

Characteristics and Electrochemical Performance of TiO₂:MWCNT Nanocomposite Anodes for Li-Ion Batteries

M.O. GULER*, T. CETINKAYA, O. CEVHER, U. TOCOGLU AND H. AKBULUT
Sakarya University, Engineering Faculty, Department of Metallurgical and Materials Engineering
Esentepe Campus, 54187, Sakarya, Turkey

In this study, highly porous buckypapers were manufactured via vacuum filtration techniques and nanocrystalline TiO₂ thin films were deposited on buckypapers using reactive radio frequency magnetron sputtering to understand the role of the deposition power. In addition, the effects of the deposition parameters on the electrochemical properties as an anode electrode for Li-ion batteries have also been studied.

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1. Introduction

High energy and high power rechargeable Li-ion battery (LIB) has become a key enabler for portable electronics such as laptops, tablets and smartphones. Advanced electrode materials with further improved volumetric and gravimetric capacity are critical for further extent of the driving range of those portable electronics. Currently, graphite is the material widely used for the negative electrode in the LIBs because of its good cycle performance and low cost. However, it has a relatively low theoretical capacity (372 mAh g⁻¹) and insufficient rate capability [1, 2]. As a transition metal oxide, TiO₂ is typical Li-ion intercalation compound with a small volume change < 4%, and has received much research spotlight for its easy control of particle morphology into nanotubes, nanowires, nanoparticles, etc. [3–5]. In bulk Li however, Li surface storage on nanometer-sized particles can be energetically more favorable than bulk insertion. However, TiO₂ host for Li-ion intercalation has intrinsically low electronic conductivity [6]. Therefore, enhancement of electronic conductivity for the host TiO₂ material is also required to decrease the polarization. Free-standing carbon nanotube (CNT) films with paper-like morphology, known as buckypapers (BPs), have been demonstrated for applications such as catalysis, filtration, and energy storage. The aim of producing TiO₂ based CNT composites is to exploit the CNT's inherent properties of stiffness, mechanical strength, electrochemical properties, etc.

In this study, multiwall CNT (MWCNT) based BPs were produced by vacuum filtration techniques and were then coated with TiO₂ in order to obtain a highly conductive nanocomposite anode electrode for Li-ion batteries.

2. Experimental details

The MWCNTs used in this study were provided by Arry International Co., Ltd. (Germany) having diameter of 50 nm in diameter and 1.00 μm in length and have been produced via chemical vapor deposition (CVD) method. The as received MWCNTs were heat treated in order to remove the contaminants such as amorphous carbon at 350 °C for 8 h. The catalysts were then removed at 90 °C by using a magnetic stirring by using HCl solution. Chemical oxidation of MWCNTs was carried out with a mixture of H₂SO₄ and HNO₃ 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 subjected to coated with TiO₂ via rf magnetron techniques. High purity Ti target (99.99% purity) having a diameter of 2'' and 75, 100, and 125 W rf powers were employed under 10% oxygen atmospheres for the deposition process. 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 titanium 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 TiO₂ coated CNT buckypapers as the working electrode, a lithium metal foil as the counter electrode, a micro-porous polypropylene (PP) membrane (Cellgard 2400)

*corresponding author

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 different current densities over a voltage range of 1–3 V. All tests were performed at room temperature (25 °C).

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.

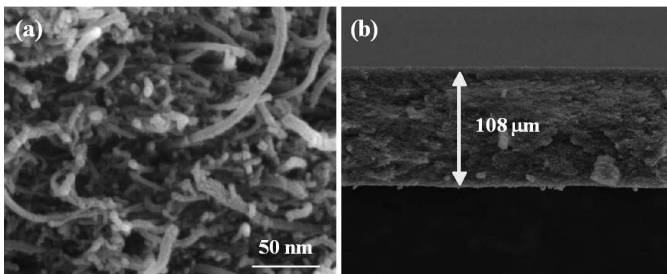


Fig. 1. SEM images of (a) surface and (b) cross-section area of the MWCNT based buckypapers.

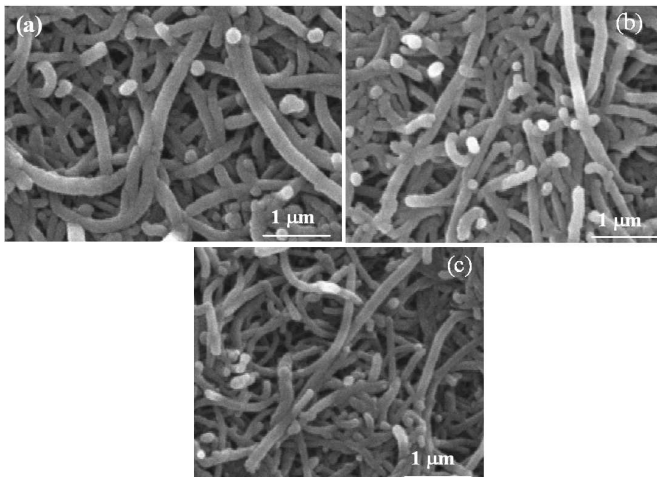


Fig. 2. SEM images of the films deposited by using (a) 75 W, (b) 100 W, and (c) 125 W rf powers under 10% oxygen gas pressures.

Figure 2 shows the TiO_2 coated surfaces of the buckypapers after deposition process. As can be concluded

from the figures, TiO_2 nanocrystals are well attached to the surfaces of individual CNT surfaces. No individual TiO_2 crystals are evident from the CNT surfaces. A highly mesoporous MWCNT skeleton type structure with a thin layer of TiO_2 were obtained after the deposition.

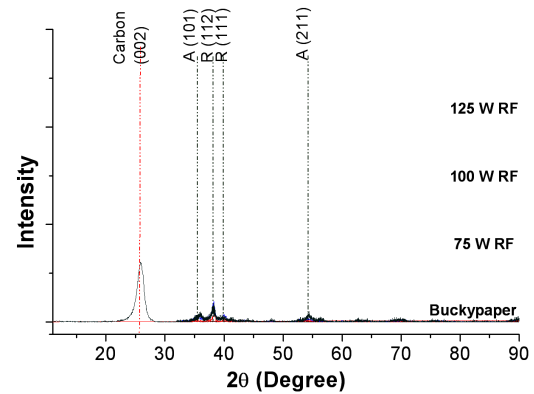


Fig. 3. XRD spectra of the as-produced buckypaper and thin films deposited with varying rf powers.

Figure 3 shows the X-ray diffraction patterns of nano- TiO_2 deposited at different rf powers. The diffractograms show clearly the formation of phase TiO_2 in anatase and rutile phases. However, the intensities of the same planes were altered with increasing rf powers. The Scherrer formula was also applied to the X-ray diffractograms and the mean grain sizes of the films were obtained as 2.57, 4.56, and 7.96 nm for the films deposited with 75, 100, and 125 W, respectively.

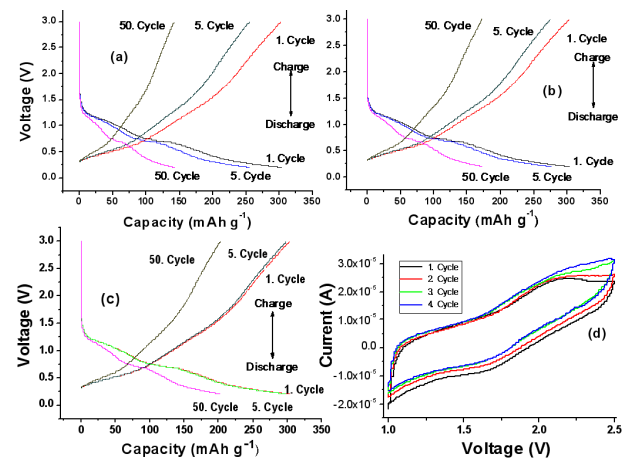


Fig. 4. Voltage-capacity curves of the deposited under (a) 125 W, (b) 100 W, and (c) 75 W rf powers and (d) cyclic voltammograms of $\text{TiO}_2/\text{MWCNT}$ nanocomposite anode electrodes.

The galvanostatic discharge-charge tests were performed at room temperature with a current density of 21 mA dm^{-2} (1 C) for the electrochemical characteriza-

tions and presented in Fig. 4a–c. As can be seen from the figures, best results were obtained for the films deposited by using 75 W rf power. 156, 182, and 208 mAh g⁻¹ discharge capacities were obtained after 50 cycles for the films deposited under 125, 100, and 75 W rf powers. Figure 4d shows the cyclic voltammogram of the TiO₂/MWCNT nanocomposite anode electrodes. The voltage is scanned from 2.5 to 1 V, and at a scan rate of 0.1 mV s⁻¹. Only one pair of cathodic/anodic peaks located at 1.69 and 2.04 V (versus Li⁺/Li) can be observed. The cathodic (insertion) and anodic (extraction) peaks (the actual peak potentials depend on the scan rate) are in accordance with the plateaus of the discharging/charging curves. The ratio of cathodic to anodic peak current is nearly 1, and the integral voltammetry area of the discharging/charging branches is almost equal. This demonstrates that the insertion/extraction of Li ions in TiO₂ thin films is highly reversible and this redox system remains in equilibrium throughout the potential scan.

4. Conclusions

In this study, nanocrystalline TiO₂/MWCNT based composites were successfully prepared by the vacuum filtration techniques followed by an rf magnetron sputtering techniques. X-ray diffraction studies showed double-phase anatase and rutile structures nucleated over the individual MWCNTs. The average particle size for the particle prepared at 75 W rf power was about 2.57 nm as evidenced by XRD studies. Nanocrystalline TiO₂/MWCNT based composites showed excellent electrochemical properties. Increase in the deposition power did not show any appreciable results due to the increment in

the particle size. The cycling performance was also found to be the best for this system with a cycling efficiency of 95% for five cycles. Increase in the rf power although did not show any appreciable change in the capacity value, but the cycling performance showed dependence due to the increases in the mean grain sizes. The strategy presented in this paper could be extended to the synthesis of other metal oxide (e.g., MnO_x, FeO_x, CoO_x, ZnO, and SnO₂) composites with different carbon materials.

Acknowledgments

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