

Influence of perfluorinated surfactants on the electrochemical behaviour of a lead electrode in sulfuric acid solution

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Abstract

The influence of various types of perfluorinated surfactants and their analogous hydrocarbon chain surfactants on the electrochemical behaviour of a lead electrode in sulfuric acid is studied by linear sweep voltammetry and cyclic voltammetry. The hydrogen evolution reaction is affected mainly by the type of the hydrophobic chain of the added surfactant (perfluorinated or hydrogenated). Nevertheless, these surfactants exert little expander action on the negative electrode, or even show an adverse effect on the discharge capacity of the lead electrode. A possible explanation is given in terms of the adsorption properties of different surfactants on the electrode surface during charge and discharge. © 1998 Elsevier Science S.A.

Keywords: Battery; Electrochemical behaviour; Perfluorinated surfactants; Lead electrode; Sulfuric acid; Charge–discharge

1. Introduction

It has been shown recently that the utilization of positive active-material in lead–acid batteries can be raised when certain perfluorinated surfactants (PFSAS) are used as additive [1,2]. Because the solubilities of the PFSAS are generally good in H₂SO₄ solution, and the PFSAS are also used as electrolyte additives in some cases [3], the electrochemical behaviour of a lead electrode as the negative plate in a lead–acid battery might be affected by such additives. Therefore, it is essential to study the influence of PFSAS on the electrochemical behaviour of a lead electrode together with a lead dioxide electrode. Although influence of different types of PFSAS on the properties of a PbO₂ electrode in H₂SO₄ have been studied previously [2], there has been little investigation of the influence of the various types of PFSAS on the electrochemical behaviour of the lead electrode in H₂SO₄.

In general, the materials used as negative-plate additives are mainly classified as two types, namely, inhibitors

and expanders. The role of inhibitors is to increase the overvoltage for the hydrogen-evolution reaction (HER) on negative plates and to lower the self-discharge rate of negative plates, while expanders are used to restrain the surface area shrinkage of negative active materials during cycling and to postpone the passivation of negative plates. Therefore, the influence of PFSAS on the electrochemical behaviour of a lead electrode in H₂SO₄ will be studied from these two aspects.

The action of expanders is often studied by cyclic voltammetry (CV), as just proposed by Mahato [4,5]. The effects of additives on the properties of negative plates obtained by CV were compared with those displayed by charge–discharge cycling with a 98-Ah battery, and it was found that the results were the same. Now, the CV technique is used widely in the pre-selection of additives for negative plates as a quick, semi-quantitative method [6–9]. On the other hand, the inhibitor action of an additive is usually studied by linear sweep voltammetry (LPV) [6] in order to illustrate the effect of the additive on the gassing behavior on the negative electrode.

The main purpose of the work reported here is to compare the effect of PFSAS and their analogous hydrogenated chain surfactants on the electrochemical behaviour of a lead electrode in 5 M H₂SO₄, and to obtain a comprehensive understanding of the use of PFSAS as additives in lead–acid batteries.

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2. Experimental

The working electrode was a spec-pure lead disc (Johnson Matthey Chemicals, Royston, UK) that was embedded in a PTFE holder with an exposed area of 0.283 cm^2 . A platinum sheet was used as the counter electrode, and the reference electrode was a saturated calomel electrode (SCE), against which all potentials are reported. The electrochemical cell was maintained in a thermostatically controlled water bath at $25 \pm 0.2^\circ\text{C}$. The treatment of the electrode prior to the experiment, the electrolytic cell, and the instrumentation used have been described previously [9,10].

The molecular formula of various types of PFSAS and other properties are given in Ref. [2]. Three types of carbon–hydrogen chain surfactants (CHSAS) were used in present work, i.e., cationic type: cetyltrimethyl ammonium bromide (CTAB) (BDH, Pool, UK); anionic type: sodium dodecyl-benzenesulfonate (SDBS) (BDH) and sodium dodecyl sulfate (SDS) (Sigma Chemical); non-ionic type: (Tween-20) (Sigma). The surfactants (SAS) were added to the H_2SO_4 electrolyte before a chemically polished lead electrode was introduced to the cell.

3. Results and discussion

3.1. Effects on HER

The negative potential sweep curves at 5 mV s^{-1} from the rest potential of the lead electrode to -1.0 V in $5 \text{ M H}_2\text{SO}_4$ with different types of SAS (30 ppm) are shown in Figs. 1–3, respectively. The rate of the HER at the lead

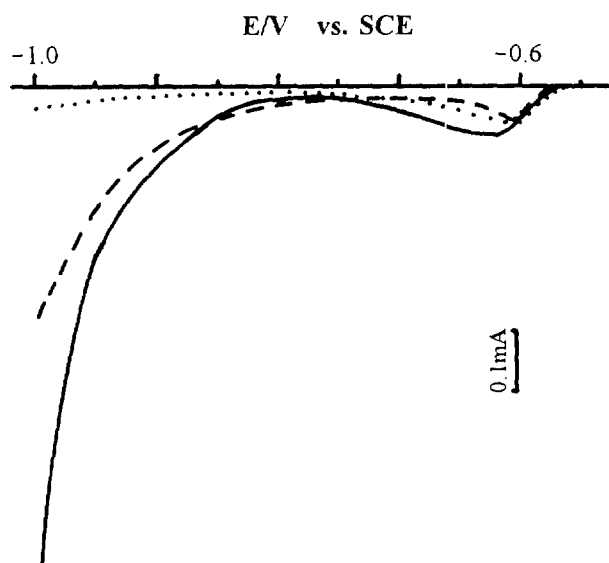


Fig. 1. The effect of non-ionic SAS (30 ppm) on the HER on a lead electrode in $5 \text{ M H}_2\text{SO}_4$. Solid line, SAS absent; dashed line, FSN; dotted line, Tween-20.

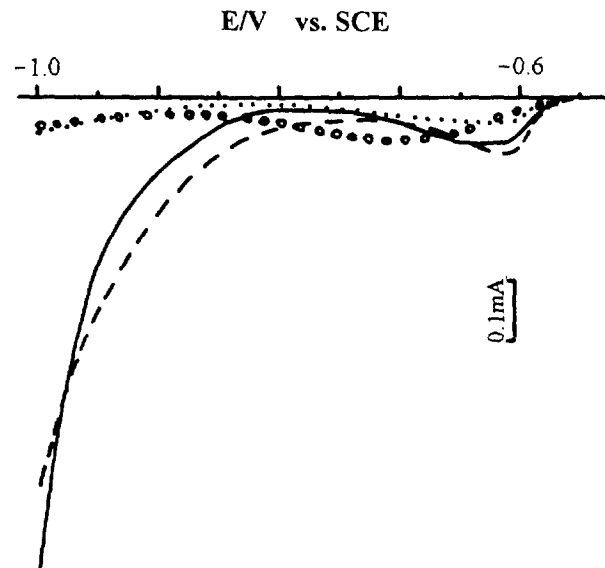


Fig. 2. The effect of anionic SAS (30 ppm) on the HER on a lead electrode in $5 \text{ M H}_2\text{SO}_4$. Solid line, SAS absent; dashed line, FC-99; dotted line, SDBS; circled line, SDS.

electrode is decreased markedly when any types of CHSAS is added to the electrolyte. This indicates that the presence of all types of CHSAS can raise the overvoltage of the HER. By contrast, the presence of various types of PFSAS exerted different influences on the overvoltage of HER. The addition of FSN increases the overvoltage of HER slightly, but the effect is much less than that of its analogous CHSAS (Tween-20). On the contrary, the presence of FC-99 in $5 \text{ M H}_2\text{SO}_4$ causes little decrease of the overvoltage of HER, and the potential of HER is shifted to much more positive potential when the electrolyte contains

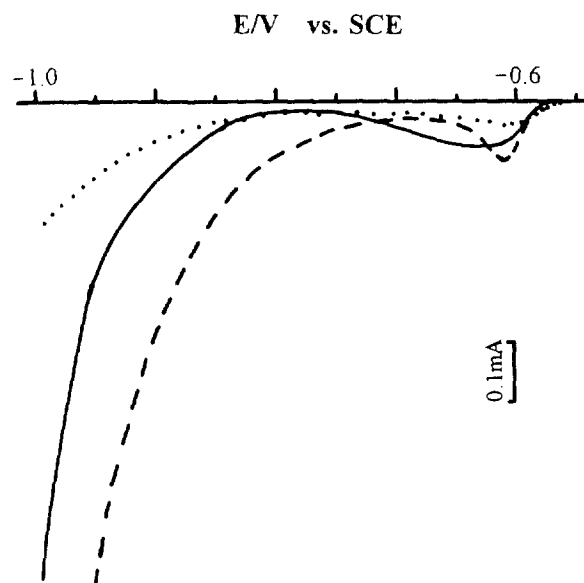


Fig. 3. The effect of cationic SAS (30 ppm) on the HER on a lead electrode in $5 \text{ M H}_2\text{SO}_4$. Solid line, SAS absent; dashed line, FC-135; dotted line, CTAB.

FC-135. The later effect indicates that FC-135 is unsuitable as an inhibitor in lead–acid batteries.

Obviously, the differences in the influence of the different SAS on the overvoltage of the HER caused by the different hydrophilic groups, or by the different function groups in the same type of hydrophobic chain, are much less than those caused by the different types of the hydrophobic chains of these SAS (perfluorinated chain or hydrogenated chain). In brief, the overvoltage of the HER is increased if the hydrophobic chain of the surfactant is hydrogenated, irrespective of whether its hydrophilic group is anionic (SDBS, SDS), cationic (CTAB), or non-ionic (Tween-20) type, or whether its hydrophobic chain is an aliphatic (SDS, Tween 20, CTAB) or aromatic (SDBS) species. On the other hand, when the hydrophobic chain is perfluorinated there is only a slight beneficial effect of the SAS, or even a deleterious effect. The mechanism of the different influences of the various types of SAS has still to be determined.

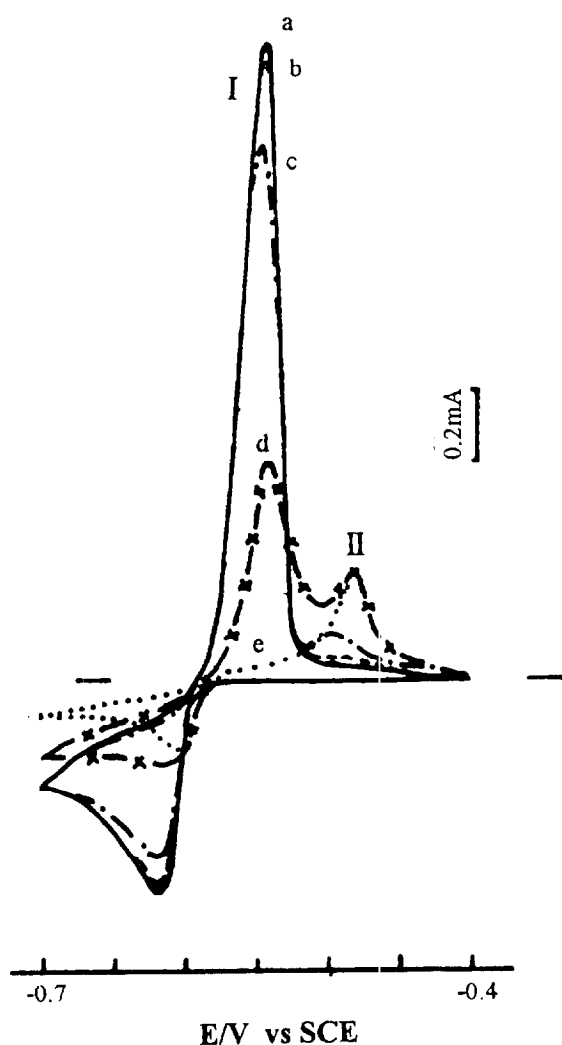


Fig. 4. The effect of FC-99 concentration in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. FC-99 concentration: (a) 0; (b) 10; (c) 20; (d) 30; and (e) 40 ppm.

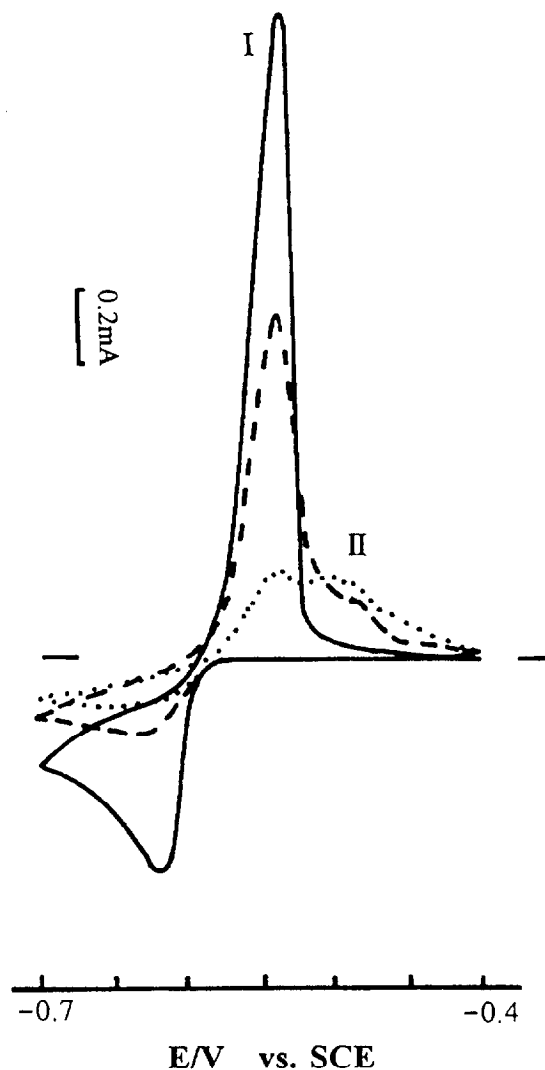


Fig. 5. The effect of anionic SAS in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. Solid line, CHSAS absent; dashed line, 30 ppm SDS; dotted line, 30 ppm SDBS.

3.2. Effects on the cyclic voltammetric curves

The influence of various SAS on the voltammograms of a lead electrode in 5 M H_2SO_4 over the potential range -0.7 to -0.4 V after 15 cycles at a scan rate of 5 mV s^{-1} is illustrated in Figs. 4–9. The solid lines represent the ‘typical voltammogram’ obtained in the absence of additive. The anodic current is due to the oxidation of lead to lead sulfate and the cathodic current is due to the reverse reaction. The area under the anodic and cathodic peaks gives the charge involved in anodic (Q_a) and cathodic (Q_c) reactions on the lead electrode, respectively.

The effect of the concentration of FC-99 on the cyclic voltammograms is presented in Fig. 4. Not only the Q_a and Q_c charges, but also the anodic and cathodic peak currents, decrease gradually as the concentration of FC-99 increases from 0 to 30 ppm. In addition, a new anodic peak (II) appears in the voltammograms at -0.47 V,

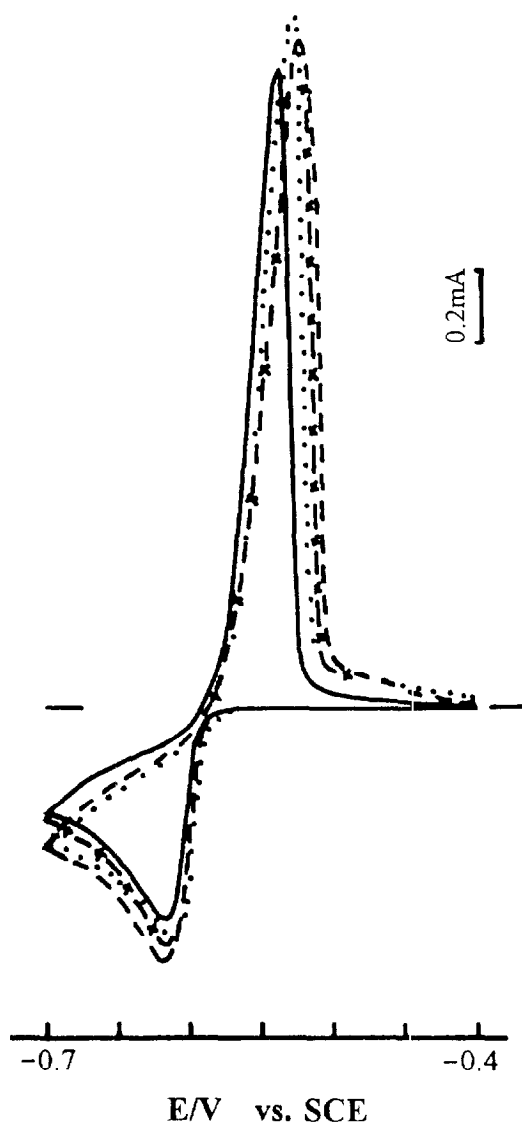


Fig. 6. The effect of FSN concentration in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. FSN concentration: (a) 0; (b) 10; (c) 20; and (d) 30 ppm.

which is positive to the anodic peak (I) at -0.55 V that corresponds to the oxidation of lead. The height of peak II rises gradually with increase in the FC-99 concentration. Moreover, peak II becomes the only anodic peak when the FC-99 concentration is ≥ 40 ppm. On the other hand, this is only a single cathodic peak that shows little shift in potential. The current of this peak and the Q_c charge decrease with increase in the concentration of FC-99.

There are also two anodic peaks in the CV curves in the presence of 30 ppm SDS and SDBS, whose hydrophilic group is the same or similar to FC-99. These peaks correspond to the process that occurs on the lead electrode with 30 ppm FC-99 (Fig. 5). The potential of the cathodic peak ($E_{p,c}$) is unaffected by the presence of SDBS and SDS, but the cathodic peak current and the Q_c are decreased markedly.

The addition of FSN increases both the Q_a and the Q_c charge (Fig. 6 and Table 1). This beneficial action diminishes as the FSN concentration is increased above 10 ppm. The presence of non-ionic CHSAS (Tween-20) also increases both Q_a and Q_c , though its benefit is smaller than that of FSN at the same concentration (Fig. 7). The potential of the anodic peak ($E_{p,a}$) is shifted to positive values in the presence of FSN and Tween-20. This suggests that the oxidation of lead is hindered by either FSN or Tween-20.

The influence of FC-135 concentration is different from that of FC-99 or FSN (Fig. 8). At a low concentration (10 ppm), the Q_a is virtually unaffected but the Q_c is increased. $E_{p,a}$ and $E_{p,c}$ are both shifted to a more positive potentials, showing that the oxidation of lead is hindered but the reduction of $PbSO_4$ is enhanced by the addition of

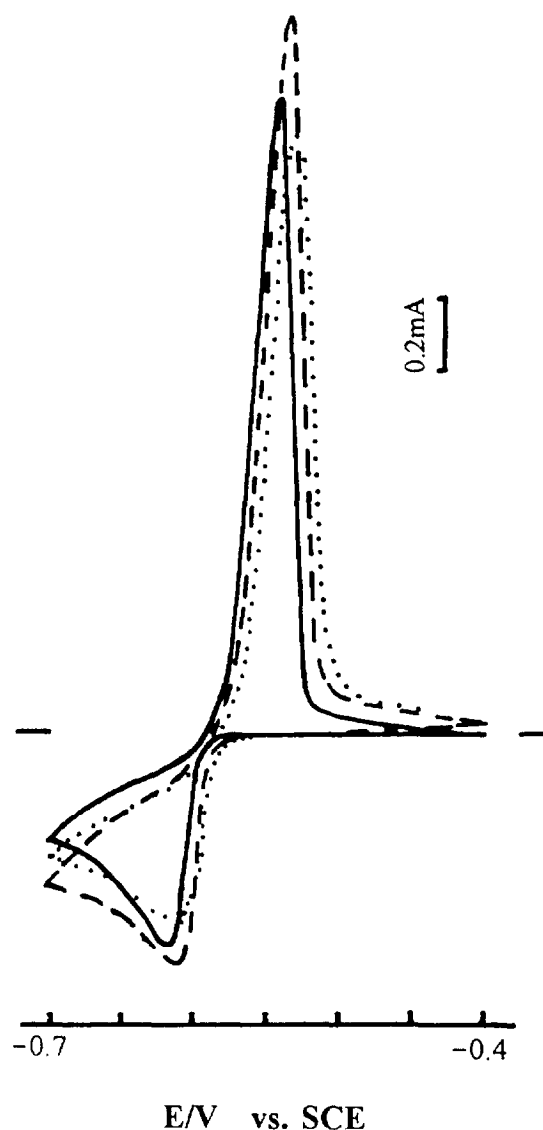


Fig. 7. The effect of non-ionic SAS in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. Solid line, SAS absent; dashed line, 30 ppm FSN; dotted line, 30 ppm Tween-20.

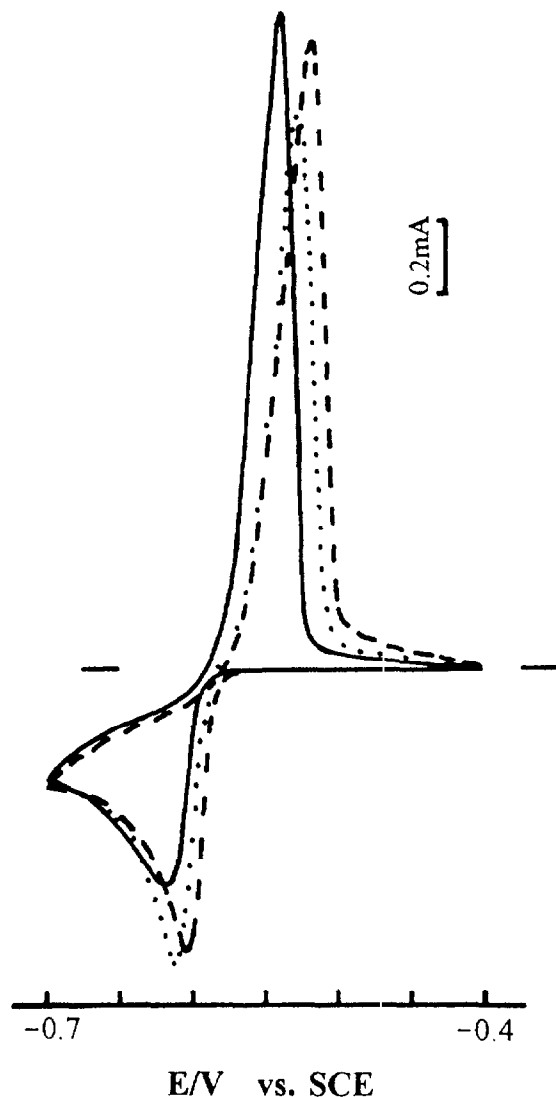


Fig. 8. The effect of FC-135 concentration in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. Solid line, FC-135 absent; dashed line, with 10 ppm FC-135; dotted line, with 30 ppm FC-135.

FC-135. By contrast, the Q_a is reduced by the presence of FC-135 at a higher concentration (30 ppm), and the Q_c is increased further. The effect on $E_{p,c}$ disappears but $E_{p,a}$ is shifted to a higher value. The Q_a and Q_c charges at a lead electrode in H_2SO_4 with 30 ppm CTAB are much less than those in the absence of CTAB, and $E_{p,a}$ and $E_{p,c}$ are unaffected by the presence of CTAB (Fig. 9).

In view of the effect of an additive on the discharge capacity of the negative plate in a lead–acid battery, which corresponds to the Q_c charge of a lead electrode in sulfuric acid, the anionic SAS (FC-99, SDS, SDBS) and the cationic CHSAS (CTAB) are unfavorable. The effect of FC-135 is negligible. Only the non-ionic SAS (FSN and Tween-20) display expander action on the lead electrode. The different behaviour may be due to the differences in the adsorption behaviour of the different SAS molecules on the electrode surface.

There are two factors that are responsible for the adsorption that occurs between the surfactant molecules and the electrode surface. One is the electrostatic force and the other is the specific chemical interaction [11]. The adsorbed molecules can affect the electrode kinetics in two ways. First, if the adsorbed molecules do not take part in the electrochemical reaction, the surface phase of the electrode and the distribution of potential at the interface will be affected by the adsorbed molecules. Furthermore, the surface concentration of the reactive particles and the activation energy of the electrochemical reaction will be changed. Second, if the reactive particles or the produced material (including intermediate particles) adsorb on the electrode surface, then the electrode kinetics are directly influenced by these adsorbed particles. No matter which way the adsorbed molecules influence the electrochemical

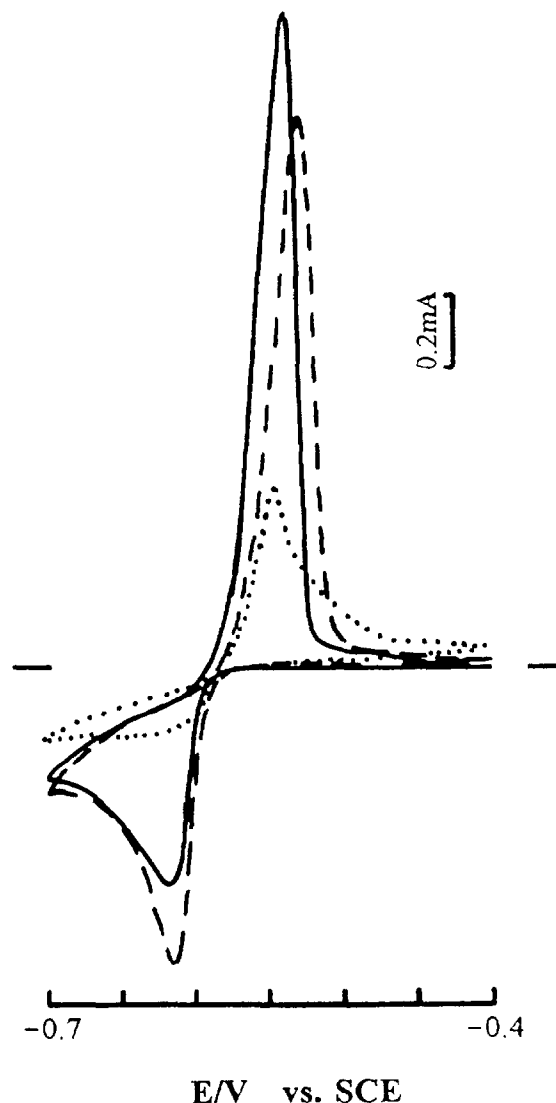


Fig. 9. The effect of cationic SAS in 5 M H_2SO_4 on voltammograms for a lead electrode on 15th cycle. Solid line, SAS absent; dashed line 30 ppm FC-135; dotted line, 30 ppm CTAB.

Table 1

The characteristic values of the cyclic voltammograms obtained for a lead electrode in 5 M H₂SO₄ with different concentrations of FSN

Concentration (ppm)	$I_{p,a}$ (mA)	$E_{p,a}$ (V)	$I_{p,c}$ (mA)	$E_{p,c}$ (V)	Q_a (mC)	Q_c (mC)
0	1.75	-0.538	0.58	-0.618	9.76	11.56
10	1.84	-0.525	0.70	-0.619	14.62	15.58
20	1.82	-0.525	0.66	-0.615	12.62	14.98
30	1.97	-0.530	0.64	-0.615	12.42	13.74

behaviour of a electrode, the molecular orientation of the adsorbed molecules is the most important factor.

Unfortunately, because of the complicated composition of the surface of a lead electrode in H₂SO₄ in different potential ranges, it is difficult to obtain a clear description of the molecular orientation of the adsorbed SAS molecules on the electrode surface. The following qualitative discussion on the molecular orientation of the various adsorbed surfactant molecules is based simply on the above two factors.

First, it is useful to recall the mechanism of a lead electrode in the charge–discharge process. The oxidation of lead in sulfuric acid can take place via two parallel paths: a dissolution–pre-cipitation process, and a solid-state reaction that involves direct attack by the sulfate anion on the lead surface [12]. In the oxidation process, lead dissolves to produce lead ions (Pb²⁺) or soluble Pb(II) ions when the voltage is below a critical potential, and these soluble ions diffuse through the electrolyte and react with sulfate ions in the diffusion layer. The resulting PbSO₄ crystals deposit on the lead surface if the solubility product is exceeded. The deposition process occurs in the diffusion layer. When the voltage is moved to a positive potential and reaches the critical value of solid reaction, the sulfate ions in the electrolyte can react directly with the lead to form a solid PbSO₄ phase instead of via a dissolution process. Thus, the discharge process of a lead electrode in sulfuric acid is an anodic oxidation in concert with a following chemical deposition reaction. On the other hand, the charge process involves the reduction of Pb(II) ions

that arise from the dissolution of PbSO₄ crystals. The dissolution and recrystallization of PbSO₄ crystals is an important step in the oxidation–reduction reactions on a lead electrode in H₂SO₄.

The value of the potential of zero charge of lead in 4 M H₂SO₄ is about -0.84 V [13]. Therefore, there are positive charges on the surface of a lead electrode in the potential range -0.7 to -0.4 V. Also, anions in the electrolyte (including sulfate ions and other negative additives) and the molecules that contain electron-rich groups are preferentially adsorbed on the positive-charged lead surface.

Since FC-99 is a single-chain, strongly polar, perfluoroalkylsulfonate salt, its molecules might adsorb perpendicularly on the metallic lead surface via their hydrophilic heads together with sulfate ions. The soluble Pb(II) ions produced from the oxidation of lead might react with the sulfonate groups of the adsorbed FC-99 molecules to form a ‘lead–sulfonate’ complex intermediate, together with SO₄²⁻ to form a PbSO₄ passive film. This would explain the appearance of two anodic peaks in the voltammograms. The coverage of the adsorbed FC-99 molecules on the active sites of the lead electrode increases with an increase in the FC-99 content in the electrolyte (Fig. 10). It is possible that the adsorbed FC-99 molecules form a hydrophobic layer between the lead surface and the bulk solution and thus, exert a repulsive force upon the encroaching hydrous sulfate ions. As the concentration of FC-99 reaches 40 ppm, a dense hydrophobic layer is formed by the adsorbed molecules (Fig. 10e) and the hydrous sulfate ions of the bulk solution are prevented completely from approaching the surface of the electrode, and the soluble Pb(II) ions react totally with the adsorbed FC-99 molecules. Hence, only one anodic peak corresponds to the formation of ‘lead–sulfonate’ on the voltammogram and the formation process of PbSO₄ is completely suppressed (Fig. 4). Fig. 4e also shows that the reduction potential of ‘lead–sulfonate’ is identical to that of PbSO₄, which means that the cathodic peak corresponding to the reduction of ‘lead–sulfonate’ overlaps the cathodic peak of the reduction of lead sulfate and, thereby, the cathodic

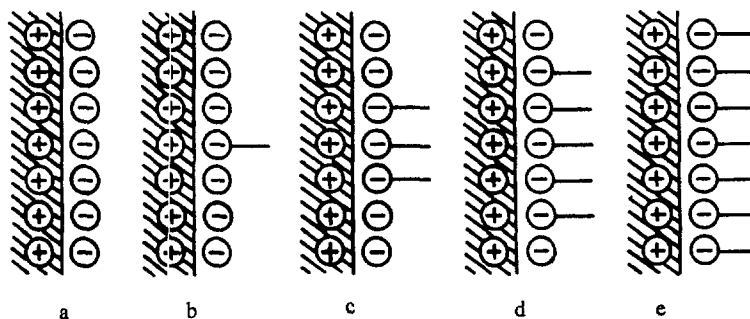


Fig. 10. The adsorption model of FC-99 molecules on lead electrode in 5 M H₂SO₄ at various concentrations of FC-99: (a) 0; (b) 10; (c) 20; (d) 30; (e) 40 ppm. ⊖ = HSO₄⁻, ⊖ ————— = FC-99 molecule.

peak always remains a single peak, whether the concentration is 10 or 40 ppm.

When a chemically-polished lead electrode is introduced into the electrolyte with a linear CHSAS, whose hydrophilic head is a sulfate group, the molecular orientation of SDS molecules adsorbed on the positively charged electrode surface is also similar to that of adsorbed FC-99 molecules. The hydrophobic layer formed by SDS molecules on the surface shows, however, less repulsive force on the approaching sulfate ions from the H_2SO_4 than that of FC-99 because of the weaker polarity of the SDS molecule. Therefore, despite the two anodic peaks in the voltammogram with SDS, the anodic peak due to the oxidation of lead is higher than that obtained in the presence of FC-99.

The SDBS molecules adsorb on the opposite-charged lead substrate by ion-pairing and by polarization of π electrons [14]. Because the adsorbate contains electron-rich aromatic nuclei and the substrate has strongly positive sites, attraction between the electron-rich aromatic nuclei of the adsorbed molecules and positive sites on the substrate results in adsorption, and the sulfonate groups of SDBS molecules also interact with the positive sites of the electrode by electrostatic force. Therefore, the orientation of the SDBS surfactant is parallel to the electrode surface, or somewhat tilted away from the parallel (Fig. 11). During the oxidation process, soluble Pb(II) ions can react with the sulfonate groups of the adsorbed molecules to form a 'lead-sulfonate' complex together with the formation of $PbSO_4$. Thus, there are two anodic peaks on the voltammogram. Moreover, because the cross-sectional area of the adsorbed SDBS molecules on the surface is greater than that of the perpendicularly adsorbed FC-99 or SDS molecules at the same concentration, the hydrous sulfate ions are less able to approach the surface and the peak corresponding to the formation of $PbSO_4$ is thus, less than that with FC-99 or with SDS.

The non-ionic SAS molecules, FSN and Tween-20, might adsorb on the lead electrode surface by hydrophobic bonding [14]. To maintain the lowest energy of the system, the hydrophobic groups of the adsorbed molecules tend to escape from an aqueous environment and keep their hy-

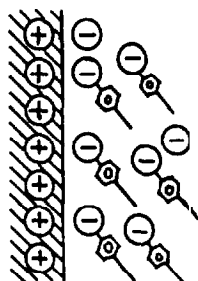


Fig. 11. The adsorption model of SDBS molecules on lead electrode in 5 M H_2SO_4 . $\oplus = HSO_4^-$, $\ominus \text{---} \text{---} \text{---} =$ SDBS molecule.

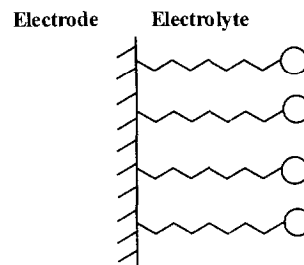


Fig. 12. The adsorption model of SAS molecules on electrode via hydrophobic bonding.

drophilic heads in the electrolyte (Fig. 12). The structure of the adsorption layer renders the interface hydrophilic which allows hydrous ions (including soluble Pb(II) ions and sulfate ions in the electrolyte) through the adsorption layer during the oxidation process, but the rate of diffusion is lower than that without SAS. As the concentration of FSN increases, the adsorbed layer becomes dense and causes a decrease in Q_a .

With respect to the electrostatic repulsive force, the hydrophilic heads of the cationic surfactant molecules might leave from the positively charged surface. If there is not an electron-rich group contained in the hydrophobic chain of the cationic surfactant molecule, hydrophobic bonding is the main cause of the adsorption between the surfactant molecules and the lead surface, or even the cationic surfactant molecules cannot adsorb on the positively charged surface if the electrostatic repulsive force is sufficiently strong. Since there is an electron-rich group, $-SO_2-NH-$, on the hydrophobic chain of a FC-135 molecule, the FC-135 molecules can adsorb on the positively charged lead surface via their electron-rich groups. The possible molecular orientation of the FC-135 molecules is shown in Fig. 13. The formation of $PbSO_4$ might be hindered by the adsorbed layer, and the potential of the anodic peak is therefore shifted to more positive values (as is also the case in the presence of FSN and Tween-20). On the other hand, the CTAB molecules have no electron-rich groups and the adsorption of CTAB on lead surface may be weak. It is more likely that the CTAB molecules adsorb on the $PbSO_4$ crystal instead of on the charged lead surface, given the lack of a change in the potential of the oxidation process.

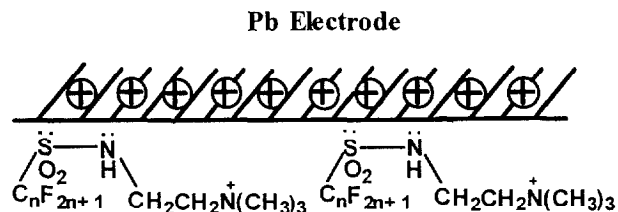


Fig. 13. The adsorption model of FC-135 molecules on lead electrode in H_2SO_4 .

4. Conclusions

The inhibitor and expander action of various types of SAS as negative additives in a lead–acid battery have been studied. The presence of the CHSAS in the electrolyte solution cause the HER to move to more negative potentials, but the cationic PFSAS (FC-135) exerts the opposite effect. The addition of FSN or FC-99 shows a negligible effect on the potential of the HER. On the other hand, only the non-ionic SAS (FSN, Tween-20) can raise the discharge capacity of the negative electrode in a lead–acid battery. The addition of anionic SAS (FC-99, SDS, SDBS) and the cationic CHSAS (CTAB) has a negative effect on the discharge capacity, and the influence of the cationic PFSAS (FC-135) on the discharge capacity is negligible. By combining the results in this work with those reported elsewhere [2], it is concluded that the various types of PFSAS can be used as additives in a lead–acid battery in different situations. That is, FC-99 is used in the positive plate, FSN could be an expander for the negative plate, and FC-135 could be either a positive-plate additive or an electrolyte additive.

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