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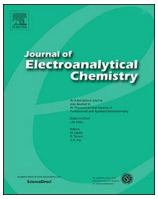

The impact mechanism of Mn^{2+} ions on oxygen evolution reaction in zinc sulfate electrolyte

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ABSTRACT

The impact mechanism of Mn^{2+} on the oxygen evolution reaction (OER) on the fresh lead-based anode in zinc sulfate electrolyte has been studied in detail by several electrochemical methods, XRD, SEM and EDX. The kinetics analysis suggested that the Mn^{2+} could significantly enhance OER, which was controlled by the electron transfer process between the active site S and H_2O (step (2)). This positive effect of Mn^{2+} on OER was limited with the increase of Mn^{2+} because of the approaching saturation of active sites. Results obtained from the Arrhenius equation disclosed the larger bond strength of MnO_2-OH in decreasing the activation energy of OER (from 55.08 to 47.04 kJ/mol), meanwhile, it also further supported the fact that the OER was electrochemical-controlled and it would not be changed in essence with the addition of Mn^{2+}, which is subject to the activation energy barrier of electron transfer induced by the active site S (step (2)). EIS data revealed adsorption resistance of the intermediate (S-OH_{ads}), R_a played a major role among the whole reaction resistance, whereas, the impact contribution of charge transfer resistance, R_t became larger as the Mn^{2+} increases, which revealed that the inhibition of electron transfer process due to the changes of the anode surface microstructure. Electron microscope technology suggested the key role Mn^{2+} played in the modification of the active interface structure, and its influence process on OER was revealed by the microstructure analysis of anode surface. Considering the potential of Mn^{2+} concentration optimization in reducing heavy metal pollutants and energy consumption, enhancing the understanding of impact mechanism of Mn^{2+} on OER provides a feasible proposal in zinc electrolysis industry.

1. Introduction

Zinc is one of the most important base metals required for various applications in metallurgical, textile and chemical industries [1,2]. Over decades of development, more than 85% of the world's zinc products are produced by the hydrometallurgical process [3]. As is known to all, the lead-based anodes are widely employed in the zinc electrolysis industry [4]. Apart from the benefits of its high corrosion resistance and availability in acidic sulfate [5], there are still several shortcomings, such as excessive lead content of the cathode zinc products, poor mechanical properties, high consumption of rare metals and high anodic over-potential [6]. The high level of energy consumption is one of main factors restricting the development of the zinc electrolytic industry, which is resulted from the high anodic potential during the actual production process [7]. The mainly anodic reaction during zinc electrolysis process is the oxygen evolution reaction (OER), accompanied by the relatively minor dissolution of lead-based anode and oxidation of Mn^{2+} (reaction (1)).

$$\begin{aligned}
&MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O\, E^{\theta} = 1.23\ (\mathrm{V\,vs\,NHE})\\
&\alpha - PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O\, E^{\theta} = 1.468\ (\mathrm{V\,vs\,NHE})\\
&\beta - PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O\, E^{\theta} = 1.46\ (\mathrm{V\ vs\ NHE})\\
&O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\, E^{\theta} = 1.23\ (\mathrm{V\,vs\,NHE})
\end{aligned} \tag{1}$$

This over-potential for OER determines the anodic potential and affects the total cell potential [8]. In view of this, some scholars have reported that the over-potential for OER could be reduced effectively by optimizing the silver content in the lead-based anodes [9,10]. But the cost of the significant amount of silver requited is also very considerable. Besides, Lai et al. prepared porous lead-based anode material, which could change the actual current density, thereby reduce the anodic potential [11]. Besides, many literatures have reported the effect of impurity metal ions such as Na^+, Ca^{2+}, Cu^{2+} and Co^{2+} on the energy consumption and current efficiency during zinc electrolysis process [12].

Actually, Mn^{2+} ion in sulfate electrolyte is an essential component, which is quite different from the other metallic impurities during zinc

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electrolysis process. As an important factor, the Mn^{2+} has been reported to be oxidized to form an oxide layer on the anode surface, which is considered to not only favor the corrosion resistance of lead-based anode, but also reduce the OER over-potential [13,14]. Therefore, many scholars have conducted a large number of studies in regards to the preparation and optimization of the MnO_2 layer on lead-based anode surface under laboratory conditions. Mohammadi et al. found that the over-potential for OER in sulfuric acid electrolyte could be reduced due to the presence of MnO_2 particles embedded into the lead matrix [15]. Jaimes et al. observed that the microscopic appearance of this MnO_2 layer changed with the addition of Mn^{2+}, directly affecting the electrochemical performance of the electrode [16]. And this oxide layer is considered as a diffusion barrier layer for oxygen species, significantly decreasing the oxidation rate and overvoltage of the lead anode [17]. Besides, some scholars prepared a Pb-MnO_2 composite anode containing composite particles dispersed through the entire anode by electrodeposition, which provided better electrocatalytic activity than the traditional Pb-Ag anodes in sulfate electrolyte [18]. Nevertheless, most of the above-mentioned researches could only provide some apparent information on electrode properties, and little attention is spent on the impact mechanism of Mn^{2+} on OER. Moreover, the presence of Mn^{2+} inevitably results in the generation of the anode slime in the electrolytic zinc system, which contains high lead content. And this anode slime recycled within electrolysis system usually causes lead accumulation as well as a lot of lead hazardous wastes in zinc electrolysis industry [19]. In general, there is still a great lack of adequate understanding of the influence mechanism of Mn^{2+}, which leads to different requirements for Mn^{2+} among the zinc electrolysis enterprises. And the accompanying issues for resource consumption of Mn and potential heavy metal contamination of the anode slime have not been given adequate attention. Considering the competitive relationship between the OER and the generation of the anode slime, the impact mechanism of Mn^{2+} on anodic polarization reaction is interesting and needed to be investigated.

In this paper, an attempt was conducted with the aim of increasing the understanding of the impact mechanism of Mn^{2+} for OER in zinc sulfate electrolyte. The effect of Mn^{2+} on the kinetic parameters for OER were detailed investigated in acid zinc sulfate electrolyte using anodic polarization curves, quasi-stationary polarization (Tafel), Arrhenius formula and electrochemical impedance spectroscopy (EIS) measurements. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed in the analysis of the morphology and composition of anode surface.

2. Experimental

2.1. Reagents

The electrolyte used in this study was prepared with 45 g/L Zn^{2+} and 160 g/L H_2SO_4, Mn^{2+} ions were added into the electrolyte to get the desired solution composition. All reagents ($ZnSO_4 \cdot 7H_2O$, H_2SO_4 and $MnSO_4 \cdot H_2O$) were guaranteed reagent grade. The zinc sulfate solution was further purified to make sure the composition of the electrolyte met the requirements of electrochemical deposition.

2.2. Electrochemical measurements

The electrochemical experiments, including linear sweep voltammetry tests (LSV) and electrochemical impedance spectroscopy (EIS) and were based on a CHI608D electrochemistry workstation (Shanghai Chenhua, China) using a three-electrode system. A lead-based anode sample with geometric areas 0.196 cm^2 was used as the working electrode, the corresponding aluminum sheets were used as cathodes, and the reference electrode was a saturated mercurous sulfate electrode (MSE). Unless otherwise specified, all potentials were recorded with respect to the MSE. All experiments were carried out from the electrolyte with designed temperature and Mn^{2+} ions concentrations. Before each group of experiments, the anode samples were polished using 400, 800, and 1200 mesh sandpapers to obtain a fresh surface, then washed thorough ultrasonic cleaning with distilled water before being ready for use. And N_2 was poured to the electrolyte for 30 min in order to get rid of the oxygen dissolved. For LSV measurements, the potential was scanned from 1.2 V to 1.5 V for anodic potentiodynamic polarization with a constant scan rate of 1 mV/s. The EIS tests were performed by applying alternating current amplitude of 5 mV root mean square among the 10^5 Hz to 10^{-1} Hz frequency range. All anodic polarization curves and EIS measurements were repeated three times.

2.3. Morphology measurements

The morphology of the anode surface deposits was examined by scanning electron microscope (SEM, Qunata FEG 250) and Energy Dispersive X-Ray Spectroscopy (EDX) to obtain high resolution images and element analysis. X ray diffraction (XRD, Rigaku Ultima IV) was used to analyze their phase composition. After LSV measurements mentioned above, the anode samples were immediately removed from the electrolyte then immersed into ultra-pure water with ultrasonic cleaning for a period of 10 min to minimize the amount of ions on the surface of anode samples that can be carried from electrolyte. Each SEM, EDX or XRD measurement corresponded to a new anode sample.

3. Results and discussion

3.1. Effect of Mn^{2+} kinetic parameters for OER

In order to obtain the information about OER on the lead-based anodes from zinc sulfate electrolyte, steady polarization curves were performed in the absence and presence of Mn^{2+}. Based on the past extensive reports, the mechanism of OER on active metal oxide electrodes could be proposed as the following reaction steps [20].

$$S + H_2O \rightarrow S - OH_{ads} + H^+ + e^- \tag{2}$$

$$S - OH_{ads} \rightarrow S - O_{ads} + H^+ + e^- \tag{3}$$

$$2S\text{–}OH_{ads} \rightarrow S - O_{ads} + S + H_2O \tag{4}$$

$$S - O_{ads} \rightarrow S + 0.5O_2 \tag{5}$$

Where S represents the active site on the electrode surface and S-OH_{ads}, S-O_{ads} are adsorption intermediates. In view of these four steps, the rate determination step for a specific electrode is normally judged by the corresponding tafel slope for OER. This is because the tafel slope of the oxide electrodes largely depends on its type, composition and physical properties. These factors effectively dominate the rate of electron transfer in multiple step reactions, which determines the rate determination step in essence [21,22]. And for the lead dioxide electrode, the rate determination step could generally be judged by that when the tafel slope b was $\geq 120\ mV\ dec^{-1}$, step (2)- the electron transfer process between the active site S and H_2O was rate determining; when b is $\sim 40\ mV\ dec^{-1}$, the rate determination step was suggested to be step (3) and (4); and when b was $\sim 15\ mV\ dec^{-1}$, step (5)-the generation of O_2 was rate determining. In this case, the determination of rate control steps (2) or (3) could be used to corroborate that the whole electrode reaction process is electrochemical-controlled due to the electron transfer procedure that is included.

In this work, the anodic kinetic parameters such as Tafel slope b, Transfer coefficient β and anodic exchange current density j_0 are determined from the anodic polarization curves (Fig. 1) using the Tafel formula [23].

$$\eta = a + b \log j \tag{6}$$

$$\log j_0 = -\frac{a}{b} \tag{7}$$