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High capacity TiO_2 anode materials for Li-ion batteries

Mehmet Oguz Guler *, Ozgur Cevher, Tugrul Cetinkaya, Ubeyd Tocoglu, Hatem Akbulut

Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

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ABSTRACT

Carbon nanotube thin sheets – buckypapers – were prepared from multi-walled carbon nanotubes oxidized with different oxidation agents. Titanium dioxide films were then deposited by magnetron sputtering of Ti films on buckypapers substrates followed by in situ DC plasma oxidation. The effect of oxygen partial pressure on the structural, compositional and electrochemical properties of the films was investigated. The mean grain sizes of the deposited films were found to be in the range of 2.27–7.39 nm as revealed by the SEM and XRD studies. The electrochemical studies were performed with pure metallic Li foil cathode with the best performing nanostructured-TiO_2 as anode. Cyclic voltammetry and impedance tests were also performed in order to evaluate the battery capacity.

1. Introduction

Highly porous materials with a large active surface area are the current choice of electrodes for electrochemical energy storage devices. Literature is replete with reports corroborating the desirable behavior of electrode materials with enhanced porosity that leads to low current densities at the electrode–electrolyte interface [1–4]. The use of electrode materials with a large active surface area allows the utilization of high electrochemical reaction rates per unit volume making porous electrode materials very attractive for battery applications. In recent years, mesoporous electrode materials with pore size varying from 2 to 50 nm have become increasingly important. This is because these materials have a large surface area that enhances diffusion kinetics by reducing the diffusion pathway for electronic and ionic transport, resulting in excellent power density [5–7]. Mesoporous TiO_2 has acquired much attention as a promising material for photocatalysis, as separators, sensors and electrochemical energy convertors (i.e., lithium batteries) due to its versatility and multiple technological consequences. Furthermore, the reason behind the wider investigation of TiO_2 as negative electrode for lithium battery applications lies in the fact that it is one of the transition metal oxides that can be reduced upon lithium insertion at lower potential. In addition, the TiO_6-edge sharing octahedra in the TiO_2 crystal lattice structure share vertices and edges allowing the build-up of a three-dimensional network. The ability to develop such networks creates favorable empty sites for lithium insertion [8–10]. In general, the wide band gap semiconductor TiO_2 mainly exists in two polymorphic phases, anatase and rutile, wherein both crystallizes in tetragonal crystal lattice arrangement. In many cases, the anatase phase TiO_2 exhibits a higher activity than other TiO_2 polymorphs as a result of enhanced electrochemical behavior. Anatase phase of TiO_2 has an average lithium insertion and deinsertion potential of 1.8 V which accommodates 1 Li per formula unit at room temperature. There has been a profound investigation attempting the exploitation of anatase phase mesoporous TiO_2 for high power lithium battery application till date [11,12].

TiO_2 based Li-ion battery is a modified lithium-ion battery that uses TiO_2 nanocrystals on the surface of its anode instead of carbon. This gives the anode a surface area of about 100 square meters per gram, compared with 3 square meters per gram for carbon, allowing electrons to enter and leave the anode quickly. This makes fast recharging possible and provides high currents when needed. The main problem of TiO_2 based anode electrodes in Li-ion batteries is the poor electronic conductivity. Free-standing CNT films with paper-like morphology, known as buckypapers (BPs), have been demonstrated for applications such as catalysis, filtration, and energy storage [13–15]. BPs have been fabricated using single-walled CNTs [13–17], double-walled CNTs [18] and multi-walled CNTs (MWCNTs) [19]. The properties of BPs – electrical conductivity, tensile strength, and specific surface area, to name a few – depend on the composition of the CNTs, e.g., length or single-walled vs. multiwalled, their alignment in the BPs, and whether any polymer binders or fillers are included. The aim of is producing TiO_2 based CNT composites is to exploit the CNT's inherent properties of stiffness, mechanical strength, electrochemical properties, etc. Nanostructured TiO_2 thin films were manufactured in two steps. TiO_2 thin films were deposited buckypaper substrates via DC magnetron sputtering process followed by in situ DC plasma oxidation.

* Corresponding author. Tel.: +90 264 295 5782; fax: +90 264 295 5601.
E-mail address: guler@sakarya.edu.tr (M.O. Guler).

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2. Experimental details

The MWCNT employed in this work was supplied by Arry International (Germany). The nanotubes were synthesized by catalytic carbon vapor deposition (CCVD) and had a purity of around 90%. The CNT diameter ranged between 10 and 20 nm. Purification and chemical oxidation of MWCNTs [18,19] was carried out with different oxidation agents supplied by Aldrich. Concerning the fabrication of MWCNT buckypapers, stable aqueous CNT suspensions at a concentration of 1 mg/ml were prepared by tip sonication for 60 min. These dispersions were then vacuum filtered through polycarbonate membrane filters of 450 nm pore size. The average thickness of the produced buckypapers is approximately 100 μm and their diameter about 16 mm. The coating and oxidation processes have been performed in a multifunctional magnetron sputtering unit equipped with thermal evaporation, DC and RF units. Nanostructured TiO_2 thin films were deposited in two steps. In the first step, pure metallic titanium is coated on CNT buckypapers via DC magnetron sputtering. Before starting to deposition, coating chamber is evacuated to 10^{-4} Pa by a turbo molecular pump and then back filled with argon up to 1 Pa pressure. High purity metallic titanium target (99.99% purity) having a diameter of 2″ and 90 W DC power was employed under pure argon atmosphere for the deposition process. In the second step, nanostructured TiO_2 thin films were obtained via DC plasma oxidation process. Plasma oxidations of the titanium films were carried out at high purity oxygen (99.999%) and argon (99.9999%) gas mixture in a ratio of 1:1, 1:3 and 1:4. The oxidation time and total chamber pressure for each oxidation condition was kept constant for 1 h and at 1 Pa, respectively. 100 W DC powers were chosen for plasma oxidation and the effect of DC power on the titanium dioxide formation and battery performance was investigated. The phase structures of the deposited films were investigated by X-ray diffraction (XRD) (Rigaku D/MAX 2000 with thin film attachment) with Cu Kα radiation. The grain size of the thin films was calculated from the Scherrer's formula [20];

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

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 [21].

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 TiO_2 coated buckypaper substrates 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 aged for 12 h before measurements. The cells were cyclically tested on a MTI Model BST8-MA electrochemical analyzer using 1 C current density over a voltage range of 1–2.5 V. Cyclic voltammetry (CV) was recorded over a potential range of 2.5–1 V at a scan rate of 0.1 mV s^{-1} using a electrochemical workstation (Gamry Instruments Reference 3000). The electrochemical impedance spectrum of the electrodes was carried out with a small AC signal of 5 mV from 0.001 Hz to 100 kHz after 4 discharge–charge cycles on electrochemical Workstation (Gamry Instruments Reference 600). The electrode was subjected to a galvanostatic charge injection followed by an open circuit equilibration for an hour before performing impedance tests, so that the equilibrium of the electrode can be ensured. The current density and specific capacity were calculated based on the mass of active materials in the electrode. All electrochemistry tests were carried out at room temperature (25 °C).

3. Results and discussion

Fig. 1 show the buckypapers produced via vacuum filtration. As confirmed by SEM images well-dispersed CNT aqueous suspensions were found to be uniform, smooth and crack-free disks exhibiting significant structural integrity. The produced buckypapers consist of randomly interconnected CNTs forming a porous structure as it is apparent from the figure. 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 coated buckypapers are shown in Fig. 2a–c, respectively. As could be seen from the figures, surfaces of the randomly oriented CNTs were coated with TiO_2 and as a result volume of the individual CNTs is increased. The surfaces of the on randomly oriented CNTs indicate an almost homogeneous, smooth and uniformly coated with TiO_2.

Fig. 3 shows the X-ray diffraction pattern of the MWCNT based buckypaper, as-deposited and oxidized films. All reflexes were assigned to Carbon (JCPDS 026-1080), TiO_2 anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276). From the figure, it was observed that the TiO_2 thin films oxidized at different DC powers are polycrystalline having tetragonal structure. From the XRD pattern it was revealed that the films show both anatase [(101), (211)] and rutile [(112), (111)] structures but the degree of orientation of different planes are not similar. The preferred texture orientations were also shown a change by increasing the oxygen partial pressure. Increasing in oxygen partial pressure leads to alter of the texture in the deposited titanium dioxide films.

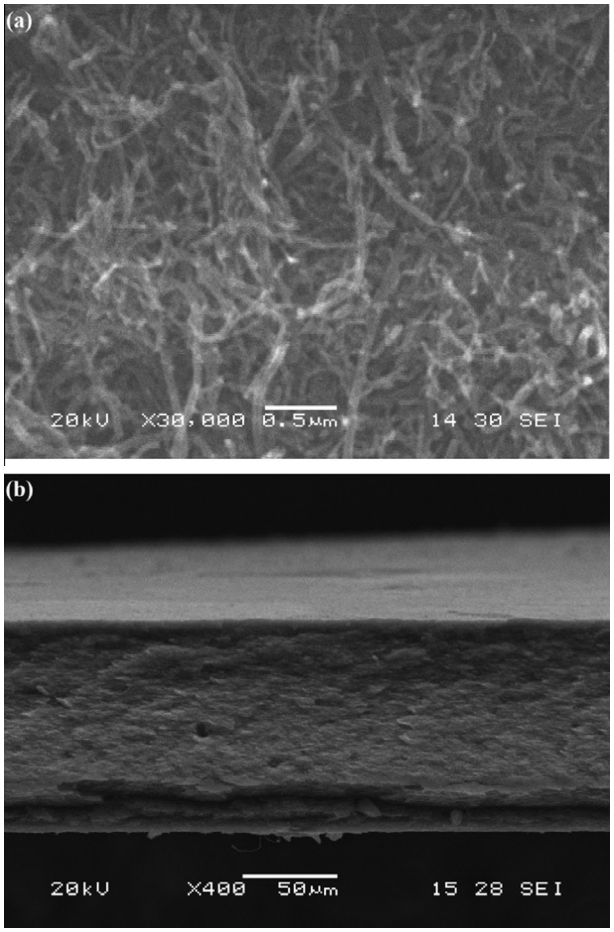

Fig. 1. SEM images of (a) surface and (b) cross-section area for the buckypaper.