Fabrication of three-dimensional porous ZnMn₂O₄ thin films on Ni foams through electrostatic spray deposition for high-performance lithium-ion battery anodes

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Three-dimensional (3D) porous ZnMn₂O₄ thin films on nickel foam substrates have been successfully synthesized through electrostatic spray deposition (ESD) method followed by an annealing process for lithium-ion battery anodes. These films exhibit excellent cycling performance with a reversible capacity of around 982 mAh g⁻¹ after 100 cycles at 400 mA g⁻¹. The ZnMn₂O₄ films also display good rate capability with 455 mAh g⁻¹ at 5 A g⁻¹. The superior battery performances of ZnMn₂O₄ films are ascribed to 3D porous ZnMn₂O₄ film directly deposited on Ni foam, which can offer effective empty space to accommodate the large volume variation during cycling, increase reaction sites, and improve the electron transport. The ESD strategy is facile, cost-effective, which can be potentially utilized to construct other 3D porous mixed transition-metal oxides materials as well.

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1. Introduction

As one of important green energy-storage devices, lithium-ion batteries (LIBs) have been widely applied in numerous portable electronic devices [1-3]. However, in order to meet high energy storage systems for the ever-growing electrical vehicles (EV), it is still a challenge to design and synthesize effective anode materials for LIBs with high capacity, long cycle life, and good rate capability [4,5]. In recent years, simple transition metal oxides (TMO) such as Mn_3O_4 [6], Co_3O_4 [7], ZnO [8], and NiO [9], have been widely researched for high-performance LIB anodes. However, simple TMOs usually show intrinsically low electronic conductivity and ionic conductivity, which lead to the serious capacity fading in the cycling processes. To resolve this issue for LIB anodes, one effective method is to synthesize metal/metal oxide hybrid for improving the electronic conductivity [10-12]. Another important method to fabricate mixed transition-metal oxides (MTMOs, spinel AB_2O_4 ; A, B = Co, Ni, Zn, Mn, Fe, etc.), which exhibit higher specific capacity and improved electronic conductivity [13-18]. Compared with metal/metal oxide hybrid, the MTMOs usually present higher electrochemical activities because of complex chemical compositions with two different metal cations acting as counter “matrix” for each other, which can make contribution to exceptionally high specific capacity of MTMOs for LIB anodes [19,20].

Among the MTMO-based anode materials, ZnMn_2O_4 has attracted much attention recently for high-performance LIBs due to its superior properties including cost-effective, environmental benignity, and high theoretical capacity (1008 mAh g^{-1})

due to both conversion and alloying reaction mechanisms [21-23]. Although attractive, practical application of the ZnMn_2O_4 is impeded by its fast capacity fading because of large volume variation upon lithiation/delithiation. As a consequence, rational design and construction of ZnMn_2O_4 nanostructures with different morphologies have been utilized to overcome this issue [24-32]. Among these strategies, synthesis of porous or hollow structures is investigated as effective means to improve the cyclability of ZnMn_2O_4 based anode materials [26-32]. Specifically, the porous or hollow structures can not only offer effective empty space to the volume variation during cycling, but also increase reaction sites. Up to date, most porous or hollow ZnMn_2O_4 architectures have been fabricated via hydrothermal (or solvothermal) [26] and templating method [30,31]. The common drawback of hollow or porous power materials is that the electrode was prepared through mixing carbon and polymer binder with these active materials and fastening on current collectors, which would increase “dead surface”, reduce the reaction sites, and decrease the electrical conductivity.

Electrostatic spray deposition (ESD) technique developed by Schoonman et al. has been utilized as an effective strategy to fabricate binder-free film with porous structures [33-35]. Many TMOs films including Fe_2O_3 [36], Co_3O_4 [37], CoO [38], MnO [39], etc, have been prepared through this ESD method, but few MTMO films have been synthesized by this technique. Herein we report the synthesis and electrochemical performances of novel ZnMn_2O_4 films on Ni foam substrate with a 3D porous structure prepared through ESD followed by annealing in Ar atmosphere. Owing to the unique 3D porous ZnMn_2O_4 architecture directly deposited on Ni foam,

the ZnMn_2O_4 electrodes exhibit stable and large reversible capacity and good rate capability.

2. Experimental

2.1 Synthesis of sample

The ZnMn_2O_4 films on Ni foams were synthesized through ESD method. 0.12 mmol of $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and 0.06 mmol of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ were dissolved in a 30 ml of solvent mixture of 1,2-propanediol and ethanol (1:1 in volume ratio) to form precursor solutions. The distance between the metal nozzle and substrate was fixed at about 3-4 cm. The DC voltage was kept at about 6-8 kV to form a spray. The precursor flow rate was 2 mL h^{-1} . The ZnMn_2O_4 films were prepared on Ni foam substrates with an area of 14 mm at 250°C for 4 h. The as-prepared films were calcined at 500°C for 2 h in Ar atmosphere.

2.2 Characterizations and electrochemical measurements

The structure and morphology of the samples were characterized by X-ray diffraction via Cu $\text{K}\alpha$ radiation (XRD, SIEMENS-D5000) and field-emission scanning electron microscopy (FESEM, JEOL 6335), respectively. The surface chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XI). Electrochemical test was carried out using CR2032 coin type cells assembled in an argon filled glove box (VAC Nexus I). As-prepared or annealed ZnMn_2O_4 films fabricated on the nickel foams were used as working electrodes, while lithium foils were used as counter and reference electrodes. The typical loading mass of active materials was 0.7 mg cm^{-2} . Celgard 2400 was used as the separator and the

electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate: diethyl carbonate (1:1 v/v). Electrochemical characterization was measured on a Versatile Multichannel Potentiostat (VMP3, Bio-Logic). The cells were cycled in the voltage range of 0.01-3 V at room temperature through a NEWARE BTS-610 Battery Test System.

3. Results and discussion

The structures of the ZnMn_2O_4 samples were analyzed through XRD pattern. In order to reduce the strong impact of the substrates on the experiment results, the ZnMn_2O_4 films were peeled off from the Ni foam for XRD analysis (Fig.1). No well-defined peaks can be found in the XRD patterns of as-prepared sample, implying amorphous nature of the film. Through the annealing process, it can be seen that the diffraction peaks appear at $2\theta=18.6, 33.2, 36.6$ and 61.3° , which can be indexed to (101), (103), (211), and (224) planes of the tetragonal ZnMn_2O_4 phase (JCPDS card No. 24-1133), indicating the high purity of the annealed sample.

Fig. 2 presents the SEM images of the ZnMn_2O_4 films on Ni foams before and after the annealing at 500°C . For the as-prepared ZnMn_2O_4 film (Fig. 2a and b), it is observed that the Ni foam substrate is uniformly covered with 3D porous reticular-like morphology. The porous structure could be related to the solvent evaporation and decomposition of organic salts [33,35,37]. Through the annealing process (from Figs. 2c and d), the surface morphology of ZnMn_2O_4 film become relatively rough with small particles on the walls, which could be assigned to ZnMn_2O_4 crystal growth [39,40].

The surface chemical compositions and the valence states of the ZnMn_2O_4 film were illustrated by XPS (Fig. 3). In Fig. 3a, the survey spectrum of ZnMn_2O_4 film shows the presence of Zn, Mn, and O elements. The high-resolution of Zn 2p spectrum was shown in Fig. 3b. Two peaks at 1144.7 and 1021.6 eV are ascribed to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of Zn^{2+} , respectively [25]. Fig. 3c reveals high-resolution of Mn 2p spectrum with two peaks at 653.6 and 641.7 eV, which can be assigned to Mn $2p_{1/2}$ and Mn $2p_{3/2}$ of Mn^{3+} [30]. It can be observed that the O 1s peak is deconvoluted into two peaks at 531.2 and 529.9 eV, corresponding to the lattice oxygen in ZnMn_2O_4 and physically adsorbed oxygen, respectively (Fig. 3d) [30].

The electrochemical performances of the 3D porous ZnMn_2O_4 films for LIB anodes are examined through cyclic voltammograms (CV) and galvanostatic cycling. Fig. 4a,b show CV curves for as-prepared and annealed ZnMn_2O_4 films in the first three cycles between 0.01 and 3 V at 0.2 mV s^{-1} . It can be seen that both CV curves for as-prepared and annealed samples present similar reduction and oxidation peaks, implying similar electrochemical behavior. For annealed ZnMn_2O_4 films, in the first discharge cycle (Fig. 4b), the peak is observed at 1.15 V, which can be ascribed to the reduction of Mn^{3+} to Mn^{2+} and the solid electrolyte interface (SEI) formation [15]. The cathodic peak at 0.29 V correlates to the reduction of Mn^{2+} and Zn^{2+} cations to metallic nanograins Mn^0 and Zn^0 and ZnLi alloying reaction [30]. In the first discharge cycle, the wide peak at approximately 0.5 V can be assigned to a ZnLi dealloying reaction, and the two broad peaks at 1.28 and 2.19 V can be assigned to oxidation of Mn^0 to Mn^{2+} and Zn^0 to Zn^{2+} [41,42], respectively. In subsequent cycles,

the reduction peak shifts from 0.29 to 0.53 V, revealing the different electrochemical mechanisms from the first cycle. The overlap of the CV curves of 2nd and 3rd cycle implies the good reversibility of the electrochemical reactions. The electrochemical reactions occurred in the discharge and charge processes are concluded below [23,25,30,43]:

The first discharge process:

The subsequent reversible reaction:

Fig. 5a,b display charge-discharge curves for the 1st, 2nd, 3rd, 50th, and 100th cycles of the as-prepared and annealed ZnMn_2O_4 electrodes at a current density of 400 mA g^{-1} between 0.01 and 3.0 V (vs. Li/Li^+). The first discharge curves of the two electrodes present similar voltage profile with two voltage plateaus. For the annealed (as-prepared) ZnMn_2O_4 films, the former plateau around 1.19 (1.24) V is related to the reduction of Mn^{3+} to Mn^{2+} and SEI formation, while the latter plateau around 0.42 (0.50) V is ascribed to the formation of Mn^0 , Zn^0 and ZnLi alloy. The as-prepared and annealed ZnMn_2O_4 electrodes exhibit initial discharge/charge capacities of 2211/1335 mAh g^{-1} (Fig. 4a) and 1789/1259 mAh g^{-1} (Fig. 4b) with the coulombic efficiency of 60.4% and 70.4%, respectively. For ZnMn_2O_4 electrodes, the irreversible reaction (the reduction of Mn^{3+} to Mn^{2+}), SEI formation, and electrolyte decomposition could be the main reasons for the low coulombic efficiency in the first cycle. However, the

value of coulombic efficiency quickly gets up to 96% (94%) for the second cycle and stabilizes above 96% (94%) in the subsequent cycles (Fig. 6a) for annealed (as-prepared) electrode, revealing good reversibility of the electrode.

Fig. 6a shows the curves of the charge-discharge capacity for as-prepared and annealed ZnMn_2O_4 films in the first 100 cycles at 400 mA g^{-1} . The as-prepared ZnMn_2O_4 film shows a higher capacity of 662 mAh g^{-1} after 100 cycles. Noticeable, for the annealed samples, excellent cycle ability is gained. The capacity gradually decreases and levels off at around 982 mAh g^{-1} after 100 cycles. The excellent cycling properties of the annealed ZnMn_2O_4 electrodes are better than those of ZnMn_2O_4 nanomaterials in previous reports (table 1), which reveals that the 3D porous ZnMn_2O_4 films can be used as promising LIB anodes for high energy storage system. The improved cycling performance is attributed to 3D porous ZnMn_2O_4 films directly deposited on Ni foams, which can offer effective empty space to accommodate the large volume variation during cycling, increase reaction sites, and improve the electron transport.

The rate capability was examined at different current densities using the same cell after the first 100 cycles (Fig. 6b). It is observed that a stable specific capacity of 1079 mAh g^{-1} is gained at 200 mA g^{-1} for annealed ZnMn_2O_4 films, which is higher than theoretical capacity of ZnMn_2O_4 . The excessive capacity phenomenon should correlate to the formation/dissolution of a polymeric gel-like film attached to active materials [28,39]. Even at the high current density of 5 A g^{-1} , the reversible capacity is still maintained as high as 455 mAh g^{-1} . Furthermore, when the current rate is reduced

to 200 mA g⁻¹, the capacity can be recovered to 1131 mAh g⁻¹, revealing an excellent rate-cycling stability of this sample.

Fig. 6c presents the subsequent cycling performances of as-prepared and annealed ZnMn₂O₄ films at 400 mA g⁻¹ using the same cell after 170 cycles. The capacity increases gradually and can reach a high value of 934 and 1670 mAh g⁻¹ after 300 cycles for the as-prepared and annealed ZnMn₂O₄ electrodes, respectively. This capacity rise phenomenon has also been found in other ZnMn₂O₄ anode materials for LIBs [26,31,44], which should be also attributed to the formation/dissolution of a polymeric gel-like film [45,46].

The electrochemical impedance spectra of as-prepared and annealed ZnMn₂O₄ electrodes were tested after 10 cycles by CV measurement at 0.2 mV s⁻¹ (Fig. 7). As can be seen, the two samples present similar impedance profile, which contains a semicircle in the high-medium frequency region and an inclined line in the low frequency region. It is obvious that radius of the semicircle for the annealed ZnMn₂O₄ films is smaller than that of the as-prepared ZnMn₂O₄ films, revealing that the annealed electrodes behaves faster charge transfer. Based on the above electrochemical results, it is proved that the annealed ZnMn₂O₄ films show better battery performances than that of the as-prepared ZnMn₂O₄ films, which should be ascribed to the improved crystal quality of annealed ZnMn₂O₄ [40,47,48].

4. Conclusions

In summary, 3D porous ZnMn₂O₄ thin films on nickel foam substrates have been successfully synthesized through ESD technique followed by an annealing process for

LIB anodes. By synergizing advantageous features of 3D porous ZnMn_2O_4 architectures and Ni foams as a current collector, ZnMn_2O_4 electrodes exhibit large specific capacity, high rate capability, and excellent cycling performance. This ESD method provides a facile strategy to fabricate other 3D porous MTMO (e.g. CoMn_2O_4 , NiCo_2O_4 , ZnCo_2O_4) as promising candidate materials for LIB anodes in high energy storage system.

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Figure captions

Fig. 1. XRD patterns of the as-prepared and annealed ZnMn_2O_4 films.

Fig. 2. SEM images for (a,b) as-prepared ZnMn_2O_4 films and (c,d) annealed ZnMn_2O_4 films at different magnifications, respectively.

Fig. 3. XPS spectra of (a) full scan, (b) Mn 2p, (c) Zn 2p, and (d) O1s region of ZnMn_2O_4 film.

Fig. 4. Cyclic voltammetry for (a) as-prepared ZnMn_2O_4 films and (b) annealed ZnMn_2O_4 films, respectively.

Fig. 5. Charge and discharge profiles for (a) as-prepared ZnMn_2O_4 films and (b) annealed ZnMn_2O_4 films, respectively, at the current of 400 mA g^{-1} between 0.01 and 3 V.

Fig. 6 (a) Capacity retention of the as-prepared and annealed ZnMn_2O_4 films. (b) Rate capability of the as-prepared and annealed ZnMn_2O_4 films. (c) Subsequent capacity retention of the as-prepared and annealed ZnMn_2O_4 films, respectively.

Fig. 7 AC impedance spectra of the as-prepared and annealed ZnMn_2O_4 films after 10 cycles CV tests, respectively.

Table 1. The electrochemical performances of ZnMn_2O_4 electrodes with different morphologies synthesized by different strategies.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1

Morphology	Synthesis method	1st discharging–charging capacity (mAh g ⁻¹)	Capacity retention (mAh g ⁻¹)	Rate properties (mAh g ⁻¹)	Reference
rGo-ZnMn ₂ O ₄ composite	Bottom-up wrapping	1412/960 at 100 mA g ⁻¹	707 (50 cycles)	450 at 2000 mA g ⁻¹	23
ZnMn ₂ O ₄ nanoplates	An “escape-by-crafty-scheme” method	1277/730 at 100 mA g ⁻¹	502 (30 cycles)	324 at 1800 mA g ⁻¹	24
Ball-in-ball ZnMn ₂ O ₄ hollow microspheres	Thermally driven contraction process	945/662 at 400 mA g ⁻¹	790 (120 cycles)	396 at 1200 mA g ⁻¹	26
ZnMn ₂ O ₄ hollow microspheres	Coprecipitation	1325/722 at 400 mA g ⁻¹	607 (100 cycles)	361 at 1600 mA g ⁻¹	27
ZnMn ₂ O ₄ porous Microspheres	Solvothermal	1718/1090 at 100 mA g ⁻¹	800 (100 cycle) at 500 mA g ⁻¹	395 at 2000 mA g ⁻¹	29
ZnMn ₂ O ₄ mesoscale tubular arrays	Reactive template (ZnO) method	1198/~750 at 100 mA g ⁻¹	784 (100 cycle)	244 at 3200 mA g ⁻¹	30
ZnMn ₂ O ₄ hollow Nanotubes	Template (CNT) method	1793/1055 at 200 mA g ⁻¹	360 (100 cycle) at 200 mA g ⁻¹	272 at 2000 mA g ⁻¹	31
ZnMn ₂ O ₄ hierarchical tubular structures	Template (CNF) method	1793/1055 at 200 mA g ⁻¹	981 (30 cycle)	478 at 2000 mA g ⁻¹	32
Loaf-like ZnMn ₂ O ₄ nanorod	Hydrothermal+solid state reaction	1357/839 at 100 mA g ⁻¹	517 (100 cycles) at 500 mA g ⁻¹	457 at 1000 mA g ⁻¹	44
3D porous ZnMn ₂ O ₄ film	Electrostatic spray deposition method	1789/1259 at 400 mA g ⁻¹	982 (100 cycles)	455 at 5000 mA g ⁻¹	This work