



Effect of lead and tin additives on surface morphology evolution of electrodeposited zinc



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ABSTRACT

Effects of Pb and Sn additives on electrodeposition of Zn were investigated for the applications in Zn secondary battery, focused on their roles on morphological evolution. Similarly to well-known effect of Pb addition to smoothly electrodeposit Zn film surface, Sn also exhibited to suppress the formation of mossy structures, which were highly filamentous Zn electrodeposits to cause frequently battery failure. Pb significantly shifted deposition potential of Zn to negative value at concentration less than 1.0 mmol dm^{-3} , while Sn showed no substantial effect even at 50 mmol dm^{-3} . The morphological evolution analysis demonstrated that the addition of 1.0 mmol dm^{-3} Pb significantly altered nucleation behavior of Zn at initial stages of deposition; stacking of layer-like structures (microsteps) were altered to discrete and uniform nuclei of Zn preferentially oriented to (002) direction. In contrast, with Sn additive, morphological features at the initial stage of deposition were similar to that without additive. However, microsteps evolution was gradually suppressed and relatively strong (002) texture of electrodeposited Zn was mitigated by Sn addition. These results suggested that the beneficial roles of Pb and Sn addition on Zn morphological evolution were ascribed to different reasons; Pb diminished the active growth sites of Zn surface by suppressing the deposition reaction of Zn, while Sn suppressed microsteps evolution by different texture evolution of Zn.

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1. Introduction

The development of advanced energy storage devices for electrical power distribution system is urgently required today since it is indispensable to introduce the renewable energy in a large scale; the intermittent renewable energy is timely saved by charge-discharge operation of these energy storage devices [1,2]. Towards the establishment of feasible energy storage devices linked with electrical power distribution system, several aspects must be discussed on battery manufacturing or operation, e.g., scalability to MWh capacity, low cost and safety (flammability).

Taking account of these aspects, Zn negative electrodes are attractive due to material abundance, compatibility with aqueous electrolyte and low cost. Gong et al., for example, estimated a capital cost less than $100 \text{ \$/kWh}$, which met the cost requirement

for the application in power distribution system [3]. Moreover, a flexible battery design such as flow assisted battery is adopted based upon non-flammability and compatibility with aqueous electrolyte [3–6].

The development of rechargeable Zn battery is, however, not straightforward despite successful commercialization of Zn negative electrode in primary battery. The main reason lies in severe morphological changes of the negative electrode during charge-discharge cycles [7–10]. Highly filamentous Zn morphology called mossy structure often results in battery failure even under the electrolyte flowing conditions although electrolyte flow is generally effective to achieve uniform electrodeposition [7–9]. This morphological evolution is rather unique since structural features and deposition conditions of mossy structures are apparently different from well-known dendritic growth under mass transfer limited conditions [11].

The formation of mossy structures by eventual suppression of layer-like growth accompanying dynamic variations in local current density was described in previous work [12]. In the present work, we aim to understand nucleation & growth process behind irregular morphological evolution further in detail and to

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rationalize metal additive effects in the growth process of Zn; metal ions with more positive deposition potential than Zn are codeposited with Zn and they sometimes show beneficial effects to obtain uniform Zn deposits [13–24]. Especially, codeposition with Pb has been known to suppress both dendrites and mossy structures [13–16,18,19]. Moreover, Sn is also focused as the additive species in present study because Sn is attractive for large scale applications in terms of low toxicity compared to Pb. Although some articles described Sn addition effects on dendrite growth of Zn at high overpotential [16,23,24], its effects on mossy structure formation at low overpotential have not been investigated yet.

In acidic media for electrowinning and electrogalvanized steel, influences of metal impurities on deposition behavior of Zn were widely investigated [25–31]. Both Pb and Sn are expected to codeposit during the Zn deposition because they have more positive standard potential than Zn (Zn/Zn^{2+} : -0.763 V, Pb/Pb^{2+} : -0.125 V and Sn/Sn^{2+} : -0.138 V vs. SHE) [32]. However, several studies showed different effects of Pb and Sn on Zn electrodeposition [25–28,31]. Changes in morphological features by additive species were also investigated, but mossy structure formation is less evident even without additives in these studies probably due to relatively high current density used for electrowinning and electrogalvanized steel in acidic media compared to alkaline zincate solution for battery application [25–27,31].

Thus, it is of interest to understand the effect of Pb and Sn on nucleation & growth behavior of Zn in alkaline zincate solution for secondary batteries application. This paper especially focuses on their effects on mossy structures suppression in order to attain uniform Zn electrodeposits. The different roles of Pb and Sn on morphological evolution of Zn are also compared.

2. Experimental

Zn electrodeposition was performed from alkaline zincate solution containing 6.0 mol dm^{-3} KOH (Kanto Chemicals, UGR grade) + 0.25 mol dm^{-3} ZnO (Kanto chemical, reagent grade). In the analysis on metal additives effects, solution containing Pb or Sn were prepared as follows. In the case of Pb addition, PbO (Kanto Chemicals, >99.9%) was first dissolved into 48 wt% of KOH and 5.0 mmol dm^{-3} of PbO solution was prepared, which was diluted to desired concentrations (1.0 , 0.10 and $0.010 \text{ mmol dm}^{-3}$ of PbO) by pure water and KOH. Then, ZnO was dissolved into it. Subsequently, 6.0 mol dm^{-3} of KOH + 0.25 mol dm^{-3} of ZnO + $0.010 - 1.0 \text{ mmol dm}^{-3}$ of PbO was prepared. For preparation of Sn containing solution, 0.10 mol dm^{-3} of $K_2SnO_3 \cdot 3H_2O$ (Sigma Aldrich, 99.9%) dissolved into pure water was added to 48 wt% of KOH and ZnO was dissolved. Concentrations of K_2SnO_3 in 6.0 mol dm^{-3} of KOH + 0.25 mol dm^{-3} of ZnO were ranged from 5.0 mmol dm^{-3} to 50 mmol dm^{-3} . All solutions were deaerated by nitrogen bubbles prior to electrochemical measurements.

For the analysis on electrochemical behavior and morphological evolution of electrodeposited Zn, working electrode was prepared by electron beam evaporation (ULVAC, EBX-6D) to form Cu (100 nm)/Cr (10 nm) layer on Si(111) wafer. For comparison, Sn plate (Nilaco, 99.9%) was also used as working electrode. Surface of Sn plate was mirror finished by automatic lapping polishing machine (MA-400D, Musashino Denshi Co., Ltd.) with a colloidal silica (Semi-Sperse 25, Cabot Microelectronics Corp.). Surface area of working electrode was confined to 0.50 cm^2 . Counter electrode was $6.0 \text{ cm} \times 1.5 \text{ cm}$ Zn plate (Nilaco, >99.5%) and reference electrode was Hg/HgO (Inter Chemie, Inc.). All potentials shown below were reported vs. Hg/HgO. Reaction of Hg/HgO couple is [Eq. (1)] [32,33].

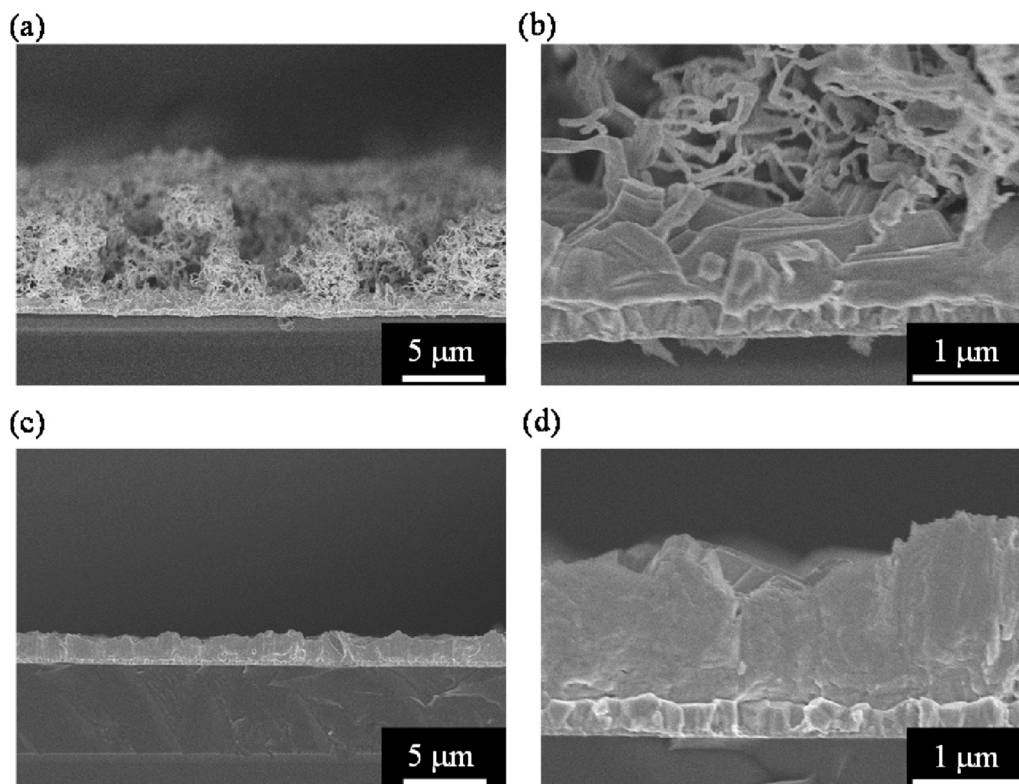


Fig. 1. Cross-sectional SEM images of electrodeposited Zn at (a), (b) -5.0 mA cm^{-2} and (c), (d) -10 mA cm^{-2} . Note that (b) and (d) are higher magnification images than (a) or (c) respectively. Passed charge for deposition was set at 5.0 C cm^{-2} .

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