



Electrochemical behavior of zinc particles with silica based coatings as anode material for zinc air batteries with improved discharge capacity



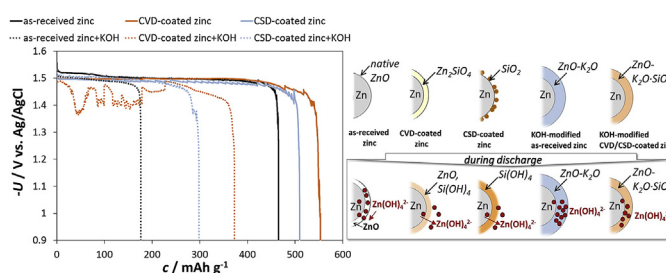
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HIGHLIGHTS

- Electrochemical behavior of silica coated zinc particles is discussed.
- Silica coatings are realized by CVD/CSD processes and modified by KOH treatment.
- SiO₂-coated zinc improves discharge capacity by reducing formation of ZnO layers.
- KOH-modified SiO₂-coated zinc particles improve rechargeability after 100% DOD.
- Diffusion coefficients, charge carrier numbers and activation energies are shown.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 January 2017
Received in revised form
2 March 2017
Accepted 21 March 2017

Keywords:

Zinc anode
Silica coatings
Electrochemical oxidation behavior
Discharge capacity
Charge carrier numbers
Electrochemical activation energies

ABSTRACT

Silica coatings on zinc particles as anode material for alkaline zinc air batteries are expected to reduce early formation of irreversible ZnO passivation layers during discharge by controlling zinc dissolution and precipitation of supersaturated zincates, Zn(OH)₄²⁻. Zinc particles were coated with SiO₂ (thickness: 15 nm) by chemical solution deposition and with Zn₂SiO₄ (thickness: 20 nm) by chemical vapor deposition. These coatings formed a Si(OH)₄ gel in aqueous KOH and retarded hydrogen evolution by 40%. By treatment in aqueous KOH and drying afterwards, the silica coatings were changed into ZnO-K₂O-SiO₂ layers. In this work, the electrochemical performance of such coated zinc particles is investigated by different electrochemical methods in order to gain a deeper understanding of the mechanisms of the coatings, which reduce zinc passivation. In particular, zinc utilization and changes in internal resistance are investigated. Moreover, methods for determination of diffusion coefficients, charge carrier numbers and activation energies for electrochemical oxidation are determined. SiO₂-coated zinc particles show improved discharge capacity (CVD-coated zinc: 69% zinc utilization, CSD-coated zinc: 62% zinc utilization) as compared to as-received zinc (57% zinc utilization) at C/20 rate, by reducing supersaturation of zincates. Additionally, KOH-modified SiO₂-coated zinc particles enhance rechargeability after 100% depth-of-discharge.

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1. Introduction

Zinc metal is widely known as anode material for zinc air batteries with high theoretical specific energy. Advantages of this cell system, such as high safety and low cost, are summarized in Ref. [1],

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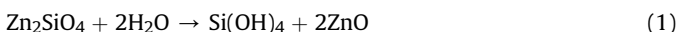
together with the restrictions in terms of electrode material degradation in alkaline electrolyte, limiting its application to a primary battery up to now.

ZnO and Zn(OH)₂ passivation layers on zinc metal, formed during discharge in alkaline solutions, lead to a decrease in electrical conductivity. Thus, the active material utilization during initial discharge is reduced and electrochemical reversibility impeded [1–6]. Zinc passivation occurs by dissolution and precipitation mechanism: during discharge zincate ions get dissolved into the electrolyte and precipitation of supersaturated zincate ions results in formation of Zn(OH)₂ layers on top of the zinc surface. Dehydration of the discharge product Zn(OH)₂ leads to formation of a dense passive ZnO film limiting further zinc utilization. The ZnO layer may be covered with a porous Zn(OH)₂ film due to redissolution of ZnO and re-precipitation [6–11].

Another problem is electrochemical corrosion of zinc in aqueous electrolytes. This leads to self-discharge, due to zinc oxidation with hydrogen evolution as side reaction [6–11].

Measures to control the kinetic of zinc oxidation during discharge as well as to improve hydrogen overvoltage have been widely reported [2–4,12–20], whereby structuring of the active material, protective zinc coatings or electrolyte additives are quite common approaches. Lee et al. [4] reported, that Al₂O₃ as a coating layer on zinc particles prevented zinc from exposing to the KOH electrolyte, resulting in improved active material utilization and less self-discharge. Less hydrogen evolution as well as higher discharge capacity was obtained by lithium boron oxide coatings on zinc particles [14]. Another possibility to improve self-discharge in battery applications is the usage of alloying elements, like Pb, In and Bi in zinc metal [17–19]. The effect of silica based coatings under atmospheric conditions [20] and of SiO₃²⁻ ions in alkaline electrolytes [21] were investigated to influence the zinc oxidation. But up to now, there have been no approaches to improve the discharge capacity of battery grade zinc particles by coating with silica and no reports about rechargeability of coated zinc particles after 100% depth-of-discharge (DOD).

In our previous paper [22] battery grade zinc particles were coated with silica based layers by chemical vapor deposition (CVD) and chemical solution deposition (CSD) with tetraethyl orthosilicate (TEOS) as precursor. As shown in Ref. [22], by CVD process Zn₂SiO₄ coatings on zinc with a thickness of 20 nm were established during hot air oxidation. Zinc particles coated by CSD in a polyol solution exhibited a SiO₂ layer with 15 nm thickness. Hydrogen evolution of CVD- and CSD-coated zinc particles in 6 M KOH could be reduced by 40% [22], because exposure of zinc metal to the aqueous electrolyte is inhibited due to the coatings. By swelling of the silica layers in aqueous KOH a Si(OH)₄ gel was formed (Eqs. (1) and (2)). This clarifies, that these coatings do not have insulating properties, but accessibility of OH⁻ ions is possible [22]:



Further modifications of as-received zinc and silica coated zinc particles were realized by treatment in 6 M KOH [22]. In Table 1 the resulting coating compositions and coating thicknesses of the differently coated zinc particles are shown, which are discussed in detail in Ref. [22] and used for electrochemical characterization in this work.

In this work, the electrochemical oxidation behavior of the CVD- and CSD-coated zinc particles, with and without KOH modification, is introduced. Different electrochemical methods are applied, in order to characterize the passivation behavior of these particles.

Table 1

Overview of silica coated zinc particles, according to [22]: composition and coating thickness.

Coated zinc particles	Composition of the coating	Coating thickness
CVD-coated zinc	Zn ₂ SiO ₄	20 nm
CSD-coated zinc	SiO ₂	15 nm
KOH-modified zinc	75ZnO: 1K ₂ O	40–70 μm
KOH-modified CVD-coated zinc	160ZnO: 2K ₂ O:1SiO ₂	30–50 μm
KOH-modified CSD-coated zinc	160ZnO: 2K ₂ O:1SiO ₂	30–70 μm

These investigations include active material utilization after discharge to 100% DOD, electrochemical impedance spectroscopy (EIS) measurements and methods to determine charge carrier numbers, electrochemical activation energies as well as diffusion coefficients at different current rates in 6 M KOH. The behavior of zinc dissolution and precipitation of supersaturated zincates during electrochemical oxidation of the silica coated zinc particles is discussed. Additionally, the rechargeability of the differently coated zinc materials after 100% DOD is investigated.

2. Experimental section

2.1. Synthesis

Zinc granules ($d_{50} = 250 \mu\text{m}$; alloying agents analyzed by ICP-OES: 516 ppm Pb, 306 ppm In, 301 ppm Bi) were used as substrate material. As SiO₂ coating methods CVD and CSD processes were applied. For both, CVD as well as CSD process, the same SiO₂ precursor tetraethyl orthosilicate (TEOS, (C₂H₅O)₄Si, Sigma Aldrich, ≥99.0%) was used. CVD was performed at atmospheric pressure p_0 in synthetic air (nitrogen with $p_{O_2} p_0^{-1} = 0.2$) by use of a fluidizing bed reactor heated up to 623.15 K, resulting in a Zn₂SiO₄ coating (coating duration 4 h). CSD process was realized in a solution of TEOS in the polyol ethylene glycol (Merck, 99.9%) under inert atmosphere (argon) at 469.15 K (coating duration 60 s). Due to the reducing behavior of the polyol solution, formation of a SiO₂ coating without any oxidation of the zinc particles was ensured. Additionally, naturally grown ZnO on as-received zinc was transformed into a ZnO-K₂O layer, and CVD as well as CSD coatings formed a ZnO-K₂O-SiO₂ layer during KOH modification. The KOH treatment of the differently coated zinc particles was performed by swelling in 6 M KOH electrolyte (20 h, 313.15 K), rinsing with distilled water and ethanol and drying in air at 353.15 K afterwards. More details of the coating synthesis and coating compositions were described earlier in Ref. [22] and summed up in Table 1.

2.2. Morphology characterization

The morphology and the elemental composition of the zinc particles after electrochemical measurements were determined by a scanning electron microscope (SEM) together with EDX at 10 kV (JSM-840A, JEOL, Japan; INCA 4.05 EDS, Oxford Instruments Microanalysis Limited, UK) and by a field emission scanning electron microscope (FE-SEM) at 3 kV (Leo Gemini 1530, Zeiss, Germany). For post-mortem analysis the electrode materials were rinsed with distilled water and dried in air at 353.15 K. The particles were embedded in epoxy resin, cut and polished, in order to analyze the cross section of the materials. EDX measurements were applied on the cross sections.

By gas adsorption (N₂, Micromeritics, ASAP 2020, US) the specific surface area (BET) of differently coated zinc particles was measured.

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