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Homologous V_2O_3/C box-in-box and V_2O_5 box for lithium-ion full cells

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Rational construction of metal oxides based electrode materials for Li-ion batteries (LIBs) is crucially essential to simultaneously get over their low conductivity and vulnerable nanostructure. Here, we demonstrate the design and synthesis of homologous V_2O_3/C box-in-box and V_2O_5 box as anodes and cathodes for all-nanobox based LIBs full cell, which are subsequently obtained by thermal treatment in different atmospheres. Except that the V_2O_5 box cathodes can provide abundant active sites, short ions diffusion distance and part volume flexibility, the key design concept of the V_2O_3/C box-in-box is the carbon box-in-box can further enhance the structural durability during lithiation/delithiation, and hence giving rise to an extended lifespan. As proof-of-concept, the V_2O_3/C box-in-box anodes deliver a high reversible capacity of 641 mAh g⁻¹ even after 1200 cycles at 1000 mA g⁻¹, while the $V_2O_3/C/V_2O_5$ box cathodes possess a specific capacity of 119 mAh g⁻¹ at 10 C with superior cycling stability. Importantly, the $V_2O_3/C/V_2O_5$ LIBs full cell is assembled, which shows an impressive specific capacity of 97 mAh g⁻¹ at 500 mA g⁻¹ with capacity retention of 81 mAh g⁻¹ even after 100 cycles based on the cathode material weight.

Introduction

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Hollow nanostructures, with the advantages of large surface area, low effective density as well as good permeation, have been widely used in optoelectronics, catalysis, drug delivery, energy storage, and so forth.¹⁻⁵ Especially in recent years, hollow-structured transition metal oxides (TMOs) based electrode materials have shown a huge potential for promoting lithium-ion batteries (LIBs), owing to low cost, abundant source and high theoretical capacity.⁶⁻⁷ To date, various hollow-structured TMOs have been synthesized to enhance LIBs performance, including Fe₃O₄ hollow nanospheres,⁸ scroll-shape VO_x,⁹ multi-shelled Co₃O₄ hollow microspheres,¹⁰ as well as V₂O₅-SnO₂ nanocapsules,¹¹ and so on. Meanwhile, hollow TMOs/C and even more complex nanohybrids have also been extensively developed, e.g. MnO/C hollow microspheres,¹² carbon-coated CNT@Fe₂O₃ nanohorns,¹³ hollow and Fe₃O₄@Fe₃C-C yolk-shell nanospindles,¹⁴ etc. Among them, box structure inherits all merits of these hollow structures, being a key morphology of hollow family with excellent electrochemical performance. For example, Lou et al.¹⁵ synthesized TiO₂ submicroboxes, delivering an improved specific capacity of 210 mAh g^{-1} at 1 C compared to TiO₂ microparticles. Accordingly, Paik et al.¹⁶ designed Fe₃O₄/C yolk-shelled nanoboxes, which exhibited a high reversible capacity of around 470 mAh g⁻¹ after 8000 cycles even at 10 C. It can be observed that the box structures possess abundant active sites, short ions diffusion distance and part volume flexibility, and hence remarkably enhancing their electrochemical performances. Nevertheless, a main contradiction between high capacity and long cycle life still exists for both hollow TMOs and their corresponding hybrids because the incorporation of abundant Li⁺ will cause in the structure collapse, resulting in a limited cycle lifespan. Therefore, the exploitation of the controllable metal oxides based nanobox is very meaningful for achieving high energy/power densities and extended lifespan for LIBs.

Among various metal oxides, vanadium oxides have attracted much attention in energy storage and conversion fields in view of their rich valence states, e.g. V₂O₅, V₂O₃, VO₂, etc. Detailed speaking, the high valence V₂O₅ is a promising substitute for the conventional LiMn₂O₄, LiCoO₂ and LiFePO₄ cathodes owing to its higher specific capacity of binding multiple lithium ions, e.g. 294 mAh $g^{\text{-}1}$ for intercalating two lithium ions. $^{\rm 17\text{-}19}$ While for low valence $V_2O_3,$ it shows a huge potential as LIBs anode materials considering that the electrical resistance of bulk V_2O_3 (~ 10 Ω at 150-350 K) is much lower than other TMOs (Co₃O₄, MnO₂, etc.), as well as its high theoretical capacity (1070 mAh g^{-1}).²⁰⁻²² Furthermore, the anode/cathode materials from the same source are reckoned to achieve strong synergistic effects between them, and hence further optimizing specific capacity of the full cell. Although these unique advantages of vanadium oxides, an all-nanobox based LIBs full cell using a V₂O₃ based anode and a V₂O₅ based cathode has yet not to be reported so far.

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(C)

mass ratio of 7:2:1. Coin cell (type CR2016) was assembled with Li foil as counter electrode and 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by weight) as electrolyte. For full cell assembly, the V_2O_3/C box-in-box and pre-lithiated V_2O_5 box were serving as anodes and cathodes with optional capacity match. Cyclic voladtammetry (CV) experiments were performed with an Autolab PGSTAT302N at a scan rate of 0.2 mV s⁻¹. Galvanostatic charge/discharge measurements were conducted by LANDCT2001A test system. The impedance spectra were recorded on constant voltage mode over the frequency range between 100 kHz to 0.01 Hz.

Results and discussion

The synthesis process for hierarchical V₂O₃/C box-in-box is schematically depicted in Scheme 1. The C-box was firstly synthesized by using Fe_2O_3 as a template (Figure 1a), and then coated a layer of polydopamine (PDA) on its surface. With the assistance of rich functional groups of PDA, vanadium oxytriisopropoxide (VOT) is very easy to nucleate and grow into vanadium oxide precursor nanoflakes on C-box surface by a simple hydrothermal method (Figure 1b). After annealing in argon, the precursor nanoflakes are converted into the V₂O₃ multi-scaled hierarchically nanostructures composed of nanoparticles (NPs) and nanoflakes, which firmly attached on carbon box-in-box. Figure 1c shows the panoramic morphology of as-obtained products with uniform nanoboxes. The mean size is about 500 nm. An enlarged SEM image (Figure 1d) reveals that the outer shell of V_2O_3/C box-in-box is composed of many nanoparticles lied on ultrathin nanoflakes, forming a hierarchical nanostructure. Additionally, the formation of carbon box-in-box can be attributed to their different densities of V_2O_3 and carbon. The shell V_2O_3 with a larger density can

1Um

(d)

Figure 1. (a) SEM image of carbon hollow cubes, (b) SEM image of VO_X/C precursor, (c) low- and (d) high-magnification SEM images of V₂O₃/C box-in-box.

500nm

spectrometer.

Electrochemical Measurements. The working electrode was prepared by mixing active materials, carbon black, and poly(vinyl difluoride) (PVDF) binder into N-methyl-2-pyrrolidone (NMP) with a

box and V₂O₅ box were studied by X-ray diffractometer (XRD) with Cu Ka radiation. Scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, JEOL-2100) were performed at 200 kV to investigated microscopic morphologies. The surface area was tested on a Micromeritics ASAP 2010 analyzer at 77K. Thermogravimetric analysis (NETZSCH STA409PC) was carried out with a temperature ramp of 10 °C min⁻¹ under air flowing. Raman spectrum was obtained using NEXUS 670 FT-IR Raman



Herein, we demonstrate a new type of all-nanobox based LIBs full cell with V_2O_3/C box-in-box anode and V_2O_5 box cathode, homologously obtained from the same precursors with different thermal treatment atmospheres. The key design concept for the V₂O₃/C box-in-box is the carbon box-in-box can further enhance the structural integrity during lithiation/delithiation. As a consequence, the V₂O₃/C box-inbox anodes deliver a high reversible capacity of 641 mAh g⁻¹ even after 1200 cycles at 1000 mA g^{-1} . Meanwhile, the V₂O₅ box cathodes also show a specific capacity of 119 mAh g^{-1} at 10 C with superior cycling stability. To top it off, the assembled $V_2O_3/C//V_2O_5$ LIBs full cell shows an impressive specific capacity of 97 mAh g⁻¹ at 500 mA g⁻¹ with capacity retention of 81 mAh g⁻¹ even after 100 cycles based on the cathode material weight. The present work might shed more light on the importance of structural design and provide a new insight on constructing high-performance LIBs full cells.

Experimental section

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Synthesis of the V2O3 box-in-box and the V2O5 box. Typically, Fe_2O_3 nanocubes serving as templates were obtained firstly via previous report.¹⁵ Subsequently, as-synthesized Fe₂O₃ and dopamine were dispersed into 2-amino-2-hydroxymethylpropane-1,3-diol (Tris) solution (10 mM) with a mass ratio of 1:1 under continuous stirring for 5 h at ambient temperature. The black products were acquired by centrifugation and washed with deionized water and ethanol, followed with drying at 60 °C. The carbon hollow cube (C-box) was obtained by annealing the precipitates in argon and subsequent removing the iron oxide core by HCl etching (4 M). And then, 10 mg of C-box and 50 mg of dopamine were dispersed into Tris solution (100 mL, 10 mM) again with magnetic stirring for 2 h. The precipitates were collected and then dissolved into 30 mL of isopropanol (IPA). After sonicating for 5 min, 0.2 mL of vanadium oxytriisopropoxide (VOT) was added into above mixture with stirring for 30 min. The suspension was transferred into an autoclave and maintained at 200 °C for 12 h. Finally, V_2O_3/C box-in-box and V_2O_5 box were obtained by treating hydrothermal products at 500 °C for 2 h in argon and at 350 °C for 2 h in air, respectively.

Characterization. The crystal phases of as-prepared V₂O₃/C box-in-

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(b) d 0.37nm 5nm 0.37

Figure 2. (a) Low-, (b-c) high-magnification and (d) high-resolution TEM images of the V_2O_2/C box-in-box (insert of (d) showing the corresponding FFT pattern).

provide a strong driving force to promote the shrinkage outward from the core C-box during the carbonization, and therefore generating the unique V_2O_3/C box-in-box architectures.

Detailed interior structure of the V_2O_3/C box-in-box is further elucidated by TEM (Figure 2). Clearly, a double-shell hollow nanocube can be observed in Figure 2a. The V_2O_3 nanoflakes as well as nanoparticles are strongly contacted with carbon box-in-box, being in good agreement with the corresponding SEM observations. Partial precursor nanoflakes are preserved during annealing process. No other separated nanoparticles can be observed even through ultrasonic treatment, implying a strong adhesion force between V₂O₃ and outer carbon. A representative morphology is also provided in Figure 2b, obviously observing the coexistence of V₂O₃ nanoparticles and nanoflakes in the shell, as well as the carbon box-in-box carbon structure with an obvious gap. When we removed the V_2O_3 by HCl etching, the distinct carbon box-inbox nanostructure can be observed in Figure S1. In addition, we also find a V_2O_3/C box-in-box (Figure 2c), where the V_2O_3 nanoflakes have been fully well-maintained. From highresolution TEM image (Figure 2d), clear lattice fringes are visible. The interconnected distance is measured to be about 0.37 nm, matching well with the distance of the (012) plane of pure V₂O₃. A fast Fourier transformation (FFT) pattern is also provide in insert of Figure 2d, showing pure V₂O₃ with high crystallinity. The corresponding XRD pattern is shown in Figure S2. All peaks can be assigned to standard pattern of the rhombohedra V_2O_3 phase (JCDPS card No.: 34-0187).^{23,24} No other detectable impurity exists, further demonstrating the successful preparation of the target products. The content of carbon is estimated to ~ 29.3% (Figure S3) with relatively high graphitization degree (Figure S4a), which will be favorable to accelerate electrons rapid transfer.²⁵ Combining with the large specific surface area of 45.2 $\mbox{m}^2\mbox{ g}^{-1}$ (Figure S4b), the unique V₂O₃/C box-in-box is reckoned to deliver high energy/power



Figure 3. (a) The capacity retention of the V_2O_3/C box-in-box, V_2O_3 HNSs and V_2O_3 NPs at 100-5000 mA g^{-1} , (b) cycling behaviour and Columbic efficiency of the V₂O₃/C box-inbox and V₂O₃ HNSs at 1000 mA g⁻¹, respectively. (c) Electrochemical impedance spectra of the V2O3/C box-in-box before and after cycling and the V2O3 HNSs, (d) SEM image of V₂O₃/C box-in-box after cycling.

densities for LIBs.

The electrochemical performances have been evaluated through assembling our V_2O_3/C box-in-box powder in coin-type 2016 half-cells. The initial three cyclic voltammograms (CVs) of the V_2O_3/C box-in-box are tested in the potential window of 0.01-3.0 V at 0.2 mV s⁻¹ (Figure S5a). In the first cathodic scan, a well-defined peak around ~ 0.61 V appears but disappears in the following cycles, which is closely related to the formation of solid electrolyte interface (SEI) film.^{20,25} Notably, the CVs of V_2O_3/C box-in-box are nearly overlapped in the subsequent two cycles, suggesting highly electrochemical reversibility. The charge-discharge curves for an initial three cycles at 100 mA g⁻¹ within 0.01-3.0 V are also provided in Figure S5b. The first discharge capacity can reach 993 mAh g⁻¹ with a Coulombic efficiency (CE) of 74.8%. The rate performance of V₂O₃/C boxin-box is further evaluated at various current densities from 100 to 5000 mA g^{-1} , as shown in Figure 3a. The as-obtained V₂O₃/C box-in-box delivers a mean reversible discharge capacity of 794, 693, 614, 544, 481 and 406 mAh g^{-1} at a current rate of 100, 300, 500, 1000, 3000 and 5000 mA g^{-1} , respectively. After through five deep charge/discharge cycles, a reversible capacity as high as 778 mAh $\mathrm{g}^{\text{-1}}$ can still be obtained when scanned again at 100 mA g⁻¹, which further proves the superior Li⁺ storage. Accordingly, the pure carbon box electrodes were also tested under the identical current densities (Figure S6). For comparison, we also synthesized the pristine V_2O_3 NPs with sizes of ~ 100 nm and the V_2O_3 hollow nanospheres (HNSs), as shown in Figure S7. It can be found that they deliver a lower discharge capacity of 479, 694 mAh g ¹ at 100 mA g⁻¹, respectively. Particularly at a high rate of 5000 mA g^{-1} , only 197, 279 mAh g^{-1} can be retained for each of them. The remarkably enhanced electrochemical performance can be mainly attributed to the V₂O₃ multi-scaled hierarchical nanostructures with rich active sites and short ions diffusion path as well as their hybridization with high-conductive carbon

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boxes. We further evaluate the cycling performance of the V_2O_3/C box-in-box for another 1200 cycles at 1000 mA g⁻¹, as shown in Figure 3b. The discharge capacity gradually increases and reaches the maximum value of 641 mAh g^{-1} after nearly 700 cycles, and then keeps stable for the subsequent 500 cycles. For the V₂O₃ HNSs, they also show an increasing trend in the first 400 cycles and then gradually decrease to 422 mAh g^{-1} after 700 cycles. The increasing capacity for both samples in the beginning has been widely attributed to the activation process with the appearance of high valence vanadium, confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Figure S8).^{20,26,27} It can be observed that a relative V^{3+} content reduces from 59% to 27% for the V_2O_3/C box-in-box, suggesting its partial oxidation of V^{3+} into $V^{5+,28-30}$ The long cycle life is mostly related to its unique and robust structure. In particular, the carbon box-in-box plays a crucial role in maintaining the structural integrity during repeated charge/discharge process, which at least possesses dual functions. The void space between carbon boxes will accommodate the distinct volume expansion when lithiation. And meanwhile, the inner carbon box can be expected to support the outer V_2O_3/C shell/core hybrids, and therefore strongly enhancing the structural durability, giving rise to an extended lifespan.

Electrochemical impedance spectra (EIS) were characterized to provide further insights on the electron/ion transfer characteristics within the electrodes and the corresponding structural robustness, as shown in Figure 3c. The V₂O₃/C box-in-box exhibits a much lower charge transfer resistance (~ 99 Ω) than the V₂O₃ HNSs (~ 176 Ω). After cycles, a little bit drop can be seen for the V_2O_3/C box-in-box due to the full infiltration by the electrolyte, which also implies the structural stability. To further clarify it, the SEM image of V₂O₃/C box-in-box after cycling is provided in Figure 3d. The cubic shape has been well-maintained without obvious pulverization. In addition, there is no obvious change about



Figure 4. (a) SEM and (b) TEM images of the V_2O_5 box, (c) rate performance of the V_2O_5 box at various rates in the voltage range of 2.5-4 V, (d) cycling behaviour and Columbic efficiency of the V_2O_5 box at 10 C.



Figure 5. (a) Schematic illustration of the all-nanobox based $V_2O_3/C//V_2O_5$ LIBs full cell. (b) Rate performance of $V_2O_3/C//V_2O_5$ full cell at 100-5000 mA g⁻¹ within 1-3.5 V, (c) cycling behaviour and Columbic efficiency of the full cell at 500 mA g⁻¹ (insert of (c) showing the lighted LEDs).

the electrode surface before and after cycles, as shown in Figure S9. These results are good at supporting our forecast that the carbon box-in-box is favorable to improve the structural stability of electrode materials. Therefore, the present V₂O₃/C box-in-box demonstrates an excellent and comprehensive electrochemical performance in terms of high energy/power densities and extended lifespan.

On the other hand, the V₂O₅ box can also be obtained if annealing the same precursor in air at 350 °C for 2 h. The pure and orthorhombic phase V_2O_5 has been confirmed by the corresponding XRD pattern (Figure S10). The SEM (Figure 4a) and TEM (Figure 4b) images show the typical and uniform V_2O_5 box morphology composed of V₂O₅ nanoflakes with the almost similar diameter with V2O3/C box-in-box. When served as cathode materials for LIBs, the V₂O₅ box delivers a high specific capacity of 142 mAh g⁻¹ at 2/3 C, closed to the theoretical capacity of 147 mAh $\mathrm{g}^{\text{-1}}$ when tested within 2.5-4 V, as shown in Figure 4c. Even at a very high current density of 50 C, the specific capacity can still be maintained as high as 83 mAh g⁻¹. Importantly, The V₂O₅ box also demonstrates a good cycling stability with nearly 100% Coulombic efficiency at 10 C, as shown in Figure 4d. The specific capacity can retain 111 mAh g-¹ at the 400th cycle with only 7.5% capacity fading. Considering their much lower specific capacity of cathode materials compared to anode materials, the volume change is also inconspicuous. Therefore, the unique V_2O_5 box structure is enough for ensuring a superior electrochemical performance in terms of its abundant active sites, short ions diffusion distance and part volume flexibility. Such an excellent performance with a high output voltage makes V₂O₅ box be a desired cathode to couple with V_2O_3/C box-in-box anode for assembling all-nanobox based LIBs full cell.

Before assembling a full cell, the V₂O₃/C anode was prelithiated by electrochemically activated for 6 cycles within 0.01-3 V, subsequently discharged to 0.01 V. And then, a V₂O₃/C box-in-box//V₂O₅ box LIBs full cell was obtained (Figure

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5a), which has been evaluated by galvanostatically charge/discharge measurement at 1.0-3.5 V. The initial 3 charge-discharge curves were shown in Figure S11 at 100 mA g^{-1} . A high reversible capacity of 130 mAh g^{-1} is achieved based on the cathode materials weight, which can still be maintained 43 mAh g^{-1} even at a very high rate of 5000 mA g^{-1} (Figure 5b). The full cell also possesses a high cycling stability. It can still deliver a high specific capacity of 81 mAh g⁻¹ (~ 80% capacity retention) after 100 cycles with nearly 100% Coulombic efficiency at 500 mA g^{-1} , as shown in Figure 5b. It is worth noting that the comprehensive electrochemical performance of the all-nanobox based full cell is superior, at least comparable to the most reported full cells in the literatures (Table S1), possibility due to the strong synergistic effects from the homologous anode and cathode materials. Furthermore, our $V_2O_3/C//V_2O_5$ full cell is able to lighten the ECUST logo composed of 220 light-emitting diodes (LEDs) with rated voltage of 3.7 V (insert of Figure 5c). Such an excellent electrochemical performance will promote the design and synthesis of other homologous electrode materials for high energy/power LIBs.

Conclusions

In conclusions, we developed an effective strategy for the synthesis of homologous V_2O_3/C box-in-box anodes and V_2O_5 box cathodes by thermal treatment of the same precursor in different atmospheres. As for the V_2O_3/C box-in-box, the unique carbon box-in-box can greatly enhance the structural stability during lithiation/delithiation, leading to an extended lifespan. The V₂O₃/C box-in-box anodes deliver a high reversible capacity of 641 mAh g⁻¹ even after 1200 cycles at 1000 mA g^{-1} . Accordingly, the V₂O₅ box cathodes with abundant active sites and part volume flexibility also show a desirable specific capacity of 119 mAh g⁻¹ at 10 C with superior cycling stability. Importantly, an all-nanobox based $V_2O_3/C//V_2O_5$ LIBs full cell is also assembled, which exhibits an impressive specific capacity of 97 mAh g^{-1} at 500 mA g^{-1} with capacity retention of 81 mAh g⁻¹ even after 100 cycles based on the cathode material weight. The present work not only clarifies the importance of the structural design, but also paves the way to fabricate other homologous electrode materials for enhanced LIBs.

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