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Influences of zinc oxide and an organic additive on the electrochemical behavior of pure aluminum in an alkaline solution

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Abstract

The corrosion behavior of pure aluminum in inhibited and uninhibited 4 M KOH was investigated by means of hydrogen collection, polarization curve measurement and electrochemical impedance spectroscopy (EIS). The results showed that the corrosion of pure aluminum was greatly inhibited by the addition of ZnO and dimethyl amine epoxy propane (designated as DE). EIS and EDAX analyses revealed that ZnO produces its effect by depositing on the aluminum surface, which increases the overpotential of hydrogen evolution. It was also found that the addition of DE could greatly improve the deposition of zinc layers.

1. Introduction

Aluminum is a very attractive anode material for batteries [1–12] because of its negative standard potential, high specific capacity and abundance in nature. However, in alkaline electrolytes pure aluminum self-discharges readily by corrosion, resulting in utilization of much less than 100%. With the purpose of improving the behavior of the aluminum anode, two methods are usually used: (1) alloying aluminum with other elements [13–15]; (2) modifying the electrolyte by adding inhibitors [15–20].

It was found that the addition of zinc oxide to the alkaline solution significantly inhibited the corrosion of aluminum anodes [21, 22]. However, when ZnO was the only additive, loose and spongy zinc was deposited on the aluminum surface. In order to obtain a better zinc deposit, we are trying the addition of DE to the zincate-containing alkaline solution in this work.

2. Experimental methods

Electrochemical measurements were made in a classical three-electrode glass cell. The working electrode was prepared from specpure aluminum rod (6 mm in diameter). The electrode surface was polished with 1500-grit waterproof abrasive paper, degreased in acetone and rinsed with deionized water. The reference electrode was a Hg/HgO electrode and the counter electrode was a platinum foil. All the solutions were prepared from A.R. grade reagents and deionized water. The electrochemical measurement system included an EG & G model 273 A potentiostat and a model 5210 lock-in amplifier, controlled by a microcomputer. The potentiodynamic polarization curves were measured at a sweep rate of 1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was measured in the frequency range 120 kHz ~5 mHz and at a.c. signal amplitude of 5 mV. All measurements were made at 25 °C. Before each measurement the electrode was kept in test solution for no less than half an hour, during which a steady open circuit potential was obtained.

3. Results and discussion

Table 1 lists the current densities of hydrogen evolution and inhibition efficiencies obtained from hydrogen collection. The experimental results show that ZnO inhibits the corrosion of aluminum in 4 M KOH solution and its inhibition effect is further enhanced by the addition of DE at certain concentrations, while DE itself has little inhibition effect. It can also be seen that the system containing 0.2 M ZnO and 0.3 ml L^{-1} DE provides the largest inhibition efficiency. When the content of DE in the solution with 0.2 M ZnO is further increased (>0.3 ml L^{-1}), the inhibition efficiency decreases due to the increasing inhibition effect of DE on the zinc deposit on the aluminum surface.

Figure 1 gives the polarization curves of Al in inhibited and uninhibited 4 M KOH solutions. It can

Table 1. The hydrogen evolution current densities and inhibition efficiencies of additives in 4 M KOH solutions

	Hydrogen evolution current density/mA cm^{-2}	η/%
Blank solution (4 M KOH)	12.93	0
0.05 M ZnO	2.91	77.5
0.1 M ZnO	0.76	94.1
0.2 M ZnO	0.32	97.5
0.3 M ZnO	0.94	92.7
0.4 M ZnO	2.70	79.1
0.05 ml L^{-1} DE	9.43	27.1
0.1 ml L^{-1} DE	10.34	20.0
0.2 ml L^{-1} DE	12.25	5.2
0.3 ml L^{-1} DE	8.55	33.9
0.4 ml L^{-1} DE	11.73	9.3
0.6 ml L^{-1} DE	12.78	1.2
0.2 M ZnO + 0.05 ml L^{-1} DE	0.43	96.7
0.2 M ZnO + 0.1 ml L^{-1} DE	0.39	97.0
0.2 M ZnO + 0.2 ml L^{-1} DE	0.35	97.3
0.2 M ZnO + 0.3 ml L^{-1} DE	0.27	97.9
0.2 M ZnO + 0.4 ml L^{-1} DE	0.72	94.4
0.2 M ZnO + 0.6 ml L^{-1} DE	0.88	93.2

be seen that in the zincate-containing alkaline solution the OCP (open circuit potential) shifts in the positive direction by ~200 mV, with an apparent increase in overall current density. The overall current density is contributed to by the following four processes: dissolution of aluminum, hydrogen evolution and deposition and dissolution of zinc. As shown in Table 1, the current density of hydrogen evolution is very small, so the increase in overall current density is mainly attributable to the processes of zinc deposition and dissolution, and this increase does not imply an increase in the corrosion rate of aluminum. Since the potential of zinc is much more positive than that of aluminum, the OCP shifts in the positive direction. It can also be seen that both the anodic and cathodic processes are inhibited by the addition of DE to the zincate-containing alkaline solution. DE increases the anodic and cathodic overpotentials by adsorption on the electrode surface, and higher cathodic overpotential may improve the deposition morphology of zinc.

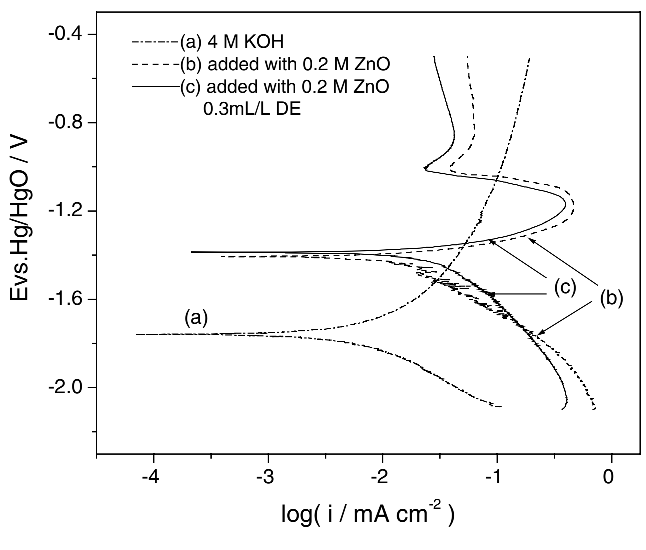

Fig. 1. Polarization curves of Al in 4 M KOH solution with and without additives.

Figure 2 illustrates the EIS of aluminum in 4 M KOH with and without additives at OCP. The differences in EIS indicate that the additives change the electrochemical processes. Figure 2(a) gives the EIS of aluminum in 4 M KOH solution, which reflects the processes of aluminum dissolution and hydrogen evolution. This EIS consists of three parts: a high-frequency capacitive loop, a small middle-frequency inductive loop and a low-frequency capacitive loop [19, 20]. The high-frequency loop is caused by the charge transfer resistance in parallel with the double-layer capacitance. The inductive loop may be attributed to the adsorbed intermediate, and the low-frequency loop to the growth and dissolution of the surface film [19, 20, 23]. The EIS greatly changes when 0.2 M ZnO is added to the electrolyte, and includes a small high-frequency capacitive loop and a

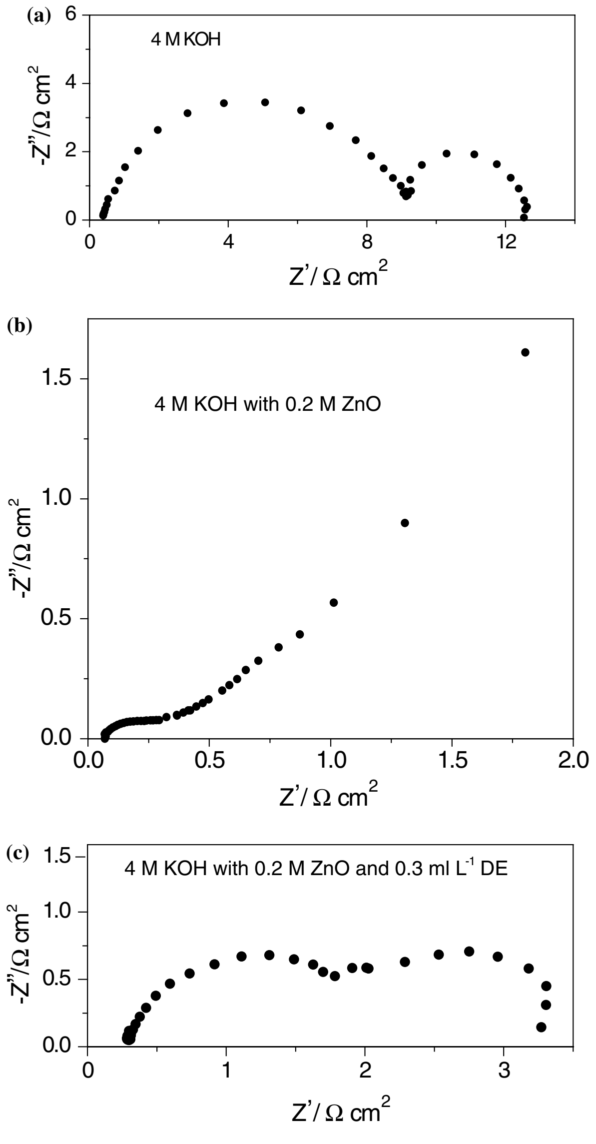

Fig. 2. EIS of pure aluminum in 4 M KOH solutions with and without additives at OCP.

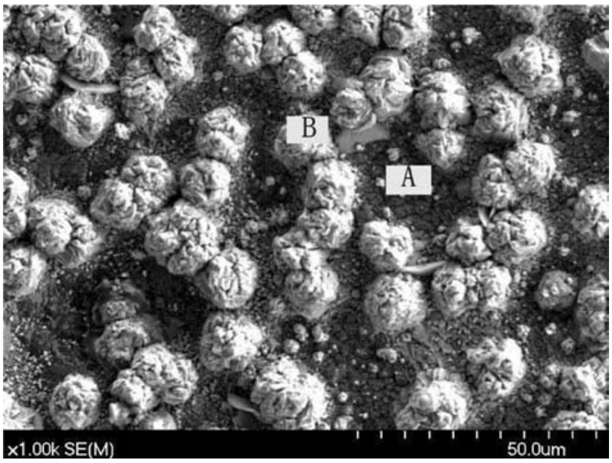

Fig. 3. SEM image of the surface of Al anode after immersion in 4 M KOH containing 0.2 M ZnO and 0.3 ml L^{-1} DE for 2 h.

line with a slope of 1 (Warburg impedance) (Figure 2(b)). The high-frequency loop is mainly caused by the charge transfer resistance in parallel with the double layer capacitance, and semi-infinite diffusion of zincate leads to the Warburg impedance. Figure 2 (c) displays the EIS of aluminum in 4 M KOH containing 0.2 M ZnO and 0.3 ml L^{-1} DE. The EIS consists of two capacitive loops. The high-frequency loop has the identical meaning with those in Figures 2(a) and (b), while the low-frequency loop may result from the adsorption of DE on the electrode surface. It can be inferred from Figures 2(b) and (c) that the addition of DE changes the deposition mechanism of zinc, increases the value of the charge transfer resistance, and then improves the deposition of zinc by increasing electrochemical polarization.

Figure 3 shows the SEM image of the surface of an aluminum electrode after immersion in 4 M KOH containing 0.2 M ZnO and 0.3 ml L^{-1} DE for 2 h. The surface is covered with a granular zinc deposit. The EDAX results in Table 2 show that the aluminum surface (region A in Figure 3) consists of aluminum and a little Zn and ZnO, and the particle (region B in Figure 3) is of Zn and a little ZnO. The ZnO on the electrode surface is probably due to the reaction of freshly deposited zinc with oxygen in air.

The above results indicate that the following reactions occur in the zincate-containing system:

Table 2. The atomic percentage of Al, O and Zn in different regions of aluminum surface*

		Atomic percentage/%			Atomic percentage/%
A:	Al	79.62	B:	Al	0
	O	4.39		O	6.89
	Zn	15.99		Zn	93.11

*Regions A and B are marked in Figure 3.

$$ZnO + H_2O + 2OH^- = Zn(OH)_4^{2-} \tag{1}$$

$$3Zn(OH)_4^{2-} + 2Al = 3Zn + 2Al(OH)_4^- + 4OH^- \tag{2}$$

When the KOH solution only contains ZnO, loose and spongy zinc is obtained, and the adhesion between the zinc layer and the aluminum is poor. In our experiments, the zinc deposit fell into the solution when the Al electrode was removed from the cell, due to the poor adhesion. Therefore, no SEM image of the electrode surface was obtained. However, the addition of DE to the alkaline zincate solution brings about a granular zinc deposit, and the corrosion of Al is effectively and safely inhibited.

4. Conclusions

The corrosion of aluminum in 4 M KOH solution can be greatly inhibited by the addition of ZnO, but the poor adhesion between the zinc layer and the aluminum surface possibly affects the safe use of aluminum anodes in batteries. The addition of DE can bring about a granular zinc deposit on the aluminum surface, and the corrosion of aluminum can be effectively and safely inhibited. EIS and EDAX analyses reveal that ZnO produces an inhibition effect on the corrosion of aluminum by the formation of a zinc deposit on the aluminum.

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