Synthesis and electrochemical properties of artificial graphite as an anode for high-performance lithium-ion batteries

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ABSTRACT
Artificial graphite containing abundant in situ grown onion-like carbon hollow nanostructures (OCHNs) was prepared from nickel nanoparticles doped pitch and natural graphite flakes by hot-pressing sintering method. Galvanostatic discharge–charge tests indicate that the synthetic graphite with abundant OCHNs exhibits a high specific capacity of 460 mA h g⁻¹ at 20 mA g⁻¹ as well as an excellent rate capability, with a reversible capacity of 220 mA h g⁻¹ at 1 A g⁻¹. Besides the advantages of common graphite anode materials, these superiorities make synthetic graphite a very promising anode for high-performance lithium-ion batteries.

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Lithium-ion batteries (LIB) are key components of portable equipments, e.g., it can be used on hybrid electric vehicles and power backup that require rechargeable batteries with combination of high energy density and high charge/discharge rate [1]. Nowadays, graphitic carbon is the foremost commercial anode for LIB due to their advantages in terms of long discharge/charge voltage platform, well cycling performance and low cost. As a result, it has become the first choice for the high-performance lithium-ion batteries (HPLIBs). However, the traditional graphitic carbon cannot meet the increasing demands for HPLIBs due to the limits of its own structure feature [2] and the theoretical capacity of 372 mA h g⁻¹.

Recently, higher lithium storage capacities have been achieved over some carbon materials through lithium storage in micropores, at defects or as a result of nanosize effects [3]. Meanwhile, the carbon material with high graphitization shows good electrical conductivity, which is essential for providing stable high rate performance. For instance, Zhou et al. presented a hollow carbon cage with graphene shells over which a high reversible capacity of 1135 mA h g⁻¹ at 50 mA g⁻¹ and an excellent charge/discharge rate of 163 mA h g⁻¹ at 15 A g⁻¹ is obtained [3]. However, most of these anode materials are non-graphitic carbon and suffer from the disadvantages of voltage hysteresis and big initial irreversible capacity, which limit their practical application.

Therefore, if it is possible to introduce hollow nanostructures into a graphite material, the anode material will have the advantages of both graphitic carbon and nanoporous carbon. The reversible capacity and rate properties of graphitic carbon will be obviously improved. Hollow carbon nanostructures (HCNs), such as the carbon nano-onions [4] and hollow carbon cages can be prepared by chemical reaction [4] and transition-metal catalytic graphitization [3,5]. Meanwhile, the nanoscale transition metal doped carbon could enhance the electrical conductivity of electrode and thus obviously promote the rate performance [6]. From this point of view, we intended to utilize the nickel nanoparticle-doped pitch (NNDP) [7] and natural graphite (NG) flakes as the precursors to fabricate the synthetic graphite by hot-pressing sintering method. The product might contain the structure of both HCNs and nickel nanoparticles, simultaneously, which might then enhance the reversible capacity and rate capability.

The typical preparation process can be divided into two steps: firstly, the NG and NNDP were mixed with a weight pro-
portion of 75:25; secondly, the mixture was compacted in a graphite mold and pressed uniaxially with a hot-pressing sintering device to prepare the resulting block. The hot-pressing temperature and pressure was 2700 °C and 25 MPa, respectively. The NNDF had undergone the softening, bonding with NG, carbonization and graphitization during the raising of temperature. The prepared graphite was denoted as NiP + G. Both NiP + G and NG were ground and sifted to approximately 325 mesh (average diameters are around 18.45 μm) to be used as active materials to measure their electrochemical properties. As illustrated by ICP analysis, the Ni content in NNDF and NiP + G is 9.44% and 2.54%, respectively, which suggested that the nickel still remained in the system after the formation of NiP + G.

The representative microstructure of the as-prepared product is presented in Fig. 1a, b, and f. Abundant and widespread HCNs in the samples can be found and the HCNs show polyhedral morphology, which are consisting of concentric graphite sheets, somewhat like an onion structure. Herein, this kind of HCNs is noted as onion-like carbon hollow nanostructures (OCHNs). The whole generation process of OCHNs could be described as semi-solid encapsulated nickel nanoparticles diffused, migrated and escaped from the carbon shells by the heat treatment, which is similar to the reference [5]. However, the differences are that OCHNs is the polyhedral morphology and the average diameter is around 25 nm, which may be derived from the effect of the pressure during the hot-pressing process. These OCHNs are closely integrated with NG by pitch-based graphitic carbon (Fig. 1c), which could improve the transfer of lithium-ion. The inter-layer spacing derived from the shell of OCHNs (Fig. 1d) shows that the graphite plane is apparent, indicating the graphene layers developed well in the shells. The corresponding SAED pattern (Fig. 1e) according to the red circle region of Fig. 1b revealed that the graphitization degree of the OCHNs was lower than that of NG but higher than that of amorphous carbon. The

Fig. 1 – High revolution transmission electron microscope images of the artificial graphite. (d) Magnified image of the red rectangle region of (c). (e) Selected area electron diffraction (SAED) of the red circle region of (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
image in Fig. 1f shows that the spherical particles are surrounded by OCHNs. Fig. 1g shows that numerous nanopores are formed around the OCHNs and the spherical particle is located in the center of the OCHN. The spherical particles should be nickel nanoparticles, which is further verified by the XRD analysis (ESI Fig. S1). Fig. 1f and g directly confirm the transfer of small nickel nanoparticle and the formation of OCHNs and large nickel nanoparticles. In addition, defects which may provide a channel for nickel diffusing were also observed in Fig. 1c and g. Therefore, the obtained synthetic graphite is made up of NG flakes, graphitic carbon, OCHNs and nickel nanoparticles. It is well known that the low-temperature nitrogen adsorption method could not measure the BET surface area of closed pore. Although the artificial graphite possesses abundant OCHNs, its BET surface area is closed to that of NG (around 4.65 m$^2$/g), which might be due to the OCHNs is closed pore nanostructure and disperse in the graphite matrix. Meanwhile, the electrical conductivity of NiP + G is similar to that of NG (ESI Table S1), which is demonstrated by impedance analysis (ESI Fig. S2).

Typical discharge/charge curves of the NiP + G (Fig. 2a) and NG at the first cycle (Fig. 2b) and the differential capacitance plots of the second discharge/charge cycle (Fig. 2c) are shown in Fig. 2. The reversible capacity of NiP + G is 425.8 mA h g$^{-1}$ at 50 mA g$^{-1}$ which is much higher than that of NG (305.9 mA h g$^{-1}$). At the same time, it is found that the first coulombic efficiency is 85.9% and 67.3% for NiP + G and NG, respectively, which demonstrate that the coulombic efficiency of synthetic graphite is enhanced due to the fact that the pitch-based carbon covered the active sites of NG. It can be observed that the electrochemical behavior of the NiP + G is similar to that of NG. The discharge curves exhibits one short potential plateau at 0.21 V and two long potential plateaus at 0.13 and 0.08 V (Fig. 2a, b). On the charge curve, the three potential plateaus occur at around 0.1, 0.14 and 0.23 V. However, the low voltage plateau of NiP + G is longer than that of NG, which means that more lithium was stored in OCHNs. It can be seen from Fig. 2c that the anode peak of NiP + G right shifted comparing with that of NG, demonstrating that it has safer potential plateaus. Meanwhile, the left shift of the cathodic peak of NiP + G comparing with that of NG, revealed that it could have higher operating voltage.

The galvanostatic discharge–charge cycling of the cell with NiP + G was carried out in the potential region of 0.005–3.0 V at the current densities from 20 to 1000 mA g$^{-1}$ (Fig. 3). The cell (NiP + G) was firstly cycled at 50 mA g$^{-1}$ for five times, under which a stable specific capacity of 425 mA h g$^{-1}$ was obtained. After increasing the current density to 400 mA g$^{-1}$, the reversible capacity was 308 mA h g$^{-1}$ which was still higher than that of NG (295 mA h g$^{-1}$) at the current density of 50 mA g$^{-1}$. Even at a high current density of 1 A g$^{-1}$, the specific capacity is still 220 mA h g$^{-1}$, which was much higher than that of NG and Graphitized mesophase carbon microspheres [8], suggesting this material could satisfy the demand of high-rate. A specific capacity of 370 mA h g$^{-1}$ was achieved at 20 mA g$^{-1}$ for NG, which is nearly the same as the theoretical capacity of 372 mA h g$^{-1}$. Meanwhile, a higher reversible capacity of 460 mA h g$^{-1}$ was obtained at 20 mA g$^{-1}$ for NiP + G. It is further proved that large amount of lithium ions could be stored in such a structure as OCHNs besides graphene layers. This result should be attributed to the high nanoporosity (OCHNs) and nickel doping structure, which
naturally leads to an increase in capacity and good electron transfer. Therefore, this synthetic graphite can stand high rate charge/discharge and thus be promising for commercial utilization.

In conclusion, the reversible capacity and rate capability of synthetic graphite had been improved obviously by the introduction of abundant OCHNs and Ni nanoparticles. The reversible capacity could reach 460 mA h g⁻¹. What is the most important is that, as one kind of synthetic graphite, it exhibited an excellent charge/discharge rate of 220 mA h g⁻¹ at 1 A g⁻¹. In addition to the advantages of commercial graphite, the superior electrochemical properties make it a promising anode material for HPLIBs.

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**Appendix A. Supplementary data**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.07.089.

**REFERENCES**


