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A facile synthesis of zinc oxide/multiwalled carbon nanotube nanocomposite lithium ion battery anodes by sol–gel method

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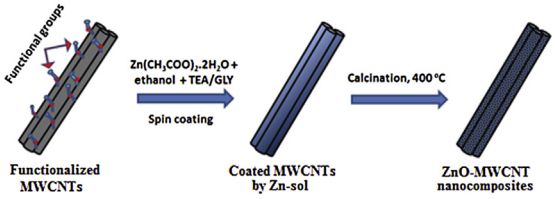
HIGHLIGHTS

- ZnO/MWCNT free-standing anodes were prepared by a novel spin coating method.
- MWCNT buckypapers were used to prevent mechanical disintegration of anode material.
- The effects of chelating agents on the properties of ZnO electrodes were researched.
- ZnO/MWCNT/GLY free-standing electrode provided better capacity retention.
- After 100 cycles, this anode showed as high as of 460 mAh g^{-1} discharge capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Free standing zinc oxide (ZnO) and multiwalled carbon nanotube (MWCNT) nanocomposite materials are prepared by a sol gel technique giving a new high capacity anode material for lithium ion batteries. Free-standing ZnO/MWCNT nanocomposite anodes with two different chelating agent additives, triethanolamine (TEA) and glycerin (GLY), yield different electrochemical performances. Field emission gun scanning electron microscopy (FEG-SEM), energy dispersive X-ray spectrometer (EDS), high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) analyses reveal the produced anode electrodes exhibit a unique structure of ZnO coating on the MWCNT surfaces. Li-ion cell assembly using a ZnO/MWCNT/GLY free-standing anode and Li metal cathode possesses the best discharge capacity, remaining as high as 460 mAh g^{-1} after 100 cycles. This core–shell structured anode can offer increased energy storage and performance over conventional anodes in Li-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) are one of the most popular types of rechargeable battery for portable electronics, providing one of the highest energy densities. They are also the choice power source for electric and hybrid vehicles [1]. LIBs have attracted attention due to

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their high energy density, high voltage, stable cycling, and environmentally friendly properties [2]. In the last few decades, transition metal oxides have attracted interest for use in electrode materials in LIBs due to their higher theoretical capacity and safety compared with conventional carbon materials. Among transition metal oxides, ZnO features low cost, easy preparation, morphologic diversity, and environmental benignity, among other benefits [3]. ZnO is attractive as a potential substitute for the conventional graphite anode in lithium-ion batteries, as the theoretical capacity (978 mAh g^{-1}) has been estimated to be superior to that of graphite (372 mAh g^{-1}) [4].

ZnO is a semiconducting material with a wide band gap of 3.37 eV and a high excitonic binding energy of 60 meV at room temperature [5]. ZnO is useful in electronics and optoelectronic devices because of its excellent electrical and optical properties [6]. For their high electrochemical activity, ZnO nanomaterials have widespread applications in electrode active materials such as Ni–MH cells, lithium cells, solar cells, and fuel cells [7]. To produce ZnO, various methods have been employed, such as vapor decomposition, precipitation, thermal decomposition, and the sol–gel process. Among these methods, the sol–gel process is favored due to providing good homogeneity, low process temperature, ease of composition control, good optical properties, and low equipment costs [8,9].

High capacity metal oxides, such as ZnO based anodes, typically suffer severe capacity fading, which results from both the quick aggregation of zinc particles and the huge volume expansion during Li^+ insertion/extraction cycles, causing pulverization of the anodes and subsequent electrical detachment of active materials. Therefore, a great deal of effort has been devoted to overcome these problems, and many methods have been developed [10,11]. In most of these methods, it is claimed that carbon nanotubes (CNTs) will radically improve the performance of batteries, because their unique structure may especially enhance the kinetic properties of the electrodes and result in an extremely high specific charge compared with the theoretical limits of graphitic carbon [12]. Due to outstanding properties of CNTs, MWCNT buckypaper substrate is considered a buffer material to prevent mechanical disintegration of anode material during the battery applications. Most notably, “free-standing” carbon nanotube paper electrode, which there is no need an external current collector, may be used for this purpose. Free standing electrodes also cause to eliminate to use binder materials which result in decreasing the active materials content in the electrode. This also served to eliminate the use of solvent materials during electrode preparation. CNT papers, also called buckypapers, are self-supporting networks of entangled CNT assemblies indiscriminately arranged and held together by van der Waals interactions at the tube–tube junctions [13].

In this work, ZnO/MWCNT buckypaper nanocomposite electrodes were prepared as free-standing anode materials by sol–gel spin coating method. First, ZnO coating solutions were fabricated by sol–gel method with TEA and GLY as chelating agents. This was intended to investigate the effect of organic chelating agents on the structure of ZnO nanoparticles and electrochemical performance for Li-ion battery electrodes. To the best of our knowledge, there has been no published work concerning highly porous MWCNT buckypapers infiltrated with ZnO sol by spin coating. The coating is intended to accommodate the stresses arisen from the volume increase during the charging process using a highly porous MWCNT network coated with a thin layer of the ZnO. The structural properties and electrochemical performance of free standing ZnO/MWCNT buckypaper nanocomposite anodes of CR2016 type Li-ion batteries were investigated.

2. Experimental

2.1. Preparation of ZnO/MWCNT buckypaper nanocomposites

In this work, the MWCNTs were supplied from Arry International Group (Germany) with an outer diameter of 50 nm over 1.0 μm in length. Carbon nanotubes need to be first purified to make them amenable to aqueous processing. Purification was performed using hydrochloric acid (HCl). MWCNTs were functionalized using an acid mixture of HNO_3 (65%):H_2SO_4 (98%) (1:3 v/v), filtered from acid solutions and washed with deionized water several times, then dried in an oven as suggested in the literature [14].

The buckypapers were prepared using functionalized MWCNTs suspended in aqueous solutions. To prevent the agglomeration of MWCNTs, sodium dodecyl sulfate (SDS) was added to the solution as a surfactant. This solution was ultrasonicated for 1 h, and vacuum filtered through PVDF membrane filters with a diameter of 47 mm and pore size of 220 nm (Millipore). After the filtration process, MWCNT buckypapers were washed with deionized water several times to remove the surfactant from the structure. Finally, the MWCNT papers were dried and peeled off the filtration membrane. Fig. 1(a) illustrates the production stages of MWCNT buckypapers. The average thickness of the produced buckypapers was 80 μm, with a diameter of 16 mm.

For producing ZnO/MWCNT nanocomposites, two sols were prepared. Firstly, a $Zn(CH_3COO)_2{\cdot}2H_2O$ precursor was added to 40 mL absolute ethanol. The solutions were stirred with a magnetic stirrer and heated to 50 °C. The solutions were cloudy during the stirring at 50 °C. TEA and GLY were separately added to different sols until the formation of a complex reaction between Zn^{2+} cation and organic chelating agents. After the addition of these chelating agents, the solutions became transparent [15]. The sols were then stirred and heated for a few hours. As a result, the ZnO precursor sols were synthesized using the sol–gel method from $Zn(CH_3COO)_2{\cdot}2H_2O$ precursor solution. All chemicals were of analytical grade and were used without further purification.

After several preliminary studies, it was noted that the prepared sols with two different chelating agents were completely infiltrated into the MWCNT buckypapers and deposited on the individual MWCNTs at a 3000 rpm spin coating rate. Therefore, MWCNT buckypaper substrates were coated with synthesized sols using a spin coater with a 3000 rpm spin rate. By using the precursor solutions, ZnO/MWCNT nanocomposites were prepared by coating ZnO sol–GLY and ZnO sol–TEA, and the resultant nanocomposites were coded as ZnO/MWCNT/GLY and ZnO/MWCNT/TEA, respectively. ZnO precursors with chelating agent infiltrated MWCNTs were dried at 50 °C in air for 15 min. Finally, the free-standing ZnO/MWCNT nanocomposites were calcinated in an Ar atmosphere at 400 °C with a heating rate of 2 °C/min for 2 h. A schematic illustration of facile sol–gel synthesis of nanocomposite anodes is presented in Fig. 1(b). The strategy was based on producing a thin core layer on the individual MWCNT surfaces in the buckypaper network to alleviate the huge volume variation of ZnO, therefore accommodating the stress formed during discharge/charge process, as well as preventing the ZnO from aggregation and pulverization.

2.2. Physical characterization of materials

The structure of the free-standing nanocomposites was analyzed using field emission gun-scanning electron microscopy (FEG-SEM, FEI QUANTA 450) and HRTEM (JEOL 2100). The chemical