



Electrodeposition of preferentially oriented zinc for flow-assisted alkaline batteries



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HIGHLIGHTS

- Compact zinc deposited on brass is shown to have ~60% $11\bar{2}2$ preferred orientation.
- Preferentially oriented zinc has a coulombic efficiency of 99% over 100 cycles.
- Texture is observed in the orientation with the lowest nucleation work function.
- Highest preferred texture is observed at the minimum in the total cell resistance.

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ABSTRACT

Preferred orientation of zinc deposits during charging is shown to significantly improve performance and cycle life in flow-assisted alkaline zinc batteries, which has not been demonstrated earlier. The preferred orientation of zinc deposits was investigated using X-ray diffraction (XRD). Compact zinc is found to have $(11\bar{2}2)$ preferred orientation on brass, which contributes to ~60% of the texture. The effect of charging current and zincate concentration on morphology was investigated in a rotating hull cell and correlated with anodic efficiency. Compact zinc deposits are found to have a fine-grained, bright finish and the highest anodic efficiency. Electrochemical impedance spectroscopy (EIS) proves that compact zinc corresponds to the minimum in the half-cell resistance. Morphological control using compact zinc could be accomplished using innovations such as pulse charging or enhanced mass-transfer to improve anode performance without affecting the cathode.

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1. Introduction

The demand for grid-scale energy storage has necessitated the development of batteries with high energy and power densities. Alkaline zinc-anode batteries offer a low-cost, scalable solution to meet this requirement. However, zinc redistribution on periodic cycling and dendrite formation is known to severely limit battery life to 200 cycles [1]. Growth of mass-transfer limited zinc dendrites leading to an internal short circuit is the primary failure mode of these batteries. In recent years, flow-assisted Zn–NiOOH batteries have been developed to circumvent this limitation and offer a significant improvement in cycle life up to 1000–1500 cycles [2,3].

Preferred orientation in electrodeposited metals was first reported by Pangarov [4], and nanocrystalline zinc with preferred orientation is reported to offer superior protection on galvanized steels [5]. The development of texture on alkaline zinc deposits and the effect on morphology has not been previously explored. Textured zinc electrodes, with their lower corrosion rates and fewer grain boundaries offer a potential improvement in flow-assisted zinc batteries. The effect of operating conditions of choice of substrate, current density and concentration on texture have not been explored, and it is desirable to be able to determine *a priori* the conditions in which preferred orientation is highest. Due to the complex kinetics of zinc deposition and dissolution, there is considerable discrepancy in the literature values for exchange current density (i_0) and Tafel slopes [6–8]. The timescales of the ohmic, kinetic and mass-transport processes have been reported and explained by EIS models [9,10]. However, these models address either the kinetically limited formation of mossy zinc or the mass-

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transfer limited formation of zinc dendrites but cannot do both simultaneously.

The morphologies of zinc have been previously reported as mossy, compact and dendritic [8,11,12], and have been correlated to the ratio of applied to limiting current density (i/i_{lim}), or the CD-ratio [13]. Mossy zinc deposited at $i/i_{lim} < 0.2$ is porous, adheres poorly to the current collector and eventually fails by the loss of electrical contact. This loss of active material is the cause of progressive loss of battery capacity. Mossy zinc has a larger specific surface area, so the nominal corrosion/self-discharge currents are proportionately higher. Hydrogen evolution occurs at low current densities due to zinc corrosion by equation (1):



Compact zinc is reported to deposit at $i/i_{lim} > 0.2$ and is reported to have a dense structure that is conformal with the current collector [14]. Relatively low surface area and compact profile are desirable to ensure low self-corrosion rates and prevent the initiation of dendritic growth [15–17] to have highly efficient long-cycling anodes with negligible capacity degradation. By comparison, dendritic zinc is deposited at $i/i_{lim} > 1$ and is accompanied by vigorous hydrogen evolution. Inefficient zinc deposition coupled with the increased likelihood of battery failure through an internal short circuit makes dendritic zinc particularly undesirable. Morphological control in battery electrodes, specifically compact zinc deposition, has not been effectively explored. The lack of research interest probably stems from the older batteries operating in a stagnant electrolyte. The stringent mass-transport led to mossy zinc deposits being the morphology of choice, since their larger surface area reduced the effective current density. The advent of flow-assisted batteries has made it possible to explore faster charging protocols and morphology control to improve the performance and cycle life of zinc anodes.

The purpose of this study is to investigate the performance of compact zinc deposits with preferred orientation in concentrated alkaline electrolyte. X-ray diffraction (XRD) is used to investigate the effect of current density ratio (i/i_{lim}) on phase composition and the development of preferred orientation. The degree of texture is quantified from the XRD peaks using the method of Berube and L'Esperance [18] and reported as a relative texture coefficient (RTC). Rotating cylinder Hull (RCH) cell [19] experiments were performed to parameterize the effect of zincate concentration and current density on morphology and determine the transition between mossy, compact and dendritic zinc. Scanning electron microscopy (SEM) is used to determine the microstructure of zinc deposits. The regime of compact zinc formation is determined and optimized to improve electrode performance. Electrochemical impedance spectroscopy (EIS) is used to deduce the timescales of the microscopic processes in zinc deposition, and the current density ratio for minimum impedance is determined. The optimal operating conditions also correspond to the maximum preferred orientation. Galvanostatic half-cell cycling experiments are performed to compare the improvement in performance of preferentially-oriented zinc.

2. Experimental

2.1. Materials

All the experiments were performed using zinc oxide (ZnO) dissolved in 45 wt% potassium hydroxide (11.6 mol L^{-1}) as the electrolyte purchased from Sigma–Aldrich (ACS grade). Unless specified explicitly, the ZnO concentration was 60 g L^{-1} (0.74 mol L^{-1}). The electrolyte was freshly prepared by dissolving a

mixture of zinc oxide and potassium hydroxide at $60 \text{ }^\circ\text{C}$ before experiments were conducted. De-aeration was not performed and experimental conditions sufficiently mimic battery operation. The reference electrode was Hg/HgO in 20 wt% KOH (Koslow Industries).

2.2. Rotating cylindrical hull cell setup

The primary current distribution varies predictably across the length of a cylindrical Hull cell electrode in a control, which means that the effect of current density on morphology can be analyzed in a single experiment. A rotating cylinder Hull cell (HT Autolab) was used to investigate the dependence of zinc morphology on current density. The working electrode was a cylindrical brass rod 0.6 cm diameter, and 8 cm long. The zincate concentration in the electrolyte was varied ($0.38\text{--}1.24 \text{ mol L}^{-1}$) to validate that the transition between different zinc morphologies is independent of zincate concentration. The rotation speed was varied in a manner such that i/i_{lim} varied in the same regime across all the experiments. The average thickness of zinc deposited (50 C cm^{-2}) was kept constant across all the experiments. The samples were titrated with acetic acid using bromothymol blue as indicator to a neutral pH ($6.0\text{--}7.6$), rinsed multiple times with DI water, rinsed with acetone, and vacuum dried at room temperature. This sample preparation step helped minimize ex-situ oxidation of the electrode.

2.3. X-ray diffraction setup

X-ray diffraction (XRD) was used to investigate the material composition and preferred orientation of the zinc morphologies. All flat-plate experiments were performed with the flow-assisted prismatic cell described in our previous work [13]. A $3.5 \times 1.8 \text{ cm}$ brass sheet (Orbel Industries) was used as anode with a $3.5 \times 1.8 \text{ cm}$ sintered nickel cathode (Jiangsu Highstar Battery Manufacturing). The nominal thickness of the electrodeposited zinc was $25 \text{ }\mu\text{m}$ across all the experiments, at which the zinc would be impervious to X-rays. X-ray diffraction (XRD) experiments were carried out in a Philips Panalytical XRD operating at $40 \text{ kV}/40 \text{ mA}$ with a Cu-K α filter. Pole figures were generated using a Bruker D8 diffractometer, and inverse pole figures were generated using the MTEX algorithm [20].

2.4. Electrochemical impedance spectroscopy (EIS) setup

EIS half-cell experiments were performed using the frequency response mode on the Versastat 4 (Princeton Applied Research) to investigate the timescales of the processes in zinc deposition. A 0.5 cm copper rotating disk electrode (Pine Instruments) was used as the anode and a single $3.5 \times 1.8 \text{ cm}$ sintered nickel sheet was the cathode. The reference electrode was paralleled with a platinum wire using a $0.05 \text{ }\mu\text{F}$ capacitor to eliminate stray impedances associated with the reference electrode at frequencies in excess of 10 kHz [21].

3. Results and discussion

3.1. Morphologies of zinc deposition

A rotating cylindrical Hull (RCH) cell was used to investigate the effect of local current density on the morphologies of zinc deposition. The benefit of using an RCH cell is that the local current density varies as a function of electrode position, making it possible to investigate morphological transitions in a range of current densities in a single experiment.

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