

Surface-Coverage-Dependent Cycle Stability of Core-Shell Nanostructured Electrodes for Use in Lithium Ion Batteries

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Li ion batteries are widely utilized as rechargeable energy sources for compact electronics and portable devices. Recently, a dramatic increase in the use of smartphones and hand-held tablet devices that offer PC-like performance have accelerated the production of Li ion batteries. Such applications demand long battery life and high power generation, thus increasing the demand for alternative electrode materials and other advanced designs in Li ion based storage devices. Graphitic carbon is widely used as an anode electrode material in the current Li ion batteries. However, graphitic carbon electrode is not suitable for exceptional energy densities due to its modest theoretical capacity (372 mAh g⁻¹). High capacity electrode materials that include lithium metal alloys (Si, Ge, and Sn) and transition metal oxides (TMO, M = Co, Ni, Cu, or Fe) have been extensively investigated as potential alternatives to replace the conventional graphite. However, these materials undergo severe volume expansion during the lithiation and deliation. Such volume expansion leads to mechanical fracture or pulverization of materials and electrodes, causing rapid, significant capacity fading with cycles.

To successfully address the issue of volume expansion, efforts have focused on various factors including crystal $linity^{\left[1\right]}$ and $dimension^{\left[2\right]}$ of the active materials, structure of electrodes^[3] and mechanical properties^[4] of the electrode components. Recently, three-dimensionally constructed electrodes directly fabricated on the current collector have been

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DOI: 10.1002/aenm.201300472

proposed as a promising solution to overcome the limitations of the high capacity materials. For example, vertically aligned conducting pathways, usually copper nanorods, were fabricated on the current collector and then electrochemically active materials were successively coated on the resulting nanostructured electrodes. Large surface area and nanoscale dimensions of these structures enable rapid, fast Li insertion, and diffusion. Also, the direct contact of electrode on the current collector provides unimpeded, fast conducting pathways for electron transport. Such advantages lead to much improved rate capability and capacity retention of these 3D nanostructured electrodes.^[5] In addition, the presence of large free space between nanostructured pillars in these structures offers the possibility of accommodating the large volume expansion/contraction during lithiation and delithiation cycles.^[5b] However, this approach has an obvious limit that the capacity fading can occur when thick materials or continuous film type of materials are coated or coalesced particles are deposited on the nanostructured electrodes. For example, Reddy et al.^[6] constructed 3D architectures consisting of vertically aligned disordered carbon nanotube arrays and MnO₂ shell layers to increase the electrical conductivity of the MnO₂ electrode and provide mechanical stability to the resulting hybrid nanostructure. This 3D architecture resulted in higher specific capacity (2170 mAh g⁻¹) and exhibited improved cycle performance compared to bulk or particle-type MnO₂ electrodes. Such improvements are attributed to the dual mechanism of lithium storage in both MnO₂ and carbon nanotubes and the presence of electrically conductive carbon nanotube core in the hybrid electrode. This work proposed new guidance for structuring hybrid type electrodes to overcome the drawbacks of single component-based electrode. Despite the advancements in electrode designs, only ≈23% of the initial discharge capacity is retained after 15 cycles,^[6] indicating poor cycle performance compared to previously reported results of other electrodes. Therefore, the development of new strategies, materials, and fabrication techniques might be necessary to improve the electrochemical performance further.

Here, we report a new design strategy to resolve the capacity fading issue in the core-shell nanostructured electrode. This approach considers the influence of surface coverage of a conducting nanostructured electrode with an electrochemically active electrode material on the stress evolution induced by the lithiation and delithiation. Our recent work on Si nanotube anode^[3] supported that free surface can play a critical role in minimizing stresses associated with lithiation. Based on this motivation, we investigate the relationship between the surface coverage and the mechanical stress



during the lithiation and delithiation, and correlate this relationship with the resulting electrochemical performance of 3D constructed electrode. In this study, vertically aligned, multiwalled carbon nanotubes (MWNTs) were directly grown on the copper current collector, which produced 3D nanostructured conducting pathways. The use of MWNTs has the advantage compared to the previous copper nanorods because MWNTs also play a role of lithium storage. We select MnO_2 as a main electrode material that covers the surface of vertically aligned MWNTs electrode because the capacity fading issue in the MnO₂ electrode has not been completely resolved.^[6,7] Different concentrations of MnO₂ precursor yield the MWNT-MnO2 nanostructures with different surface coverages of MnO₂. Based on the systematic experiments and theoretical calculation of stress evolution, we optimize the surface coverage of MWNT with MnO₂ shell layer and resolve the capacity fading issue in MnO₂-based electrodes completely. The modeling shows that mechanical stress in MnO₂ increases with increasing surface coverage of MnO₂ layer. The electrode that has an optimized surface coverage exhibits 910 mAh g⁻¹ of initial capacity and it is successfully maintained even after 50 cycles. MWNT electrodes that are fully covered with a continuous film of MnO₂ deliver a higher capacity of 1071 mAh g⁻¹, however the electrodes are mechanically fractured with repeated cycles; at the same time the capacity is severely faded, which is entirely consistent with the modeling results. We verify that the design strategy demonstrated here resolves the capacity fading issue in core-shell nanostructured electrode completely. It is also expected that this strategy can be utilized to develop novel material and design concepts to improve the electrochemical performance for lithium ion batteries, which suffers from the capacity fading induced by the mechanical stress. The advantages of this type of electrode structure and the electrochemical performance of the anode based on the MnO₂ content are examined in detail here.

Arrays of MWNTs were formed in vertically aligned configuration on the copper foil by chemical vapor deposition (CVD) using an acetylene source gas and a mixed carrier gas of hydrogen and argon. Figure S1 (Supporting Information) shows a crosssectional scanning electron microscopy (SEM) image of pristine MWNT (Figure S1a) and MnO₂-coated MWNTs (Figure S1b). MnO₂ layers were deposited on the surface of MWNTs by submerging the MWNTs array electrodes in a KMnO₄ solution. MnO₂ layers can be formed on the surface of the MWNTs via a reaction between surface carbons and MnO₄⁻ ions.^[8] The thickness and morphology of the MnO₂ layer can be controlled by varying the concentration of KMnO₄ solution, reaction time, and temperature.^[8,9] In this study, three different concentrations of KMnO₄ solutions were prepared to control the thickness and morphology of the MnO₂ shell layers. Figure 1 shows the transmission electron microscopy (TEM) images that show the morphological changes of MWNT-MnO2 nanostructures with increasing concentration of KMnO₄ solution. Pristine MWNT have a diameter of ≈ 15 nm and inner layers of ≈ 8 (Figure 1a). In this experiment, we observed that the diameter and inner layer had distributions in the ranges 7-15 nm and 5-10 layers, respectively. For electrodes immersed in a lower concentration of KMnO4, an island-type surface coverage of MnO2 nanostructures on the walls of MWNTs was observed





Figure 1. TEM images of MWNT-MnO₂ nanostructures: a) pristine MWNT and b–d) MWNT-MnO₂ nanostructures with $MnO_2/MWNT$ weight ratios of b) 0.5, c) 1.5, and d) 5.4. All scale bars are 10 nm.

solution (see the white arrows in Figure 1b). As anticipated, the deposition of MnO_2 increased with increasing concentration of the $KMnO_4$ solution. At higher concentrations (Figure 1c), most of the nanotube surface was covered with a layer of MnO_2 . By immersing the nanotubes in the highest concentration of $KMnO_4$ solution, the nanotube surfaces were completely saturated with MnO_2 shell layers (Figure 1d). Larger areas of MWNT-MnO₂ nanocomposites were also observed (Figure S2, Supporting Information) to ensure the uniform coating of MnO_2 over the full length of the CNTs. The weight fraction of MnO_2 in the MWNT-MnO₂ core-shell nanostructure was determined by measuring the mass after reaction, which is specified on the each panel of Figure 1.

Figure S3a (Supporting Information) shows high-resolution TEM images, indicating lattice fringes with two different spacings of 3.4 and 2.4 Å, corresponding to the (002) plane of the carbon nanotube and the (006) plane of birnessite-type manganese oxides, respectively.^[10] Figure S3b (Supporting Information) shows the X-ray diffraction patterns of MWNTs covered with MnO₂ nanostructures. The lowest peak at 25.8° arises due to the trace of (002) basal plane of nanotubes and the latter two peaks at 37.6° and 66.3° can be ascribed to (006) and (119) planes of birnessite-type MnO₂ (JCPDS 18–0802),^[10] which is consistent with the d-spacing data obtained from HR-TEM image.

The influence of MnO₂ surface coverage on the stress evolution in MWNT-MnO₂ electrode was examined using an analytical model. The stress evolution induced by the lithiation and delithiation in the MWNT-MnO₂ core-shell electrode was simulated with different MnO₂ weight fractions. For the MnO₂/MWNT ratio η larger than 1.5, MWNTs are fully covered by MnO₂. The strain in the MWNT-MnO₂ electrode results from the volumetric expansion due to lithiation and the elastic mismatch between MWNT and MnO₂. Previous

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experiments^[3] clearly showed that the expansion in the radial direction is much larger than that in the axial directions of MWNTs, which is also confirmed by the present experiments and analysis (see Supporting Information for details). Therefore, the expansion is mainly in the radial direction and that in the axial direction is negligible. The difference of volumetric expansions in MnO2 and MWNTs leads to a different radial expansion in these two materials, which in turn gives rise to a tensile normal stress on the interface. Continuity of radial displacement across the MWNT/MnO₂ interface requires $\sqrt{\Delta V_{\text{MWNT}}} R_{\text{interface}} + (u_{\text{r}})_{\text{MWNT}} = \sqrt{\Delta V_{\text{MnO}_2}} R_{\text{interface}} + (u_{\text{r}})_{\text{MnO}_2}$, where $R_{\text{interface}}$ is the outer radius of MWNTs, ΔV_{MnO_2} and ΔV_{MWNT} are volumetric expansions in bulk MnO₂ and MWNTs, (u_r)_{MWNT} and $(u_r)_{MnO_2}$ are displacements at outer radius of MWNTs and inner radius of MnO2, respectively. Taking together with a similar continuity equation of axial displacement across the interface and force equilibriums in axial direction and at the MWNT/MnO2 interface, the axial stresses and pressures at the MWNT/MnO2 interface are derived analytically (see Supporting Information).

The maximum strain in MWNTs is reached in the circumferential direction as

$$\varepsilon_{\max} = \frac{2 E_{\text{MnO}_2}}{\left(1 + v_{\text{MnO}_2}\right) E_{\text{MWNT}}} \\ \times \frac{\left(\sqrt{\frac{\Delta V_{\text{MnO}_2}}{\Delta V_{\text{MWNT}}}} - 1\right) \left(1 - \sqrt{\frac{\Delta V_{\text{MnO}_2}}{\Delta V_{\text{MWNT}}}} v_{\text{MnO}_2} v_{\text{MWNT}}\right)}{\frac{2\left(1 - v_{\text{MnO}_2}\right)}{\eta} \frac{\rho_{\text{MnO}_2}}{\rho_{\text{MWNT}}} + 1 - \frac{R_{\text{MWNT}}^2}{R_{\text{interface}}^2}}$$
(1)
for $\eta \ge 1.5$

where the mass density of $MnO_2\rho_{MnO_2} = 3.40 \text{ g cm}^{-3[10]}$ and the mass density of MWNT $\rho_{MWNT} = 1.90 \text{ g cm}^{-3}$ is the same as that of graphite,^[11] R_{MWNT} and R_{MnO_2} are the inner radius of MWNTs and outer radius of MnO_2 before lithiation, $E_{MnO_2} = 2.56 \text{ GPa}$ and $v_{MnO_2} = 0.20$ are the Young's modulus and Poisson's ratio of lithiated MnO_2 measured in experiments and $E_{MWNT} = 500 \text{ GPa}$ and $v_{MWNT} = 0.20$ are for lithiated MWNT.^[3]

For the MnO₂/MWNT ratio $\eta = 1.5$, the thickness of MnO₂ shell is $R_{MnO_2} - R_{interface} = 1.45$ nm for the inner and outer radii $R_{MWNT} = 2.95$ nm and $R_{interface} = 5.5$ nm. For the MnO₂/MWNT ratio η less than 1.5, the surface of MWNT is not fully covered by MnO₂, but the thickness of MnO₂ shell remains constant at $t \approx 1.45$ nm for the covered part as shown in Figure 1. Similar to the theory of composite materials, the maximum strain in MWNTs can be obtained by the weighted average of strains in the covered and uncovered parts as

$$\varepsilon_{\text{max}} = \frac{4\eta E_{\text{MnO}_2}}{3\left(1 + v_{\text{MnO}_2}\right) E_{\text{MWNT}}} \times \frac{\left(\sqrt{\frac{\Delta V_{\text{MnO}_2}}{\Delta V_{\text{MWNT}}}} - 1\right) \left(1 - \sqrt{\frac{\Delta V_{\text{MnO}_2}}{\Delta V_{\text{MWNT}}}} v_{\text{MnO}_2} v_{\text{MWNT}}\right)}{\frac{4\left(1 - v_{\text{MnO}_2}\right)}{3} \frac{\rho_{\text{MnO}_2}}{\rho_{\text{MWNT}}} + 1 - \frac{R_{\text{MWNT}}^2}{R_{\text{interface}}^2}}$$
(2)
for $\eta < 1.5$.

Figure 2 shows that the maximum strain in MWNTs, obtained in Equations (1) and (2), increases with the $MnO_2/MWNT$ ratio η . For $\eta = 5.4$ as in experiments, the maximum strain in MWNT is 0.73%.



Figure 2. The maximum strain in MWNT as a function of the $MnO_2/$ MWNT ratio $\eta.$

To examine the effect of MnO₂ content on the electrochemical performance of MWNT-MnO2 nanostructured electrodes, galvanostatic tests were carried out with a two electrode configuration. All capacities noted here correspond to the capacity contributed from both MnO₂ and MWNT components in the nanocomposites. We prepared MWNT-MnO₂ nanostructures with different MnO₂ contents ranging from 0 to 5.4, which were utilized as working electrodes without the addition of polymeric binder. Li metal foil was used as a counter electrode. Figure 3a shows the first charge and discharge curves at a current density of 100 mAg⁻¹ between 0.01–3 V vs Li/Li⁺. For pristine MWNT electrode, a discharge capacity of \approx 1900 mAh g⁻¹ was observed at the first cycle. However, the poor extraction of Li ions from the nanotubes resulted in low reversible capacity of \approx 393 mAh g⁻¹. A plateau at \approx 0.9 V was observed at the first discharge cycle. This large irreversible capacity and the plateau region could arise from the presence of surface defect sites, and electrolyte decomposition resulting in the formation of solid electrolyte interface (SEI) layers on CNT surface.^[12] The initial Coulombic efficiency (23.2%) well represents the irreversibility of CNT electrode (Figure S4, Supporting Information).

MWNT-MnO₂ electrodes (MnO₂/MWNT ratio of 0.5) exhibit similar electrochemical behavior to that of pristine MWNT electrodes. However, it delivers slightly increased charge and discharge capacities of ≈ 666 and ≈ 2478 mAh g⁻¹, respectively. A new plateau appears at ≈ 0.5 V, which corresponds to the reduction potential of MnO2.^[13] Lithium ions can be intercalated into MWNT and attached on the sidewalls (intercalation type).^[14] On the other hand, lithium insertion into MnO₂ electrode produces Li2O and metallic Mn (conversion type).^[6,15] At higher MnO₂/MWNT weight ratio (MnO₂/MWNT ratio of 1.5), the electrodes show higher charge and discharge capacities of ≈909 and ≈2063 mAh g⁻¹, respectively. There is a clear plateau at ≈0.5 V and a smaller one at ≈ 0.9 V. MWNT fully covered with MnO₂ (MnO₂/ MWNT ratio of 5.4) shows charge and discharge capacities of \approx 1071 and 1975 mAh g⁻¹, with a discharge curve that is similar to that of MWNT-MnO₂ electrodes (MnO₂/MWNT ratio of 1.5).

Although the irreversibility of MWNT electrode is much improved with the increase in MnO₂ content, MWNT-based electrodes show relatively large irreversible capacity at the first cycle compared to typical anodes. The initial Coulombic efficiency in Figure S4 (Supporting Information) clearly shows the WWW.advenergymat.de

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Figure 3. Electrochemical performance of MWNT-MnO₂ core-shell nanotube electrodes. a) Charge-discharge curves and b) cycling performance; numbers in the panel indicate MnO_2/CNT weight ratio, scanning electron microscopy (SEM) images of MWNT-MnO₂ electrodes after 50 cycle (current density: 100 mA g⁻¹). c) Robust MWNT-MnO₂ electrode ($MnO_2/MWNT = 1.5$) and d) pulverized electrode ($MnO_2/MWNT = 5.4$).

influence of MnO₂ content on the reversibility at the first cycle. The difference between charge and discharge capacities was assumed to be due to the drastic, lithium-driven, and structural or textural modifications of the transition-metal-oxide-based electrode.^[15] Figure S4-6 (Supporting Information) shows such structural and chemical changes of the MnO₂ electrode during the lithiation and delithiation. The irreversible capacity can be related to the decomposition of electrolyte and results in the formation of SEI layers on the electrode surface.^[16] The electrochemical properties of MWNT-MnO2 electrodes with increasing MnO₂ fraction show a clear, direct dependence on MnO₂ surface coverage. It is evident from the TEM images that when the MnO₂/MWNT weight ratio is less than 1.5, bare surfaces of the MWNTs are exposed to electrolyte (Figure 1b), suggesting the ability of MWNT (intercalation) and MnO₂ (conversion) to participate in the electrochemical reaction. The electrochemical measurements also showed plateaus at \approx 0.9 and 0.5 V in the discharge curve of the first cycle. At higher concentration $(MnO_2/MWNT$ weight ratio >1.5), the surface is nearly or fully covered with MnO₂, leading to MnO₂-like electrochemical behavior. Thus, the plateau at ≈ 0.9 V related to the SEI formation on the CNT surface disappears and the dominant plateau at ≈ 0.5 V related to the reduction of MnO₂ is observed. Electrochemical impedance spectroscopy was employed to investigate the electrochemical properties of MWNT-MnO₂ electrode. The results were presented as Nyquist plots (Figure S8, Supporting Information). The plots consist of a semicircle and an inclined linear line. In the semicircle, the leftmost x-intercept corresponds to the Ohmic resistance, while the rightmost x-intercept indicates the polarization resistance consisting of solid-electrolyte interface layer resistance and charge-transfer resistance. All electrodes exhibit similar Ohmic resistance of



≈5 Ω . With increasing the surface coverage of MWNT with MnO₂, the polarization resistance significantly decreases. At the MnO₂/MWNT ratio of 5.4, the polarization resistance falls <150 Ω .

To evaluate the cycle performance, charge and discharge cycles were repeated up to 50 cycles at a current density of 100 mA g^{-1} (Figure 3b). No capacity fading was observed at higher cycles except for the electrode with a MnO₂/MWNT weight ratio of 5.4. The electrodes that use MWNT and MWNT-MnO₂ core-shell structures show improved cycling stability compared to that of MnO₂ nanowire,^[17] coaxial MnO₂/carbon nanotubes (CNT) array electrodes,^[6] and porous MnO₂/carbon nanotubes (CNT).^[7] The reversible capacity of MnO2 nanowire electrode was reported^[17] to decay with cycling. After 50 cycles, it delivered only 61% of the reversible capacity observed in the first cycle. The coaxial MnO₂/CNT array electrodes^[6] also showed a significant capacity fading, which resulted in the reversible discharge capacity as low as ≈23% after 15 cycles. Alternatively, highly porous interconnected MnO₂ nanostructures were coated on the CNTs,^[7]

however this electrode also showed the moderate decrease in the capacity with cycles. After 50 cycles, ≈70% of the initial capacity was maintained. A high irreversible capacity in the first cycle can be explained by the formation of SEI layer at the interface between electrolyte and electrode, and the isolation of active manganese metal by insulating Li₂O.^[17] However, the continued decay in capacity with repeated cycles is not related to these issues. In general, lithium insertion and extraction induces volume changes in the electrode, causing severe cracking that leads to partial and/or complete disconnection. The cracking also leads to the formation of SEI layer on the newly exposed surface. The inserted lithium can be trapped within the electrode material due to various kinetic and thermodynamic reasons, resulting in capacity fading with increasing cycles.^[18] Such capacity fading is also observed in this experiment when MWNTs are fully covered with MnO₂ shell layer. The electrode with the MnO₂/MWNT ratio of 5.4 showed a high charge capacity of 1070 mAh g⁻¹ at the first cycle, but only delivered 340 mAh g⁻¹ at the 50th cycle. In other words, the capacity retention is only 32% compared to the first cycle. The rate capability of the MWNT-MnO₂ electrodes was investigated (Figure S9, Supporting Information); however, this is beside the discussion on surface coverage-dependant cycle stability of core-shell nanostructured electrodes. Therefore, the detailed explanation is noted in the Supporting Information (Figure S9).

Figure 3c,d shows SEM images of the MWNT-MnO₂ coreshell electrodes with different $MnO_2/MWNT$ ratios, each after 50 cycles. At lower weight ratios of $MnO_2/MWNT$ (Figure 3c), the MWNT-MnO₂ core-shell nanostructure still remains connected to the Cu current collector and exhibits its original structure even after 50 cycles. However, at higher $MnO_2/MWNT$





Figure 4. Microstructural evolution of MWNT-MnO₂ electrodes (MnO₂/MWNT = 5.4) at each cycle. Left graph is taken from Figure 3b. SEM images of a) as-prepared MWNT-MnO₂ electrode and b–d) MWNT-MnO₂ electrodes after charge and discharge of b) 5th, c) 20th, and d) 50th cycle.

(Figure 3d) weight ratios, the nanostructures were broken, leaving behind only the base part of nanostructures on the Cu current collector after 50 cycles.

Figure 4 correlates the cycle performance and microstructural changes of MWNT-MnO2 nanostructures with a weight ratio of 5.4 MnO₂/MWNT. The initial microstructure is maintained at 5th cycle. However, most of nanostructures are pulverized at the 20^{th} cycle when the capacity starts to fade severely. Finally, only the base parts of nanostructure are left after the 50th cycle. The different microstructural evolution supports the MnO₂ weight fraction dependent cycling stability of MWNT-MnO₂ electrode. This suggests that the surface coverage of MWNT with MnO₂ can be related to different mechanical relaxation during the charging and discharging processes. This relationship is fully supported by the modeling results (Figure 2) that the maximum strain increases with increasing the surface coverage. A continuous film of MnO₂ cannot endure the stress induced by the lithiation and delithiation. During the repeated cycles of charge and discharge, mechanical stress can accumulate in the electrode, resulted in the severe capacity fading of MWNT electrodes fully covered with MnO₂ with increasing cycles. Although MWNTs have superior mechanical properties, MnO2-MWNT nanostructures were broken and became shorter with repeated cycles of lithiation/delithiation process, indicating that the accumulated stress may exceed the stress relaxation ability of MWNTs. In addition, the adhesion of shell layer to core structure can contribute to such pulverization of core-shell nanostructure. Weak adhesion of shell layers causes the detachment of the layers from the core structure. However, MnO₂ layer has strong adhesion to the surface of MWNTs, which can result in the pulverization of MnO2-MWNT nanostructure. The consideration of the morphology of electrode material would be beneficial to design an electrode material that expands dramatically by the lithiation. For example, recent works on the silicon-carbon nanostructured electrodes reported stable cycling performance.^[19] These electrodes were fabricated by the CVD of Si nanoparticles on the surface of nanotube with a random spacing between the nanoparticles. Such excellent cycling performance can be systematically explained using our design concept. Therefore, the results shown here suggest a general design rule for high performance lithium ion battery

electrodes that suffer from significant capacity fading by the accumulated stress in the electrode.

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In summary, the relationship between the surface coverage of 3D constructed electrode with electrochemically active materials and the resulting electrochemical performance of the electrode is described. MWNT- MnO_2 core-shell nanostructured electrode is selected in this demonstration and its coverage of MnO_2 shell layer is controlled. Systematic studies and analytical mechanics modeling reveal that the surface coverage is a critical factor in determining the mechanical stress induced by lithiation and delithiation. The optimized condition, MWNT partially covered with MnO_2 , prevents the pulverization of the electrode by releasing the internal

stress in the electrode structure, leading to the excellent cycle performance. This electrode exhibited specific capacities of \approx 910 mAh g⁻¹ and the ability to maintain this capacity after 50 cycles. On the other hand, electrodes of MWNTs fully covered with MnO₂ showed high specific capacity of ≈ 1070 mAhg⁻¹ but the pulverization of electrode was started after ≈ 20 cycles. After 50 cycles, its capacity was significantly faded to 370 mAh g^{-1} . These collective observations with the MWNT/MnO₂ core-shell nanostructure systems provide valuable insights into the fabrication of other lithium ion battery electrodes that suffer from poor cycle performance induced by the drastic, lithium-driven structural, or textural modifications of the electrode. These and related concepts could contribute to the development of high performance anodes for lithium ion batteries that avoid some of the limitations associated with conventional graphitic carbon anode materials.

Experimental Section

Preparation of Vertically Aligned MWNTs and Vertical Arrays of MWNT-MnO2 Core-Shell Structures: Prior to the deposition of metal catalyst, the surface oxide of the Cu foil substrate was removed by immersion in acetic acid with subsequent cleaning in acetone and 2-propanol. Al/Fe thin film bi-layer catalyst (10-20/1-5 nm) was deposited on cleaned Cu foils using an e-beam evaporator. The foils containing the catalysts were placed in a quartz tube CVD chamber and annealed to the growth temperature (650-800 °C) with an Ar flow (300 sccm). The CVD growth of MWNTs on Cu foils were performed by flowing acetylene source gas (5-25 sccm) with a mixed carrier gas of hydrogen and argon. For the preparation of MWNTs/MnO2 coreshell nanostructures, the precursor solution was prepared by dissolving potassium permanganate (KMnO4, Aldrich, ACS reagent) in de-ionized water with different concentrations. The MWNT-grown Cu foils were submerged in the KMnO₄ precursor solution at room temperature for 24 h. The samples were removed from the precursor solution, washed with de-ionized water thoroughly, and finally dried in vacuum oven at 80 °C overnight.

Lithium Ion Battery Fabrication: The electrochemical properties of $MWNT-MnO_2$ core-shell electrodes were investigated using a coin-type half cell (2032R type). Pure lithium metal foil was employed as a counter electrode. Vertical arrays of $MWNT-MnO_2$ core-shell structures on the Cu foil current collector served as a working electrode. 1.0 M LiPF₆ solution in a mixture of ethylene carbonate and diethylene carbonate (EC/DEC,





3:7 vol%) was used as an electrolyte. The cells were assembled in an Ar-filled glove box.

Evaluations: The precise masses of the MWNT-MnO₂ nanostructures were estimated using a microbalance (Sartorius SE2, resolution 0.1 µg, Sartorius, Germany). The cells were galvanostatically discharged and charged in a voltage range from 0.01 V to 3 V vs Li/ Li⁺ at various current densities using a battery cycle tester TOSCAT 3100 (Toyo Systems, Japan). The electrochemical impedance spectroscopy (EIS) was conducted using a Princeton Applied Research PARSTAT 2273 potentiostat/galvanostat apparatus in the frequency range of 250 kHz to 10 mHz at an excitation amplitude of 5 mV. A field emission scanning electron microscope (FE-SEM, JSM 7600F, [EOL) and a field emission transmission electron microscope (FE-TEM, JEM 2100F, JEOL) were used to observe the morphology of the MWNT-MnO₂ core-shell nanostructures. The crystallographic structure was determined using X-ray diffraction patterns obtained by a Bruker Miller diffractometer using Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Sigma Probe (Thermo VG Scientific, USA) with Al-Ka X-ray radiation. A nanoindenter (Nano Indenter XP, MTS Systems Corp., USA) with a Berkovich indenter tip was used for nanoindentation. The measured indenter tip drift rate was within ± 0.05 nm s⁻¹. The result is shown in Figure S10 (Supporting Information).

Acknowledgements

S.L. and J.H. contributed equally to this work. This work was supported by the Global Research Laboratory (GRL) Program (K20704000003TA050000310) through the National Research Foundation of Korea (KRF) funded by the Ministry of Science, ICT (Information and Communication Technologies) and Future Planning, the International Cooperation program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government of Ministry of Trade, Industry & Energy (2011T100100369), and the World Class University (WCU) Program (R31-10092) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT (Information and Communication Technologies) and Future Planning. Y.H. acknowledges supports from NU ISEN and NSF Grant Nos. ECCS-0824129 and OISE-1043143.

Received: May 2, 2013 Revised: June 5, 2013 Published online: July 31, 2013

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