A facile synthetic strategy to three-dimensional porous ZnCo₂O₄ thin films on Ni foams for high-performance lithium-ion battery anodes

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ABSTRACT

Three-dimensional (3D) porous ZnCo₂O₄ thin films on nickel foam substrates have been fabricated through a facile strategy of electrostatic spray deposition (ESD) followed by annealing in Ar atmosphere for lithium-ion battery anodes. The obtained ZnCo₂O₄ films on Ni foams show excellent cycling performance with a reversible capacity of over 1726 mAh g⁻¹ after 100 cycles at 400 mA g⁻¹. The ZnCo₂O₄ electrodes also present good rate capability with 811 mAh g⁻¹ at 5 A g⁻¹. The improved electrochemical performances should be ascribed to 3D porous ZnCo₂O₄ architecture directly grown on Ni foam current collector, due to the synergistic advantages of offering more reaction sites, effective void space to the volume variation during cycling, and improving of electron transport. It is proposed that this facile strategy of ESD technique can be extended to synthesize other 3D porous mixed transition-metal oxide materials.¹

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1. Introduction

In the past few years, lithium-ion batteries (LIBs) have been widely utilized as main power sources for numerous portable electronic devices and become promising energy storage systems for use in upcoming high energy area including electric vehicles (EVs), hybrid electric vehicles (HEVs), and so on [1,2]. To meet the ever-growing large energy requirements, many efforts have been devoted to develop high-performance anode materials for replacing traditional graphene based materials with low theoretical capacity of 372 mAh g^{-1} [3-5]. Recently, transition metal oxides (TMO) such as SnO_2 [6], Co_3O_4 [7,8], Mn_3O_4 [9], and Fe_3O_4 [10] have been widely researched for high-performance LIB anodes. Particularly, Co_3O_4 has been considered as one of the most promising anode candidates in view of its high capacity and good rate capability [11,12]. However, the practical application of cobalt oxides is hindered owing to their disadvantages of high cost and toxicity for cobalt. Thus, partially replacing cobalt in Co_3O_4 by cost-effective and environment-friendly metals (Zn, Mn, Ni, Cu, etc) to constitute the mixed transition-metal oxides (MTMOs) [13-20], has been regarded as ideal LIB anode materials.

Among the above MTMOs, ZnCo_2O_4 is a quite attractive candidate for substitution of the Co_3O_4 anode in LIBs. ZnCo_2O_4 presents many advantages such as lower cost, low toxicity, and high theoretical capacity (975 mAh g^{-1}), which could be assigned to both conversion and alloying mechanisms [21,22]. Nevertheless, ZnCo_2O_4 still suffers from fast capacity fading because of large volume variation in the process of lithiation/delithiation. Up to now, many ZnCo_2O_4 micro/nanostructures such as nanowires [23-25], nanosheets [26], and hollow or porous architectures [27-34], have been synthesized to improve the cycle life and rate capability of ZnCo_2O_4 for LIB anodes.

It should be pointed that hollow or porous architecture has shown promising results for enhancing electrochemical performance of LIBs owing to the advantages of offering more reaction sites and effective void space to the volume variation during cycling. Porous and hollow ZnCo_2O_4 structures have been fabricated through different strategies including solvothermal process [27-29], electrospinning technique [30,31], template-assistant synthesis [32,33], co-precipitation [34,35], and so on. The common weakness of hollow or porous power materials is that the electrodes was prepared through mixing carbon and polymer binder with these active materials, and fastening on current collectors, leading to an increase of “dead surface”, reduction of the reaction sites, and decrease of the electrical conductivity. It is proposed that synthesizing hollow or porous ZnCo_2O_4 structures directly on the current collector will be promising method to resolve the problem.

Electrostatic spray deposition (ESD) technique has been regarded as a simple and facile method for fabricating binder-free film of metal oxide electrodes with porous structures for LIBs [36-38]. However, there are few researches on the preparation of MTMOs film using ESD technique. Herein in this paper, we present a facile strategy for the synthesis of three-dimensional (3D) porous ZnCo_2O_4 thin film via ESD method followed by annealing in Ar atmosphere. Electrochemical properties of 3D porous ZnCo_2O_4 thin film were researched. The ZnCo_2O_4 films on Ni foams exhibit excellent cycling performance and good rate capability for LIB anodes.

2. Experimental

2.1. Synthesis of materials

The ZnCo_2O_4 films were fabricated via ESD technique. 13.22 mg of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 30 mg of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (4 mM) were dissolved in

the solvent mixture of 1,2 propanediol and ethanol (1:1 V/V) to form precursor solutions. The precursor flow rate was set at 2 mL h⁻¹. The ZnCo₂O₄ films were prepared on Ni foams (Φ =14 mm) substrates at 250 °C for 4 h. The distance between the substrate and the spray nozzle was about 3.5 cm and the applied direct current voltage was 6.5-7.5 kV to form a stable spray. The as-prepared samples were annealed at 500 °C for 2 h under Ar atmosphere.

2.2. Characterizations and electrochemical measurements

The crystalline structure of the samples was characterized by X-ray diffraction via Cu K α radiation (XRD, SIEMENS-D5000). The morphology of the samples was observed by field-emission scanning electron microscopy (FE-SEM, JEOL 6335). The surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI). Electrochemical test was carried out using coin type cells (CR2032) assembled in an argon filled glove box (VAC Nexus I). The ZnCo₂O₄ film synthesized on the nickel foam was used as a working electrode, while a lithium foil was used as a counter and reference electrode. The typical loading mass of active materials was around 0.6 mg cm⁻². A microporous polypropylene (Celgard 2400) was used as a separator. The electrolyte was 1 M LiPF₆ dissolved in mixture of ethylene carbonate and diethyl carbonate (1:1 v/v). Cyclic voltammetry and electrochemical impedance spectroscopy (EIS) were measured on a Verstile Multichannel Potentiostat (VMP3, Bio-Logic). The cells were cycled in the voltage range of 0.01-3 V at room temperature by a NEWARE BTS-610 Battery Test System.

3. Result and discussion

Fig. 1 shows the XRD pattern of the annealed ZnCo₂O₄ thin film, which was stripped from Ni foam substrate to reduce strong impact of the substrate on the XRD

result. It can be seen that the diffraction peaks at 2θ values of 31.22° , 36.80° , 59.37° and 65.15° are assigned well to (220), (311), (511), and (440) planes of pure ZnCo_2O_4 phase with cubic spinel structure (JCPDS card No. 23-1390). No diffraction peaks for ZnO and CoO phases were found in XRD pattern, indicating the high purity of the product. Fig. 2 presents SEM images of the as-prepared and annealed ZnCo_2O_4 thin films on Ni foam. As-prepared ZnCo_2O_4 film exhibits 3D network porous structure on nickel foam with a pore size in the range of 2-3.5 μm (Fig. 2a and b), which is similar to the morphology of other metal oxide materials synthesized by ESD method in previous literatures [36,38]. Through high-temperature calcinations' process, the annealed ZnCo_2O_4 film (Fig. 2c and d) still maintains the 3D porous structure and shows good mechanical attachment with Ni foam.

The surface chemical compositions and the valance states of the ZnCo_2O_4 film were illustrated by XPS (Fig. 3). In Fig. 3a, the survey spectrum of ZnCo_2O_4 film shows the presence of Zn, Co, and O elements. The high-resolution of Zn 2p spectrum was shown in Fig. 3b. Two peaks at 1044.6 and 1021.5 eV are ascribed to Zn 2p_{3/2} and Zn 2p_{1/2} of Zn^{2+} , respectively. Fig. 3c presents high-resolution of Co 2p spectrum. Two strong peaks at 796.2 eV for Co 2p_{1/2} and 780.2 eV for Co 2p_{3/2} are observed [25,39]. Each peak presented a +6.0 V satellite peak at ~ 786.2 (Sat.2) and ~ 802.2 (Sat.1) eV [33]. The position of Co 2p major and satellite peaks indicate the Co (III) oxidation state. The O 1s peaks at 529.6 eV correspond to the oxygen species in ZnCo_2O_4 (Fig. 3d).

The electrochemical performances of the annealed ZnCo_2O_4 film are examined through cyclic voltammograms (CV) and galvanostatic discharge-charge measurements. Fig. 4a presents the CV curves of ZnCo_2O_4 film in the first three cycles with the voltage window of 0.01-3 V at a scan rate of 0.2 mV s^{-1} . In the first cathodic process, the peak at

around 0.82 V could be assigned to reduction reaction of Co^{3+} cations to metallic Co, and the other peak at around 0.52 V could be assigned to the reduction of Zn^{2+} to metallic Zn, the generation of a ZnLi alloy, and the solid electrolyte interface (SEI) formation [40,41]. In the first anodic process, the wide peak nearby 0.75 V corresponds with ZnLi dealloying reaction, while the two broad peaks at approximately 1.60 and 2.10 V could be ascribed to oxidation of Zn^0 to Zn^{2+} and Co^0 to Co^{3+} , respectively [23]. In the subsequent cathodic processes, the peak is moved to 0.98 and 1.34 V, respectively, indicating different electrochemical mechanisms. This phenomenon was also found in the CV curve of other ZnCo_2O_4 anode materials in the previous reports [27, 41, 42]. The overlap of the CV curves of 2nd and 3rd cycle implies the good reversibility of the electrochemical reactions.

According to previous discussions, the electrochemical reactions occurred during charge/discharge process are concluded below [23,27]:

Fig. 4b shows charge-discharge curves for the 1st, 2nd, 3rd, 50th, and 100th cycles of the ZnCo_2O_4 electrode at a current density of 400 mA g^{-1} between 0.01 and 3.0 V (vs. Li/Li^+). It is observed that there are two voltage plateaus in the first discharge cycle. The former plateaus at 1.10 V is related to the reduction of Co^{3+} to Co^0 , while the latter plateaus around 0.57 V is attributed to the formation of Zn^0 , Li-Zn alloy and SEI layer. In the first discharge step, the ZnCo_2O_4 electrode delivers a specific capacity of 1363

mAh g⁻¹, while in the first charge step up to 3.0 V, the electrode display a capacity of 1032 mAh g⁻¹. The Coulombic efficiency of the first cycle is 76%. For ZnCo₂O₄ electrodes, the SEI formation and electrolyte decomposition should be the two main reasons for the low Coulombic efficiency, which has been reported for the ZnCo₂O₄ materials in previous literatures [27, 43]. However, the value of Coulombic efficiency quickly gets up to 96% for the second cycle and stabilizes above 96% in the subsequent cycles (Fig. 4a), revealing good reversibility of the electrode.

Fig. 5a displays the discharge/charge cyclic properties of the annealed ZnCo₂O₄ films with mass loading of 0.6 mg cm⁻² and 2 mg cm⁻², respectively, between 0.01 and 3.0 V at 400 mA g⁻¹. It is observed that ZnCo₂O₄ electrode with mass loading of 0.6 mg cm⁻² shows relatively high discharge capacity loss with a value of 27% in the first 6 cycles. Nevertheless, from the 7th cycle, the specific capacity is gradually increased to get a high value of 1726 mAh g⁻¹ after 100 cycles, which is much higher than the theoretical capacity of ZnCo₂O₄. The similar capacity rise phenomenon has also been observed in other ZnCo₂O₄-based electrode materials including ZnCo₂O₄ nanosheets [25], ZnO-ZnCo₂O₄ hybrid hollow microspheres [41], flake-by-flake ZnCo₂O₄ [34], and so on. The extra specific capacity should be ascribed to the reversible growth and dissolution of a polymeric gel-like film attached to active materials during cycling [25,34,41]. Additionally, it can be seen that ZnCo₂O₄ film with active mass loading 2 mg/cm² show the capacity value of 1074 mAh g⁻¹ after 100 cycles. The electrode with low mass loading of 0.6 mg cm⁻² exhibits a higher capacity. It is demonstrated that mass loading of the electrode shows strong influence for electrochemical performance of the ZnCo₂O₄ film.

Fig. 5b presents the rate capability of ZnCo₂O₄ film using the same cell with mass loading of 0.6 mg cm⁻² after the initial 100 cycles. With the current densities

increasing from 0.2 to 0.4, 0.8, 1.6, 3.2 A g⁻¹, ZnCo₂O₄ electrode retains the specific capacity of 1986, 1900, 1669, 1372, 1042 mAh g⁻¹, respectively. Even at a high current density of 5 A g⁻¹, the electrode still can retain a high capacity of 811 mAh g⁻¹. When the current density reduces to 200 mA g⁻¹, the capacity can recover a value as high as 2179 mAh g⁻¹, indicating an excellent rate-cycling stability of this electrode.

To further test the cycle stability of the ZnCo₂O₄ electrode, the subsequent cycling performance of the electrode was evaluated at 400 mA g⁻¹ using the same cell with mass loading of 0.6 mg cm⁻² after the first 170 cycles (Fig. 5c). It can be seen that the specific capacity of ZnCo₂O₄ electrode further increases gradually and reach a high value of 2457 mAh g⁻¹ after 300 cycles. The capacity rise phenomenon can also be related to the reversible growth and dissolution of a polymeric gel-like film attached to active materials during cycling.

The EIS of ZnCo₂O₄ electrode were analyzed before and after 10 cycles by CV measurement at 0.2 mV s⁻¹. From Fig.6, it can be observed that all three Nyquist plots consist of one semicircle in the high frequency region and a linear line in the low frequency region. The semicircle's diameter of ZnCoO after 100 cycles is smaller than those of the fresh cell and the cell after 10 cycles, indicating charge-transfer resistance has significantly decreased after cycling. The slope of linear line after 100 cycles is steeper in comparison to the fresh cell and the cell after 10 cycles, indicating the Li ion diffusion kinetics has increased after cycling. The decreased charge transfer resistance and enhanced Li ion diffusion kinetic could also be the contribution of capacity increase [44].

Fig.7 shows SEM images of the fully charged ZnCo₂O₄ film electrode after 270 cycles. It is observed that the ZnCo₂O₄ electrode remains a three-dimensional porous structure during the cycling, indicating that the 3D porous architecture not only acts as a

cushion but also facilitate an enhanced material stability during Li alloying/de-alloying.

Based on the above electrochemical results, it is demonstrated that the 3D porous ZnCo_2O_4 films on Ni foams exhibit excellent cycling performance and good rate capability. The unique morphology on Ni foam plays a key role on improving the electrochemical performances for LIBs. Firstly, the 3D porous ZnCo_2O_4 structure not only can offer more reaction sites, but also can offer effective void space to the volume variation during cycling. Secondly, the Ni foam with porous network architecture can further increase the contact areas between the ZnCo_2O_4 film and the electrolyte, and improve the electron transport. Additionally, reversible growth and dissolution of a polymeric gel-like film attached to the surface of the ZnCo_2O_4 film can strengthen the capacity of ZnCo_2O_4 electrode.

4. Conclusions

In summary, we report the preparation of 3D porous ZnCo_2O_4 thin films on Ni foam substrates through ESD method and followed by an annealing process for LIB anodes. It is demonstrated that the ZnCo_2O_4 films exhibit large specific capacity, excellent cycling performance, and good rate capability, which can be assigned to the unique 3D porous ZnCo_2O_4 architecture directly grown on Ni foam current collector. Considering the excellent electrochemical properties of 3D porous ZnCo_2O_4 films on Ni foams, the above researches suggest that the 3D porous ZnCo_2O_4 films on Ni foams are favorable for the applications on high performance LIB anodes.

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Figure captions

Fig. 1. XRD patterns of the annealed ZnCo_2O_4 film.

Fig. 2. SEM images for (a,b) as-prepared ZnCo_2O_4 film and (c,d) annealed ZnCo_2O_4 film at different magnifications.

Fig. 3. XPS spectra of (a) full scan, (b) $\text{Zn}2\text{p}$, (c) $\text{Co} 2\text{p}$, and (d) $\text{O}1\text{s}$ region of ZnCo_2O_4 film.

Fig. 4. (a) Cyclic voltammetry for annealed ZnCo_2O_4 film. (b) Charge and discharge profiles for annealed ZnCo_2O_4 film at the current of 400 mA g^{-1} between 0.01 and 3 V.

Fig. 5. (a) Capacity retention of the annealed ZnCo_2O_4 film. (b) Rate capability of the annealed ZnCo_2O_4 film. (c) Subsequent capacity retention of the annealed ZnMn_2O_4 film.

Fig.6. Impedance spectra of the annealed ZnCo_2O_4 film before and after 10 cycles, 100 cycle CV tests.

Fig.7. SEM image of the fully charged ZnCo_2O_4 film electrode after 270 cycles.

Fig. 1

Fig.2

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Fig. 4

Fig. 5

Fig. 6

Fig. 7