



Development of silica based coatings on zinc particles for improved oxidation behavior in battery applications

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ABSTRACT

ZnO and Zn(OH)₂ layers formed on zinc metal upon contact with aqueous media, like 6 M KOH electrolyte used in zinc air batteries, do not provide sufficient protection against further zinc oxidation leading to hydrogen evolution as well as self-discharge of the battery itself. In this work, the syntheses of artificial coatings based on silica, SiO₂, were investigated, which should improve zinc metal oxidation stability to reduce aqueous corrosion of battery grade zinc particles. For synthesis of silica coatings the precursor tetraethyl orthosilicate (TEOS) was used. Chemical vapor deposition (CVD) in synthetic air and chemical solution deposition (CSD) under argon in polyol media were used for synthesis of these coatings on zinc under different thermal conditions. Zinc silicate formation was observed upon CVD while silica was formed upon CSD. The capability of the silicate based coatings to enhance oxidation resistance of zinc was analyzed via volumetric measurement of hydrogen evolution upon wet corrosion in 6 M KOH. Thermodynamic calculations were used to analyze the composition of the synthesized coatings and their compositional changes in concentrated KOH. As a result, silicate based coatings are able to reduce zinc corrosion by almost 40% by formation of protective layers in 6 M KOH. These results were confirmed by hot air corrosion tests.

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1. Introduction

Zinc metal is used as an anode material for zinc air batteries. Since corrosion of zinc in aqueous electrolyte leads to formation of ZnO or Zn(OH)₂ layers, self-discharge of the battery occurs [1,2]. Oxidation of zinc metal in alkaline aqueous media is a thermodynamically favored reaction, which - depending upon a certain hydrogen overvoltage of zinc [3] as well as upon thickness and density of the formed ZnO/Zn(OH)₂ layers - can only be reduced slightly [4]. Naturally grown ZnO films on zinc metal do not provide sufficient protection against corrosion due to their porosity and semiconducting properties. The ZnO layers grow outwards from the metal and are prone to spallation, therefore zinc metal surface is again exposed to the electrolyte (breakthrough oxidation) [5,6]. In aqueous solution the adsorbed species are OH-groups on the zinc surface, therefore Zn(OH)₂ can be formed along with ZnO accompanied by H₂ evolution as side reaction, Eqs. (1)–(3):



In strong alkaline solutions these compounds dissolve and react to Zn(OH)₃⁻ or Zn(OH)₄²⁻. After supersaturation precipitation of Zn(OH)₂ occurs. A dense ZnO layer is formed after dehydration of Zn(OH)₂, while the OH-containing compounds remain at the outer surface forming a porous Zn(OH)₂ layer on top of the ZnO layer [6–9]. The overall mechanism of wet electrochemical corrosion is shown in Eq. (4):



Hydrogen evolution itself leads to battery leakage or voltage drops during battery operation [3]. A strategy to inhibit corrosion of zinc metal in aqueous solution should concentrate on reducing semiconductive properties of the corrosion layer as well as preventing direct contact of zinc with the electrolyte. Thus, a compromise has to be found between reducing conductivity of the layer to minimize zinc corrosion and ensuring electrochemical accessibility for high zinc utilization during discharge of the battery.

For inhibition of aqueous corrosion of zinc different measures are known [1,10–13]. Lee et al. [11] reported that alumina as a coating layer on zinc can prevent zinc from exposure to the alkaline electrolyte. Moreover, inhibition of zinc oxidation and H₂ evolution is achieved by introduction of alloying elements, like Pb, In and Bi in battery grade zinc particles [1]. Corrosion protection of metals, e. g. zinc or steel,

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with silicate based layers are investigated and discussed in [14–19], where corrosion stability is mainly investigated in salt solutions or under atmospheric conditions.

In the present work, artificial functional oxide coatings were developed for zinc particles with the aim to improve wet corrosion stability in 6 M aqueous KOH and reduce self-discharge of zinc batteries. Thus, formation of porous ZnO or Zn(OH)₂ layers should be avoided in order to achieve less hydrogen evolution. Silica coatings were chosen, due to their electronic insulation properties as well as ability to form hydroxides, Si(OH)₄, which prevent hydroxide-adsorption on zinc metal and therefore zinc corrosion [14,15]. A widely used method for synthesis of silica coatings on zinc substrates is sol deposition as discussed in [17–20]. In [21] electrodeposition of SiO₂ on Zn has been performed.

As an alternative approach, in the present work chemical vapor deposition (CVD) is compared with chemical solution deposition (CSD). Tetraethyl orthosilicate (TEOS, (C₂H₅O)₄Si) was used as SiO₂ precursor. Beside different temperature regimes (CVD: 350 °C, CSD: 196 °C), different oxygen activities were investigated. CSD was carried out under argon, while CVD was performed in synthetic air (nitrogen with $p_{O_2}/p_0 = 0.2$, $p_0 = 1$ atm).

Thermodynamic calculations were performed on oxide forming reactions in synthetic air and inert atmosphere, and compared with experimental results. Composition, layer thickness and morphology of the various zinc coatings were investigated by spectroscopic and microscopic methods. The performance of the coatings under wet corrosion was characterized by volumetric measurements of the amount of evolved hydrogen gas in 6 M KOH. Thermodynamic considerations as well as experimental data were used to analyze oxidation stability in aqueous media. These results were confirmed by hot air corrosion measurements.

2. Material and methods

2.1. Synthesis of SiO₂-based coatings

2.1.1. CVD process

CVD with TEOS can be conducted in two different ways: as pyrolysis according to Eq. (5) under reducing conditions or as partial oxidation under presence of oxygen, according to Eq. (6) [22–24]:

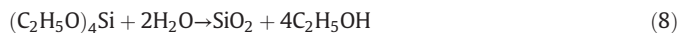


In order to enable control on oxygen activity the CVD process in this work was performed in synthetic air and partial oxidation of TEOS was assumed (Eq. (6)). An in-house built fluidized bed reactor was used for CVD process. Fig. 1a shows a flow chart of the system. Battery grade zinc granules ($d_{50} = 250 \mu\text{m}$; alloying agents, analyzed by ICP-OES: 516 ppm Pb, 306 ppm In, 301 ppm Bi) were fluidized and oxidized at atmospheric pressure p_0 in synthetic air (nitrogen with $p_{O_2}/p_0 = 0.2$), with TEOS (Sigma Aldrich, $\geq 99.0\%$) as SiO₂ precursor. Synthetic air was used as carrier gas for TEOS, which was saturated to air in a stainless steel bubbler heated to 60 °C. The fluidizing gas was bypassing the bubbler using a gas flow rate of $180 \text{ dm}^3 \text{ h}^{-1}$. The reactor was heated to 350 °C. In order to achieve sufficient coating thickness, coating duration was 4 h.

2.1.2. CSD process

CSD was performed in a solution of TEOS in the polyol ethylene glycol (Merck, 99.9%) under inert atmosphere (argon). In Fig. 1b, a flow chart of this set-up is depicted. By applying the polyol solvent under inert gas, oxidation of zinc was avoided. Near the boiling point of ethylene glycol (196 °C), its dehydration leads to formation of acetaldehyde [25], and subsequently hydrolysis of TEOS forms silica and ethanol

[26] as shown in Eqs. (7) and (8):



Silica was deposited on the zinc granules at a temperature of 196 °C during 60 s processing time.

2.2. Analysis of coating thickness and composition

Cross sections of the zinc particles were investigated by a field emission scanning electron microscope (FE-SEM with in-lens detector; 3 kV; Leo Gemini 1530, Zeiss, Germany), and by a scanning electron microscope (SEM with SE detector), which is equipped with a unit for energy dispersive X-ray spectroscopy (EDX) for elemental analysis (JSM-840A, JEOL, Japan; INCA 4.05 EDS, Oxford Instruments Microanalysis Limited, UK). For preparation of cross sections the zinc particles were embedded in epoxy resin and ground and polished until the cross-section was laid open.

Powder X-ray diffraction using CuK α could not resolve the crystal structure of the coating layers due to their thin thickness of only few nm or due to small amount of some of their compounds, respectively.

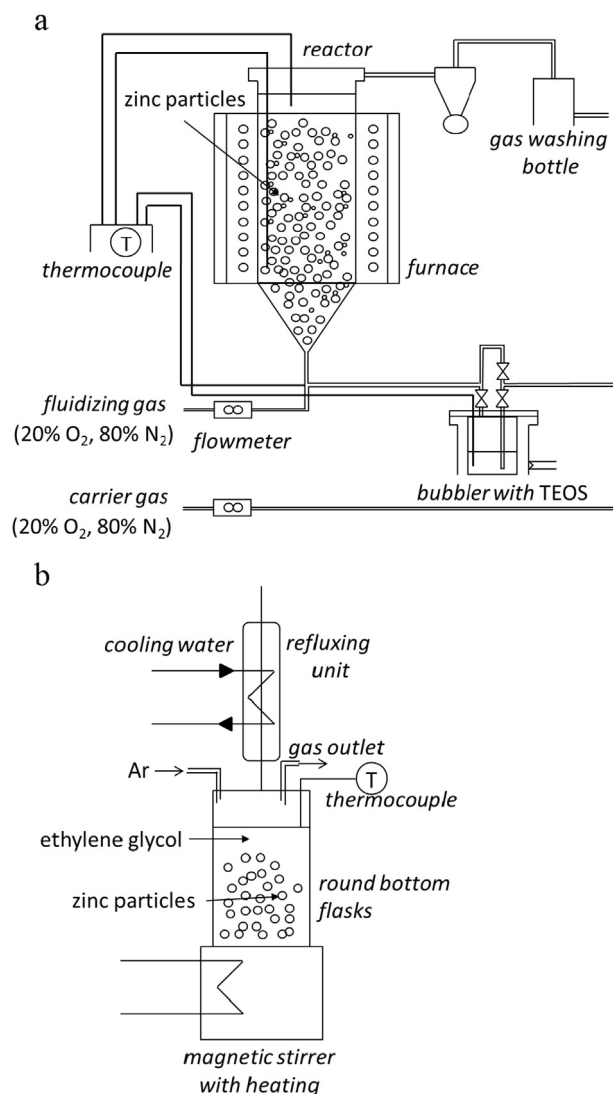


Fig. 1. Flow chart of a: fluidized bed reactor used for CVD process (350 °C, nitrogen with $p_{O_2}/p_0 = 0.2$), b: polyol set-up for CSD process (196 °C, argon atmosphere).

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