Functionalized 3D Porous Carbon as Anode for High-Performance Lithium-Ion Batteries

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Introduction

Anode material is a key component that determines the capacity, stability and performance of lithium-ion batteries. However, graphite, the most commonly used commercial anode material, has a low theoretical specific capacity (372 mAh g^{-1}) and limited rate capability. Thus, intense efforts have been devoted to searching for new carbon-based anode materials with enhanced Li-ion storage capacity. It has been determined that porous nanostructure and incorporation of heteroatoms are both desirable for excellent Li^+-ion storage performance of the carbon-based anode materials.[1] Herein, we report a temple-free method to synthesize functionalized 3D porous carbon (3DPC) by chemical activation of polypyrrole (PPy) microsheets with KOH. The as-obtained 3DPC shows large surface area, high-level N, O contents, and demonstrates outstanding rate and cycling performances as anode for lithium ion batteries.

Experimental

PPy microsheets were synthesized by a modified oxidative template assembly route. Typically, cetrimonium bromide was dissolved into HCl solution under ice bath, and then ammonium persulfate was added. After being ultrasonically treated for 4 h and cooled down to 0−5 °C, pyrrole monomer was added into the as-formed reactive template solution. The reaction was carried out at 0-5 °C for 24 h. A black precipitate (PPy microsheets) was obtained. Functionalized 3DPC was synthesized by chemical activation of the as-obtained PPy microsheets. A mixture of KOH and PPy was heated up to 700 °C at a heating rate of 3 °C min^{-1} and kept for 2 h under nitrogen atmosphere. The activated mixture was then washed with 1 mol L^{-1} HCl solution and deionized water till the filtrate became neutral. The sample was finally dried overnight at 80 °C in an oven. The electrochemical performance of the porous 3DPC was measured with 2032 coin cells. Li metal was used as anode, 1 mol L^{-1} $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as electrolyte, and Celgard 2300 as separator. The working electrode was made of 3DPC (85 wt%), super P (5 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) slurry coated onto a copper foil substrate.

Results and Discussion

After carbonize PPy precursor under severe activation conditions (KOH/PPy = 5), the sheet-like microstructures (**Fig. 1a**) were totally destroyed and a sponge-like porous carbon was obtained, which shows 3D interconnected structures (**Fig. 1b**). Beside the macropores in the range of 200−500 nm, 3DPC also processes uniform micropores below 2 nm and mesopores about 10−20 nm (**Fig. 1c,d**). Such a pore size distribution is desirable for various energy conversion and storage applications.

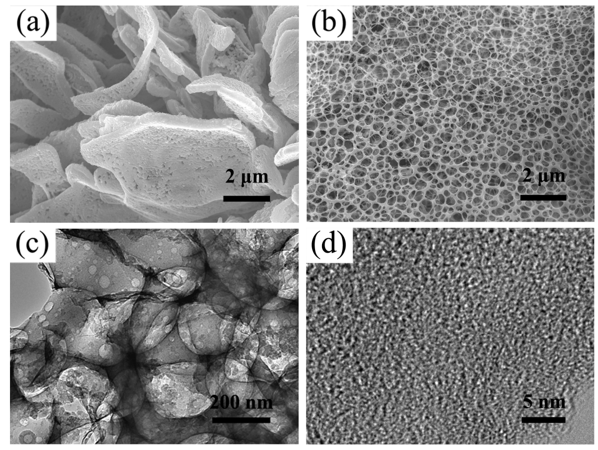

Figure 1. SEM images of (a) PPy microsheets and (b) 3DPC; (c) TEM and (d) HRTEM images of 3DPC.

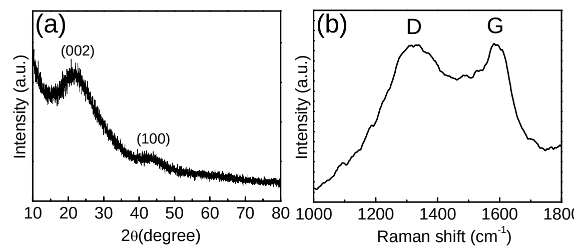

Figure 2. (a) XRD pattern and (b) Raman spectrum of 3DPC.

XRD pattern of 3DPC (**Fig. 2a**) shows two broad and low intensity peaks located at about 24º and 43º, suggesting that 3DPC possesses low degree of graphitization, which is also confirmed by Raman spectrum (**Fig. 2b**) and HRTEM.

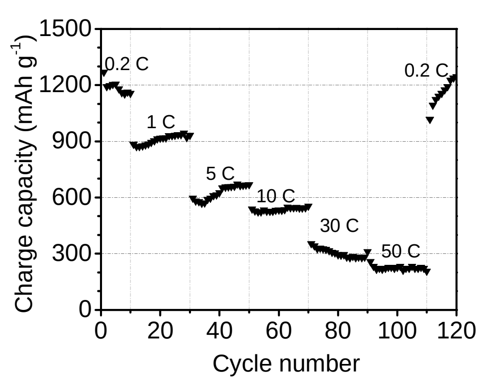

Figure 3. Charge capacity of 3DPC over cycling at different rates between 0.01 − 3.0 V *vs.* Li^+/Li.

As anode materials for lithium ion batteries, 3DPC shows high Li^+-ion storage and excellent cycling stability even at very high rate (**Fig. 3**). The charge capacities are 1268, 944, 668, 553, 354, and 259 mAh g^{-1} at 0.2, 1, 5, 10, 30 and 50 C, respectively.

The obtained 3DPC can also exhibit excellent performance when it is used as electrode material for supercapacitor. What's more, we believe that it may also be applicable for Li-S batteries, catalysis supports, gas separation, water purification, and so on.

References

[1] L. Qie, W. M. Chen, Z. H. Wang, Q. G. Shao, X. Li, L. X. Yuan, X. L. Hu, W. X. Zhang, Y. H. Huang, Adv. Mater. 24 (2012) 2047-2050.