



# Electrochemical lithium storage performance of ternary Zn–Co–Ni alloy thin film as negative electrodes by electrodeposition method

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## ABSTRACT

Ternary Zn–Co–Ni alloy film electrode as an anode has been investigated, for the first time, for the purpose of electrochemical lithium storage in lithium-ion batteries. In this study, the ternary Zn–Co–Ni alloy film electrode is prepared by electroplating method. The electrodes were examined using X-ray diffraction (XRD), FE-SEM with EDX, and impedance studies. The electrochemical results demonstrate that the Zn–Co–Ni alloy film electrode delivers an initial discharge capacity of 281 mAh g<sup>-1</sup> and improves to 650 mAh g<sup>-1</sup> at the end of 30th cycling with no capacity fading at 0.1 C rate. The charge–discharge properties of the Zn–Co–Ni alloy film electrode are as follows: insertion capacity of 650 mAh g<sup>-1</sup> and delithiation capacity of 512 mAh g<sup>-1</sup> in the 30th cycling, coulombic efficiency of about 80.0% and good cycling behavior. The results suggest that the ternary Zn–Co–Ni alloy thin film electrode obtained via electroplating shows a good candidate anode material for lithium-ion batteries.

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## 1. Introduction

Lithium ion batteries have widely been used as a power source for portable electronic devices such as cellular phones. The main goal is to replace the conventional graphite anode to achieve higher capacity content. In the recent years, lithium metal alloys, LiM, have received greater attention in the lithium ion battery industry. The materials have a very high specific capacity and are considered very promising negative electrodes to replace conventional carbon electrodes. Significant research efforts have recently focused on M1–M2 types of alloys, such as Sn–Co, Sn–Ni, Sn–Cu; however, to the best of our knowledge, M1–M2–M3 type alloy materials have never been explored. In these electrodes, M1 acts as an active phase, while M2 and M3 are inactive. Generally, a very high irreversible capacity loss of M–M alloys (>50%) in the first cycle and deep capacity fade (~40%) in the consecutive cycles are observed due to exorbitant volume expansion that make the compounds unsuitable for global and practical lithium-ion battery applications [1].

Alternatively, it is well known that zinc metal reversibly reacts with lithium to produce a maximum alloy composition of LiZn [2]. In addition to its familiarity as a battery-active material, Zn is known for its high dissolution and the subsequent dendrite formation, which impinges on the battery performance and extends cycle life [3]. Alloying of Zn with an inactive metal element (e.g.,

Ni, Fe, and In) may minimize the dissolution to exploit the maximum electrochemical performance of Zn as a potential lithium battery anode active material. Recently, tin-based ternary alloys were developed as anode materials with improved cycle ability [4–8]. Alloy electrodeposition is widely used in the production of new materials that require specific mechanical, chemical and physical properties [9–11]. This technique has demonstrated to be very convenient because of its simplicity and low cost in comparison with the other methods such as mechanical alloying, sputtering and vapor deposition [12]. In the present study, the ternary Zn–Co–Ni alloy film electrodes were prepared via electroplating on copper foil using a DC power supply and were characterized using XRD, FE-SEM, EDX, impedance and the electrochemical characterization of charge–discharge studies.

## 2. Experimental

### 2.1. Preparation of anodes

Zn–Co–Ni alloy anode materials were synthesized via electroplating, as shown in Fig. 1(a). The electrolyte contained 0.40 M ZnSO<sub>4</sub>, 0.40 M CoCl<sub>2</sub>, 0.20 M NiCl<sub>2</sub>, 0.50 M H<sub>3</sub>BO<sub>3</sub>, 0.30 M CH<sub>3</sub>COONa, and 0.50 M NaCl. The bath pH range was adjusted to 3.5 and distilled water was used to prepare a 1 l volume. The temperatures of these baths were maintained at 50 °C for all experiments. The copper foil substrate was decreased in acetone, electrocleaned with an alkaline bath and etched in 10% H<sub>2</sub>SO<sub>4</sub>. The graphite and copper foil substrate was connected to the anode and cathode in the plating system. The direct current depositions (DCDs) of the Zn–Co–Ni alloy were performed using an Aplab Model rectifier source. The deposition was performed in 5 min plating times, and 1 A dm<sup>-2</sup> current densities were applied using the rectifier source to produce alloy deposits with thicknesses of approximately 2 μm. Fig. 1(b) shows the punched 2032 coin-type electrode at the electrodeposited Zn–Co–Ni alloy

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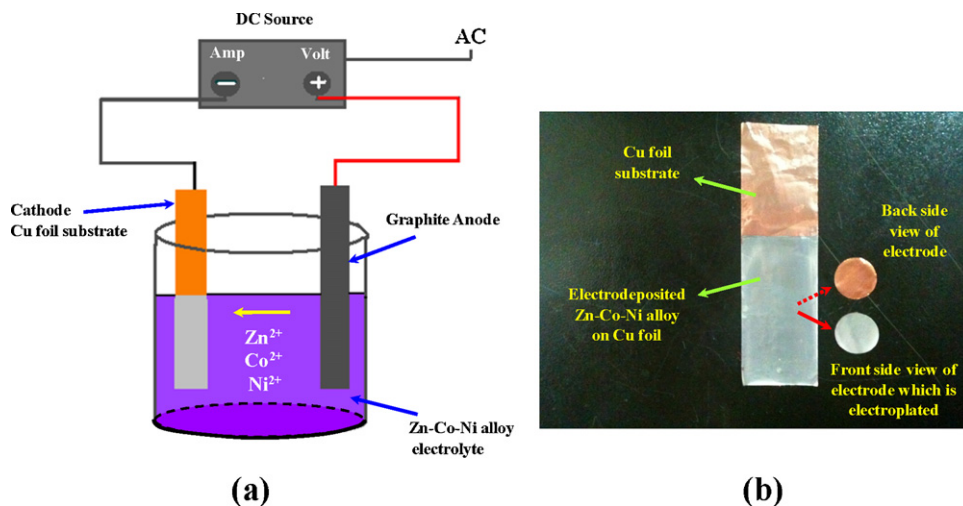


Fig. 1. Schematic representation: (a) ternary Zn–Co–Ni alloy electrode prepared by electroplating method and (b) prepared electrode images.

surface. The surface morphologies of the electrode were characterized using FE-SEM with EDX, and the crystal sizes were assessed using the XRD technique.

## 2.2. Electrochemical characterization

The electrodeposited Zn–Co–Ni alloy anodes were electrochemically characterized using the electrochemical impedance spectroscopy (EIS) measurements by applying an ac voltage of 10 mV amplitude over the frequency range from 0.1 Hz to 100 kHz using IVIUM technologies instruments. The cells were left at the delithiated state for 12 h prior to EIS measurements in order to obtain equilibrium state. Cells were assembled in an argon-filled glove box. The cell consisted of a prepared Zn–Co–Ni alloy anode, pure Li metal as a cathode, a microporous membrane (Celgard 3501) as a separator, and a non-aqueous 1 M LiPF<sub>6</sub> in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1 vol/vol) as an electrolyte. Also, electrochemical charge–discharge evaluation was performed on 2032 coin cells fabricated using the prepared Zn–Co–Ni alloy materials. Charge and discharge were conducted using an ARBIN battery cycler at a 0.1 C rate to a cut-off potential of 0.01 and 1.20 V vs. Li/Li<sup>+</sup>.

## 3. Results and discussion

### 3.1. Surface morphologies of the ternary Zn–Co–Ni alloy film coatings

The X-ray diffraction (XRD) patterns of the electrodeposited Zn–Co–Ni alloy film on Cu foil are as shown in Fig. 2. The XRD result reveals that it is mainly composed of a cubic  $\gamma$ -Co<sub>5</sub>Zn<sub>21</sub> alloy phase, Ni and Co matrix phase are observed in the deposition of Zn–Co–Ni

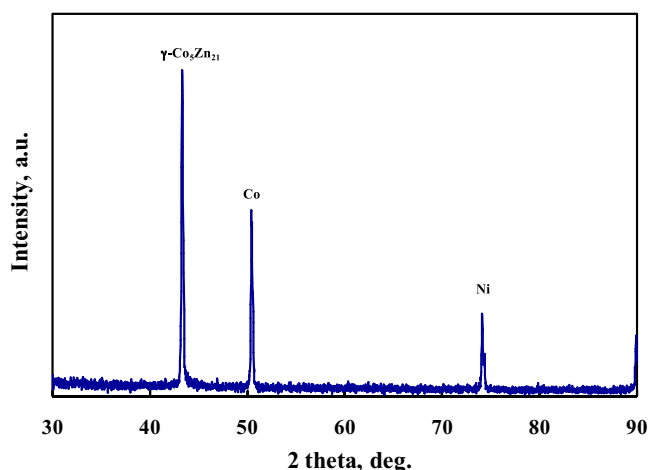


Fig. 2. XRD pattern of the deposited ternary Zn–Co–Ni alloy on Cu foil.

alloy film electrode. The main strong peaks of cubic  $\gamma$ -Co<sub>5</sub>Zn<sub>21</sub> phase are at  $2\theta = 43.33^\circ$ . These phases were referred to the JCPDS card (04–0887) used in the analysis and as previously reported [13]. Also, the minor quantities of Co and Ni phase at  $2\theta = 50.45^\circ$  and  $74.13^\circ$  were present (JCPDS card 15–0806 and 87–0712). Thus, the patterns demonstrated that the pure crystalline nature of the coatings can be prepared by electrodeposition method. The calculated crystallite sizes of particles were 40, 48, and 77 nm, respectively, using the Debye–Scherrer formula. Such small crystalline sizes not only contribute to the smooth surface morphology but also have a beneficial effect on the improvement of microhardness of the coatings [14]. Furthermore, the crystalline size reduction to the nanometer range results in considerable improvement in their corrosion resistance [15].

Fig. 3 shows the FE-SEM images of the prepared ternary Zn–Co–Ni alloy thin film deposited on copper foil for 5 min plating time at  $1 \text{ A dm}^{-2}$  current. A large number of alloy particles and uniform deposits observed and are presented in Fig. 3(a). The thin film coatings thickness was approximately  $2 \mu\text{m}$  and 100 nm porous structure was found from the magnified view of surface as shown in Fig. 3(b). The particle sizes of the synthesized compounds were present within the desired sub-micron level at  $\sim 5 \mu\text{m}$ , which services the preferred morphological characteristics of a good battery electrode [16]. It has been concluded that the nano-porous structure of ternary Zn–Co–Ni alloy thin film anode material can be prepared using the electrodeposition method for lithium-ion battery. Additionally, Fig. 4 illustrates the EDX spectrum of the ternary Zn–Co–Ni alloy, which indicates that the average weight% of (Zn:Co:Ni)/Cu from electrodeposits onto the Cu foil substrate was approximately (38.58:12.81:1.77)/46.85 for this alloy.

### 3.2. Electrochemical performance

Fig. 5 shows the impedance response of the ternary Zn–Co–Ni alloy film electrode. The nyquist plot evolves with a convoluted semicircle at a higher frequency and a straight line at a low frequency region. The semicircle in the medium frequency region was attributed to the charge-transfer reaction of the alloy, and the sloped line corresponds to the lithium-ion diffusion process (Warburg impedance) within the electrode [17,18]. This result confirms that the ternary Zn–Co–Ni alloy film electrode shows only one depressed semicircle at the high frequency region and a  $45^\circ$  line to the axis in the low frequency region. Importantly, the ohmic resistance is quite low, i.e., approximately  $5.99 \Omega$  at real impedance axis,

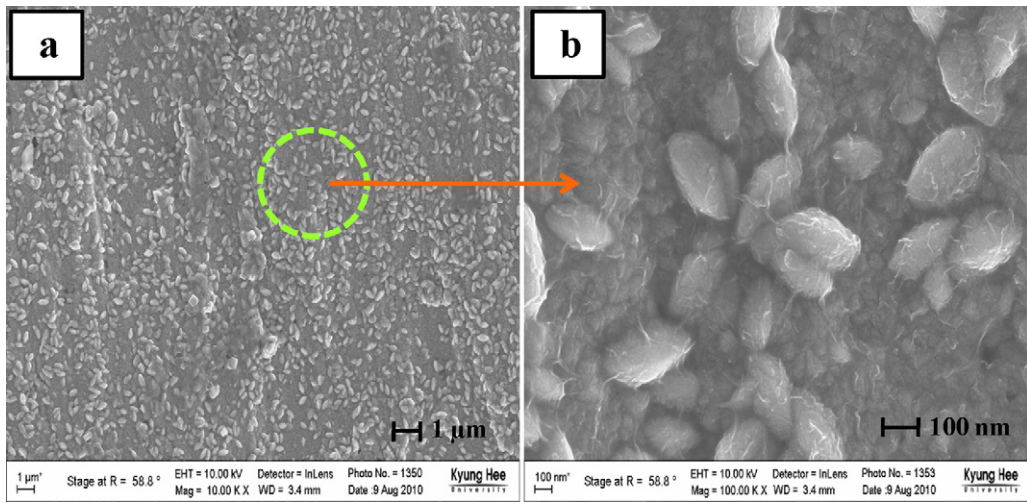


Fig. 3. The surface morphologies of the ternary nano-porous Zn–Co–Ni alloy on Cu foil.

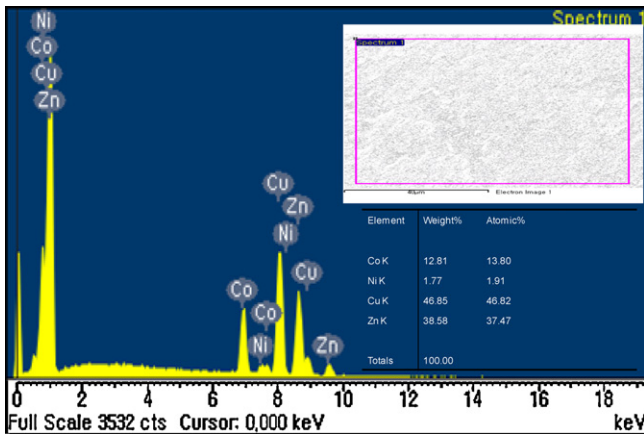


Fig. 4. EDX spectrum results of electrodeposited ternary Zn–Co–Ni alloy on Cu foil surface.

whereas the charge transfer resistance of this Zn–Co–Ni alloy layer is somewhat high due to kinetically rather sluggish electrochemical system.

The electrochemical properties of the ternary Zn–Co–Ni alloy thin film electrodes are illustrated in Fig. 6(a). The charge and

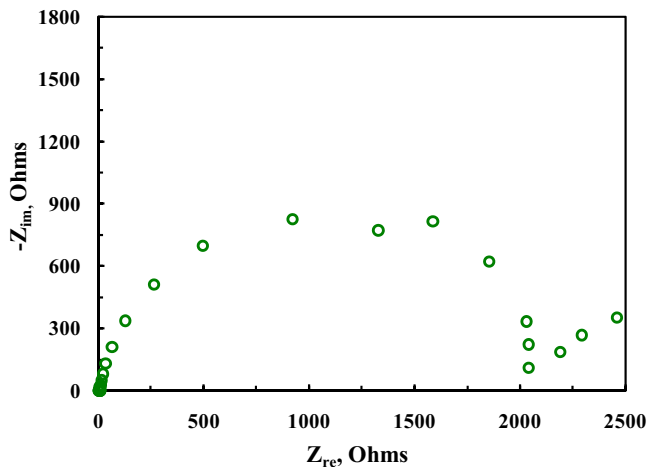


Fig. 5. The Nyquist plot of electrochemical impedance spectra of ternary Zn–Co–Ni alloy anode material.

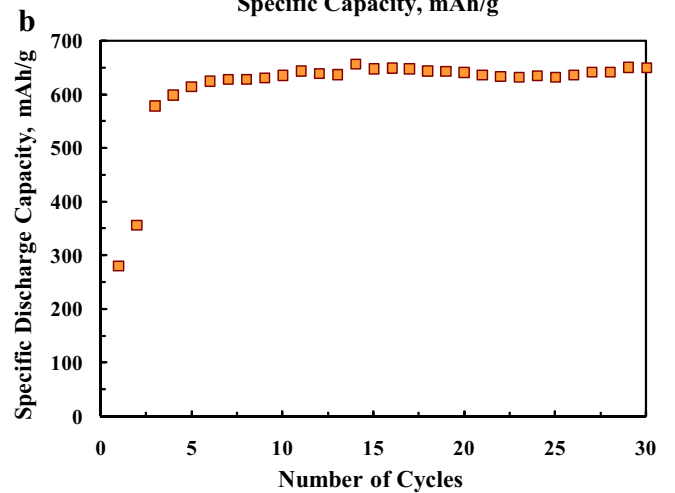
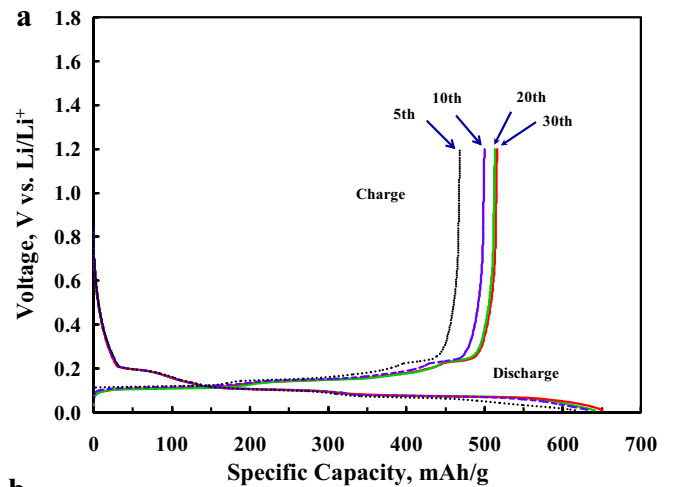


Fig. 6. (a) Charge–discharge profile of electrodeposited ternary Zn–Co–Ni alloy film negative electrode and (b) cycling behavior of electrodeposited ternary Zn–Co–Ni alloy film negative electrode at 0.1 C rate.

discharge profiles were obtained at the current rate of 0.1 C and their cut-off potentials were 1.20 and 0.01 V vs. Li/Li<sup>+</sup>, respectively. The OCV of the Zn–Co–Ni alloy anode cells were measured to be 2.52 V vs. Li/Li<sup>+</sup> in the delithiated state. Moreover, the theoretical capacity of Zn–Co–Ni alloy is 436 mAh g<sup>−1</sup> by stoichiometry. The

discharge–charge capacities were  $615 \text{ mAh g}^{-1}$  and  $468 \text{ mAh g}^{-1}$  in the 5th cycling as well as  $650 \text{ mAh g}^{-1}$  and  $512 \text{ mAh g}^{-1}$  in the 30th cycling, respectively. The coulombic efficiency in the discharge and charge processes is maintained as high as approximately 80.0%, except for the initial several cycles, with no capacity fading and good cycling behavior at the end of 30th cycling. The charge and discharge characteristics were similar to those of the electroplated ternary alloy electrode, as previously reported [19,20]. These results demonstrated that the ternary Zn–Co–Ni alloy thin film anode exhibits the good electrochemical lithium storage performance, which is attributed certainly to the nano-porous structure and multi component of the as-prepared Zn–Co–Ni alloy.

Fig. 6(b) shows the cycle performance of the ternary Zn–Co–Ni alloy electrode prepared via electroplating. The initial cycle discharge capacity was  $281 \text{ mAh g}^{-1}$  and improved to  $650 \text{ mAh g}^{-1}$  at the end of the 30th cycling. The cycling performance increased and was quite stable after the fifth cycling because the discharge capacity was likewise maintained at approximately  $650 \text{ mAh g}^{-1}$  during the extended cycling process up to 30 cycles. A similar behavior was also observed in other tin-based alloy anodes [19,21,22]. It should be noted that a high discharge capacity was obtained for 3 and 30 cycling. However, the Zn–Co–Ni alloy electrodes in the initials cycling capacities were less than those of the third and 30th cycles. The reason can be considered as follows.  $\text{Li}_3\text{Co}$  is first formed around Zn domain from alloy phase, which can reduce the volume change of following Li-insertion into Zn in the charging process. As the cycle proceeds, Zn tends to aggregate resulting in significant volume change and capacity decay. Also, the average capacity observed in the initial cycles may result from possible oxide impurities on electrode surface and the formation of a SEI layer on the surface with a large specific surface area. It was previously reported that an inactive Co matrix would prevent the aggregation during cycling [19]. However, a steady-state anode capacity of approximately  $350 \text{ mAh g}^{-1}$  was observed, which is closer to those of carbonaceous anodes [23]. The preliminary studied of charge and discharge capacities of the ternary Zn–Co–Ni alloy anode had reversibility and varied greatly with the composition of the alloy.

#### 4. Conclusion

In this work, the ternary Zn–Co–Ni alloy film anode was successfully prepared via electroplating and investigated its availability in lithium-ion batteries for the first time. The XRD pattern revealed the pure crystalline nature of the deposited ternary Zn–Co–Ni alloy

obtained by a simple and short time electrochemical deposition process. The initial cycle discharge capacity was  $281 \text{ mAh g}^{-1}$  and improved to  $650 \text{ mAh g}^{-1}$  at the end of 30th cycling with no capacity fading. The coulombic efficiency of the discharge and charge processes is maintained as high as approximately 80.0%, except for the initial several cycles, at 0.1 C rate. Moreover, the ternary Zn–Co–Ni alloy film materials are interesting candidates for the negative electrode of lithium-ion batteries.

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