

Nanocomposite ZnO:MWCNT Thin Films for Li-Ion Batteries Prepared via Reactive Magnetron Sputtering

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In this study, ZnO/MWCNT buckypaper nanocomposite structures were obtained as an anode electrode material for Li-ion batteries. MWCNT based buckypapers were produced via vacuum filtration techniques and the surfaces of the buckypapers were coated with ZnO in order to increase stability and mechanical integrity during charging and discharging processes. The effect of deposition powers on the battery performance is also investigated.

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1. Introduction

Currently, lithium ion insertion materials have attracted great interests since they can be used as active electrode materials in rechargeable Li-ion batteries (LIBs) for potential applications such as portable electronics and hybrid electrical vehicles. ZnO has been considered as one of the most important anode electrode material in LIBs due to its high theoretical specific capacity (978 mAh g^{-1}), compared to traditional graphite anode [1–4]. However, exponential volumetric expansion usually occurs during the lithiation and delithiation processes [5], which leads to pulverization of electrode and rapid capacity degradation. Therefore, its commercial application in LIBs anode has been significantly hindered.

Many metal oxide based anode electrodes having pulverization and degradation problems during lithiation and delithiation processes were widely studied. In order to prevent these obstacles and extend the cycling life of metal oxide based anode electrodes, metal oxide particles were integrated with carbon based matrices as an inactive buffer layer due to their intrinsic mechanical durability and good electronic properties [6–8]. In this study, we report a new type of nanostructure, CNTs–ZnO nanocomposite structures, which integrate both electronic conductivity and buffering matrix design strategies. The CNTs–ZnO nanostructured electrodes have been prepared and applied as anode materials for lithium-ion batteries, which exhibit higher lithium storage capacities and better cycling performance compared to single CNTs and ZnO electrodes. Thin films of ZnO nanostructures were formed via rf magnetron sputtering.

2. Experimental details

The multiwalled carbon nanotubes (MWCNTs) of 50 nm in diameter and 1.00 μm in length used in this research were provided by Arry International Co., Ltd.

(Germany), produced using a chemical vapor deposition (CVD) method. As received MWCNTs were heat treated at 350°C for 8 h in order to remove the amorphous carbon. MWCNTs were then dispersed in nitric acid solution and further refluxed at 140°C with magnetic stirring for the removal of metal catalysts contaminants. Chemical oxidation of MWCNTs was carried out with a mixture of H_2SO_4 and HNO_3 acids in ratio 3:1 for 3 h. The functionalized MWCNTs were first dispersed into water by the aid of SDS surfactant and sonicated to form a well-dispersed suspension which subsequently was vacuum filtered through PVDF membrane filters of 220 nm pore size to form buckypapers. The produced buckypapers were then coated with ZnO via magnetron sputtering techniques. The base pressure was reduced to 1.0×10^{-3} Pa, then the targets were pre-sputtered for 5 min in order to eliminate the contaminant from target surfaces under 0.55 Pa, followed by injected high purity (99.999%) oxygen reactive gas into the vacuum chamber to form zinc oxide thin films. The argon and oxygen flow rate were fixed at constant value for all coatings and the effect of coating power on the electrochemical performance is investigated.

The structure of the deposited films was characterized by means of X-ray diffraction (XRD, Rigaku D/max 2200 system with thin film attachment). The morphology was observed by scanning electron microscopy (JSM-6060 LV system). Coin-type (CR2016) test cells were assembled in an argon-filled glove box, directly using the ZnO coated CNT buckypapers as the working electrode, a lithium metal foil as the counter electrode, a micro porous polypropylene (PP) membrane (Cellgard 2400) as the separator, and 1 M solution of LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by weight) as the electrolyte. The cells were cyclically tested on a MTI Model BST8-MA electrochemical analyzer using different current densities over a voltage range of 0.2–2.5 V.

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3. Results and discussions

Figure 1 shows the SEM image of the produced buckypapers. As can be seen from the figures, a highly entangled CNT network, with numerous intersection points consists of long, curled and highly random oriented mesoporous structure. The self standing property of the produced paper-like structure is due to the Van der Waals forces and mechanical locking of the MWCNTs within the buckypaper. The SEM image of a cross-section of a representative sheet (Fig. 1b) indicates an almost homogeneous CNT deposition through the thickness giving rise to a dense morphology.

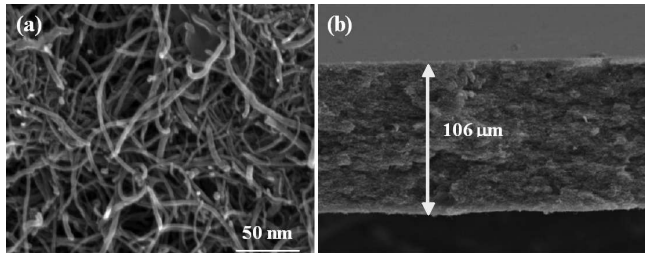


Fig. 1. SEM images of (a) surface and (b) cross-section area of the MWCNT based buckypapers.

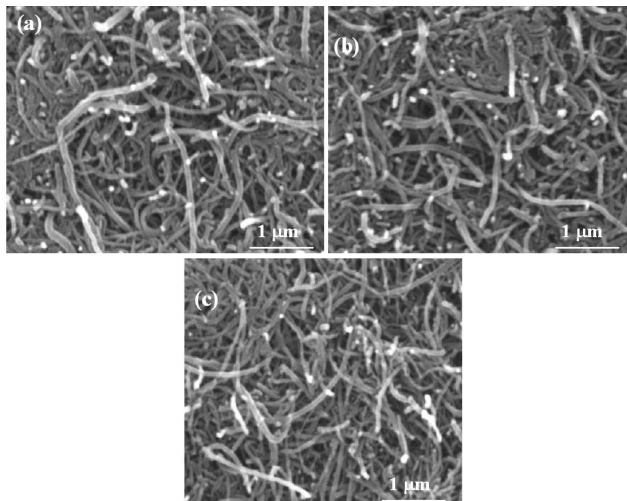


Fig. 2. SEM images of the films deposited by using (a) 75 W, (b) 100 W, and (c) 125 W rf powers under 10% oxygen gas pressures.

Figure 2 shows the surfaces of the buckypapers after reactive magnetron sputtering process. The SEM images revealed that the ZnO is considered to be selectively nucleated and uniformly deposited on the surface of CNTs by the reactive magnetron sputtering process. No obvious separated ZnO bulk particles are evident apart from those deposited on CNTs. The CNTs coated with ZnO are entangled and interconnected to form a uniform network with a three-dimensional and highly mesoporous structure.

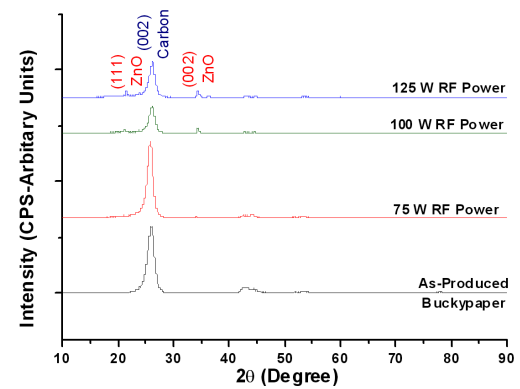


Fig. 3. XRD spectra of the as-produced buckypaper and thin films deposited by using varying RF powers.

Figure 3 shows the XRD patterns of the produced buckypaper and ZnO coated buckypaper by using varying rf powers. The XRD results indicate that the ZnO thin films were obtained on the surfaces of buckypapers. All peaks were assigned to carbon (JCPDS 026-1080) and hexagonal zinc oxide (JCPDS-36-1451). XRD patterns also exhibit the (002) and (111) peaks, which indicates that the films are highly oriented with their crystallographic *c*-axis perpendicular to the substrate, irrespective of sputtering power. However, intensities of the peaks were shown a variation with increasing RF power. The diffraction intensity of the (002) peak maximized at sputtering power of 125 W which clearly indicates that the crystallinity of the films was improved with increasing RF power.

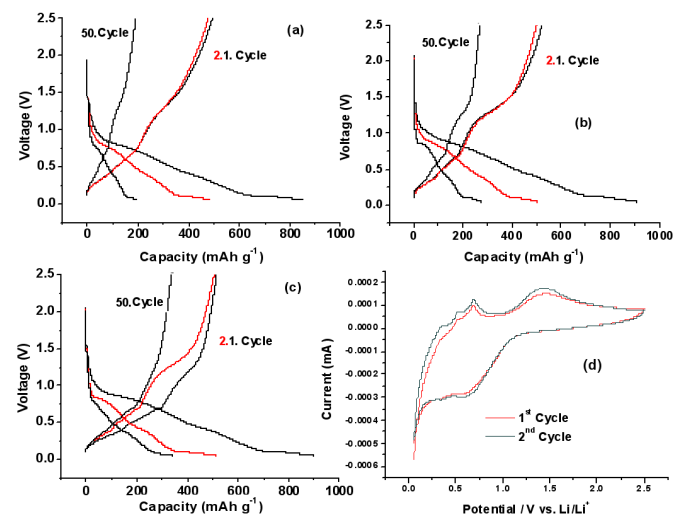


Fig. 4. Voltage–capacity curves of the deposited under (a) 125 W, (b) 100 W, (c) 75 W rf powers, and (d) cyclic voltammograms of ZnO/MWCNT nanocomposite anode electrodes.

The galvanostatic discharge–charge curves at current density 14 mA dm^{-2} (1 C) of MWCNT/ZnO anode elec-

trode between 0.2 and 2.5 V vs. Li^+/Li and cycling performances are presented in Fig. 4a–c. As can be deduced from the figures, best results were obtained after 50 cycles with a capacity of 257 mAh g^{-1} . Figure 4d shows the cyclic voltammograms (CV) of porous ZnO nanocomposite structures measured between 0 and 2.5 V at a scan rate of 0.5 mV s^{-1} . As can be seen, two peaks were obtained between 0.35 V and 0.70 V which can be attributed to the reduction of ZnO into Zn and the formation of lithium–zinc alloy. However, four oxidation peaks were obtained in the subsequent anodic scan which can be assigned to the multi-step dealloying process of lithium–zinc alloy (LiZn , Li_2Zn_3 , LiZn_2 and Li_2Zn_5). In addition, a broad oxidation peak is found at 1.54 V, which may relate to the decomposition of Li_2O . The integral area of the curves were seen to be equal which clearly indicates that ZnO/MWCNT based anode electrodes are highly reversible and MWCNT buckypapers improved the Li electroactivity of the ZnO nanoparticles because of their beneficial effect on the conductivity, efficient electron paths, and aggregation control of active nanoparticles.

4. Conclusions

In this study, highly mesoporous MWCNT based buckypapers were produced via vacuum filtration techniques. The surfaces of the MWCNT based buckypapers were then coated with ZnO in order to increase the electrochemical performance of the buckypapers which could be used as an anode material in Li ion batteries. The results have shown that best results were obtained for the deposited under 75 W rf power which could be attributed to the finer nanograins as revealed by the XRD results. Obtaining nanograins over the surfaces of the buckypapers can increase the surface area structure and may alleviate the change of the cell volume during charge

and discharge cycles. Furthermore, buckypaper shells in the composites optimize the electrochemical performances of ZnO electrode materials. Therefore, core–shell ZnO/MWCNT composites are worth extensively exploiting as anode materials for lithium ion batteries.

Acknowledgments

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