Carbon Nanotubes Coupled with Metal Ion Diffusion Layers Stabilize Oxide Conversion Reactions in High Voltage Lithium-Ion Batteries

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ABSTRACT: Creating new architectures with a combined superiority of diverse materials achieving for more fantastic performances are attracting great attention recently. Herein, we introduce a novel dual metal (oxide) microsphere reinforced by vertically aligned carbon nanotubes (CNTs) and covered with a titanium oxide metal ion transfer diffusion layer. The CNTs penetrate the oxide particles and buffer structural volume change, while enhancing electrical conductivity. Meanwhile, the external TiO_2 -C shell serves as a transport pathway for mobile metal ions (e.g., Li^+) and acts as a protective layer for the inner oxides by reducing the electrolyte/metal oxide interfacial area and minimizing side reactions. The proposed design is shown to significantly improve the stability and Coulombic efficiency (CE) of metal (oxide) anodes. For example, the as-prepared MnO -CNTs@ TiO_2 -C microsphere demonstrates an extremely high capacity of 967 mAh g^{-1} after 200 cycles, where a CE as high as 99% is maintained. Even at a harsh rate of 5 A g^{-1} (ca. 5C), a capacity of 389 mAh g^{-1} can be maintained for thousands of cycles. The proposed oxide anode design was combined with nickel-rich cathode to make a full-cell battery that works at high voltage and exhibits impressive stability and life span.

1 INTRODUCTION

2 Rechargeable lithium-ion batteries (LIBs) have dominated the energy market from
3 handheld electronic devices to electric vehicles since their commercialization;¹⁻³
4 however further enhancement of energy density remains challenging. One of the main
5 bottlenecks to achieving higher energy density in LIBs is the commonly used carbon
6 anode (e.g., graphite), which has a low lithium storage capacity (theoretical capacity
7 of graphite is 372 mAh g⁻¹).⁴⁻⁶ Thus, alternative high capacity anodes are urgently
8 needed. One potential class of materials that can replace graphite are transition metal
9 oxides due to their high theoretical capacity (>700 mAh g⁻¹) and non-flammability
10 compared to carbon anodes.⁷⁻¹² However, metal oxide-based anodes have always
11 suffered from several fatal disadvantages which prevented their use as anodes in LIBs.
12 For example, oxide anodes in LIBs typically exhibit severe capacity fading and low
13 initial Coulombic efficiency (CE). This is because most metal oxides are
14 semiconducting, meaning they have lower conductivity than carbon anodes and
15 experience a conversion reaction during the lithium process. The combination of poor
16 electrical conductivity and large volumetric expansion results in irreversible reactions
17 and fast capacity decay. Thus, developing electrode design strategies to stabilize the
18 metal oxide anodes is urgently needed.

19 To date, designing metal oxide-carbon composites has become the main trend to
20 improve the performance of oxide anode materials. Many composites consisting of
21 oxide anodes combined with some form of carbon (e.g., carbon nanotubes, graphene,
22 bio-derived carbon, etc.) are being extensively studied. Generally, introducing the
23 carbon additive and minimizing the size of the metal oxide particles have been the
24 two most common approaches used to enhance the electrical conductivity and
25 mitigating volume change of oxide anodes.¹³⁻¹⁸ However, the approach of pursuing

the high tap density metal oxide anode is rarely reported. In general, a spherical shape is preferred for achieving a high volumetric energy density because spherical particles can be easily transformed into highly compact electrodes.

Herein, we introduce a completely new architecture to design high tap density oxide anodes for LIBs. Our approach relies on using spherical metal oxide particles grown along vertically aligned carbon nanotubes (CNTs) to form a sea urchin-like structure (i.e., metal oxide-CNTs). These structures are subsequently coated by a layer of $\text{TiO}_2\text{-C}$. The CNTs penetrate deep into the particles, a feature that offers an effective pathway for electron transport and reinforces the structure by absorbing the mechanical strain that occurs during the conversion reaction. Meanwhile, the external $\text{TiO}_2\text{-C}$ shell exhibits a high lithiation plateau (1.65 V vs. Li/Li^+) which can protect the inner metal oxide nanoparticle and maximally suppress the electrolyte decomposition. This is because the Li^+ ion can be de-solvated on the $\text{TiO}_2\text{-C}$ shell and move into the inner oxide nanoparticles avoiding further side-reactions caused by the Li^+ -solvent reduction. This new design concept is demonstrated here using manganese oxide (MnO) as a conversion anode. We find that our design concept delivers a ternary anode ($\text{MnO-CNTs@TiO}_2\text{-C}$) whose electrochemical performance is superior to most, if not all, previously-reported MnO -based LIB anodes. In addition, we assembled full-cell LIBs combining our rationally-designed anode ($\text{MnO-CNTs@TiO}_2\text{-C}$) with the nickel-rich cathode (e.g., $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, NCM622), resulting in robust LIBs with excellent performance. We believe that this concept can be extended to other conversion oxide anodes and other battery systems.

RESULTS AND DISCUSSIONS

Synthetic Procedure. The structural design and synthetic procedure of the ternary $\text{MnO-CNTs@TiO}_2\text{-C}$ anodes are schematically illustrated in **Figure 1a** (see

experimental details in the supporting information). The main design feature of this unique anode can be summarized as follows: i) aligned CNTs that penetrate into the inner MnO core and connect it with the TiO₂-C shell vertically; this feature improves the electronic conductivity and structural stability of the anode; ii) the TiO₂ shell is known to be a stable and robust battery electrode, so it can provide protection for the inner MnO; iii) the coated carbon layer on TiO₂ can improve the electronic conductivity of the TiO₂ shell and the entire anode composite.¹⁹⁻²⁰ The morphological evolution observed during the synthesis process is demonstrated in **Figure 1b-i**. First, we find that the spherical features of MnCO₃ are retained when the CNTs are introduced. The MnCO₃ can be precipitated and grown on the CNTs to form a sea urchin-like structure (MnCO₃-CNTs), where the CNTs cover and penetrate the MnCO₃ particles (**Figure 1d-e**). The ultrathin TiO₂ was then coated on the MnCO₃-CNTs to form MnCO₃-CNTs@TiO₂ through a precipitation process, where the rough spherical surface becomes smooth (**Figure 1f-g**). Finally, a carbon layer was coated on the MnCO₃-CNTs@TiO₂ by a chemical vapor deposition process in Ar/C₂H₂, in which MnCO₃ decomposes into MnO and TiO₂ crystallizes²¹ to form the final MnO-CNTs@TiO₂-C anode. The carbon coating can cover the TiO₂ uniformly because the decomposition of C₂H₂ can occur on the TiO₂ surface.. The MnO-CNTs@TiO₂-C anode retains the spherical morphology after annealing, in which the penetrating CNTs can be clearly observed (**Figure 1h-i**, **Figure S1-S3**). We find that the atomic ratio of Mn:Ti in the anode is about 4.24:0.17 as can be seen in the elemental mapping images in **Figure S4**.

Structural Analysis. The microstructure of MnO-CNTs@TiO₂-C is analyzed and compared to the MnO-CNTs-C and MnO@TiO₂-C. We find that the MnO core is highly porous and penetrated by CNTs (**Figure 2a-d**). The porosity is produced by the

MnCO₃ decomposition (i.e., $\text{MnCO}_3 \rightarrow \text{MnO} + \text{CO}_2$), while the penetration of CNTs is determined by the co-precipitation process of MnCO₃ in the presence of CNTs. In parallel, the TiO₂-C shell covering MnO (MnO@TiO₂-C) confirms that TiO₂-C can be finely coated on the inner core MnO particles after annealing (**Figure 2e-h**). Thus, the formation of the core-shell anode (MnO-CNTs@TiO₂-C) has been confirmed. **Figure 2i-j** show additional features of this anode including the porous MnO core, ultrathin TiO₂-C shell, and penetrated CNTs morphology. In addition, the crystalline nature of the MnO core and TiO₂ shell is demonstrated by measuring the interplanar distance of lattices. Our results show the ~0.22 and ~0.26 nm spacings correspond to the (200) and (111) lattice planes of MnO (**Figure 2l₁-l₂**), while the 0.47 nm spacing corresponds to the (020) crystal plane of TiO₂ (**Figure 2k**). Finally, the presence of the elements Mn, Ti, C, and O is confirmed by the elemental maps shown in **Figure 2m-q**, and by the valence state measured by X-ray photoelectron spectroscopy (XPS) in **Figure S5a**. The XPS results show two peaks, one at 653.09 eV which corresponds to the Mn 2p_{1/2}, and one at 641.28 eV, which corresponds to Mn 2p_{3/2}; one satellite peak was also observed at 644.66 eV, all of which confirm the formation of MnO (**Figure S5b**).^{22, 23} In addition, the binding energy of Ti 2p_{1/2} and Ti 2p_{3/2} at 464.1 eV and 458.44 eV indicate the existence of Ti⁴⁺ (**Figure S5d**).^{24, 25} Although the crystalline information of TiO₂ is hard to be characterized by XRD (**Figure S3**) due to the low amount of TiO₂ (Mn:Ti atomic ratio is 4.24:0.17, **Figure S4**). The crystalline structure of TiO₂ might be a two-phase mixture of anatase and rutile (**Figure S6**), as confirmed by the pristine TiO₂ which was prepared using the same procedures, but without adding MnCO₃ and CNTs. Note that the MnO-CNTs@TiO₂-C has a high surface area around 319 m² g⁻¹, which is similar to 336 m² g⁻¹ of MnO-CNTs-C, but much higher than ~70 m² g⁻¹ of MnO-C and MnO@TiO₂-C, respectively (**Figure**

S7a). This data show that the CNTs can increase the surface area of the anode significantly, even though the total amount of carbon is only ~19 wt% (**Figure S8**). This is because the CNTs can penetrate the MnO particles and can become intertwined within the MnO-CNTs@TiO₂-C particles to produce enhanced porosity, as confirmed by the comparative TEM images of MnO-CNTs-C and MnO-CNTs@TiO₂-C (**Figure S9**). The volume and average pore size of MnO-CNTs@TiO₂-C are confirmed to be 0.8 cm³ g⁻¹ and 2.2 nm (**Figure S7b**). These results re-confirm the porous nature of the MnO-CNTs@TiO₂-C, which is consistent with the TEM results.

Electrochemical Performance. The lithium storage characteristics of different anode structures were studied in LIBs. We find that the MnO-CNTs@TiO₂-C anode offers the highest 1st cycle Coulombic efficiency (CE) of 73%, which is higher than 65%, 68% and 70% obtained for MnO-C, MnO-CNTs-C, and MnO@TiO₂-C anodes, respectively (**Figure 3a-b**). In addition, the stability of the MnO-CNTs-C, MnO@TiO₂-C, and MnO-CNTs@TiO₂-C are superior to MnO-C anodes made without CNTs (**Figure 3c**). These results demonstrate that the introduction of CNTs and TiO₂ can enhance cycling stability and CE. This is reasonable because the CNTs can increase the electronic conductivity and stabilize the structure upon (de-)lithiation process; while the TiO₂ can protect the MnO and reduce the side-reactions (e.g., electrolyte decomposition) to achieve higher CE. Besides, the capacity of MnO-CNTs@TiO₂-C can increase quickly after about 40 cycles (**Figure 3c**). This increase can be attributed to the activation of MnO within the electrode,^{15, 16, 26} in which the transportation of lithium ions and electrons along the CNTs can be enhanced significantly as the electrode volume changes.

Note that one probable negative effect of using the external TiO_2 layer is the lower rate capability.^{14,16} However, using our design, a high capacity of 825, 720, 623, 524, 449 and 300 mAh g^{-1} were measured for the $\text{MnO-CNTs@TiO}_2\text{-C}$ anode at the current densities of 100, 200, 500, 1000, 2000 and 5000 mA g^{-1} , respectively (**Figure 3d**). This should be ascribed to the ultrathin feature and good wettability of the $\text{TiO}_2\text{-C}$ shell. Further, we find that the CV curves of the $\text{MnO-CNTs@TiO}_2\text{-C}$ anode can be stabilized fast (after the 2nd cycle)^{26, 27} as shown in **Figure 3e**. Meanwhile, an average capacity of 972, 662 and 389 mAh g^{-1} were measured at a current density of 100, 1000 and 5000 mA g^{-1} over 1000, 2000 and 2000 cycles, respectively (**Figure 3f-g**). These results collectively confirm the highly reversible conversion reaction and good stability of the $\text{MnO-CNTs@TiO}_2\text{-C}$ anode during the repeated (de-)lithiation. This performance is much better than those of MnO-C anodes made without the CNTs and protective TiO_2 layer (e.g., 381 mAh g^{-1} at 100 mA g^{-1} after 300 cycles, 194 mAh g^{-1} at 5000 mA g^{-1}), as shown in **Figure S10**. Note that the capacity of the $\text{MnO-CNTs@TiO}_2\text{-C}$ anode initially increases with cycling up to 800 cycles after that the capacity decreases with the increasing the number of cycles (**Figure 3g**). This could be attributed to the gradual activation of MnO within the electrode, while the increase in SEI thickness on the electrode upon cycling might increase the barrier for Li^+ diffusion, resulting in electrode deactivation. The thick SEI can be inferred from the increased O 1s signal and the concurrent disappearance of the Ti 2p signal due to the formation of SEI on the electrode (**Figure S11**). Further, we characterized the performance of $\text{MnO-CNTs@TiO}_2\text{-C}$ using different amounts of CNTs and TiO_2 (TiO_2 amount was changed by changing the amount of titanium isopropoxide (TTIP) used in the reaction). We find that the average capacity and 1st CE of the as-prepared $\text{MnO-CNTs@TiO}_2\text{-C}$ using 25 mg CNTs/0.01 mL TTIP (797 mAh g^{-1} , 73%) are

1 higher than the anodes prepared using the precursors of 50 mg CNTs/0.01 mL TTIP
2 (588 mAh g⁻¹, 70.1%) and 25 mg CNTs/0.05 mL TTIP (572 mAh g⁻¹, 69.9%)
3 (**Figure S12**). The results demonstrate that the proper amounts of CNTs and TiO₂ are
4 critical, to achieve the optimal performance. Finally, the MnO-CNTs@TiO₂-C anode
5 performance is superior to most previously reported MnO-based anodes (**Figure 3h**,
6 **Table S1**),²⁸⁻⁴¹ where the high tap density of 1.49 g cm⁻³ is higher than most anodes
7 reported before (**Table S2**).⁴²⁻⁴⁸

8 **Structural Benefits for Lithium Storage.** The excellent performance of MnO-
9 CNTs@TiO₂-C benefits from its carefully-made design. The conversion reaction
10 within the MnO primary nanoparticles can be accelerated due to the shorter path for
11 ionic diffusion and faster charge transportation afforded by the integrated CNTs. In
12 addition, the TiO₂-C shell can reduce the interfacial area between MnO and the
13 electrolyte, where the lithium ions can be de-solvated on the TiO₂-C surface and then
14 diffuse into the MnO-CNTs core. Thus, the electrolyte decomposition on the MnO
15 surface can be significantly suppressed. The structural variation and comparative
16 cycling performance are summarized in **Figure 4**. For example, the MnO-C
17 microsphere anode without the protection of CNTs and TiO₂ demonstrates structural
18 and morphological collapse during the (de-)lithiation process (**Figure 4a-a'**), thus
19 giving rise to inferior cycling stability and low CE. In contrast, the structural stability
20 of MnO-C can , when the CNTs are introduced to form MnO-CNTs-C anode (**Figure**
21 **4b-b'**), thus improved stability is achieved due to the buffering effect and high
22 electrical conductivity of CNTs.⁴⁹ However, the low CE still needs to be improved
23 because of the large irreversible capacity resulting from excess side-reactions (**Figure**
24 **3a-b**). However, the CE of MnO-C anode is improved when the TiO₂ shell is
25 introduced. This is because the TiO₂ shell can reduce the electrolyte decomposition in

the MnO core (**Figure 4c-c'**)^{50, 51}. Finally, the MnO-CNTs@TiO₂-C anode possesses all the advantages of CNTs and TiO₂, thus good structural stability and good CE are obtained (**Figure 4d-d'**). The better structural stability of MnO-CNTs@TiO₂-C anode over that of the MnO-C is further confirmed by examining the cycled electrodes. We find that the MnO-CNTs@TiO₂-C anode microspheres remain stable after cycling, and retain their original morphology (**Figure 4e-i**). In contrast, the MnO-C anode microspheres experience serious pulverization during cycling (**Figure 4j-l**), which is consistent with the capacity decay observed during cycling (**Figure 3c**). Finally, the positive effect of CNTs and TiO₂ in protecting the structural stability of MnO was further confirmed in the cycling test in the results of the MnO-CNTs-C and MnO@TiO₂-C anodes (**Figure S13**).

Electrochemical Analysis. To further understand the excellent performance of our rationally-designed MnO-CNTs@TiO₂-C anodes, electrochemical impedance spectroscopy (EIS) analysis was performed (**Figure 5a-b**, **Figure S14**). We find that the charge transfer resistance (R_{ct}) and SEI layer resistance (R_{SEI})⁵²⁻⁵⁴ values of fresh MnO-CNTs@TiO₂-C are 68.5 and 16.6 Ω , respectively. These values are slightly higher than the 64.4 and 13.7 Ω obtained in the case of the MnO-C anode. This result is due to the existence of the TiO₂ shell and the core-shell boundaries between MnO-CNTs and TiO₂ shells. However, the R_{ct} and R_{SEI} of the cycled MnO-CNTs@TiO₂-C decrease significantly to values of 8.5 Ω and 8.3 Ω , respectively. These values are much lower than the 54.4 Ω and 90.1 Ω values obtained for cycled MnO-C anodes (**Table S3**). The results confirm that the SEI formation is significantly suppressed due to the presence of the TiO₂ layer. This observation is consistent with the electrochemical performance discussed earlier. Besides, the active materials (e.g., MnO) within the electrode become more compacted and interconnected by the CNTs

during the formation of SEI. Therefore, a decrease in the magnitude of the electrical impedance is observed. The defect such as the reduced Ti^{n+} ions and/or oxygen vacancies do provide charge carriers, but they barely affect the overall impedance considering the low amount of TiO_2 used. In contrast, without the TiO_2 layer to mitigate the electrolyte decomposition and CNTs to connect the MnO particles, the cycled MnO-C anode demonstrates a higher electrical impedance. Moreover, the calculated lithium diffusion coefficient in MnO-CNTs@ TiO_2 -C anode ($7.78 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) is about two times higher than the Li diffusion coefficient in MnO-C anodes ($4.2 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) (**Figure 5c**).⁵⁵⁻⁵⁷ The higher lithium transportation can be ascribed to the unique feature of our anode including the penetrated CNTs and high porosity, enabling faster electronic and ionic transportation.

Furthermore, the lithium storage contributions were studied by CV analysis (**Figure S15-S16**),⁵⁸ where the peak current (i) and scan rate (v) follow the power-law relationship $i = av^b$.^{59, 60} The diffusion-controlled current is indicated by a b value of 0.5, while the surface-mediated current is indicated by a b value of 1. These b values are obtained by plotting $\log(i)$ versus $\log(v)$. We find that the value of b for the MnO-CNTs@ TiO_2 -C anode is 0.73 and 0.74 for the cathodic and anodic peaks (vs. 0.74 and 0.69 for MnO-C) (**Figure 5d**), respectively. These results imply the co-existence of diffusion-controlled and surface-mediated processes.⁶¹ The percentage of capacitive current contribution was calculated using a previously reported approach,^{62, 63} the current response $i(v)$ is divided into surface capacitive process (k_1v) and diffusion-controlled processes ($k_2v^{1/2}$) (i.e., $i(v) = k_1v + k_2v^{1/2}$, where $i(v)$, k_1v and $k_2v^{1/2}$ correspond to the integral capacity, surface-mediated capacity, and diffusion-controlled capacity, respectively). The values of k_1 and k_2 obtained at different potentials for our anode are shown in **Figure S17**. We find that the contribution of capacitive current for MnO-

CNTs@TiO₂-C anode is 25%, 37%, 42%, 51%, 56% and 59% at a scan rate of 0.05, 0.1, 0.25, 0.5, 0.75 and 1.0 mV s⁻¹ (**Figure 5e-f**). In contrast, the capacitive contribution of MnO-C anode is lower than MnO-CNTs@TiO₂-C and is only 14% and 33% at the scan rate of 0.1 and 1.0 mV s⁻¹, respectively (**Figure S16c-d**). This result is rational because the surface area and porosity of MnO-CNTs@TiO₂-C anode are much higher than MnO-C anodes.

High Voltage Lithium-Ion Battery. The great features of MnO-CNTs@TiO₂-C anode were further confirmed by constructing a high voltage full-cell lithium-ion battery. A nickel-rich LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode was used as the cathode in combination with our optimized MnO-CNTs@TiO₂-C anode (**Figure 6a**). The N/P ratio was controlled at 1.05, where the high capacity of MnO-CNTs@TiO₂-C anode (798 mAh g⁻¹) can reduce about the amount of anode mass needed in the battery by 2.3 times compared to graphite anodes (i.e., ~340 mAh g⁻¹) to obtain the same capacity in anode side (**Figure 6b**). We find that the battery can be stabilized fast, as confirmed by the CV test, even when the battery was charged to a cut-off voltage as high as 4.5 V (vs. 4.2 V in normal) (**Figure 6c**). This result is consistent with the good cycle stability confirmed by the Galvanostatic (dis-)charge curves, where the capacity retention can be maintained at 78.4% after 200 cycles at the high rate of 0.5 C (**Figure 6d**). This cycle performance is hard to be achieved when the graphite anode is used at high voltage conditions. This is because the cation ions (i.e., Ni, Co, Mn) dissolved from the cathode can be deposited and accumulated on the graphite anode, inducing the deterioration of graphite.⁶⁴⁻⁶⁶ Obviously, the MnO-CNTs@TiO₂-C anode can overcome these disadvantages for the reasons discussed above. In addition to the good stability, the full cell also has great rate capabilities; specifically, the capacity can be maintained at 95.1%, 90.3%, 87.5%, 81.7%, 77.8% and 73.1% (vs. 2.02 mAh at 0.1C)

1 under 0.2, 0.5, 1, 2, 3 to 2 C rates, respectively (**Figure 6e**). This result is attractive
2
3 for fast charging of batteries.⁶⁷⁻⁷⁰ Thus, our preliminary results show that the MnO-
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5 CNTs@TiO₂-C anode has a high potential application as an anode in high power and
6
7 energy density LIBs.
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12 **CONCLUSIONS**
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14 In summary, a completely new sea urchin-like architecture is introduced to stabilize
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16 the metal oxide conversion reactions in lithium-ion batteries (LIBs). The presented
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18 metal oxide-CNTs@TiO₂-C microspheres are designed through the precipitation of
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20 metal oxide with CNTs first, and then coating with a TiO₂-C layer. The CNTs
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22 penetrate and intertwine with the core and shell, which reinforces the structural
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24 stability, buffers the mechanical strain, and increases the electrical conductivity.
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26 Meanwhile, the external TiO₂-C shell acts as a transport path for ions and protects the
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28 inner oxide by reducing the electrolyte/metal oxide interfacial reactions, minimizing
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30 side-reactions, thereby giving rise to better stability and higher CE. The MnO-
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32 CNTs@TiO₂-C anode demonstrates extraordinary performance in capacity, stability,
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34 CE, and high voltage full cell, which are superior to most previously reported MnO-
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36 based anodes. We believe this new concept can be extended to design other functional
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38 materials with greater capabilities for wider applications.
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Figure 1. Schematic illustration of the synthesis process and characterizations. (a) Schematic diagram to MnO-CNTs@TiO₂-C microspheres. SEM images of (b, c) MnCO₃, (d, e) MnCO₃-CNTs, (f, g) MnCO₃-CNTs@TiO₂, (h, i) MnO-CNTs@TiO₂-C microspheres with different magnifications.

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2 **Figure 2 Structural Characterizations of MnO-based microsphere anodes.** TEM
3 and HRTEM images of (a-d) MnO-CNTs-C, (e-h) MnO@TiO₂-C and (i-l) MnO-
4 CNTs@TiO₂-C microspheres. (m-q) EDS mapping images of MnO-CNTs@TiO₂-C
5 microspheres.

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Figure 3. Electrochemical performance of MnO-based microsphere anodes. Comparison of (a) the 1st Coulombic efficiency, (b) the 1st charge-discharge curves, (c) cycle performance in initial 200 cycles at the current density of 100 mA g⁻¹. (d) Typical charge-discharge curves in the rate test, (e) CV curves and (f, g) cycle performance of MnO-CNTs@TiO₂-C microspheres. (d) Comparison of electrochemical performance of MnO-CNTs@TiO₂-C and MnO-based anode reported before.

Figure 4. Summary of structural evolution of MnO-based microsphere anodes upon cycling. Schematic illustration of (a, a') MnO-C, (b, b') MnO-CNTs-C, (c, c') MnO@TiO₂-C and (d, d') MnO-CNTs@TiO₂-C microspheres upon (de-)lithiation process. SEM and TEM images of (e-i) cycled MnO-CNTs@TiO₂-C and (j-l) cycled the MnO-C electrode after 300 cycles.

Figure 5. Electrochemical analysis of MnO-based microsphere anodes.

Impedance spectroscopy of MnO-NTs@TiO₂-C and MnO-C (a) before and (b) after 100 cycles. (c) Relationship between the peak current (i_p) and the square root of scan rate ($v^{1/2}$) of the anodic peaks to calculate the lithium diffusion constant. (d) Calculated b-value determination of cathodic and anodic peaks based on the relationship between $\log(i)$ and $\log(v)$. (e) Capacitive-controlled charge storage contributions divided with the CV curve at the scan rate of 0.5 mV s⁻¹. (f) Normalized contribution ratio of capacitive (green) and diffusion-controlled (safron yellow) capacities at different scan rates.

Figure 6. Electrochemical features at high voltage conditions. (a) Schematic configuration of lithium-ion full battery consisting of MnO-CNTs@TiO₂-C and lithium layered oxide (e.g., LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂, NCM622). (b) Typical voltage vs. capacity profiles of MnO-CNTs@TiO₂-C and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ charged to the high voltage of 4.5 V. (c) CV curves, (b) typical voltage vs. capacity profiles in cycling at 0.5C and (e) rate capabilities of the lithium-ion battery at the high voltage of 4.5 V.

ASSOCIATED CONTENT

Supporting Information. A brief statement in non-sentence format listing the contents of material supplied as Supporting Information should be included.

The following files are available free of charge.

The experimental section, **Figures S1-S17**, and **Table S1-S3** are included.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Table of Contents

Carbon Nanotubes Coupled with Metal Ion Diffusion Layers Stabilize Oxide Conversion Reactions in High Voltage Lithium-Ion Batteries

Qian Li, Yingqiang Wu, Zhaomin Wang, Hai Ming, Wenxi Wang, Dongming Yin,

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A **completely new sea urchin-like architecture** is introduced to stabilize the metal oxide conversion reactions for **high voltage lithium-ion batteries** (LIBs). The presented materials consist of metal (oxide) core and TiO₂-C shell, which were connected by vertically aligned carbon nanotubes (CNTs) to form a spherical particle. As a prototype, the MnO-CNTs@TiO₂-C anode demonstrates an extremely high lithium storage capability of **967 mAh g⁻¹**, high Coulombic efficiency >99% and **extraordinary cycling performance over 2000 cycles**. The greater features of the constructed high voltage MnO₂-CNTs@TiO₂-C | Nick-rich layered oxide (e.g., LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂) battery can be further applied for many energy storage devices.