

Preparation and Electrochemical Performance of ZnO Films as Anode Materials for Li–Ion Batteries

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In this work, the effect of rf power on the structural, electrical and electrochemical properties of ZnO thin films was investigated. ZnO thin films were deposited on glass and Cr coated stainless steel substrates by rf magnetron sputtering in pure Ar gas environment. ZnO thin films for different rf powers (75, 100, and 125 W) were deposited keeping all other deposition parameters fixed. ZnO thin films were used as negative electrode materials for lithium-ion batteries, whose charge-discharge properties, cyclic voltammetry and cycle performance were examined. A high initial discharge capacity about 908 mAh g⁻¹ was observed at a 0.5 C rate between 0.05 and 2.5 V. The crystallographic structure of the sample was determined by X-ray diffraction. The electrical resistivity of the deposited films was measured by the four-point-probe method. The thickness of the ZnO thin films was measured using a profilometer.

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1. Introduction

ZnO with hexagonal structure has a wide optical band gap, 3.37 eV [1]. Zinc oxide has attracted extensive interest because of its important role in various applications, for example, gas sensor [2], surface acoustic wave devices [3], optical waveguides [4] as well as blue/UV light emitting devices [5]. Compared to other kinds of nanostructured films, the ZnO films have the advantages of structural versatility, easy fabrication and availability, which make them ideal templates for nanostructure construction [6, 7]. ZnO films can be deposited by a variety of techniques, such as sol–gel technique [8], spray pyrolysis [9], metal organic chemical vapor deposition [10], molecular beam epitaxy [11], pulsed laser deposition [12] and sputtering [13]. The properties of grown thin films depend on the deposition process and deposition parameters. Magnetron sputtering is a promising technique for the deposition of transparent oxides, which allows the deposition of films at low temperatures with good electrical and optical properties [14]. Sputtering parameters such as working gas pressure, substrate temperature, and sputtering power play important roles in controlling the properties of the films.

ZnO has a theoretical capacity of 978 mAh g⁻¹ [15], but it has rarely been used as anode materials in lithium-ion batteries because ZnO showed poor cycleability compared with other transition metal oxides. It is believed that low electronic conductivity and large volume-change during lithium insertion–extraction process are responsible for the poor electrochemical performance of ZnO electrode [16, 17]. Despite some effort had been devoted to overcome the problems, slight improvement had been achieved.

2. Experimental

ZnO thin films were deposited on glass and Cr coated stainless steel substrates by rf magnetron sputtering. The working pressure and the target substrate distance were respectively 1 Pa and 13.5 cm. In order to investigate the effect of rf power on the properties of ZnO thin films, the rf power was varied from 75 W to 125 W. All depositions were carried out for 60 min. Prior to the deposition, the glass substrates were cleaned with a hydrogen peroxide–acetone–methanol at 60 °C for 30 min and washed by deionized water. Cr coated stainless steel substrates were ultrasonically cleaned in alcohol for 15 min.

The crystal structure of the films was characterized by X-ray diffraction (XRD) using a Rigaku D/MAX 2000 diffractometer in the Bragg–Brentano configuration with Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$). The grain size was calculated by Scherrer's formula [18]:

$$D = \frac{0.9\lambda}{B \cos \theta},$$

where D is the grain size, λ is the X-ray wavelength, B is the corrected full-width at half maximum (FWHM) and θ is the Bragg angle. The resistivity of the films was also measured. Electrical resistivity measurements were performed using a four-point probe (Lucas Labs Pro4-4000). The film thickness was measured using a surface profiler (KLA Tencor P6).

The electrochemical performance was studied using 2016-type coin cells assembled in a nitrogen-filled glove box. The electrochemical performance of ZnO thin films was evaluated by galvanostatic discharge–charge measurement using a computer-controlled battery tester at a 0.5 C rate between 0.05 and 2.5 V. Cyclic voltammograms (CV) were measured on a Gamry Model 3000 electrochemical analyzer at a scan rate of 0.5 mV s⁻¹ between 0.05 and 2.5 V versus Li⁺/Li.

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3. Results and discussion

Figure 1 shows the X-ray diffraction pattern for ZnO thin films as a function of rf powers. ZnO thin films at (002) and (103) peaks were also observed. The XRD measurements indicate that the ZnO thin films have a polycrystalline structure with the hexagonal wurtzite structure and a strong preferred orientation of crystallites in the (002) direction along the *c*-axis perpendicular to the glass substrate.

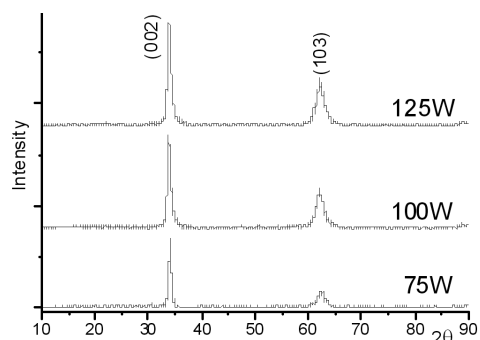


Fig. 1. X-ray diffraction patterns of ZnO thin films deposited with different rf powers under pure argon atmosphere.

Figure 2 shows the deposition rate, grain size, and resistivity of ZnO thin films deposited on glass substrates as a function of the different rf powers. Deposition rate increases with an increase in rf power at pure argon. As the rf power increased from 75 to 125 W, the deposition rate of ZnO thin films increased from 8.02 to 10.52 nm/min. The grain size increases gradually with the rf power. When the rf power is about 75 W, the average particle size is about 16 nm, when rf power is increased to 125 W, the grains also increase to about 25 nm. As the rf power increased from 75 to 125 W, the resistivity of ZnO thin films deposited on glass substrates decreased from 266 Ω cm to 89 Ω cm. This result can be explained with the enhanced crystallinity at higher rf power.

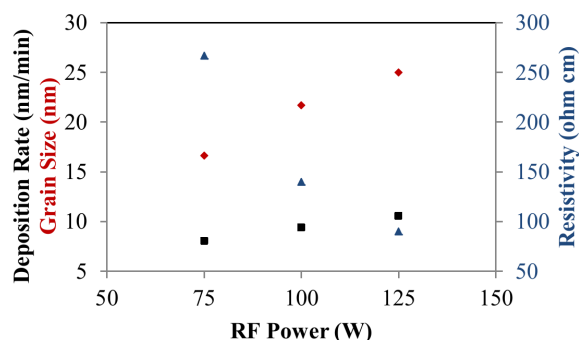


Fig. 2. The deposition rate, grain size and resistivity of ZnO thin films deposited with different rf powers under pure argon atmosphere.

Figure 3 shows the cyclic voltammograms for ZnO thin films between 0.05 and 2.5 V measured at a scan rate of 0.5 mV s^{-1} . In the cathodic scan, there are two peaks at 0.34 and 0.60 V, which are related with the alloying processes. This process contains the reduction of ZnO into Zn, the formation of Li–Zn alloy, and the growth of the gel-like solid electrolyte interphase (SEI) layer [19]. In the anodic scan, the four peaks, located at 0.35, 0.52, 0.68, and 1.43 V are ascribed to the multi-step dealloying process of Li–Zn alloy [20, 21].

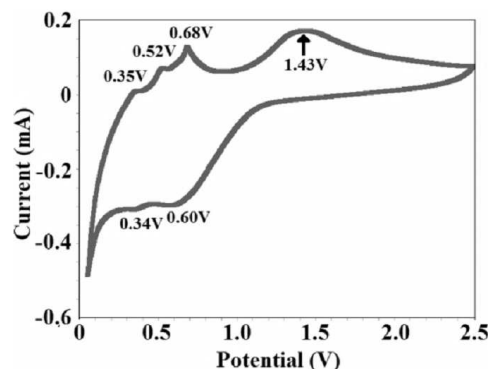


Fig. 3. Cyclic voltammograms of ZnO thin films at a scan rate of 0.5 mV s^{-1} between 0.05 and 2.5 V (vs. Li^+/Li).

Figure 4 shows the galvanostatic discharge–charge curves of ZnO thin films deposited with different rf for the 30 cycles at a 0.5 C rate between 0.05 and 2.5 V. When compared the ZnO thin films deposited at 75, 100, and 125 W rf powers, it is obvious that the ZnO thin films deposited at 125 W rf power exhibit higher discharge and charge capacities.

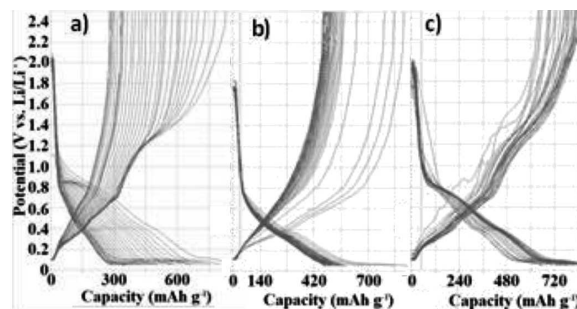


Fig. 4. The discharge/charge curves of ZnO thin films under pure argon atmosphere: (a) 75 W rf power, (b) 100 W rf power, (c) 125 W rf power.

Figure 5 shows the comparison of the cycling performance of ZnO thin films deposited at different rf powers. The test cells were cycled at a 0.5 C rate between 0.05 and 2.5 V. The profiles show that although the initial discharge capacities of ZnO thin films deposited at 125 W rf power are slightly lower than that of ZnO thin films deposited at 75 and 100 W rf powers.

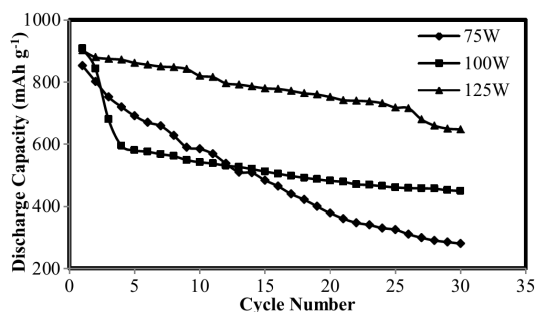


Fig. 5. Cycling behavior of ZnO thin films deposited with different rf powers under pure argon atmosphere.

4. Conclusions

Deposition rate increases with the increase in rf power. The intensity of peaks becomes more intense and sharper with the increase in rf power. The mean grain size increases with increase in the rf power. The electrical resistivity of ZnO thin film decreases with increase in the rf power. The best electrochemical results were obtained with ZnO thin films deposited at 125 W rf power (648 mAh/g) in highest discharge capacity 30 cycles.

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References

- [1] W. Yang, Z. Liu, D.-L. Peng, F. Zhang, H. Huang, Y. Xie, Z. Wu, *Appl. Surf. Sci.* **255**, 5669 (2009).
- [2] M. Suhea, S. Christoulakis, K. Moschovis, N. Katsarakis, G. Kiriakidis, *Thin Solid Films* **515**, 551 (2006).
- [3] X.Y. Du, Y.Q. Fu, S.C. Tan, J.K. Luo, A.J. Flewitt, S. Maeng, S.H. Kim, Y.J. Choi, D.S. Lee, N.M. Park, J. Park, W.I. Milne, *J. Phys. Conf. Series* **76**, 012035 (2007).
- [4] X. Ming, F. Lu, H. Liu, M. Chen, L. Wang, *J. Phys. D, Appl. Phys.* **42**, 165303 (2009).
- [5] O. Senthilkumar, K. Yamauchi, K. Senthilkumar, T. Yamamae, Y. Fujita, N. Nishimoto, *J. Korean Phys. Soc.* **53**, 46 (2008).
- [6] J.P. Liu, Y.Y. Li, R.M. Ding, J. Jiang, Y.Y. Hu, X.X. Ji, Q.B. Chi, Z.H. Zhu, X.T. Huang, *J. Phys. Chem. C* **113**, 5336 (2009).
- [7] Q.M. Pan, L.M. Qin, J. Liu, H.B. Wang, *Electrochim. Acta* **55**, 5780 (2010).
- [8] L. Znaidi, T. Touam, D. Vrel, N. Souded, S. Ben Yahia, O. Brinza, A. Fischer, A. Boudrioua, in: *Acta Physica Polonica A* **121**, 165 (2012).
- [9] M.R. Islam, J. Podder, *Cryst. Res. Technol.* **44**, 286 (2009).
- [10] J. Zhu, I.H. Lee, R. Yao, Z. Fu, *J. Korean Phys. Soc.* **50**, 598 (2007).
- [11] W.C.T. Lee, C.E. Kendrick, R.P. Millane, Z. Liu, S.P. Ringer, K. Washburn, P.T. Callaghan, S.M. Durbin, *J. Phys. D, Appl. Phys.* **45**, 135301, (2012).
- [12] A.Og. Dikovska, P.A. Atanasov, C. Vasilev, I.G. Dimitrov, T.R. Stoyanov, *J. Optoelectron. Adv. Mater.* **7**, 1329 (2005).
- [13] K.-H. Lee, N.-I. Cho, E.-J. Yun, H.G. Nam, *Appl. Surf. Sci.* **256**, 4241 (2010).
- [14] R. Kumar, N. Khare, V. Kumar, G.L. Bhalla, *Appl. Surf. Sci.* **254**, 6509 (2008).
- [15] F. Belliard, P.A. Connor, J.T.S. Irvine, *Ionics* **5**, 450 (1999).
- [16] F. Belliard, P.A. Connor, J.T.S. Irvine, *Solid State Ionics* **135**, 163 (2000).
- [17] H. Li, X. Huang, L. Chen, *Solid State Ionics* **123**, 189 (1999).
- [18] B.D. Cullity, *Elements of X-Ray Diffraction*, Addison-Wesley, Massachusetts 1956.
- [19] G. Gachot, S. Grugeon, M. Armand, S. Pilard, P. Guenot, J.-M. Tarascon, S. Laruelle, *J. Power Sources* **178**, 409 (2008).
- [20] F. Belliard, J.T.S. Irvine, *J. Power Sources* **97-98**, 219 (2001).
- [21] J. Liu, Y. Li, X. Huang, G. Li, Z. Li, *Adv. Funct. Mater.* **18**, 1448 (2008).