Structure Controlled Porous Carbon Materials as Hosts for Lithium-Ion Batteries

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To meet the ever-increasing demand of high performance lithium-ion batteries (LIBs), the existing electrode (anodes and cathodes) materials should be modified to improve their electrical conductivity and maintain the structure integrity. So far, porous carbon materials with adjustable crystallinity and stable physical, chemical properties are considered as attractive hosts and extensively applied to load active electrode materials for LIBs. In fact, different preparation strategies and carbon precursors can achieve some porous carbons with various structures and morphologies, thus the carbons as hosts play the different but key roles on improving the electrochemical performance of anodes or cathodes. Herein, we report our recent progress regarding the preparation of structure controlled carbon hosts for encapsulating different active materials as electrodes of LIBs (Figure 1). To buffer volume expansion of metal oxide anodes with a high loading, an ordered tubular mesoporous carbon with thin carbon walls (~2 nm) and high pore volume (~2.16 cm$^3$ g$^{-1}$) was purposely synthesized as a host for homogeneously encapsulating ultrafine SnO$_2$ and Fe$_2$O$_3$ anodes, respectively (Figure 1a). The unique tubular nanostructure can warrant efficient contact between nanoparticles and carbon matrix and prevent pulverization during cycling. The composites exhibit a high reversible capacity of 1039 mAh g$^{-1}$ for SnO$_2$ and 785 mAh g$^{-1}$ for Fe$_2$O$_3$ with a negligible capacity loss during 100 cycles. Meanwhile, this carbon host also can enhance the electrical conductivity of LiFePO$_4$ cathode with a good particle connectivity and uniformity to achieve a high rate performance.

To further improve the loading of LiFePO$_4$, a 3D coralloid nitrogen-containing carbon with a larger pore volume (4.68 cm$^3$ g$^{-1}$) and open-ended nanostructure was selected to fabricate a novel LiFePO$_4$/C composite (Figure 1b). The LiFePO$_4$/C cathode with a high loading of 85.4% exhibits a stable and high reversible capacity of 144.6 mAh g$^{-1}$ at 0.1 C and 60.4 mAh g$^{-1}$ at 20 C based on the total mass of LiFePO$_4$ and C. This coralloid carbon provides not only sufficient space for hosting nano-sized LiFePO$_4$, but also 3D conductive framework for fast transfer of electron and Li-ion. Moreover, the pore size of carbon hosts can be tuned rationally in the range of 7-22 nm with unchanged pore volume, thus to control the particle size of LiFePO$_4$.

Next, we also propose a controlled synthesis for porous carbon nanofibers with large ratio and tunable porosity through a hydrothermal approach. Among them, encapsulating the sulfur cathode material in microporous carbon can improve its utilization and avoid the dissolution of the Li$_2$S$_8$ species in the electrolyte solvent (Figure 1c). The suitably developed micropores and large external surfaces contribute to the good electrochemical behaviors of the Li-S batteries. Moreover, this unique 1D nanometer-scale of microporous carbon nanofibers can significantly increase electronic and ionic transport rate at the cathode, thus enhance the reversible capacity of sulfur with 950 mAh g$^{-1}$ after 50 cycles. The results show that the microporous carbon nanofibers have the apparent merits for application in Li-S batteries compared with mesoporous carbons and microporous carbon spheres.

Due to the strong binding affinity of catechol-derivative anchor groups, dopamine is considered as a carbon precursor to coat on the surface of active nanoparticles. Taking the advantages of dopamine, a core-shell N-doped carbon-coated Fe$_3$O$_4$ composite with a controlled and conformal carbon layer is prepared as an anode material (Figure 1d). The composite exhibits outstanding electrochemical performance as a LIB anode with a very high specific capacity of 817 mAh g$^{-1}$ at a current of 500 mA g$^{-1}$ and a high capacity retention of 99% after 200 cycles. This remarkably improved electrochemical performance can be undoubtedly attributed to the N-doped carbon coating layer, which not only acts as a barrier to avoid the direct contact of electrolyte and Fe$_3$O$_4$ particles, thus stabilize the formed SEI film, but also prevent aggregation and pulverization of the active nanoparticles. To further improve the rate capability, a "confined nanospace pyrolysis" strategy is developed to fabricate coaxial Fe$_3$O$_4$/C hollow particles with high surface area of 209.5 m$^2$ g$^{-1}$ and well-developed mesochannels of 18 nm.

In conclusion, the results show that the structures, morphologies of carbons and fabrication patterns of carbon-based composites strongly affect the electrochemical properties of anodes and cathodes, and help in developing a better understanding of the advantages of carbon materials in LIBs. Figure 1. (a) Tubular mesoporous carbon encapsulating SnO$_2$ anode, (b) 3D coralloid mesoporous carbon encapsulating LiFePO$_4$ cathode, (c) 1D microporous carbon nanofibers encapsulating S cathode and (d) conformal carbon layer coated Fe$_3$O$_4$ anode.

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