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High interfacial lithium storage capability of hollow porous Mn$_2$O$_3$ nanostructures obtained from carbonate precursors

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Preparation of porous Mn$_2$O$_3$ boxes has been developed via a carbonate precursor route. As a Li-ion battery anode, it delivers a high reversible capacity of 1442 mA h g$^{-1}$ over 600 cycles at 800 mA g$^{-1}$, and 65% the capacity originates from the gradually emerging interfacial storage contribution.

Mn$_2$O$_3$ has been regarded as an appealing anode material for Li-ion batteries (LIBs) owing to its high theoretical capacity, low operating voltage, earth-abundance, nontoxicity and low processing cost. In principle, the conversion reaction of a transition metal oxide (TMO) with metallic Li results in highly dispersed transition metal nanoparticles and electrochemically inactive Li$_2$O matrix, and the enhanced surface energy favors the Li$_2$O reversibility catalyzed by metallic nanocrystals. This deals with a large volume change or a high capacity loss and even destroys the integrity of assembled electrode upon discharge-charge cycling, especially at a high current rate. Aside from the bulk insertion of Li$^+$ ions, both the faradaic contribution of pseudocapacitance and nonfaradaic contribution of double-layer capacitance are reasonably referred to as an interfacial storage capability to offset the capacity loss. In most cases the interfacial storage capacity of bare TMOs can outstand when the active nanoparticles are highly dispersed and effectively stabilized by a nanostructured matrix such as carbonaceous materials.

Constructing the hollow porous nanostructures of TMO with a high specific surface area is a promising approach to improve its Li storage capacity. This structural feature facilitates the close contact of active substance with electrolyte, reduces the diffusion path of Li$^+$ ions and favors the conversion reaction of the TMO with metallic Li. Moreover, both the porous shells and hollow interiors can effectively buffer the volume change of a working electrode occurring during the reversible processes of Li-ion insertion/extraction. To date, the hollow porous nanostructures of Co$_2$O$_4$, SnO$_2$, Fe$_2$O$_4$ and LiMn$_2$O$_4$ have been prepared successfully, however, as LIB anodes only the acquired electrochemical properties of high reversible capacity, good cycling stability and/or rate capability, not the non-faradaic contribution, have been highlighted therein. Therefore, it is of crucial importance to evidence the possible relationship between the high interfacial Li$^+$ storage capability and the high specific surface area of nanostructured TMOs with a hollow porous feature.

Several experimental efforts have been carried out for the controlling synthesis and potential applicability of Mn$_2$O$_3$ applied as LIB anodes, and unfortunately its non-faradaic contribution of specific surface area to the improved lithium storage capability is still difficult to be demonstrated visually. Herein, the slow ion-exchange reaction of solid-state vaterite (i.e., the instable polymorph of anhydrous CaCO$_3$) with aqueous MnCl$_2$ was firstly adopted to prepare cube-shaped MnCO$_3$ boxes, not the loose aggregates of tiny nanoparticles in case of the structural collapse occurring during the direct transformation of MnCO$_3$ into oxides. Secondly, a well-known KMnO$_4$-assisted wet-chemical oxidation of precursor MnCO$_3$ was used to produce amorphous Mn$_2$O$_3$ boxes. And then, a high-temperature calcination of intermediate MnO$_2$ guarantees the final generation of porous Mn$_2$O$_3$ boxes, defined as Mn$_2$O$_3$-1 sample. When evaluated as a LIB anode, the reversible capacity of Mn$_2$O$_3$-1 electrode initially expresses a routine downward trend owing to gradual capacity loss and thereafter exhibits an upward trend owing to the gradually outstood interfacial storage, reaching a high value of 712 mA h g$^{-1}$ over 600 cycles at 1600 mA g$^{-1}$.

![Fig. 1](image_url) (a) A schematic drawing of porous Mn$_2$O$_3$ boxes obtained from carbonate precursors. (b-d) SEM images of precursor MnCO$_3$, intermediate MnO$_2$ boxes and finally produced porous Mn$_2$O$_3$ boxes in sequence.

Fig. 1 schematically illustrates a three-step procedure to obtain porous Mn$_2$O$_3$ boxes. The first step deals with an ion-exchange reaction from crystalline CaCO$_3$ to MnCO$_3$ driven by their different solubility products, which is slow and at least six hours are needed to obtain MnCO$_3$ cubes (Fig. S1, S2†). In the second step, at the
KMnO₄: MnCO₃ molar ratio of 1:30 the resulting MnO₂ boxes are directly rinsed using HCl aqueous solution (1.2 M) to remove unreacted MnO₃ within the cubes’ interior (Fig. 1a). By increasing the molar ratio of KMnO₄ to MnCO₃ to 1:1.5, porous MnO₂ boxes with a smaller interior can be synthesized, referred to as a comparative sample Mn₃O₄-2. The third step of MnO₂-to-Mn₃O₄ transformation is performed at an optimal temperature of 600 °C according to the TGA result of precursor MnCO₃ (Fig. S3, S4†). Similarly, under air circumstance the thermal decomposition of precursor MnCO₃ leads to the formation of porous MnO₂ cubes, defined as another comparative sample Mn₃O₄-3.

Overall and close-up SEM images of precursor MnCO₃ show irregular cube-like shapes with an average size of ca. 340 nm (Fig. 1b). At the KIrMnO₂: MnCO₃ molar ratio of 1:30, the wet-chemically transformed MnO₂ boxes succeed at the skeleton preservation of MnCO₃ cubes, obviously giving a hollow interior and a rough surface (Fig. 1c). Through the high-temperature crystallization and simultaneous release of gaseous O₂, the solid-state transformation of amorphous MnO₂ to cubic MnO₂ endues a hollow porous structure for sample Mn₃O₄-1 (Fig. 1d).

Fig. 2 (a-c) TEM images of precursor MnCO₃, intermediate MnO₂ and sample Mn₃O₄-1 in sequence. (d) A representative HR TEM image of the porous shell of a Mn₃O₄-1 box.

TEM images further prove the structural features of low-valence precursors, high-valence intermediates and middle-valence products: cube-shaped MnCO₃ (Fig. 2a and an inset), MnO₂ boxes with a thin shell and a big hollow interior (Fig. 2b and an inset) and porous MnO₂ boxes with a thin shell composed of tiny nanoparticles (Fig. 2c, the bottom-right inset). In the upper right corner of panel (c), another inset is the electron diffraction (ED) pattern of cubic MnO₂ with diffraction rings corresponding to the crystal plane (hk) d-spacing (nm) of (415)/0.15, (044)/0.17, (314)/0.18, (223)/0.20, (004)/0.24, (222)/0.27 and (112)/0.38 (Fig. 2c). Fig. 2d is a representative high-resolution TEM image taken by focusing electron beam on the shell of a porous Mn₃O₄-1 box, showing the integrative lattice fringes of crystal face (022) with an interplanar spacing of ~3.3 Å across the porous gap. Insets in Fig. 2d are the corresponding fast Fourier-transformed patterns, indicating a high crystallinity of these porous shells.

When evaluated using a standard MnO₂/Li half-cell model, the 1st discharge profile of Mn₃O₄-1 electrode experiences a monotonic voltage drop from the upper limit of 3 V to a plateau at ~1.3 V then undergoes another voltage drop to a low plateau at ~0.35 V and then sustains a further voltage drop to the lower limit of 0.01 V, giving a specific discharge capacity of 1467 mA h g⁻¹ at 800 mA g⁻¹ (Fig. 3a). This process can be associated with the stepwise reduction of Mn⁵⁺ to Mn⁴⁺ and then to Mn²⁺, accompanied by the formation of organic polymeric gel-like layer or the so-called solid electrolyte interface (i.e., SEI) film outside particles’ surface. By subtracting the theoretical Li storage capacity of MnO₂ (i.e., 1018 mA h g⁻¹), the residual value of 449 mA h g⁻¹ originates from the decomposition of electrolyte or the formation of SEI film. Considering the significant drawback of low conductivity, this working electrode delivers the decreasing discharge capacities of 1125, 580 and 301 mA h g⁻¹ in the 2nd, 10th and 50th cycles, respectively (Fig. 3a).

Over decades of continuous cycles at 800 mA g⁻¹, the capacity loss occurring at each previous-cycle may be overcompensated by an extra contribution of the gradually emerged double-layer capacitance, showing the discharge capacities of 411, 660, 880 and 1127 mA h g⁻¹ with the interfacial storage parts of 237, 353, 553 and 718 mA h g⁻¹ in the 100th, 200th, 300th and 400th cycles, respectively (Fig. 3b). According to our previous results, after a discharging process the resulting metallic Mn can hardly be converted into manganese oxides completely, which may account for the general capacity loss occurring therein, and then the surface-enhanced storage behavior could emerge from the ordered arrangement of residual metallic Mn⁰ accumulated gradually. To the best of our knowledge, so far this surface-enhanced storage phenomenon can only be observed for nanostructured composites composed of nanosized TMOs that were highly dispersed in a layered structure of conductive carbons. As shown in Fig. 3c, after ~80 cycles these porous MnO₂ boxes (i.e., Mn₃O₄-1 sample) obviously present an upward trend of discharge capacity operated at different current rates. At 200 mA g⁻¹ anode MnO₂-1 displays the discharge capacities of 663, 902, 1028 and 1145 mA h g⁻¹ with the interfacial storage parts of 291, 510, 692 and 726 mA h g⁻¹ in the 100th, 200th, 300th and 400th cycles, respectively; at 1600 mA g⁻¹ anode MnO₂-1 displays the discharge capacities of 191, 304, 430 and 529 mA h g⁻¹ with the interfacial storage parts of 138, 171, 243 and 302 mA h g⁻¹ in the 100th, 200th, 300th and 400th cycles, respectively. Therefore, in the absence of conductive carbons, the so-called surface-enhanced Li storage capability originating from non-faradaic contribution increases with the increasing of cycling numbers.

As mentioned above, another two samples were synthesized and treated as comparisons: seriously agglomerated MnO₂-2 is composed of porous boxes (Fig. S5†) and Mn₃O₄-3 clearly presents a shape of cube with the visually porous feature (Fig. S6†). As shown in Fig. 3d, at 800 mA g⁻¹ the initial discharge capacities of Mn₂O₃-1, Mn₂O₄-2 and Mn₃O₄-3 are 1467, 1046 and 1019 mA h g⁻¹.
with a retention ratio of 98.2%, 118.6% and 44.5% in the 600th cycle, respectively. Considering both the formation of SEI film at the 1st cycle and the gradual capacity loss during the subsequent ~54 cycles, the overall discharge upward trend of MnO2-1 can be attributed to the increasing interfacial storage contribution that originates from its structural characteristics similar to those of MnO2-1 (Fig. 3d, S5†). Aside from the relative big size of building blocks, both the impurity and non-hollow features of MnO2-3 may answer for the slow penetration of electrolyte and/or the gradual activation of its interior, giving a transient increase of reversible capacity occurring from the 30th to 160th cycle (Fig. 3d, S6†).

Fig. 4 (a-c) N2 adsorption-desorption isotherms and the inserted pore size distributions of three porous MnO2 products. (d) Histograms of the comparative electrochemical parameters of these porous MnO2 obtained at a current rate of 800 mA g⁻¹.

N2 adsorption-desorption results of MnO2-1, MnO2-2 and MnO2-3 demonstrate a non-mesoporous nature for all of them and give the BET surface areas of 52.23, 17.63 and 9.23 m² g⁻¹, respectively. By comparison, the higher surface area of MnO2-1 (Fig. 4a) and its achieving interfacial Li storage capability (Fig. 3d) coincide well with both the higher value of initial Coulombic efficiency (i.e., initial CE, Fig. S7†) and the lower values of charge-transfer and surface-film resistances measured at different states (Fig. S8a, b†), whereas these are reverse for the lower surface area of MnO2-3 (Fig. 4c). Furthermore, the agglomeration of hollow porous MnO2-2 accounts for both the middle BET surface area and the transient increase of reversible capacity occurring from the 35th to 160th cycle (Fig. 3d, 4b, S9†).

At 800 mA g⁻¹, the acquired electrochemical parameters of the three MnO2 electrodes are summarized for practical application purposes. As shown in Fig. 4d, the higher BET surface area of the sample corresponds to the higher initial discharge capacity (i.e., initial D-value) of the electrode with a higher initial CE, even though all the samples show high CE (>99%) after the first 80 cycles (Fig. S7†). Supposed a complete transformation of Mn⁴⁺ to Mn²⁺ in these initial discharges, the initial interfacial contributions of BET surface area can be estimated: 449 (MnO2-1), 28 (MnO2-2) and 1 mA h g⁻¹ (MnO2-3) compared to the theoretical value of 1018 mA h g⁻¹, assigned to the adverse effect of SEI film formation (Fig. S8a, b†). As for each parameter of the initial or 600th discharge capacity (i.e., 600th D-value), the fraction of interfacial storage contribution is shaded therein (Fig. 4d). In the 600th cycle, the acquired reversible capacities of MnO2-1, MnO2-2 and MnO2-3 electrodes are 1442, 1241 and 454 mA h g⁻¹ with an extra interfacial contribution of 65%, 61% and 59%, respectively. Aside from the large surface area and high electrochemical durability of porous MnO2-1 boxes (Fig. S10†), after initial 80 cycles the combination of the upward trend of reversible capacity (Fig. 3c) with the increasing plus-value of charge-transfer surface-film resistances (Fig. S6c†) implies the gradual generation of interfacial non-faradaic storage capacity.

In summary, the nanofabrication of a hollow porous MnO2 nanostructure with the possibly layered arrangement of adjacent shells at nanoscale, composed of single-crystalline building blocks, has been developed using carbonate precursors. The porous MnO2-1 sample exhibits an upward trend of reversible capacity (e.g., 1442 mA h g⁻¹, the 600th cycle, 800 mA g⁻¹) and can be mainly assigned to the extra interfacial compensation appearing after the initial ~80 cycles. In the absence or presence of conductive carbons, the non-faradaic contribution to an enhanced interfacial Li storage capacity of other hierarchically nanostructured TMOs deserves to be investigated in future.

Notes and references

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† Electronic Supplementary Information (ESI) available: experimental procedures, further SEM images, XRD, TGA, EIS and charge-discharge results. See DOI: 10.1039/c000000x/


