



Influences of carboxymethyl cellulose on two anodized-layer structures of zinc in alkaline solution



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ABSTRACT

Two anodized-layer structures of zinc in alkaline solution were obtained by different anodic polarizations in 6 M KOH, which contained different carboxymethyl cellulose (CMC) molecular weights (MWs). The electrochemical characteristics and electrodeposition behaviors of the oxide layers, which were obtained before and after passivation, were investigated. Results of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Tafel polarization curves and zinc deposition indicated that different CMC MWs showed opposite effects on the porous oxide layer and passive film. Scanning electron microscopy analyses revealed that CMC with different characteristics can influence the surface structures of the porous oxide layer and passive film.

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1. Introduction

Polymers with functional groups that are characterized by low cost, chemical stability, multiple adsorptions, and the complexation ability with metal ions are considered to be effective inhibitors of metallic corrosion in different environments [1,2]. One such polymer is carboxymethyl cellulose (CMC). The inhibitory ability of CMC on the corrosion of cadmium in 0.5 M HCl was studied by A. El-Sayed [3]. S.A. Umoren et al. [4,5] showed that CMC can physically adsorb onto mild steel and act as its corrosion inhibitor in H₂SO₄ solution. The adsorption of CMC onto the surface of mild steel followed Langmuir and Dubinin–Radushkevich adsorption isotherm models. Afterwards, the CMC was observed to be an inhibitor for the corrosion of some metals in acidic solution, for example, mild steel [6–8].

CMC has been used for a long time in zinc paste electrodes for alkaline zinc-based batteries as a common additive [9]. Alkaline zinc-based batteries are the most important type of the various commercialized batteries due to several traits, such as their low price, non-toxicity, environmental acceptability, thermodynamic stability in an aqueous electrolyte and high specific energy density

(820 Ah kg⁻¹) of zinc [10,11]. Different from the de-intercalated and re-intercalated lithium ions for Li-ion batteries, the chemical and physical properties of zinc electrodes essentially change in the charge and discharge processes of alkaline zinc-based batteries. Thus, the oxide layer, which was formed in the discharge process, would hinder the electrolyte and infiltrate the inside of the zinc electrode [12]. Due to the expansion and shrinkage of Zn/ZnO particles and the shape change of the block electrode during the charge and discharge processes, polytetrafluoroethylene was frequently used as a binder, and it would increase the hydrophobicity of the zinc electrode [13]. Meanwhile, the aqueous electrolyte can hardly soak the highly compact electrode, which was treated by the rolling process. All of these processes decrease the utilization of zinc and produce a low-capacity battery [14,15].

To address this issue, cellulose was applied in zinc paste electrode by the General Motors Corporation in 1980 [16,17]. Analogous works by Muller et al. [18] and Lee et al. [12] revealed that cellulose in zinc oxide paste electrodes suppresses hydrogen evolution as well as dendrite growth and enhances the cycle performance, and this result was attributed to the pore-forming ability of cellulose. Since then, cellulose, particularly CMC, has been introduced into zinc/zinc oxide paste electrodes as a gelling agent in many reports [9,19–22]. Our previous work [23] proved that CMC will affect the zinc anodic reaction and deposition. However, the structure of the anodic product formed in the presence of CMC with different MWs has not been studied. As the discharge product of alkaline zinc-based batteries, the anodic product affects the performance of the

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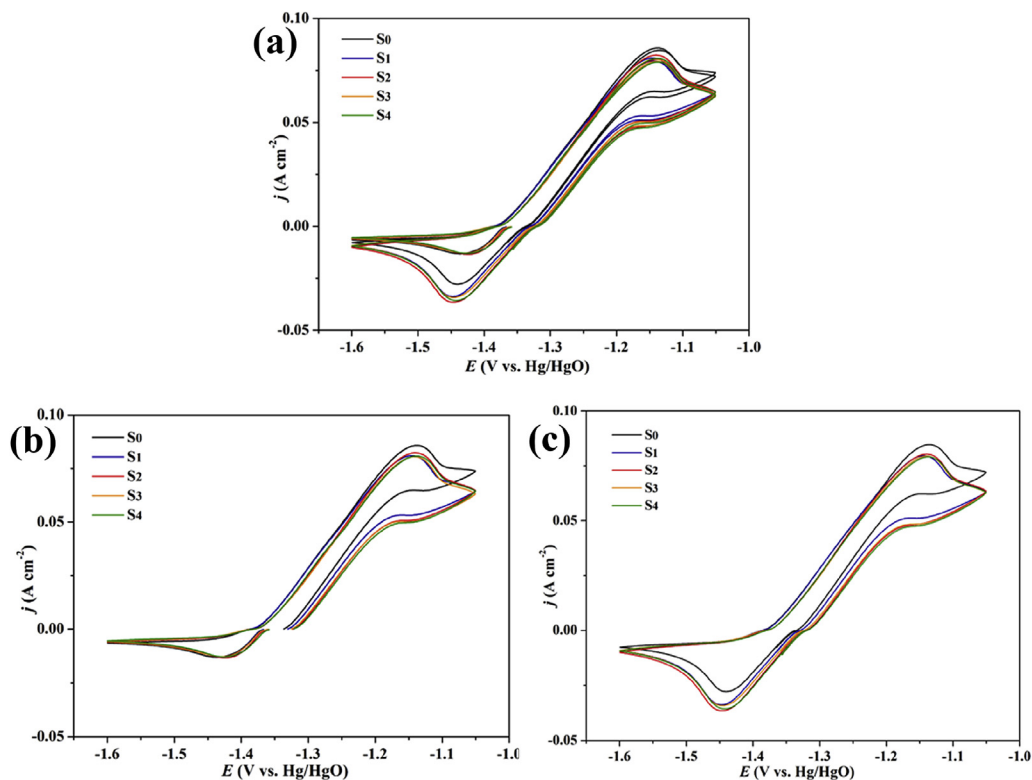


Fig. 1. Cyclic voltammograms for zinc electrodes in 6 M KOH containing 10.0 g L^{-1} CMC with different MWs and 25 g L^{-1} ZnO: (a) both cycles, (b) first cycle, and (c) second cycle.

battery to a large extent. Learning the anodic product structure is essential to understand the influence of CMC on the zinc electrode.

The effects of CMC on the electrochemical characteristics and electrodeposition behavior of zinc oxide layers in 6 M KOH were investigated. Zinc plate electrodes were utilized as the studied electrodes to avoid the influence of different effective surface areas of zinc paste electrodes on the electrochemical characteristics. The porous oxide layer and passive film were obtained by potentiodynamic and galvanostatic cathodic polarizations, respectively. Cyclic voltammetry (CV), Tafel extrapolation, electrochemical impedance spectroscopy (EIS) and zinc deposition measurements were

utilized. Scanning electron microscopy (SEM) measurements were utilized to observe morphologies of the anodic oxide layers.

2. Experimental

2.1. Electrolyte preparation

The molecular weights (MWs) of CMC (Aladdin) used were 90,000 (DS 0.7), 250,000 (DS 0.9) and 700,000 (DS 0.9). KOH (guaranteed reagent) was purchased from the Sinopharm (Shanghai) Chemical Reagent Co., Ltd. The blank solution, which

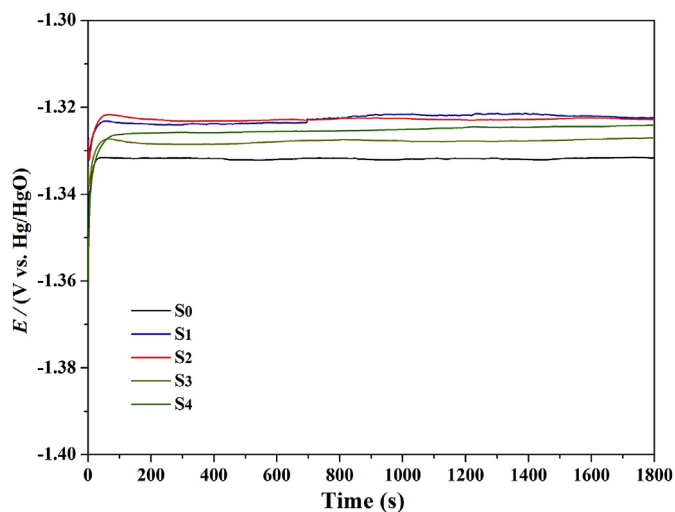


Fig. 2. Galvanostatic anodic polarization at 20 mA cm^{-2} versus time in 6 M KOH containing no or 10.0 g L^{-1} CMC with different MWs at $30 \text{ }^\circ\text{C}$.

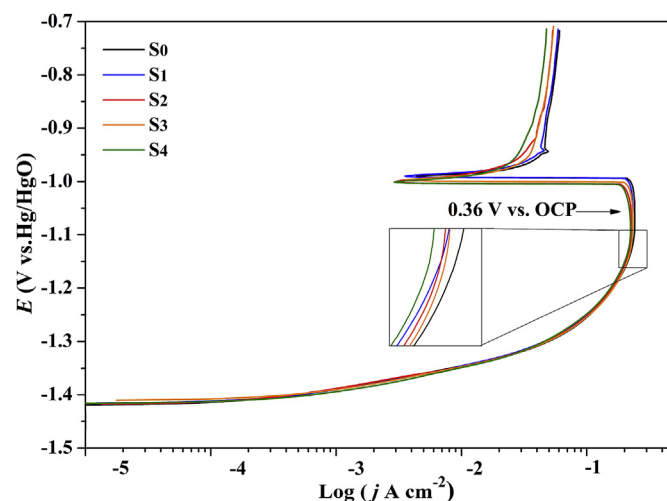


Fig. 3. Potentiodynamic anodic polarization from 0 V to 0.7 V (vs. OCP) in 6 M KOH containing no or 10.0 g L^{-1} CMC with different MWs at $30 \text{ }^\circ\text{C}$.

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