Facile fabrication of three-dimensional porous ZnO thin films on Ni foams for lithium ion battery anodes

¹Jujun Yuan^{a,b,*}, Xianke Zhang^{a,b}, Chunhui Chen^b, Yong Hao^b, Richa Agrawal^b, Chunlei Wang^{b,*}, Wei Li^c, Huajun Yu^a, Yi Yu^a, Xiurong Zhu^a, Zuzhou Xiong^a, Yingmao Xie^a

Keywords: ZnO films; Electrostatic spray deposition; Porous structure; Lithium-ion battery; Energy storage and conversion

ABSTRACT

Three-dimensional (3D) porous ZnO thin films on nickel foam substrates have been synthesized via a facile strategy of electrostatic spray deposition (ESD) followed by annealing in Ar atmosphere for lithium-ion battery anodes. The ZnO films show 3D porous structure with a pore size in the range of 3.5-5 μm . When used as anode materials for lithium ion battery anodes, the obtained ZnO films on Ni foams exhibit good cycling stability and superior rate capability. The ZnO electrode on Ni foam delivers a reversible capacity of 402 mAh g⁻¹ after 100 cycles at a current density of 200 mA g⁻¹. It is demonstrated that the improved performance is attributed to the unique 3D porous ZnO structure on Ni foam, which provide more reaction sites and effective tolerance to the volume change during cycling.

1. Introduction

Transition-metal oxides, including SnO₂ [1], Fe₂O₃ [2], MnO₂ [3], ZnO [4], etc, have drawn attentions as high-performance anode materials for lithium ion batteries (LIBs) to substitute for graphene used as commercialized anode material with low theoretical capacity of 372

1 mAh g⁻¹. Among these metal oxides, ZnO exhibits many advantages, such as low cost,
2
3 environmental friendliness, and high theoretical capacity (978 mAh g⁻¹) due to conversion
4
5 reactions and alloying/dealloying reactions mechanisms for LIB anodes [5,6]. However,
6
7 ZnO-based anodes are still subjected to capacity fading during the charge/discharge processes
8
9 because of a large volume change (~228%). To overcome this issue, the construction of
10
11 hollow or porous ZnO structure has been considered as one of effective strategies to improve
12
13 the cycle life and rate capability for LIBs, due to its advantages of offering more reaction sites,
14
15 and effective tolerance to the volume change during cycling [7-9]. Hollow and porous ZnO
16
17 materials have been prepared by different methods such as chemical solution route [7,8] and
18
19 template-assistant synthesis using nonreactive [9] or reactive template [10]. One common
20
21 drawback of hollow or porous power materials is that these active materials need be mixed
22
23 with the conductive agent and polymer binder to paste the electrodes onto the collector,
24
25 which will destroy the hollow and porous structure and reduce the reaction sites.
26
27

28
29 Electrostatic spray deposition (ESD) method has been considered as an ideal strategy to
30
31 synthesize binder-free metal oxide films with nanostructures or porous structures for LIB
32
33 anodes [11-14]. For example, nanosheet ZnO/reduced graphene oxide composites have been
34
35 fabricated using ESD method to improve the cycling performance of a LIB anode (359.6
36
37 mAh g⁻¹ after 220 cycles). However, there are no reports on the preparation of
38
39 three-dimensional (3D) porous ZnO films using ESD method for LIB anodes. Herein in this
40
41 letter, we present a facile strategy for the synthesis of 3D porous ZnO thin films by the ESD
42
43 method followed by annealing in an Ar atmosphere. The 3D porous ZnO films were
44
45 electrochemically characterized and given standard tests for LIB. The ZnO films on Ni foams
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

exhibit good cycling performance and superior rate capability for LIB anodes.

2. Experimental

2.1 Synthesis of sample

The schematic diagram of ESD setup is shown in Fig. 1a. The precursor solutions for ESD were prepared by dissolving stoichiometric proportions of 5 mM $\text{Zn}(\text{Ac})_2 \cdot 2(\text{H}_2\text{O})$ into the solvent mixture of 1,2 propanediol and ethanol (1:1 v/v). The resultant solution was pumped through a needle at a flow rate of 2 mL h^{-1} . Samples were deposited on Ni foam (Corun new energy company) substrates with $\Phi 14 \text{ mm}$ at 250°C for 4 h. The distance between the substrate and the nozzle was about 3-4 cm and the applied direct current voltage to generate a spray was about 6-8 kV. The as-prepared samples were annealed in a tube furnace at 500°C for 2 h under an Ar atmosphere.

2.2 Characterizations and electrochemical measurements

The crystal structure and morphologies of the products were characterized by X-ray diffraction using $\text{Cu K}\alpha$ radiation (XRD, SIEMENS-D5000) and field-emission scanning electron microscopy (FE-SEM, JEOL 6335), respectively.

The electrochemical characterization was carried out using button type cells (CR2032) coin type cells (CR2032) assembled in an argon filled glove box (VAC Nexus I). ZnO films on the nickel foams were used as a working electrode and a lithium foil as a counter and reference electrode. The typical loading mass of active materials was around 0.6 mg cm^{-2} .

A polypropylene microporous membrane (Celgard 2400) was used as separator. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 v/v). Cyclic voltammetry (CV) tests 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. Results and discussion

Fig. 1b presents the XRD pattern of the annealed ZnO films, which was peeled off from the Ni foam to reduce strong impact of the substrates on the experiment results. All the diffraction peaks are indexed to hexagonal wurtzite ZnO (JCPDS card No. 36-1451), indicating the high purity of the product. The SEM images of as-prepared and annealed ZnO films on Ni foam were shown in Fig. 2. As-prepared ZnO films show 3D reticular-like porous structure on nickel foam with a pore size in the range of 3.5-5 μm (Figs. 2a and b). After an annealing process (Figs. 2c and d), it can be seen that the film still has a 3D porous structures except some increasing cracks, indicating good mechanical attachment with the substrate.

Fig. 3a shows the CV curves for annealed ZnO films between 0.01 and 3 V at 0.2 mV s^{-1} . In the first cathodic sweep, the only peak at around 0.26 V is ascribed to the reduction of Zn^{2+} to Zn^0 , ZnLi alloying reaction, and the formation of a solid electrolyte interface (SEI) [15]. In the first anodic sweep, the first three peaks at 0.32, 0.57, and 0.69 V correspond to the multi-step dealloying process of LiZn alloy, and the fourth peak at 1.36 V corresponds to oxidation reactions of Zn^0 to Zn^{2+} [16]. In the subsequent cycles, there are two cathodic peak at 0.40 and 0.70 V, respectively. The peak at 0.70 V could be assigned to the reduction of Zn^{2+} to Zn^0 and the formation of LiZn alloy, while the other peak at 0.40 V may be assigned to the formation of SEI layer [17,18]. Fig. 3b displays the charge-discharge curves for the 1st, 2nd, 3rd, 50th, and 100th cycles of the annealed ZnO films on Ni foam at 200 mA g^{-1} between 0.01 and 3.0 V. The first discharge curve exhibits a plateau at approximate 0.49 V and shows

a capacity of 1784 mAh g⁻¹. The first charge capacity is 1000 mAh g⁻¹, leading an initial coulombic efficiency of 56%. The low coulombic efficiency of the first cycle should be ascribed to the SEI formation and electrolyte decomposition [19]. The electrochemical reactions occurred during charge/discharge process are concluded below [15, 20]:

Fig. 3c presents discharge/charge cyclic properties of the annealed ZnO films between 0.01 and 3.0 V at 200 mA g⁻¹. It is observed that the electrode shows a relatively high discharge capacity loss during the first 20 cycles. From 21 cycle, the capacity decayed slowly, and the specific capacity still retains a stable value of 402 mAh g⁻¹ after 100 cycles. The rate cycling performance is tested under different current rates using the same cell after 100 galvanostatic charge/discharge cycles (Fig. 3d). As can be seen, The average reversible capacities of 3D porous ZnO films on Ni foam range from 395, 331, 272, 225 to 175 mA h g⁻¹ with the current densities increasing from 200, 400, 800, 1600 to 3200 mA g⁻¹, respectively. When the current density reduces back to 200 mA g⁻¹, the specific capacity of the ZnO electrode is nearly recovered its initial values. The subsequent cycling performance of ZnO electrode are tested at 200 mA g⁻¹ after the rate capability measurement (Fig. 3d). The capacity increases gradually and can reach a value of 435 mAh g⁻¹ after 250 cycles. This capacity rise phenomenon could be attributed to the reversible formation/dissolution of polymeric gel-like film resulted from electrolyte degradation, which is often observed in TMOs [21,22]. Based on the above electrochemical results, it is proved that the 3D porous ZnO films on Ni foams show stable cycling performance and good rate capability. The improved electrochemical performances are ascribed to the unique 3D porous ZnO structures

on Ni foam, which can enhance the reaction sites and provide effective tolerance to the volume change during cycling.

4. Conclusion

In summary, a facile strategy has been reported to fabricate 3D porous ZnO films on Ni foams through ESD technique followed by an annealing process for LIB anodes. It is proved that the ZnO electrodes on Ni foams exhibit a good cycling performance and superior rate capability, which can be ascribed to the unique 3D porous ZnO structure directly grown on Ni foam current collector. It is believed that the 3D porous ZnO films on Ni foams can be applied as candidate materials for LIB anodes due to their good electrochemical properties.

Acknowledgements

This work is partially supported by the National Science Foundation (NSF) projects #1506640, #1509735, NERC ASSIST center seed funding, and National Natural Science Foundation of China (NSFC) with no. 51302118. The authors acknowledge facilities of AMERI at FIU.

References

- [1] Haag JM, Pattanaik G, Dustock F. Adv Mater 2013;25:3238-43.
- [2] Padashbarmchi Z, Hamidian AH, Zhang HW, Zhou L, Khorasani N, Kazemzad M, Yu CZ. RSC Adv 2015;5:10304.
- [3] Bai ZC, Fan N, Ju ZC, Guo CL, Qian YT, Tang B, Xiong SL. J Mater Chem A 2013;1:10985-90.
- [4] Yue HY, Shi ZP, Wang QX, Cao ZX, Dong HY, Qiao Y, Yin YH, Yang ST. ACS Appl Mater Interfaces 2014;6:17067-74.
- [5] Kim J, Hong SA, Yoo J. Chem Eng J 2015;266:179-88.
- [6] Wu XY, Li SM, Wang B, Liu JH, Yu M. RSC Adv 2015;5:81341-7.
- [7] Xie QS, Li JG, Tian Q, Shi RR. J Mater Chem 2012;22:13541-47

- [8] Xie QS, Zhang XQ, Wu XQ, Wu XB, Wu HY, Liu X, Yue GH, Yang Y, Peng DL. *Electrochim Acta* 2014;125:659.
- [9] Zeng XY, Yang J, Shi LX, Li LJ, Gao MZ. *Nanoscale Res Lett* 2014;9:468-77.
- [10] Park KT, Xia F, Kim SW, Kim SB, Song T, Paik U, Park WI. *J Phys Chem C* 2013;117:1037-43.
- [11] Yu Y, Gu L, Dhanabalan A, Chen CH, Wang CL. *Electrochim Acta* 2009;54:7227-7230.
- [12] Li XF, Wang CL. *J Mater Chem A* 2013;1:165-182.
- [13] Ma XH, Wan QY, Huang X, Ding CX, Jin Y, Guan YB, Chen CH. *Electrochim Acta* 2014;121:15-20.
- [14] Wu J, Chen CH, Hao Y, Wang CL. *Colloids Surf A: Physicochem Eng Asp* 2015;468:17-21.
- [15] Huang XH, Guo RQ, Wu JB, Zhang P. *Mater Lett* 2014;122:82-5.
- [16] Quartarone E, Dallasta V, Resmini A, Tealdi C, Tredici IG, Tambuini UA, Mustarelli P. *J Power Source* 2016;320:314-21.
- [17] Wang HB, Pan QM, Cheng YX, Zhao JW, Yin GP. *Electrochim Acta* 2009;54:2851.
- [18] Huang XH, Xia XH, Yuan YF, Zhou F. *Electrochim Acta* 2011;56:4960-4965.
- [19] Yang HJ, Lim SC, He SY, Tuan HY. *RSC Adv* 2015;5:33392-99.
- [20] Li S, Xiao Y, Wang X, Cao MH. *Phys Chem Chem Phys* 2014;16:25846-53.
- [21] Yuan CZ, Li JY, Hou LR, Zhang LH, Zhang XG. *Part Part Syst Charact* 2014;31:657-63.
- [22] Xie QS, Ma YT, Zeng DQ, Wang LS, Yue GH, Peng DL. *Sci Rep* 2015;5:8351-9.

Figures captions

Fig. 1 (a) Schematic diagram of ESD setup. (b) XRD pattern of the annealed ZnO films.

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

Fig. 3 (a) Cyclic voltammetry for annealed ZnO films. (b) Charge and discharge profiles for annealed ZnO films at 200 mA g⁻¹ between 0.01 and 3 V. (c) Capacity retention of the annealed ZnO films at 200 mA g⁻¹ between 0.01 and 3 V. (d) Rate capability of the annealed ZnO films.

Fig. 1

Fig. 2

Fig. 3