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Zinc electrodeposition from flowing alkaline zincate solutions: Role of hydrogen evolution reaction

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HIGHLIGHTS

- Hydrogen evolution reaction has a complex role during zinc electrodeposition.
- Current efficiency of zinc deposition is lowered by hydrogen evolution.
- Rising hydrogen bubbles increase zinc limiting current density.
- Current density ratio is not suitable as zinc morphology indicator.

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ABSTRACT

The hydrogen evolution reaction is known as a parasitic reaction during the zinc electrodeposition from alkaline zincate solutions and is thus responsible for current efficiency losses during the electrolysis. Besides that, the rising hydrogen bubbles may cause an extra convection within a diffusion layer, which leads to an enhanced mass transport of zincate ions to an electrode surface. In this work, the mentioned phenomena were studied experimentally in a flow through electrolyzer and the obtained data were subsequently evaluated by mathematical models. The results prove the indisputable influence of the rising hydrogen bubbles on the additional mixing of the diffusion layer, which partially compensates the drop of the current efficiency of the zinc deposition at higher current flows. Moreover, the results show that the current density ratio (i.e., the ratio of an overall current density to a zinc limiting current density) is not suitable for the description of the zinc deposition, because the hydrogen evolution current density is always involved in the overall current density.

1. Introduction

A zinc metal has been historically a very popular negative electrode material and hence was used especially in primary batteries due to its good electrochemical behavior, high electrochemical equivalence, non-toxicity, low-cost and availability [1]. Therefore, researchers attempted to develop also secondary or flow batteries based on the zinc electrochemistry especially in alkaline solutions, where a zinc electrode can be combined with a nickel [2–4] or an air [5–7] electrode, but the widespread use of zinc-based secondary batteries is restrained mainly by the poor cycle life of the zinc electrode [8].

The poor cycle life is caused by shape changes and dendritic growth of the electrode [8]. These phenomena are linked with an electrochemical dissolution and deposition of the zinc metal during cycling, so it is important to control the morphology of the zinc deposits. Many researches [9–16] paid attention to determine factors, which influence the final zinc morphology, and among them an electrolyte convection, an applied current density, a zincate concentration and a presence of additives in the electrolyte were proved to play the key role. Although the electrolyte convection was found as an important factor affecting the zinc electrodeposition, the effect of convection caused by rising hydrogen bubbles has been studied minimally.

This work aims to study the influence of the hydrogen evolution reaction on the zinc electrodeposition from the flowing alkaline zincate solutions. Since the hydrogen evolution reaction is thermodynamically preferred, as the value of the standard reduction potential for the hydrogen reduction is higher than for the zinc reduction, it can be expected that the coulombic efficiency of the zinc deposition will be lowered by the presence of the hydrogen gas evolution [17]. On the other hand, the rising hydrogen bubbles may influence the mass-

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transfer rate of zincate ions to the zinc electrode, since the effect of mass-transfer enhancement by rising bubbles within a mass-transfer boundary layer was reported in literature [18]. Therefore, the final influence of the hydrogen evolution reaction on the zinc electrodeposition is complex. Another issue related to the presence of the hydrogen evolution reaction is the characterization and the prediction of the deposited zinc metal morphology. For these purposes, a current density ratio (i.e., the ratio of an overall current density to a zinc limiting current density) is often used. Its value equal to 1 should intuitively mean the mass transfer limitation of the zinc electrodeposition, which leads to the dendritic growth of zinc metal. However, some researchers [12,13] haven't observed such correlation of the current density ratio with the zinc morphology.

The presented study consists of experimental electrodepositions of zinc metal in the electrolyzer with a convective flow of the electrolyte and of subsequent data evaluation using mathematical models describing the process with and without the dependence of the zincate mass-transfer rate on the hydrogen gas evolution. This approach enables us to reveal the complicated role of the hydrogen evolution on the zinc electrodeposition, especially the influence of the rising hydrogen bubbles on the limiting current density of the zinc deposition, which is linked with the mass-transfer rate of the zincate ions. It is also demonstrated that the correlation of the morphology of the zinc deposits with the current density ratio, which is commonly used for the characterization of deposits, is not generally applicable when used as a deposition criterion.

2. Experimental part

2.1. Experimental setup

The experiments were conducted in the in-house-designed and constructed flow through cell (see Fig. 1). The cathode for the zinc deposition was made of carbon composite plate (PPG 86, SIGRACET) with a square shaped electrode active area of 2.25 cm^2. The anode for the oxygen evolution was made of the rolled nickel foam of the same size as the cathode. These two electrodes were parallel to each other with a gap of 1.0 cm. The electrolyte inlet was connected to the bottom of the cell to ensure upward flow of the electrolyte. The electrolyte flow rate of 6 $cm^3\ s^{-1}$ was maintained by a peristaltic pump with a flow output stabilized by an air vessel. The zinc deposition was conducted using a three-electrode arrangement, in which the electric current was supplied by a power supply and both current and voltage responses were measured by universal multimeters. The Hg/HgO reference electrode was connected at the bottom of the cell via a capillary tube ended by a fritted glass.

As the electrolyte, solutions of 8 mol dm^{-3} KOH (p.a. purity) containing various concentrations of ZnO (p.a. purity) were used in a great excess. The precise ZnO concentrations were determined by a chelatometric titration. Before each experiment, the cathode was polished with a sandpaper of P2500 grit size, degreased with ethanol (95% vol. + 5% vol. methanol) and weighted on the analytical balance. Then the zinc was deposited at selected constant current densities by an electric charge of 45 A s (an equivalent of 0.152 mg zinc). Immediately after the deposition, the cathode with the deposited zinc metal was rinsed in ethanol, left for 5 min at temperature of 50 °C to evaporate possible residues and weighted again. Based on the weighting, the coulombic efficiency of the zinc deposition was calculated using the Faraday's laws of the electrolysis as follows:

$$\eta_C = \frac{m_{Zn,deposited}\frac{z_{Zn}F}{M_{Zn}}}{Q} \quad (1)$$

The oxidation of zinc deposits during the mentioned treatment, which could influence the value of the coulombic efficiency based on the weighting, hasn't happened, since the coulombic efficiencies were during the first few depositions determined also by the chelatometric titration and the provided values were very similar to the values of the weighting method. Consequently, the optical analysis of the zinc deposits was carried out using a scanning electron microscope.

2.2. Mathematical approach

The obtained data from the zinc deposition in the flow through cell were regressed with two mathematical models – the first one reflecting the additional mixing of the diffusion layer by the rising hydrogen bubbles and the second one neglecting this influence. The only chemical reactions considered for the mathematical description are zinc deposition and the hydrogen evolution as follows:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \quad (2)$$

$$[Zn(OH)_4]^{2-} + 2\,e^- \rightarrow Zn + 4\,OH^- \quad (3)$$

An overall current density at the electrode is given by the sum of corresponding current densities of the proposed chemical reactions according to the following equation:

$$j = j_{H_2} + j_{Zn} \quad (4)$$

The hydrogen evolution reaction is described by the Tafel kinetics (see equation (5)) and it is assumed that kinetics constants are identical for the hydrogen evolution that takes place on the deposited zinc of different morphology as well as on the carbon composite plate.

$$j_{H_2} = -j_{0,H_2}\exp\left[-\alpha_{C,H_2}\frac{z_{H_2}F}{RT}\left(E - E^0_{H_2}\right)\right] \quad (5)$$

The zinc deposition reaction is expressed by the Butler-Volmer kinetics combined with a mass transport limitation of the zinc reduction

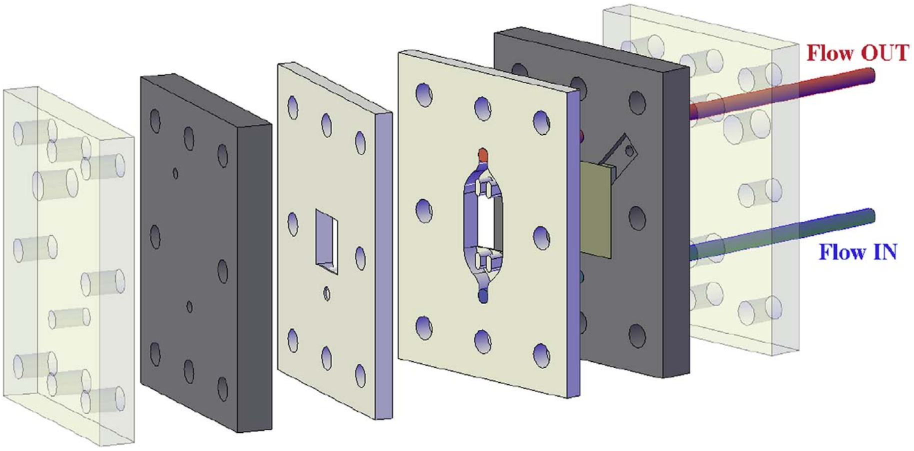

Fig. 1. Scheme of the flow through deposition cell.