Proceedings of the 2nd International Congress APMAS2012, April 26–29, 2012, Antalya, Turkey Synthesis and Characterization of Antimony Doped Tin Oxide Nanocomposites for Li-Ion Batteries

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High content carbon nanotubes mats have been produced to multi-walled carbon nanotubes. Sb doped SnO_2 films were then deposited by rf magnetron sputtering on buckypapers substrates. The effect of oxidation pressure on the structural, compositional, and electrochemical properties of the films was investigated.

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1. Introduction

Carbon nanotubes (CNTs) have been suggested as a substitute for the graphite anode in lithium-ion batteries. Their unique one-dimensional tubular structure, high electrical conductivity, and large surface area [1-6] are promising features for highly efficient Li storage. However, two disadvantages are inherent in a CNT anode: low volumetric capacity owing to the presence of a large internal void, which is of no use for Li storage [2], and a specific capacity that is limited by the theoretical maximum capacity of the graphite structure (372 mAh g^{-1}). Antimony dopped tin oxide (ATO) thin films and microspheres/nanoparticles, in particular, have also been reported as anode materials for lithium-ion battery. The Sb doping was found to increase the electrical conductivity and mechanical stability of the anode, thereby leading to improved electrochemical properties. Mats or so-called "buckypapers" that contain high concentrations of carbon nanotubes have the potential to form strong and light weight composite materials. CNT-skeleton based composites can solve so many problems faced by bulk electrode materials in Li-ion systems. The structure of the product was characterized by X-ray diffraction (XRD, Rigaku D/max 2200 system with thin film attachment). In this study, CNTs-Sb:SnO₂ nanocomposite structures are presented, which integrate both electronic conductivity and buffering matrix design strategies. The CNTs--Sb:SnO₂ 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 SnO_2 electrodes.

2. Experimental details

Buckypapers were prepared from calculated amounts (1 mg/mL) of multi-walled carbon nanotubes (MWCNTs) suspended in 50 cm³ solvent acetyl-acetone (acac) or dimethyl-formamide (DMF) by 30 min sonication in an ultrasonic bath. The suspensions were filtered through 0.45 μ m Whatman nylon filters using dead-end filtration with an effective pressure difference of 960 mbar. The samples were dried at 70 °C overnight in air on the filters and peeled off afterwards. The coating and oxidation processes have been performed in a multifunctional magnetron sputtering PVD unit equipped with thermal evaporation, dc and rf units. Nanostructured Sb:SnO₂ films were performed onto CNT based buckypapers via rf magnetron sputtering. Before starting to deposition, coating chamber is evacuated to $10^{-4}~\mathrm{Pa}$ by a turbo molecular pump and then back filled with argon up to 0.55 Pa pressure. High purity Sb:SnO₂ target $(10\% \text{ Sb}:90\% \text{ SnO}_2 - 99.99\% \text{ purity})$ having a diameter of 2" under 0%, 5% and 10% oxygen by using 100 W rf power were employed for the deposition process. The phase structures of the deposited films were investigated by X-ray diffraction (XRD) (Rigaku D/MAX 2000 with multipurpose attachment) with Cu K_{α} radiation. The grain size of the thin films was calculated from the Scherrer formula [8]:

$$D = \frac{0.9\lambda}{B\cos\theta},\tag{1}$$

where D is the mean 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 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 Sb:SnO₂ coated CNT buckypapers as the working electrode, a lithium metal foil as the counter electrode, a microporous polypropylene (PP) membrane (Cellgard 2400) as the separator, and 1 M solution of LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by weight) as the electrolyte. The cells were aged for 12 h before measurements. The cells were cyclically tested on a MTI Model BST8-MA electrochemical analyzer using different current densities over a voltage range of 1–3 V.

3. Results and discussions

Scanning electron microscopy (SEM) images of the surface and a cross-section of buckypaper electrodes are

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shown in Fig. 1. Highly porous network of randomly ordered individual and bundled CNTs is observed at the surface (Fig. 1a) and in the interior (Fig. 1b). As could also be concluded from the figures, the structure of the buckypapers is found to be uniform, smooth and crack--free disks exhibiting significant structural integrity. 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. The surfaces of the Sb:SnO₂ coated buckypapers were shown in Fig. 2a–c, respectively. As could be concluded from the figures, CNTs were coated with Sb:SnO₂ and a dense and more smooth surface is obtained by decreasing the oxygen partial pressure.



Fig. 1. Typical SEM images of (a) surface and (b) cross-section area for the buckypaper.



Fig. 2. SEM images of the films deposited under (a) pure argon, (b) 5%, and (c) 10% oxygen partial pressures.

Figure 3 shows the XRD pattern of the MWCNT based buckypaper, as-produced and SnO_2 deposited. All reflexes were assigned to carbon (JCPDS 026-1080) and SnO_2 (JCPDS 077-0447). The grain sizes of the films were calculated via Scherrer's formula and were found to increase with the decrease of oxidation power. The calculated values are 4.43 nm, 8.41 nm and 12.48 nm for the films deposited under 0%, 5% and 10% oxygen partial pressures, respectively.

The galvanostatic discharge–charge curves at current density 33.5 mAg^{-1} (1C) of nanosized SnO_2 between 0.02



Fig. 3. XRD patterns of produced MWCNT based buckypaper and SnO_2 coatings under various oxygen partial pressures.

and 2.5 V vs. Li⁺/Li is presented in Fig. 4. As could be seen from the figures, the number of active Li ions was increased via increasing oxidation power. 0.42, 3.2 and 5.1 Li ions are still active for the films deposited under 0%, 5% and 10% oxygen partial pressures, respectively.



Fig. 4. Galvanostatic charge/discharge graphics of SnO_2 coatings deposited under (a) 0%, (b) 5%, and (c) 10% oxygen partial pressures.

Figure 4 shows the cycling performance of the films deposited under (a) 0%, (b) 5%, and (c) 10% oxygen partial pressures in the potential range of 0.02-2.5 V. The capacity fading ratios for the films deposited under 0%, 5%, and 10% oxygen partial pressures are 9%, 11%, and 13% after 20 cycles, respectively. The capacity retention is also stabilized after 27th cycle and no capacity fading was observed. We conclude that the oxidized by using 10% oxygen partial pressure power contributes more to the enhancement of capacity retention due to smaller crystal size and larger surface area.



Fig. 5. Galvonastatic charge/discharge curves for SnO_2 coatings deposited under (a) 0%, (b) 5%, and (c) 10% oxygen partial pressures.

4. Conclusions

Carbon nanotube thin sheets — buckypapers — were prepared from multi-walled carbon nanotubes oxidized with different oxidation agents. Nanocrystalline SnO₂ thin films were deposited onto buckypaper substrates via rf magnetron sputtering under oxygen partial pressures as a possible anode material for lithium ion batteries. The films deposited under 10% oxygen partial pressure exhibited higher initial capacity and better cycling stability than the films deposited under 0% and 5% oxygen partial pressure.

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