Materials Chemistry and Physics 199 (2017) 73–78

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Effects of dodecyltrimethylammonium bromide surfactant on both corrosion and passivation behaviors of zinc electrodes in alkaline solution

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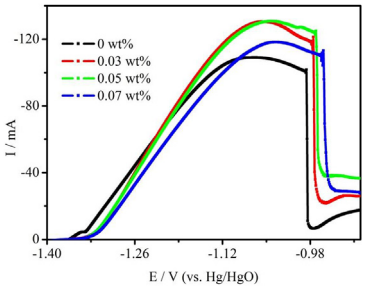
HIGHLIGHTS

- DTAB was firstly used to evaluate electrochemical behavior of Zn electrode.
- DTAB worked as an anodic-type inhibitor for Zn electrode in KOH solution.
- DTAB effectively inhibited corrosion of Zn electrode in KOH solution.
- Adsorption of DTAB on the surface of zinc obeyed Freundlich adsorption isotherm.
- DTAB delayed passivation of Zn electrode in KOH solution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 March 2017
Received in revised form
16 May 2017
Accepted 22 June 2017
Available online 23 June 2017

Keywords:
Zinc electrode
Dodecyltrimethylammonium bromide
Corrosion
Passivation

ABSTRACT

The corrosion and passivation behaviors of zinc electrodes in 7.0 M KOH saturated with ZnO in the presence of dodecyltrimethylammonium bromide (DTAB) surfactant were evaluated by Tafel, linear sweep voltammetry, electrochemical impedance spectroscopy (EIS) and field emission scanning electron microscopy (FE-SEM) tests. It was found that DTAB had a considerable effect on inhibiting zinc corrosion by the adsorption of DTAB. The adsorption of DTAB obeyed the Freundlich isotherm. Tafel polarization curves revealed that DTAB worked as an anodic-type inhibitor. The highest corrosion inhibition efficiency of DTAB was up to 80.2% in the presence of 0.07 wt% DTAB. In addition, potentials of both passivation and anodic dissolution current peak positively shifted in the presence of DTAB, indicating that the passivation was delayed. Based on the EIS tests and FE-SEM analysis in the presence and absence of DTAB, it was shown that the adsorption and favorable moisture retention of DTAB were beneficial to the formation of uniform and fluffy protective layer on the surface of zinc electrode. Such a morphological modification of zinc surface greatly improved the diffusion rate of ions and the utilization of zinc electrode.

1. Introduction

Zinc is widely used as anode materials for alkaline zinc batteries,

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http://dx.doi.org/10.1016/j.matchemphys.2017.06.050
0254-0584/

such as zinc-manganese dioxide [1,2], zinc-air [3,4], zinc-silver oxide [5] and zinc-nickel [6], owing to its low cost, abundance, high capacity, high energy density and low toxicity [7,8]. Generally, both the utilization and the discharge performance of zinc electrode for zinc-based batteries are significantly decreased due to passivation and corrosion of zinc electrode in alkaline solution [9–11].

The passivation of zinc electrode in alkaline solution is regarded as the formation of passive film on surface of zinc electrode [12], and the passive film is considered to be composed of two layers of zinc oxide (ZnO). The first one is a white, fluffy layer formed by a dissolution/reprecipitation mechanism, and the second one is a black, dense ZnO layer formed by the dehydration of discharge product [13]. In order to inhibit the passivation of zinc electrode, surfactants are normally used as electrolyte additives to enhance the diffusion of discharged zinc ions into bulk solution and improve the utilization of zinc [14]. Nowadays, numerous research works mainly focus on inhibiting corrosion of zinc [15–17] by adding inorganic [18,19] or organic compounds [20–23] as electrode additives or electrolyte additives. It was shown that, as electrolyte additive, surfactant affects not only the cathodic reaction but also the anodic reaction of zinc electrode in alkaline solution [23]. However, the effects of electrolyte additive on both corrosion and passivation behaviors of zinc electrodes in alkaline solution were rarely reported [24], especially surfactant.

As a quaternary ammonium surfactant, dodecyltrimethylammonium bromide (DTAB) has favorable chemical stability and moisture retention. DTAB is used to inhibit carbon steel corrosion in well water [25] and, due to the strong interaction with amino acids, DTAB was also widely used in the research of biological system [26].

In our work, different mass fractions of DTAB were added in 7.0 M KOH saturated with ZnO to investigate the electrochemical behaviors of zinc electrodes by Tafel, linear sweep voltammetry and electrochemical impedance spectroscopy (EIS) techniques. Field emission scanning electron microscopy (FE-SEM) was carried out to analyze the surface morphologies of zinc electrodes.

2. Experimental

2.1. Reagents and materials

DTAB was purchased from Ai Keda Chemical Technology Co., Ltd. (Chengdu, China). KOH, ZnO, acetone and zinc sheets were analytical grade and purchased from Chengdu Chemical Reagent Co., Ltd. (Chengdu, China). The reagents used in experiments were not further purified.

The electrolyte used throughout all experiments was 7.0 M KOH saturated with ZnO. The electrochemical behaviors of zinc electrodes were evaluated by adding different mass fractions of DTAB surfactant in 7.0 M KOH saturated with ZnO. Doubly distilled water was used throughout the whole experiments.

2.2. Surface treatment of zinc electrodes

Planar zinc working electrodes were used throughout the whole experiments. The surface of zinc specimens, except for the surface to be tested, was insulated with epoxy resin. Before each experiment, the surface of zinc specimens was polished with emery papers (800, 2000 and 4000 grade), next with 500 and 50 nm aluminum oxide powders until a mirror surface was obtained, and then it was cleaned with doubly distilled water to remove aluminum oxide powders. Finally, the zinc electrode was degreased with acetone and washed with doubly distilled water.

2.3. Electrochemical measurements

Electrochemical measurements were carried out using PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) in a conventional three-electrode system. A treated planar zinc electrode with effective surface area of 0.50 cm^2 was used as working electrode, a foam nickel as counter electrode and a Hg/HgO (7.0 M KOH) as reference electrode to which all potentials were referred. All electrochemical measurements were carried out at room temperature.

Tafel polarization curves were investigated in 7.0 M KOH saturated with ZnO with addition of 0, 0.03, 0.05, 0.07 and 0.09 wt% DTAB in the potential range of −1.65 ~ −1.25 V at constant scan rate of 1 mV s^{-1}.

Anodic polarization curves were investigated in 7.0 M KOH saturated with ZnO with addition of 0, 0.03, 0.05 and 0.07 wt% DTAB in the potential range of −1.40 ~ −0.90 V at constant scan rate of 1 mV s^{-1} by linear sweep voltammetry technique.

For the corrosion behavior of zinc electrodes, EIS measurements were investigated at the open circuit potential (OCP) with ac excitation signal of 10 mV with frequency range from 100 kHz to 8 Hz after immersing zinc electrodes in 7.0 M KOH saturated with ZnO with addition of 0, 0.03, 0.05 and 0.07 wt% DTAB for 1 h.

For the passivation behavior of zinc electrodes, EIS measurements were investigated at the potential of −0.90 V (vs. Hg/HgO) with ac excitation signal of 10 mV with frequency range of 100 kHz to 8 Hz after immersing zinc electrodes in 7.0 M KOH saturated with ZnO with addition of 0 and 0.07 wt% DTAB for 1 h.

2.4. FE-SEM analysis

Surface morphologies of zinc electrodes were observed by FE-SEM (JSM-6360LV, Japan) at an acceleration voltage of 15 kV. Before observation, zinc electrodes were immersed in 7.0 M KOH saturated with ZnO with addition of 0 and 0.07 wt% DTAB for 30 days at room temperature in tightly closed conditions, and then carefully cleaned with doubly distilled water and dried in vacuum.

3. Results and discussion

3.1. Tafel polarization curves of zinc electrodes

Shown in Fig. 1 were Tafel polarization curves of zinc electrodes

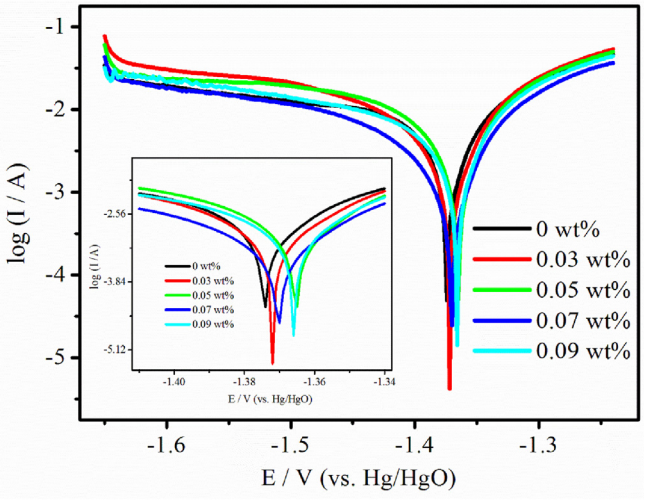

Fig. 1. Tafel polarization curves of zinc electrodes in 7.0 M KOH saturated with ZnO with addition of 0, 0.03, 0.05, 0.07 and 0.09 wt% DTAB. The inset was amplified plot of polarization curves in the potential range of −1.41 ~ −1.34 V.