Short communication

Influence of surfactants on electrochemical behavior of zinc electrodes in alkaline solution

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Abstract

The effects of different ionic types of perfluorosurfactants (including hydrocarbon chain surfactant CTAB) on the electrochemistry behavior of zinc have been examined using voltammetric and potentiostatic polarization techniques. The results show that these surfactants can be used as substitute of mercury for decreasing the corrosion in zinc batteries. It is also shown that the deposition of zinc from zincate electrolyte in the presence of these surfactants can be improved to some extent. The morphology of the electrodeposited zinc shows that these surfactants can bring about more uniform and compact deposits and, thereby, reduce dendritic growth. FC-170C and CTAB are found to be the most effective inhibitors. © 1998 Elsevier Science S.A.

1. Introduction

The secondary alkaline zinc electrode has advantages of high specific energy, high specific power, and low cost. Nevertheless, the widespread development of cells with zinc anodes has been prevented because of shape change and dendrite growth problems with the zinc electrode.

Advances in rechargeable zinc batteries have included the use of additives and modified charging methods to obtain a beneficial effect on zinc morphology [1–6]. In particular, organic additives can refine the grain size and eliminate dendrite growth [7–10]. Generally, the additives are specifically adsorbed at rapid growth sites (i.e., dendrites) on the surface of the electrode and restrict further growth at these locations [8,11–14]. This adsorption phenomenon can be caused by π-bond orbital adsorption, electrostatic adsorption, or chemisorption [15].

Perfluorosurfactant has the advantage of excellent chemical stability; it can survive the severe conditions of strong acids, bases or oxidants. It has been reported [16–18] that fluorosurfactants are efficient inhibitors of the growth of zinc moss and dendrites. The studies on this surfactant have focused only on F1110 (C_6F_{13}–$C_2H_4(OC_2H_4)_{12}OH$) [19–21].

The aim of this investigation is to examine the effects of perfluorosurfactants (including hydrocarbon chain surfactant CTAB) on the electrochemical behaviour of zinc via the techniques of voltammetry and potentiostatic polarization.

2. Experimental

2.1. Electrode and electrolytic cell

For linear and cyclic voltammetric experiments, a single-compartment electrochemical cell with five entries was used. The working electrode was a disc electrode of zinc (99.99%, Johnson Matthey Chemicals, Royston, UK) which was embedded in a Teflon (PTFE) holder so as to expose a free surface area of 0.125 cm^2. Prior to each experiment, the zinc electrode was first polished with emery paper (1200 grade), and then with aluminum oxide powders from 3 to 0.05 μm until a mirror surface was obtained. After polishing, aluminum oxide particles were removed from the surface of the electrode by ultrasonic cleaning in doubly-distilled water and acetone, alternately. Finally, the electrode was rinsed thoroughly with doubly-distilled water. A platinum sheet was used as a counter electrode. The cell was maintained in a thermostatic water bath at 25 $\pm$ 0.5°C. The electrolyte was deoxygenated by bubbling ni-

Table 1
Molecular formula and ionic type of surfactants used in this work

Surfactant	Molecular formula	Ionic type
FC-170C	$C_nF_{2n+1}SO_2(C_2H_5)(CH_2CH_2O)_xH$ ($n \sim 8$)	nonionic
FC-135	$C_nF_{2n+1}SO_2NHC_3H_6N^+(CH_3)\cdot I$ ($n \sim 8$)	cationic
FC-129	$C_nF_{2n+1}SO_2N(C_2H_5)CH_2COO^-K^+$ ($n \sim 8$)	anionic
CTAB	$C_{16}H_{33}N^+(CH_3)_3\cdot Br^-$	cationic

trogen gas through the solution prior to measurements. The latter were commenced after the zinc electrode had been immersed in the electrolyte for 0.5 h.

In potentiostatic polarization experiments, a planar zinc electrode (99.99%, apparent area 1×1 cm) was used as the working electrode; the counter electrode was a platinum sheet. Zinc electrodes were pretreated in acetone (degreasing), followed by a short immersion in 50% HCl (v/v, specific gravity 1.18) until a light, matte, clean surface became apparent [22].

A Hg/HgO reference electrode with a Luggin capillary was used in all experiments. All potentials are reported with respect to this electrode.

2.2. Electrolytes

Two base electrolytes were employed, namely, a 30% KOH solution, and a 30% KOH solution with 40 g l^{-1} ZnO (both of AR grade). The ionic type and molecular formula of the surfactants used in this work are given in Table 1.

The measurements were performed using an RDE4 bipotentiostat (Pine Instruments, USA) connected to a Type 3086 X–Y recorder (Yokogama Hokushin Electric, Tokyo, Japan).

3. Results and discussion

3.1. Effect of surfactants on hydrogen evolution reaction (HER) on zinc electrode

The need to suppress H_2 formation is critical for both primary and secondary zinc batteries. Although mercury has long been the favoured primary battery additive for this purpose, environmental pressures have provoked a worldwide effect to identify a less-toxic alternative additive. In general, the rate of the HER depends greatly on the overpotential of hydrogen on the zinc electrode. Many studies have confirmed that this overpotential can be raised by the presence of certain surfactants.

Cathodic polarization curves at 1 mV s^{-1} from the rest potential of the zinc electrode in 30% KOH with various surfactants (30 ppm) are shown in Fig. 1. The hydrogen overpotential is raised to some degree in the presence of surfactants. Thus, the addition of these surfactants can slow the rate of the HER on zinc electrodes. In other
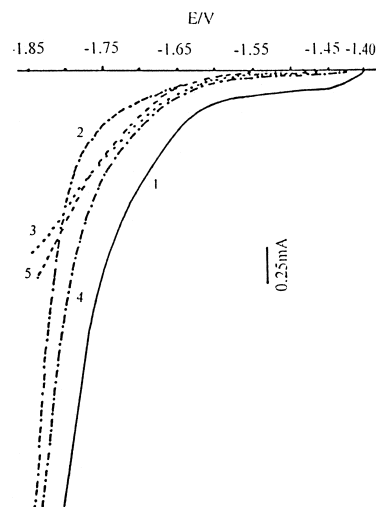

Fig. 1. Effect of surfactants (30 ppm) on hydrogen evolution reaction (HER) on zinc electrode in 30% KOH solution. (1) Surfactant absent; (2) FC-170C; (3) FC-135; (4) FC-129; (5) CTAB.

words, the surfactants can be used as substitutes for mercury as a means to decrease electrode corrosion in zinc batteries.

It is concluded that the hydrogen overpotential is raised because of the adsorption of surfactant molecules on the zinc electrode. During cathodic polarization, the surface of the zinc electrode is partially covered by adsorbed surfactant molecules, which block some of the active sites of the electrode surface [19]. From Fig. 1, in terms of raising the hydrogen overpotential on zinc electrodes, FC-170C (nonionic type) is found to be most effective, followed by FC-135 and CTAB (both of cationic type), but the hydrogen overpotential of zinc electrode is also raised in the presence of FC-129 (anionic type). The value of the potential of zero charge (pzc) of the zinc electrode is about -0.9 V vs. SCE [23,24]. Consequently, during cathodic polarization, there are negative charges on the surface of the zinc electrode. Nevertheless, an anionic type surfactant, FC-129, still induced an increase in hydrogen overpotential on the zinc electrode. Apparently, the adsorption of these surfactant molecules is not caused by the electrostatic attraction between the polar group of the surfactant molecules and the surface of zinc electrode. Moreover, because the valence electron orbitals of the zinc atoms are fully filled and, therefore, do not leave empty d orbitals to accept electrons, chemical adsorption by means of electron exchanging between the surfactant molecules and the surface of electrode is also impossible. Thus, these surfactants may be adsorbed on the surface of the zinc electrode via non-polar groups, with the polar groups oriented towards the bulk solution. Through such action, the main function of the polar groups is to increase the solubility of the surfactants in electrolyte, there is only a slight effect on adsorption free energy. When the cathodic polarization potential is negative to -1.80 V, the nonionic type FC-170C begins to de-adsorb from the surface of the zinc

electrode (the anionic type FC-129 de-adsorbed before the FC-170C type), however, the cationic type FC-135 and CTAB maintain a steady adsorption on the surface of the zinc electrode. Cationic type surfactants may be adsorbed by the electrostatic attraction between the polar group of the molecules and the surface of zinc electrode, so that the rate of the HER increases more slowly in the presence of FC-135 or CTAB when the potential of zinc electrode is more negative than −1.80 V.

3.2. Effects on cyclic voltammetric curves of zinc electrode

Cyclic voltammograms (1st cycle) for a zinc electrode between −1.30 and −1.60 V in 30% KOH containing 40 g l^{-1} ZnO in the presence of various surfactants (30 ppm) are presented in Fig. 2. The dotted lines represent voltammograms obtained in the absence of surfactants. The addition of FC-170C, FC-135, FC-129 or CTAB in electrolyte containing zincate all affected the voltammetric behaviour of the zinc electrode to some degree, especially the cathodic part of voltammograms (corresponding to zinc deposition). Except for FC-129, the potential of the cathodic peak of zinc deposition is shifted towards a most negative value by about 80 mV. The onset potentials of zinc deposition are also shifted to a negative value to some extent by the addition of surfactants; FC-170C and CTAB give the most pronounced shifts, namely, 45 and 100 mV, respectively. These shifts of the onset potential of deposition and the potential at the cathodic current maximum

indicate that the deposition of zinc from zincate electrolyte is inhibited to a certain degree in the presence of surfactants. The reason is that the surfactants adsorb on the surface of zinc electrode to give a layer that presents an inhibitor effect on the electroreduction process of zincate [9]. Therefore, these surfactants may slow the rate of zinc deposition from zincate during electrode charging and, thereby, mitigate the dendrite growth.

It also can be seen from Fig. 2a,d that the so-called 'inductive loop' occurs on the cathodic branch of voltammograms, i.e., the cathodic current resulting from scanning in a positive-going, direction is higher than that resulting from scanning in a negative-going direction. It is assumed that the occurrence of the 'inductive loop' is caused by the nucleation process of the zinc [25]. The 'inductive loop' occurs at a negative overpotential. This means that the mature nuclei are formed under conditions of overpotential deposition. A possible explanation is as follows. The molecules of FC-170C or CTAB adsorb on the active sites of the electrode surface and block the deposition of zinc on these points. This, in turn, makes it necessary for new nuclei to form at a higher overpotential and, thus, the rate of zinc deposition from zincate solution is suppressed. The data in Fig. 2 also show that the addition of the surfactants in the electrolyte exert little effect on the anodic process of the zinc electrode. The anodic polarization is slightly increased in the presence of FC-170C and FC-135. The effect of CTAB on the anodic behaviour of the zinc electrode is unlike that of the quaternary ammonium salt of
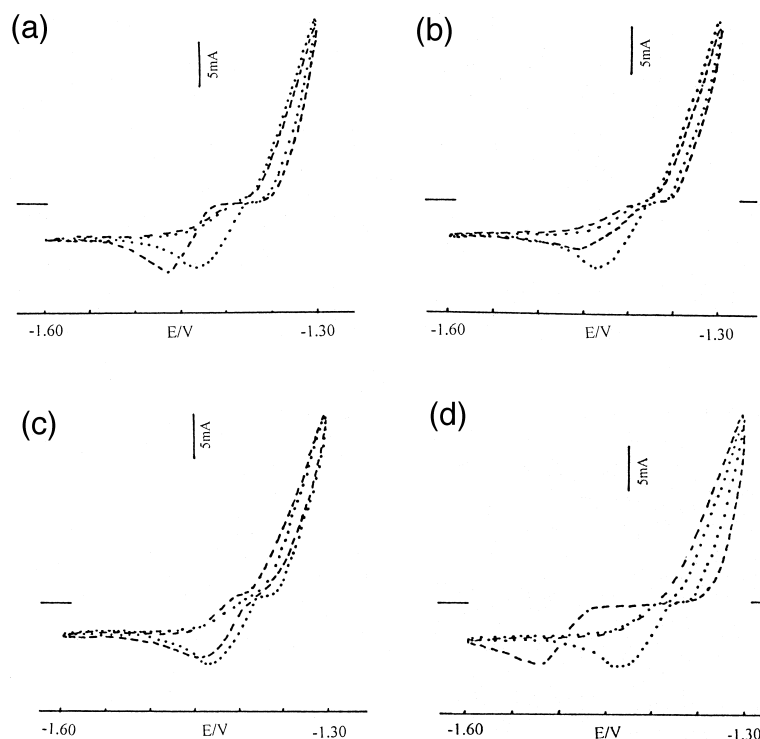

Fig. 2. Cyclic voltammograms for zinc electrode in 30% KOH containing 40 g l^{-1} ZnO and various surfactants (30 ppm) on first cycle: (a) FC-170C; (b) FC-135; (c)FC-129; (d) CTAB. Dotted line: surfactant absent. Dashed line: with surfactant.
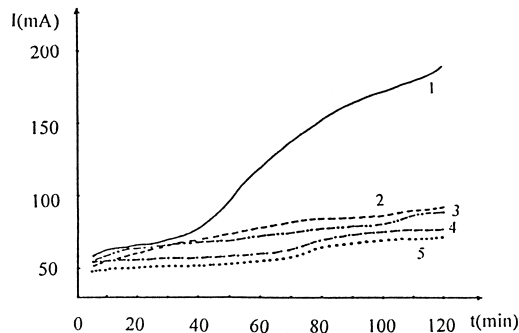
Fig. 3. Current-time curves for zinc electrode in 30% KOH containing 40 g l^{-1} ZnO with various surfactants (60 ppm): (1) surfactant absent; (2) FC-135; (3) FC-129; (4) CTAB; (5) FC-170C.

NBu_4Br [8,10], namely, it can inhibit the deposition of zinc, but does not increase the electrode anodic polarization.

3.3. Effect on electrodeposition of zinc

Current-time data for electrolytes containing FC-170C, FC-135, FC-129 or CTAB are given in Fig. 3. The curves

are for the addition of various surfactants at a cathodic overpotential of 100 mV. Baugh et al. [26] have claimed that the limiting diffusion current of oxygen reduction in 7 M KOH that results from air saturation is only 4 μA cm^{-2}. That is to say, oxygen reduction is a very minor reaction at this KOH concentration. Therefore, the electrodeposition of zinc at this potential can be regarded as the only significant cathodic reaction under the conditions of these experiments. Current-time data can be considered as being representative of the change in surface structure during a potential-controlled electrodeposition [22]. If the deposition of zinc is uniform and compact, and therefore does not cause a change in the real electrode surface-area, then the current through the electrode will not rise. By contrast, if the zinc deposition is non-uniform, especially in the case of dendrites, the real electrode surface-area will be greatly increased. Thus, if the cathodic overpotential applied to the zinc electrode is still 100 mV, then the current through the electrode will rise with the increase in electrode surface-area. That is to say, any rise in current indicates an increase in electrode surface-area. It can be seen from Fig. 3 that the cathodic current is about 58 mA
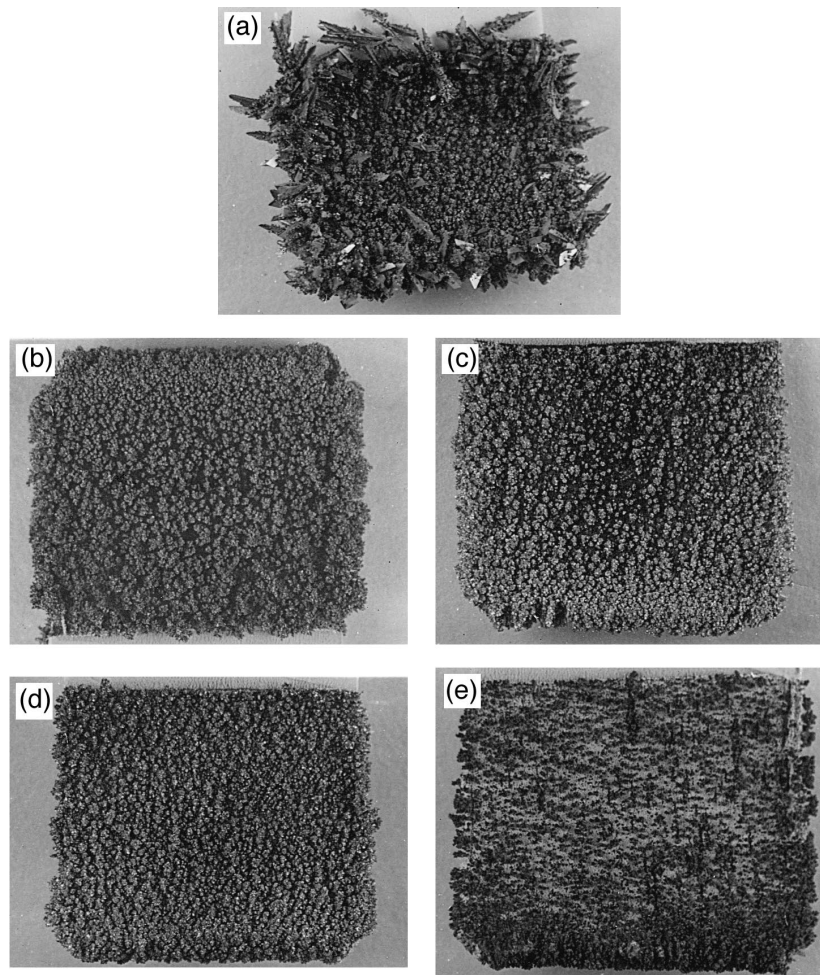

Fig. 4. Photographs of zinc electrodeposit from 30% KOH containing 40 g l^{-1} ZnO and various surfactants (60 ppm) (magnification, ×30): (a) surfactant absent; (b) FC-135; (c) FC-129; (d) CTAB; (e) FC-170C.

at the beginnings, and then rises slowly to about 70 mA in 35 min. In the following 85 min, the increase in current become more rapid in a surfactant-free solution, such that a cathodic current of $\sim$ 190 mA is attained at 120 min. This behaviour indicates an increase in surface area brought about by a non-uniform (and ultimately, dendritic) deposit. On the other hand, solutions in the presence of various surfactants display a lower initial current profile and continue at this level throughout the 120-min test, thus indicating a compact growth morphology.

The morphologies of the deposited zinc after the 120-min test, are shown in Fig. 4. A deposit from a 'blank' solution containing no surfactant is presented in Fig. 4a. As can be clearly seen, the zinc has deposited as a large quantity of dendritic crystallites and the deposition is uneven. The effects of adding various surfactants, are shown in Fig. 4b–e. In all cases, a uniform and compact deposit is observed, especially for the addition of CTAB (Fig. 4d) and FC-170C (Fig. 4e).

4. Conclusions

The effectiveness of FC-170C, FC-135, FC-129 and CTAB as inhibitors of zinc corrosion and dendritic growth has been examined. The addition of these surfactants to the electrolyte can decrease the rate of the HER on the zinc electrode. This demonstrates that these surfactants can be used as a substitute for mercury in order to decrease electrode corrosion in zinc batteries. The initial potential and the potential at cathodic current maximum of zinc deposition are shifted to a negative value in the presence of these surfactants. Thus means that the deposition of zinc from zincate electrolyte can be inhibited to some degree. Potentiostatic polarization experiments in zinc electrodes show that these surfactants can bring about a significant improvement in deposit morphology and result in the reduction of dendritic growth. Of those surfactants examined in this work, FC-170C and CTAB are found to be most effective inhibitors.

The excellent stability of perfluorosurfactants and the negligible effect on the corresponding anodic reaction favour the possibility of applying FC-170C as an electrolyte additive to secondary zinc technology. Nevertheless, the stability of CTAB to prolonged cycling has still to be confirmed.

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