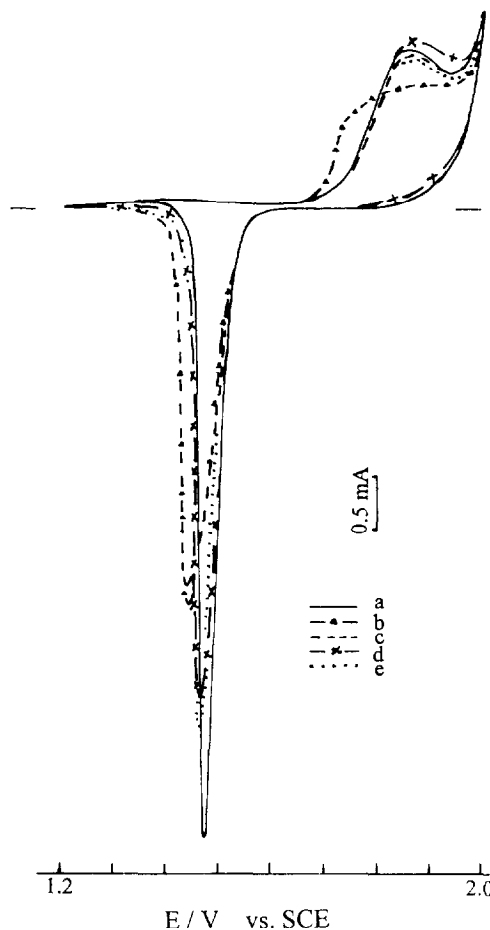

Fig. 4. Cyclic voltammograms for PbO_2 electrode in 5 M H_2SO_4 with various surfactants (30 ppm) at the 10th cycle: (a) SAS absent; (b) FC-135; (c) FC-170C; (d) FC-129, and (e) CTAB.

1.35 to 2.05 V (versus SCE) range for 50 cycles in the absence of any additive. The results were the same as those obtained on a PbO_2 electrode formed on a gold substrate. The shapes of the voltammograms of the lead electrode in H_2SO_4, with or without PFSAS, are somewhat similar to each other at any given cycle number, except for those obtained with 20 ppm FC-135. Typical cyclic voltammograms for the lead electrode in 5 M H_2SO_4 with 20 ppm FC-99 and 20 ppm FC-135 are shown in Figs. 5 and 6, respectively. The potential of point A is taken as the initial potential ($E_{i,o}$) for the oxygen evolution reaction (OER). The characteristic parameters of the cyclic voltammograms obtained in the 5 M H_2SO_4 without PF-

Fig. 3. Cyclic voltammograms for PbO_2 electrode (supported on a gold disc) in 5 M H_2SO_4: (a) without, and (b) with 30 ppm FSN.

Table 2
Charge involved in anodic (Q_a) and cathodic (Q_c) reactions on PbO_2 electrode in 5 M H_2SO_4 with different types of PFSAS (30 ppm)

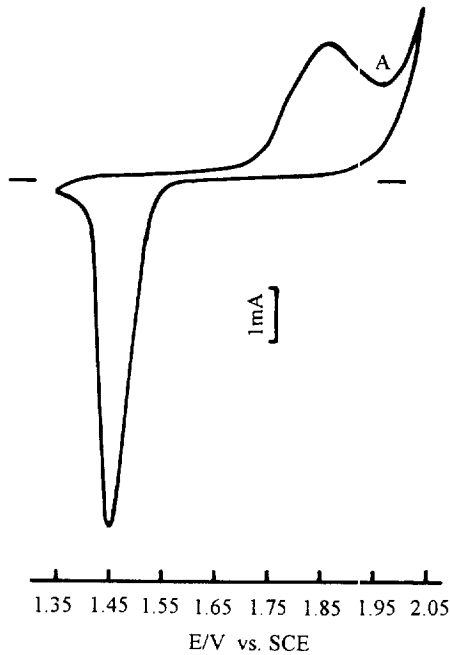| Surfactant	Q_a^0 (mC)	Q_a' (mC)	Q_c^0 (mC)	Q_c' (mC)
FC-99	258.64	292.75	194.73	232.29
FC-135	309.21	347.8	266.67	306.58
FSN	300.08	304	269.43	279.34

Fig. 5. Typical cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ with 20 ppm FC-99 at the 50th cycle; scan rate = 5 mV s^{-1}.
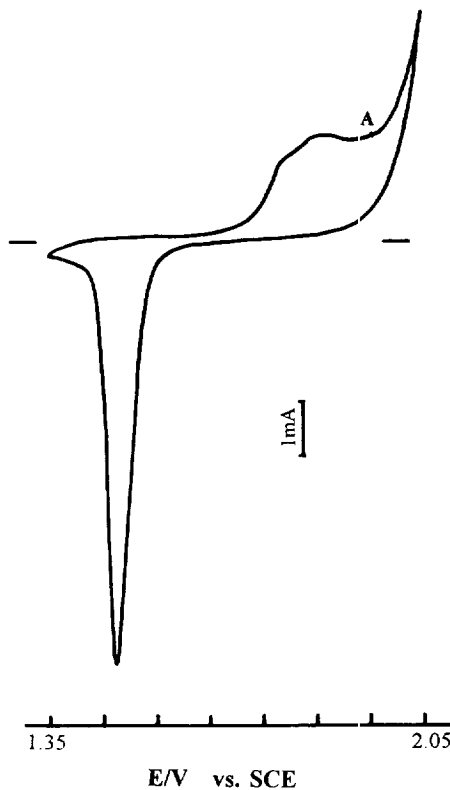
Fig. 6. Typical cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ with 20 ppm FC-135 at 50th cycle; scan rate = 5 mV s^{-1}.

Table 3
Characteristic parameters of cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ at different cycles

Cycle no.	$E_{p,a}$ (V)	$I_{p,a}$ (mA)	$E_{p,c}$ (V)	$I_{p,c}$ (mA)	$E_{i,o}$ (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	65.26	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 4
Characteristic parameters of cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ with 20 ppm FC-99 at different cycles

Cycle no.	$E_{p,a}$ (V)	$I_{p,a}$ (mA)	$E_{p,c}$ (V)	$I_{p,c}$ (mA)	$E_{i,o}$ (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

Table 5
Characteristic parameters of cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ with 20 ppm FC-135 at different cycles

Cycle no.	$E_{p,a}$ (V)	$I_{p,a}$ (mA)	$E_{p,c}$ (V)	$I_{p,c}$ (mA)	$E_{i,o}$ (V)	Q_a (mC)	Q_c (mC)
0	1.85	1.5	1.48	5.7	1.95	62.07	48.44
20	1.85	1.5	1.48	7.1	1.96	78.36	57.74
50	1.86	1.9	1.48	8.4	1.96	109.7	86.85
75	1.86	2.0	1.47	7.9	1.97	129.78	108.9
100	1.88	1.9	1.46	6.3	1.97	116.97	108.2
150	1.88	1.8	1.45	5.6	1.97	115.59	107.3

Table 6
Characteristic parameters of cyclic voltammograms for PbO$_2$ electrode in 5 M H$_2$SO$_4$ with 20 ppm FSN at different cycles

Cycle no.	$E_{p,a}$ (V)	$I_{p,a}$ (mA)	$E_{p,c}$ (V)	$I_{p,c}$ (mA)	$E_{i,o}$ (V)	Q_a (mC)	Q_c (mC)
0	1.85	1.7	1.48	3.7	1.95	61.3	45.37
20	1.86	1.7	1.48	6.6	1.95	65.26	55.35
50	1.88	2.4	1.48	6.8	1.95	83.39	77.19
75	1.86	2.1	1.48	7.0	1.95	92.02	83.03
100	1.87	2.2	1.48	7.4	1.95	90.25	88.92
150	1.87	2.1	1.48	7.1	1.96	90.04	84.72
175	1.87	1.9	1.48	6.9	1.95	94.82	90.54
200	1.88	2.0	1.48	6.8	1.95	105.13	93.07

SAS and with various PFSAS at different cycle numbers are presented in Tables 3–6, respectively. There is little shift in the potentials of the anodic ($E_{p,a}$) and the cathodic ($E_{p,c}$ peaks when FC-99 is contained in the electrolyte. On the other hand, the $E_{p,c}$ is virtually unchanged but the $E_{p,c}$ is shifted to more negative potentials at the presence of FC-135. This behaviour indicates that the reduction process of PbO_2 is hindered. The $E_{i,o}$ is shifted to more positive values, and the anodicand cathodic peak current, as well as the Q_a and Q_c charges, are increased when FC-99 or FC-135 is added to the electrolyte. The rate of PAM shedding is accelerated and the cycle life of the PbO_2 electrode is decreased after the addition of FC-99 or FC-135. The PAM begins to shed from the electrode at the 170th cycle and the 152nd cycle when the electrolyte contains FC-99 and FC-135, respectively. Alternatively, the addition of FSN has a slight influence on the characteristic values of the cyclic voltammogram obtained on a PbO_2 electrode in 5 M H_2SO_4, and the cycle life is greater than 200 cycles when the PbO_2 electrode is cycled in

Fig. 8. Changes in the (a) charging and (b) discharging capacity of a Planté positive electrode in 5 M H_2SO_4 with various surfactants during first 60 cycles. $I_c = I_d = 2$ mA, depth-of-discharge = 100%.
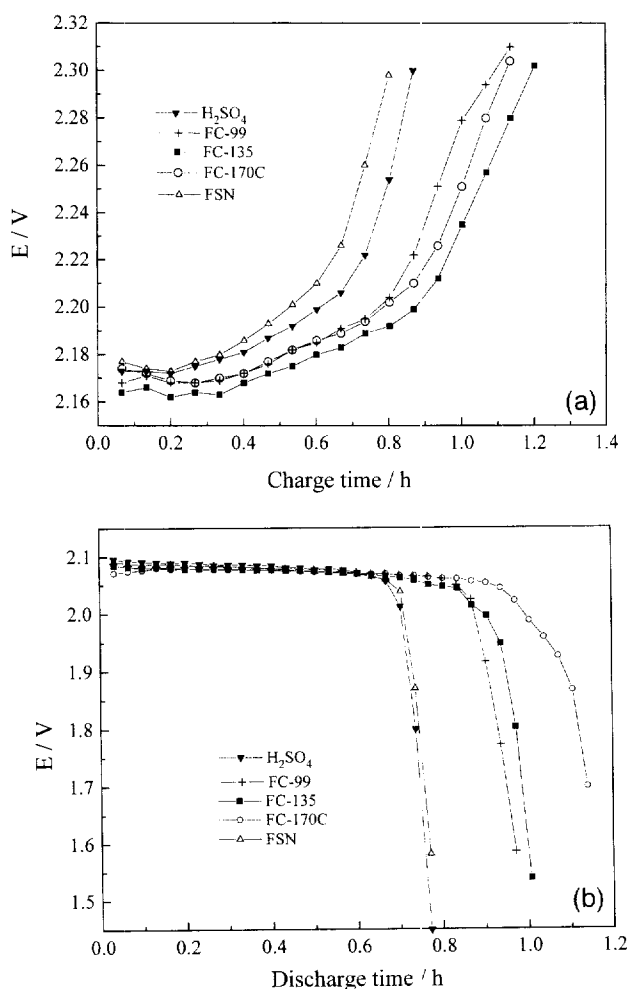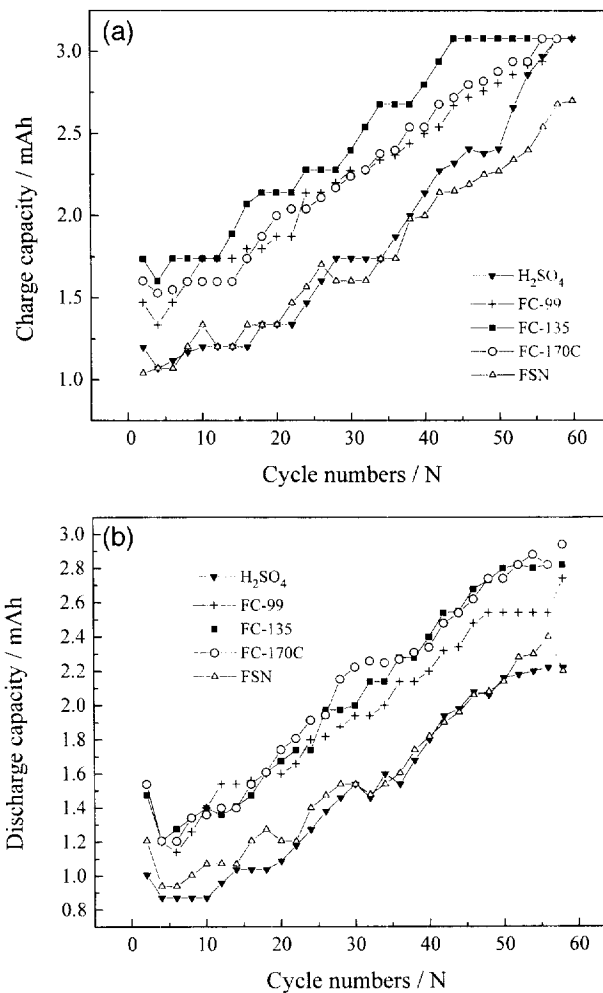

Fig. 7. (a) Charge and (b) discharge curves for Planté positive electrode in 5 M H_2SO_4 with various surfactants at the 30th cycle; $I_c = I_d = 2$ mA.

H_2SO_4 with FSN or without PFSAS. From these results, it can be concluded that the long-term stability of either FC-99 or FC-135 in the $PbO_2/PbSO_4/H_2SO_4$ system is good, and that the addition of FC-99 or FC-135 improves the active-material utilization before the onset of shedding from the positive electrode.

3.2. Charge / discharge cycling

The charge/discharge cycling experiments were carried out with Planté positive electrodes in 5 M H_2SO_4, with or without various types of PFSAS. The Planté positive electrodes were formed according to the procedure reported elsewhere [7], and then cycled in 5 M H_2SO_4 with 20 ppm of different PFSAS. The charge and discharge curves at the 30th cycle for Planté electrodes in 5 M H_2SO_4, with and without PFSAS, are presented in Fig. 7. The discharge potential of the PbO_2 electrode is affected negligibly when the electrolyte contained each type of PFSAS, but the

Table 7
XRD lines from a charged PbO_2 electrode in 5 M H_2SO_4 with various surfactants (30 ppm)

None d (Å)	I/I^0 (%)	FC-99 d (Å)	I/I^0 (%)	FC-135 d (Å)	I/I^0 (%)	FC-170C d (Å)	I/I^0 (%)	FSN d(Å)	I/I^0 (%)
4.246[a]	28.7	4.25[a]	65.8	4.267[a]	82.9	4.248[a]	72.1	4.259[d]	65.4
3.798[a]	19.1	3.798[d]	47.9	3.808[a]	38.2	3.808[a]	42.3	3.804[d]	47.4
3.501[b]	61.7	3.501[b]	58.2	3.511[b]	36.2	3.501[b]	79.8	3.506[b]	75.6
3.323[a]	70.2	3.323[a]	67.1	3.331[a]	45.4	3.328[a]	100	3.331[d]	91.0
2.997[a]	37.2	3.211[a]	20.5	3.217[a]	35.5	3.211[a]	32.7	3.215[a]	74.4
2.791[b]	100	2.997[a]	84.9	3.005[a]	50	3.001[a]	82.7	3.005[a]	98.7
2.693[a]	23.4	2.792[b]	75.3	2.798[b]	55.3	2.791[b]	86.4	2.794[b]	79.5
2.476[b]	27.6	2.693[d]	100	2.697[a]	100	2.691[b]	78.8	2.792[a]	43.6
2.27[a]	21.3	2.615[a]	23.3	2.619[a]	21	2.61[d]	59.6	2.697[a]	60.2
2.159[a]	27.6	2.479[b]	23.3	2.275[a]	26.3	2.476[b]	30.8	2.616[a]	28.2
2.063[a]	18	2.402[a]	11.6	2.161[a]	27.6	2.272[a]	28.8	2.48[b]	25.6
2.024[a]	14.4	2.27[d]	30.1	2.066[a]	80.3	2.161[a]	31.7	2.406[b]	23.1
1.853[b]	68	2.159[a]	38.4	2.03[a]	17.1	2.063[a]	72.1	2.275[a]	28.2
1.752[b]	19.1	2.064[a]	65.8	1.855[b]	43.4	2.026[a]	40.4	2.163[a]	34.6
1.567[b]	23.4	2.02[a]	30.1	1.569[b]	18.4	1.989[a]	25	2.066[a]	100
		1.853[b]	68.5			1.852[b]	90.4	2.028[a]	56.4
		1.752[b]	16.4			1.567[b]	34.6	1.971[a]	34.6
		1.567[b]	23.3					1.855[b]	73.1
								1.569[b]	21.8

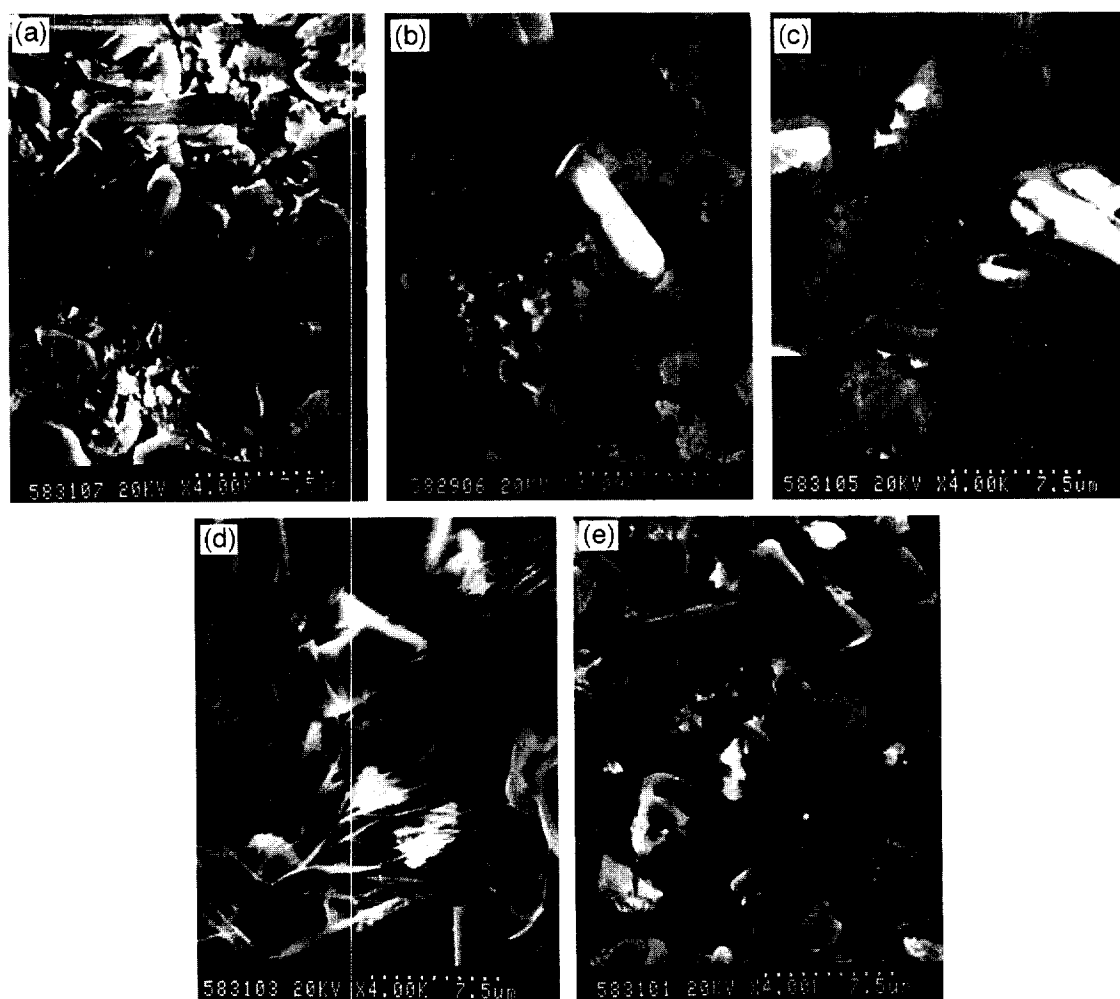[a] PbO_2.
[b] $PbSO_4$.

Fig. 9. SEM for a Planté positive electrode after 6C cycles (charged phase) in 5 M H_2SO_4 with various surfactants (20 ppm): (a) SAS absent; (b) FC-99; (c) FC-170C; (d) FC-135, and (e) FSN.

charge potential is lower when the electrolyte is doped with FC-99, FC-135 or FC170C, compared with that for PbO_2 in 5 M H_2SO_4 without PFSAS. By contrast, the charge potential is increased in the presence of FSN. Furthermore, the charge time is prolonged and the discharge capacity of the positive electrode is increased, to varying degrees, when the electrolyte contains FC-99, FC-135 or FC-170C.

From the dependence of the capacity of the PbO_2 electrodes on cycle number during charge/discharge cycling (Fig. 8), it can be seen that the discharge and charge capacities of positive electrodes in 5 M H_2SO_4 with FC-99, FC-135 or FC-170C are greater than those in electrolyte without PFSAS at each corresponding cycle number. These results agree with those obtained from previous cyclic voltammetric (CV) experiments. Similarly, the presence of FSN in the electrolyte exerts a negligible effect on the charge/discharge capacity of the Planté electrode. It is interesting to note, however, that the presence of FSN in the electrolyte is somewhat beneficial to the discharge capacity of the Planté positive electrode in H_2SO_4 during the first 25 cycles (Fig. 8(b)). As cycling proceeds, the beneficial effect of FSN on the discharge capacity becomes smaller and smaller, and is lost after 30 cycles.

The crystal structure of PbO_2 in a positive electrode cycled in H_2SO_4 solution with or without PFSAS for about 60 cycles was analyzed by the X-ray diffraction (XRD) technique. Even in the charged state, the surface of the PbO_2 electrode is still comprised of $PbSO_4$ crystals (Table 7). In addition, there are marked differences in the morphology of these positive electrodes (Fig. 9). The particle size of the PbO_2 crystals is obviously smaller and the porosity of electrode surface is larger in the presence of some PFSAS (FC-99, FC-135, FC-170C) than in the absence of PFSAS or with FSN. Moreover, the network structure of the electrode surface is excellent in the presence of these PFSAS. The smaller particle size of the PbO_2 means that the surface area is enlarged, and the higher porosity of the electrode creates a higher contact area between the active material and the electrolyte. All of these changes increase the discharge capacity of positive electrode, i.e., raise the utilization of PAM. On the other hand, the smaller particle size and the higher porosity of the electrode surface decrease the contact density between the PAM and the substrate metal (especially, in the case of the needle shape that is formed when FC-135 is present in the electrolyte). This promotes the shedding of PAM from the grid and, thus, the cycle lives of positive electrodes in lead/acid batteries are decreased. The particle size of the PbO_2 crystals is still large and the porosity of electrode surface does not change when the electrolyte contains FSN. These results indicate that the changes in the porosity and the particle size of the PAM are the main reasons for the changes in the discharge capacity and cycle life of the positive electrode.

4. Discussion

The different influence of various types of PFSAS on the utilization of PAM are mainly due to different adsorption degrees of various types of PFSAS on the positive electrode, together with the stability of various PFSAS molecules on the positive electrode in 5 M H_2SO_4.

It is well known that the adsorption of compounds at the electrode/electrolyte interface is governed by, at least, two important factors: (i) electrostatic force (attraction, repulsion), and (ii) specific chemical interactions (such as the chemical interaction between the specific group of the adsorbate and specific sites on the electrode surface) [10]. The first factor is determined by the sign and the magnitude of the surface charge. The surface charge can be obtained once the differential double-layer capacitance and the potential of zero charge (PZC) are known. If the double-layer capacitance not available, however, only the sign of the surface charge can be determined if the PZC is known.

The value of the PZC of lead dioxide in 4 M H_2SO_4 is about 1.46 V (versus SCE) [11]. Therefore, the surface of a PbO_2 electrode is charged positively during overcharge and the later stages of charging, and charged negatively during discharge and the early stages of charging. Because FC-99 is an anionic and FC-135 a cationic surfactant, the FC-99 molecules can adsorb on the electrode surface of the positively charged electrode during overcharge and the later stages of charging, and the FC-135 molecules can adsorb on the electrode surface during discharge and the early stages of charging. The adsorption of PFSAS on the electrode surface causes the PbO_2 crystals to become smaller and more porous thus, the porosity of the PAM and the electrode surface area are both enlarged (Fig. 9(b) and (d)). At the same time, the addition of PFSAS may reduce the surface tensions of the electrode/electrolyte interface and enable the electrolyte to reach the inner parts of the micropores on the electrode surface. Consequently, the discharge capacity of the positive electrode is significantly increased when the PbO_2 electrode is cycled in electrolyte with FC-99 or FC-135. Nevertheless, the higher porosity of the electrode weakens the contact between the positive active material and the substrate metal, i.e., accelerates the rate of PAM shedding from the substrate metal. Therefore, the cycle lives of positive electrodes are shortened with these two PFSAS (see Tables 4 and 5).

On the other hand, the presence of FSN in the electrolyte has negligible effect on the overvoltage of the OER and the utilization of the PAM. FSN is a non-ionic type of PFSAS, and there is no electron-rich group in its molecular structure. In aqueous solution, the FSN molecules remain neutral and the adsorption of FSN on the solid surface is weak. Another, or maybe more important, reason is that FSN might be decomposed on the positive electrode at a high potential (Table 1). Cha and Zu also found that FSN can be oxidized on a platinum electrode at positive poten-

tials (i.e., above 1.0V versus SCE) [12]. The increase in discharge capacity of the PbO_2 electrode during the first 25 cycles when the electrolyte contains FSN indicates that FSN can adsorb on the electrode surface during this earlier stage of cycling (Fig. 8(b)). On the other hand, the long-term stability of FSN under strongly oxidizing conditions is bad so that FSN might be decomposed progressively during cycling and the favorable effect of FSN cannot be maintained after 30 cycles.

In most studies of the OER on lead dioxides [13–16], a generalized theory for the mechanism is formulated in which the first step usually involves adsorption of the OH_{ad} intermediate from discharge of H_2O in acid or OH^- in alkaline solution, followed by a rate-controlling step of electrochemical oxidation of OH_{ad} to form a second intermediate O_{ad} which undergoes chemical recombination and gives rise to O_2 evolution [17]. The adsorption process of OH_{ad} intermediate would be hindered by the presence of FC-99 because the active sites of the electrode surface are occupied by the molecules of FC-99 during the overcharge and the later stages of charging, and thus shift the OER to more positive potentials (Table 4). Nevertheless, the potential of the OER is also shifted to positive values when the electrolyte contains a cathodic type of PFSAS, namely FC-135 (Table 5). This behaviour conflicts with the electrostatic theory of adsorption. To understand this conflict, it is necessary to consider the second factor that influences the adsorption of compounds on the electrode/electrolyte interface, viz., chemical interactions. A electron-rich group, $-SO_2-NH-$, is contained in the molecule of FC-135. Thus, during overcharge and the later stages of charging, the electron-rich group in the FC-135 molecules will interact with the positive sites of the positively charged PbO_2 electrode, and cause adsorption on the positively charged surface. Thus, the potential of the OER is shifted to more positive potentials. To prove this hypothesis, a non-ionic PFSAS, FC-170C, whose hydrophobic chain contains the same electron-rich group as FC-135, was evaluated in charge/discharge cycling tests. In fact, the overvoltage of the OER was reduced when FC-170C was added to the H_2SO_4 electrolyte (Fig. 7(a)). Therefore, the FC-135 molecules can adsorb on the positive electrode during either charge or discharge and, thereby invoke a large influence on the formation of the crystals of $PbSO_4$ and PbO_2. During discharge, the molecules of FC-135 adsorb on the PbO_2 crystals via their hydrophilic groups to hinder the reduction process of PbO_2 and the deposition process of the reaction product ($PbSO_4$) on the surface of PbO_2 crystals; simultaneously, molecules of FC-135 can both adsorb on the electrode surface via their hydrophilic group during the early stages of charging, and on the positively

charged electrode surface via their electron-rich groups at the end of charge and the overcharge. This behaviour gives rise to a smaller particle size of formed PbO_2 crystals in the charge process and a larger surface area of the positive electrode, and also inhibits blockage of the micropores of the electrode surface by $PbSO_4$ crystals (Fig. 9(d) and Table 5).

5. Conclusions

The addition of various types of PFSAS to 5 M H_2SO_4 electrolyte exert different effects on the discharge capacity and the cycle life of the PbO_2 electrode. In general, molecules of the PFSAS that can adsorb on the positive electrode during either charge or discharge all reduce the particle size of PbO_2 crystals and increase the porosity of the electrode surface when the PbO_2 electrode is cycled in electrolyte with these PFSAS (FC-99, FC-135 and FC-170C). By virtue of this behaviour, the utilization of the positive active-material is enhanced. This advantage is offset, however, by a reduced cycle life of the positive electrode because of the weakening of the contact between the active material and the grid. On the other hand, FSN molecules are unstable in strong oxidization conditions and can be decomposed after a few charge/discharge cycles, so that there is little influence of FSN on the active-material utilization and the cycle life of the positive electrode.

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