Short communication

Improved discharge capacity and suppressed surface passivation of zinc anode in dilute alkaline solution using surfactant additives

Hanxi Yang, Yuliang Cao*, Xinping Ai, Lifen Xiao

Department of chemistry, Wuhan university, Wuhan 430072, China

Abstract

The capacity utilization of zinc anode is usually very low in dilute alkaline solution or at high rate discharge because of the passivation of zinc surface. This problem can be considerably overcome by use of surfactant additive in electrolyte. In this work, it is found that with addition of 2% sodium dodecyl benzene sulfonate (SDBS) in 20% KOH solution, the discharge capacity of zinc anode increases from 360 to 490 mAh/g at moderate discharge rate of 40 mA/g, corresponding to a 35% increase in the capacity utilization. Based on the electrochemical and morphological observation of the anodic passivation behaviors of zinc electrode, this effect is revealed that due to the SDBS adsorption, the passive layer formed on the zinc surface has a loose and porous structure rather than a dense and compact film. This type of surface layer facilitates the diffusive exchange of the solution reactant and discharged product through the surface deposit layer and therefore effectively suppresses the surface passivation of zinc anode.

1. Introduction

Zinc is widely used as a high capacity anodic material for primary and secondary alkaline batteries because of its high specific energy, low cost and non-toxicity. However, the high capacity of zinc anode can only be obtained in very concentrated alkaline solution. In dilute alkaline solutions, the discharge capacity and power capability of zinc anode decrease dramatically with decreasing OH^- concentrations due to the passivation of zinc surface.

The passivation of zinc anode in dilute alkaline solution is known to result from the formation of passive film on zinc surface. In past decades, numerous works have been undertaken to evaluate the anodic passivation mechanism and the properties of the passive film of zinc electrode in alkaline solution [1–5]. It is now well agreed that the passivation of zinc takes place by a dissolution–precipitation mechanism and the dissolution of zinc is the rate-determining step [4,5]. The passive film formed at the surface of zinc anode was postulated to consist of two layers: the outer layer is white and flocculent, formed by precipitation of

the supersaturated zincate in the vicinity of the electrode surface. The inner layer is a dense ZnO film adhered on zinc surface and formed from the dehydration of the discharge product $Zn(OH)_2$, behaving as a barrier for further dissolution of zinc when it is formed [2]. To suppress the anodic passivation and improve the utilization of zinc, one usually use very concentrated alkaline solution to increase the solubility of ZnO or use electrolyte additives to modify the electrode surface to depress the blocking effects of the passive film on the diffusion of discharged zinc ions into bulk solution [6–8]. However, most research works on the electrolyte additives were focused on the inhibition of zinc corrosion [9–11] and dendritic formation in secondary zinc batteries [12–14], the effects of surfactant additives on the utilization and discharge performances of zinc in dilute alkaline solution are rarely reported.

In the studies of the effects of electrolyte additives on the anodic passivation of zinc, we found that sodium dodecyl benzene sulfonate (SDBS) in alkaline electrolyte as a surfactant additive can effectively depress the surface passivation and greatly improve the discharge capacity of zinc anode, particularly in dilute alkaline solution. Here we report the results of electrochemical behaviors of zinc in dilute alkaline solution containing SDBS molecules and

* Corresponding author. Tel.: +86-27-8787-3526;
fax: +86-27-7888-4476.
E-mail address: ece@whu.edu.cn (Y. Cao).

discuss the working mechanism of the additive on the improvement of discharge capacity of zinc.

2. Experimental

2.1. Preparation of materials and test cells

Zinc anode used for discharge measurements was a gelled zinc slurry and prepared by mixing 66.3% zinc powder (Micore Corp. Belgium), 0.67% polyacrylate and 33.3% (by weight) ZnO-saturated alkaline solution, which is similar to those used in commercial alkaline manganese battery. The surfactant additive was added in the zinc slurry by mixing together with zinc powder.

The discharge performances of zinc anode with or without electrolyte additives were examined by gavanostatic method using AA-sized zinc-air test cells. The test cells were constructed in laboratory with air electrode as cathode and gelled zinc slurry as anode. The air electrode was a U-shaped container fabricated by mould pressing a powder mixture of 70 wt.% carbon black and 30 wt.% polyethylene. The catalyst for the air cathode was manganese dioxide loaded on activated carbon, coated in the inner wall of the air electrode tube by hot spraying method. The separator was non-woven fabric of nylon usually used in alkaline Zn-MnO$_2$ batteries. In general, a laboratory zinc-air battery of AA size contained 7.0 g of zinc slurry (ca. 4.6 g zinc powder) in the experiments.

2.2. Electrochemical characterization

All the electrochemical measurements of the anodic dissolution and passivation behaviors of zinc electrode were performed using three electrode cells. Working electrode was a zinc rod of 5 mm diameter (99.9% purity). The zinc rod was sealed with epoxy resin with one end exposed to electrolyte. The exposed surface of the zinc rod was firstly polished with fine grade emery papers, then degreased with acetone and finally washed with the twice-distilled water. The reference electrode and counter electrode were an Hg/HgO electrode and a larger platinum sheet, respectively. The electrolyte used in the experiments was ZnO-saturated 20% KOH solution. The linear voltammometric measurements were carried out using a CHI 660 type electrochemical system (Shanghai, China). The impedance spectra measurements were carried out on an impedance spectroscopy system (EG&G PARC model 273) coupled with M398 software and the frequency range typically used was from 100 KHz to 8 Hz with an ac amplitude of ±10 mV.

2.3. SEM measurements

The samples of discharged zinc anode for the surface morphological examinations were taken from the fully discharged zinc-air cells and directly sent for SEM analysis using a SEM ISI-SX-40.

3. Results and discussion

3.1. Effects of electrolyte additives on the discharge capacity of zinc

Since air cathode is inexhaustible and the capacity limit of Zn-air cells depends uniquely on the amount of zinc added, we used zinc-air test cells to calibrate the discharge capacity of zinc and the effects of electrolyte additives on the capacity utilization.

It is well known that the zinc utilization decreases very rapidly with decreasing OH$^-$ concentration. The reason for the very poor utilization of zinc is due to the lower solubility of the discharged product Zn(OH)$_2$ in diluted KOH concentration, which leads to a supersaturation of zincate ions and the formation of the surface passive film. In order to suppress the passivation of zinc anode in dilute alkaline solution, we tried to use various types of anionic additives to modify the surface morphology and structure of the passive film in 20% KOH solution and found that the existence of a small amount of SDBS had dramatic influence on the discharge capacity of zinc in dilute KOH solutions. Typical results are shown in Fig. 1. It can be seen from the figure that the discharge capacities of the zinc-air batteries are all increased with addition of the surfactant SDBS except for excessive addition of 7% SDBS. The highest capacity of the batteries appears in the 2% SDBS content. In the zinc-air battery with addition of 2% SDBS, the discharge capacity increases from 1690 mAh (360 mAh/g) to 2280 mAh (490 mAh/g), nearly 35% higher than that of the battery in the absence of the surfactant, suggesting an effective depression of the surface passivation of zinc anode. Lower or higher SDBS addition does not show distinct capacity improvement. This effect could be understood that due to the very limited dissolution of SDBS in the alkaline solution, very low content of the additive in electrolyte cannot
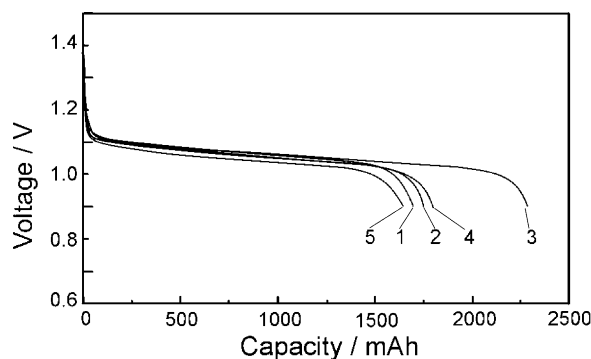

Fig. 1. Discharge curves of zinc/air batteries at constant current of 200 mA in 20% KOH solution with addition of: 1.0, 2.1, 3.2, 4.5 and 5.7% SDBS.
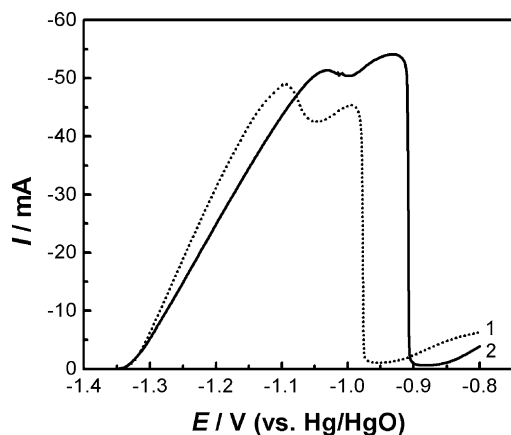
Fig. 2. Anodic polarization curves of a zinc anode in 20% KOH solution with addition of 1. Zero and 2.2% SDBS. Sweep rate of 10 mV/s.

Fig. 3. Complex impedance spectra for a zinc disk electrode in 20% KOH solution with addition of 0 (■) and SDBS (□) at potential of −0.9 V vs. Hg/HgO.

provide an adequate surface coverage of SDBS adsorption and hence gives a limited influence on the formation of the surface passive film. When the SDBS content exceeds much more than the saturated concentration as in the case of >2% SDBS addition, the aggregate of insoluble molecules in the surface region of zinc would also impose a inhibiting effect for the discharged Zn^{2+} to diffuse into bulk solution and therefore the discharge capacity of zinc no longer increase with further addition of the additive.

3.2. Electrochemical characterization

The anodic passivation of zinc can usually be visualized by measurements of the passivation polarization curves. Fig. 2 gives the potentiostatic anodic polarization curves of zinc electrode in 20% KOH with and without the SDBS. During anodic sweep, two anodic current peaks appear at −1.1 and −1.0 V for zinc anode in blank solution, which is similar to those previously reported in [15,16]. According to previous assignments of the two peaks, the first anodic peak at −1.1 V is due to the anodic dissolution of zinc to form $Zn(OH)_4^{2-}$ and the second current peak at −1.0 V is attributed to the anodic diffusion current peak. When the potential rises to a more positive value of −0.97 V, a sudden decrease of anodic current appears, which is characteristic of zinc passivation process. If we compare the passivation curves in Fig. 2, some marked differences are observed in the anodic dissolution current and the passivation potential for the zinc anode in the electrolyte with and without the additive. Firstly, the active dissolution current peak of zinc in the presence of SDBS shifts to a more positive potential, indicating a surface inhabitation for normal anodic dissolution of zinc, possibly due to the adsorption of the surfactant SDBS. Besides, the zinc electrode in the presence of SDBS shows a larger anodic diffusion current peak and a delayed passivation potential than that in the absence of the surfactant. These phenomena indicate that the anodic passivation of zinc is postponed by SDBS adsorption.
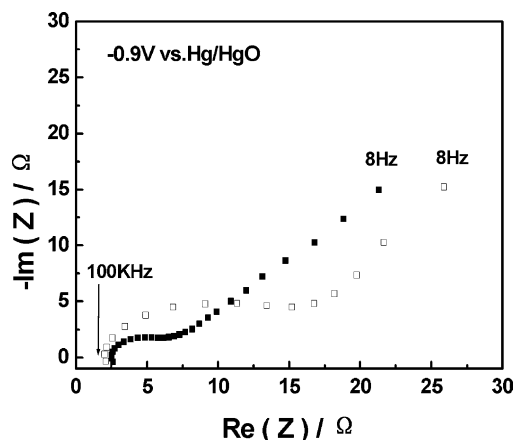
The SDBS absorption can also be seen from the impedance measurements. Fig. 3 shows the complex impedance plots obtained from the passivated zinc anode in 20% KOH solution with or without addition of SDBS. In both cases, the impedance spectra exhibit a high frequency semicircle and a low frequency sloping line. The low frequency sloping line, namely Warburg impedance, is only apparently observable from the zinc anode at the potential region of passivation, and it indicates that the electrode reaction is controlled by the diffusion of zinc ions and OH^- ions through the passive film on zinc surface. The high frequency semicircle observed in this work is analogous to that reported previously and has been already assigned to the charge transfer behavior of zinc electrode in literature [17]. In comparison, the semicircle for zinc anode in the SDBS-containing electrolyte shows a much larger diameter semicircle than that obtained in blank solution, reflecting that the addition of SDBS in electrolyte increases the charge transfer resistance of zinc-electrolyte interface. This is true since the surface of zinc electrode is occupied by absorbed SDBS and therefore the interfacial charge transfer must be impeded to some extent. The sluggish kinetics of interfacial reaction and increased diffusion current for zinc in the SDBS containing electrolyte seem to be conflict, but this could be explained by the formation of a loose and porous passive film on the zinc surface in the existence of SDBS. Although the SDBS adsorption can reduce the active surface area and the anodic dissolution rate of zinc, this could be compensated by the enhanced diffusion rate for the reactant and discharged product through the less compact passive film brought about by the adsorption of SDBS.

3.3. Effects of SDBS addition on the surface morphology of zinc anode

Fig. 4 compares the surface morphologies of the zinc anode discharged in solution with and without addition of
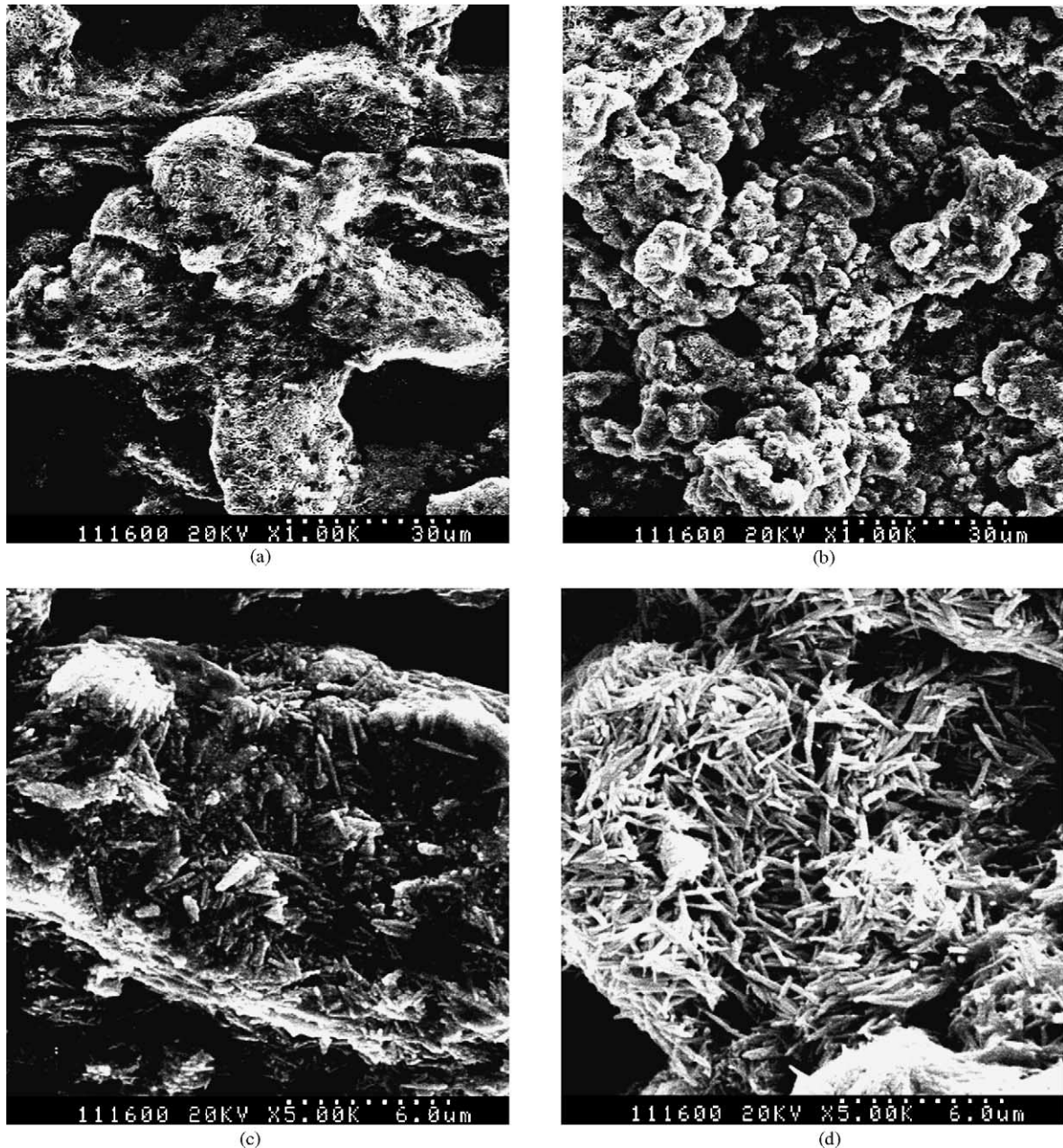
Fig. 4. SEM micrographs of zinc electrodes discharged in 20% KOH solution with addition of: (a) 0 and (b) 2% SDBS; (c) and (d) the amplified images from (a) and (b), respectively.

SDBS. The zinc electrode in blank electrolyte shows a stack of large zinc grains and each grain comprises densely packed small zinc particles. Assumedly, as long as the dense surface layer is formed during the anodic dissolution, the surfaces of zinc granules must be blocked for the diffusion of zinc ions into bulk solution or the migration of OH^- ions into the zinc surface. In this case, only parts of the zinc surface are utilized for anodic reaction, as shown as whiter edges in amplified SEM images in Fig. 4c. The effects of SDBS on the surface morphology of discharge zinc anode are shown in Fig. 4b and d. In this case, the zinc surface shows a distribution of smaller particles and each particle consists

of needle-like crystallites loosely packed together to form a porous structure. Undoubtedly, such a porous structure of deposit layer facilitates the zinc ions to diffuse into bulk solution and the OH^- ions to penetrate into zinc surface. As a result, the anodic dissolution of zinc could proceed continuously until zinc is consumed up or the zinc surface is fully inhibited. Based on these results, it could be concluded that the suppressed passivation of zinc anode is mainly due to the morphological modification of the surface layer of discharged product.

Detailed interaction of SDBS with zinc surface to produce a loose passive layer is difficult to explain. In

previous studies of the passivation mechanisms of zinc anode, it was suggested that electrochemical dissolution of zinc anode take place at first step to produce $Zn(OH)_2$ which dissolves immediately in alkaline solution to form zincate ions. When the zincate ions reaches to saturation concentration, the precipitation of solid zincate occurs to form a loosely adherent porous film in the vicinity of zinc surface. When the electrochemical oxidation continues to proceed, a dense film is formed on the zinc surface due to the depletion of OH^- ions at surface region [2,18,19].

In the solution containing SDBS, zinc surface must be occupied to some extent by SDBS adsorption. Since the surface of metallic zinc is positively charged during anodic polarization, SDBS molecules preferably adsorb with their non-polar groups bonded to the surface and the polar groups oriented towards bulk solution [20]. Moreover, due to the electrostatic repulsion between the anionic type SDBS molecules and OH^- ions, the OH^- ions are more or less excluded away from the surface. During anodic dissolution, zinc ions produced at the surface may coordinate with SDBS anions to form the surface complexes and then zinc ions are brought into solution to combine with OH^- ions to form $Zn(OH)_2$ deposits. Apparently, the occupation of SDBS at the zinc surface may also be an important cause for spatial inhibition of the formation of dense passive film.

4. Conclusions

The passivation properties of zinc anode in alkaline solution containing the surfactant additive SDBS were investigated by measurements of discharge capacity, passivation polarization curves and impedance spectra in combination with SEM observation of surface morphology. It was found that the addition of SDBS molecules in the dilute alkaline electrolyte can effectively depress the passivation of zinc surface during the electrochemical dissolution of zinc and therefore improve the discharge capacity of zinc anode up to more than 35%. The suppression effect is suggested to result from the adsorption of the electrolyte additive, which produce a loose and porous passive film at the zinc surface. Such a morphological modification of the surface structure greatly facilitates the diffusive transportation of discharged product and solution reactant, and therefore improves the anodic utilization of zinc anode.

Acknowledgements

References

[1] T.P. Dirkse, D.D. Wit, R. Shoemaker, J. Electrochem. Soc. 115 (1968) 442.
[2] R.W. Powers, M.W. Breiter, J. Electrochem. Soc. 116 (1969) 719.
[3] T.P. Dirkse, N.A. Hampson, Electrochim. Acta 16 (1971) 2049.
[4] P.L. Cabot, M. Cortes, F.A. Centellas, J.A. Garrido, E. Perez, J. Electroanal. Chem. 201 (1986) 85.
[5] P.L. Cabot, M. Cortes, F.A. Centellas, E. Perez, J. Appl. Electrochem. 23 (1993) 371.
[6] R. Shivkumar, G.P. Kalaignan, T. Vasudevan, J. Power sources 55 (1995) 53.
[7] Y. Sharma, M. Aziz, J. Yusof, K. Kordesch, J. Power Sources 94 (2001) 129.
[8] C. Cachet, U. Stroder, R. Wiart, Electrochim. Acta 27 (1982) 903.
[9] V.K. Nartey, L. Binder, K. Kordesch, J. Power Sources 52 (1994) 217.
[10] R. Shivkumar, G.P. Kalaignan, T. Vasudevan, J. Power sources 75 (1998) 90.
[11] J. Dobryszycki, S. Biallozor, Corrosion Sci. 43 (2001) 1309.
[12] G.D. Wilcox, P.J. Mitchell, J. Power sources 28 (1989) 345.
[13] J.W. Diggle, A. Dammjanovic, J. Electrochem. Soc. 119 (1972) 1649.
[14] J. Bressan, R. Wiart, J. Appl. Electrochem. 9 (1979) 615.
[15] M.C.H. McKubre, D.D. Macdonald, J. Electrochem. Soc. 128 (1981) 524.
[16] R.D. Armstrong, G.M. Bulman, J. Electroanal. Chem. 25 (1970) 121.
[17] M. Cai, S.M. Park, J. Electrochem. Soc. 143 (1996) 3895.
[18] A.H. Goff, S. Joiret, B. Saidani, R. Wiart, J. Electroanal. Chem. 263 (1989) 127.
[19] M. Liu, G.M. Cook, N.P. Yao, J. Electrochem. Soc. 128 (1981) 1663.
[20] J.L. Zhu, Y.H. Zhou, C.Q. Gao, J. Power sources 72 (1998) 231.