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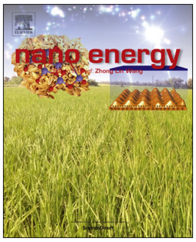

COMMUNICATION

Hard carbon nanoparticles as high-capacity, high-stability anodic materials for Na-ion batteries

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Abstract
Hard carbon nanoparticles (HCNP) were synthesized by the pyrolysis of a polyaniline precursor. The measured Na^+ cation diffusion coefficient (10^{-13}-10^{-15} cm^2 s^{-1}) in the HCNP obtained at 1150 °C is two orders of magnitude lower than that of Li^+ in graphite (10^{-10}-10^{-13} cm^2 s^{-1}), indicating that reducing the carbon particle size is very important for improving electrochemical performance. These measurements also enable a clear visualization of the stepwise reaction phases and rate changes which occur throughout the insertion/extraction processes in HCNP, The electrochemical measurements also show that the nano-sized HCNP obtained at 1150 °C exhibited higher practical capacity at voltages lower than 1.2 V (vs. Na/Na^+), as well as a prolonged cycling stability, which is attributed to an optimum spacing of 0.366 nm between the graphitic layers and the nano particular size resulting in a low-barrier Na^+ cation insertion. These results suggest that HCNP is a very promising high-capacity/stability anode for low cost sodium-ion batteries (SIBs).

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Introduction

Large scale electrical energy storage (EES) requires the supporting battery systems not only to have a sufficient large storage capacity, but also to be cost-effective and ideally environmentally benign [1,2]. Utilization of Li-ion batteries (LIBs) for EES applications may be limited by a constraint on the global lithium availability [3]. In contrast, the high abundance and low environmental impact for sodium production make Na-ion batteries (SIBs) an attractive alternative [4]. The potential of room temperature rechargeable SIBs stimulated active research on the optimization of relevant cell chemistries through the exploration of the underlying factors limiting SIB performance. The more active chemical reactivity of Na metal and larger ionic diameter relative to Li metal have been identified as critical bottlenecks in SIB development. Controlling the Na reactivity requires strict control of both the moisture and oxygen content in the experimental environment. The 40% larger radius of Na^+ cations relative to Li^+ cations leads to higher Na^+ stability in the rigid lattices of electrode materials [5]. Consequently, the insertion and extraction of Na^+ cations can induce large stress changes in the host materials, causing rapid collapse of the lattice structures and therefore poor cycling stability. In addition, the diffusion of the large Na^+ cations within lattices is sluggish, resulting in poor electrochemical utilization and rate capability [6]. These factors have seriously hindered the development of SIBs over the last two decades.

One solution proposed recently for overcoming these intrinsic difficulties in the developing of efficient electrode materials for SIBs through the use of nanotechnology. For cathode active materials [3,7-14], we [7] reported that a single crystalline $Na_4Mn_9O_{18}$ nanowire could offer a highly reversible capacity of 128 mAh g^{-1} during the first charge/discharge cycle (at a 0.1 C rate) and exhibited unprecedented cyclability (77% capacity retention after 1000 cycles at a 0.5 C rate). Yang's group [8] reported that a $Na_4Fe(CN)_6$/C nanocomposite electrode could deliver 90 mAh g^{-1} at a high potential of 3.4 V (vs. Na/Na^+) and exhibited an excellent cycling stability with 88% capacity retention after 500 cycles. Carbon-coated nanosized NASICON-type $Na_3V_2(PO_4)_3$ was found to exhibit an ultrafast rate capability [9,10,15,16]. According to Fang et al. [15], the $Na_3V_2(PO_4)_3$/C composite could exhibit superior electrochemical performance of both ultra-high rate capability (38 mAh g^{-1} at 500 C) and ultra-long cycling lifespan (20,000 cycles at 30 C), which exceeds most of the electrodes used in rechargeable batteries.

For anode active materials, Wang et al. [17] reported a layered P2-$Na_{0.66}[Li_{0.22}Ti_{0.78}]O_2$ material which exhibited zero-strain characteristics during Na^+ cation insertion/extraction. Wu et al. [18] reported a highly stable Sb-C nanofiber alloy anode which had a large initial reversible capacity of 504 mAh g^{-1} at a 200 mA g^{-1} rate and a 90% capacity retention after 400 cycles. Qu et al. [19] reported a SnS_2-RGO composite anode which demonstrated a superior reversible capacity of 630 mAh g^{-1} at a 0.2 A g^{-1} rate resulting from a combined electrochemical conversion and alloying/dealloying mechanism, and good cyclability (500 mAh g^{-1} at a 1 A g^{-1} rate for 400 cycles). While offering excellent electrochemical performance, these materials are expensive for practical applications. In contrast, carbonaceous materials are more economically viable and abundant [20,21]. Several hard carbons have been reported to have a favorable Na^+ cation storage capacity (250-300 mAh g^{-1}) and good rate capability [22-26]. For instance, Ding et al. [25] reported a highly ordered pseudographitic carbon with an intergraphene spacing of 0.388 nm derived from a biomass precursor which exhibited highly reversible capacity of 298 mAh g^{-1} (after 10 cycles at 50 mA g^{-1}) and a high rate capability (66 mAh g^{-1} at a 5 A g^{-1} rate). However, achieving a prolonged cycling stability for hard carbon anodes for Na^+ storage, in particular for high charge-discharge rates, has remained a difficult challenge [27]. Through a combined experimental and theoretical study, we have demonstrated facile Na^+ cation uptake and release in a carbon with a spacing of greater than 0.37 nm between the graphitic sheets [23]. In that study, hollow carbon nanowires synthesized by the direct pyrolyzation of polyaniline showed an initial reversible capacity of 251 mAh g^{-1} and capacity retention of 82.2% at a 50 mA g^{-1} rate after 400 cycles. Nevertheless, a further optimization of the synthesis procedure through a detailed study of the influence of the structure of the polyaniline precursor and the carbonization temperature on the Na^+ cation storage properties is desired.

Herein, we report the refined method for fabrication of hard carbon nanoparticles (HCNPs) from polyaniline. The spectroscopic characterization show that HCNPs obtained at 1150 °C have the largest interlayer distance between the graphite layers and consist of large graphitic clusters, thus displaying an optimum electrochemical performance. The measurements of the Na^+ cations diffusion variation throughout the insertion/extraction processes in HCNP by electrochemical impedance spectroscopy (EIS) show lower Na^+ diffusion rate than that of Li^+ in graphite highlighting the importance of nanostructuring.

Materials and methods

Material preparation

Polyaniline (PANI) was synthesized by a chemical oxidative method: 0.9 mL of aniline was dissolved in 80 mL of 1.5 mol L^{-1} HCl by stirring. 2.28 g of $(NH_4)_2S_2O_8$ was dissolved in 20 mL of deionized water and then quickly added to the aniline solution. The mixture was stirred at room temperature for 12 h. The resulting PANI solid product was washed with deionized water until the filtrate became both colorless and pH neutral and the solid was then dried at 50 °C overnight. Finally, the PANI was calcinated at 800, 1000 and 1150 °C for 6 h in an N_2 atmosphere to obtain the target hard carbon nanoparticles (HCNP-800, HCNP-1000 and HCNP-1150, respectively).

Structural characterization

Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM) experiments were performed on a FEI Helios Nanolab dual-beam,