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} cm² 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} cm² 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).

Keywords

Hard carbon; Ionic diffusion coefficient; Electrochemical impedance; Anode; Na-ion battery

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 $\text{Na}_4\text{Mn}_9\text{O}_{18}$ nanowire could offer a highly reversible capacity of 128 mAh g^{-1} during the first charge/discharge cycle (at a 0.1C rate) and exhibited unprecedented cyclability (77% capacity retention after 1000 cycles at a 0.5C rate). Yang's group [8] reported that a $\text{Na}_4\text{Fe}(\text{CN})_6/\text{C}$ 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 $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ was found to exhibit an ultrafast rate capability [9, 10, 15, 16]. According to Fang et al. [15], the $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ composite could exhibit superior electrochemical performance of both ultra-high rate capability (38 mAh g^{-1} at 500C) and ultra-long cycling lifespan (20000 cycles at 30C), which exceeds most of the electrodes used in rechargeable batteries.

For anode active materials, Wang et al. [17] reported a layered $\text{P2-Na}_{0.66}[\text{Li}_{0.22}\text{Ti}_{0.78}]\text{O}_2$ 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 $\text{SnS}_2\text{-RGO}$ 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 $^{\circ}\text{C}$ 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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, focused ion beam/scanning electron microscope (FIB/SEM) and a JEOL-2010 high-resolution electron microscope. X-ray diffraction (XRD) measurements were conducted on a Philips Xpert X-ray diffractometer using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$).

N₂ adsorption/desorption isotherms for surface area and pore analyses were measured with a Quantachrome autosorb, automated gas sorption system.

Electrochemical measurements

The HCNP-based anodes were prepared by mixing 80 wt% HCNP powder, 10 wt% Super P carbon black, and 10 wt% polyvinylidene difluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone (NMP) to form slurry. The slurry was pasted on Cu foil current collectors and the NMP solvent was evaporated. Electrochemical tests were performed with 2035 coin cells having Na metal as both the counter- and reference electrodes. The electrolyte was 1 M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:2 by wt.), and the separator was a microporous membrane (Celgard 2135). The cells were assembled in an Ar-filled glove box. The galvanostatic charge-discharge tests were conducted at a voltage interval of 0-1.2 V (vs. Na/Na⁺) with a BT-2000 Arbin battery testing system. Cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.1 mV s⁻¹ using a SI 1287 electrochemical interface (Solartron). To obtain the diffusion coefficient of the Na⁺ cations within the hard carbon anodes, EIS measurements were conducted with a frequency response analyzer (Solartron, SI 1260) in the frequency range 100 kHz to 3 mHz with an AC signal amplitude of 10 mV. The cells for the EIS measurements were cycled galvanostatically twice and were charged (or discharged) at a 30 mA g⁻¹ rate for 1 h. After the cells relaxed to equilibrium potentials (i.e., open circuit voltage (OCV) condition) for 3 h, the impedance response was measured.

Results and discussion

The polyaniline precursor was readily synthesized by a chemical oxidative method (see experimental section). It follows from the SEM data that the precursor has a uniform nanoparticle morphology with particles diameters around 70-100 nm (Fig. 1a). After being pyrolyzed at 1150 °C for 6 h in an N₂ atmosphere, the resulting hard carbon material (HCNP-1150) shows no obvious morphological modifications relative to its precursor (Fig. 1b and c). The HRTEM image of an individual carbon nanoparticle shows that it has regions of stacked graphite sheets, as well as amorphous regions (Fig. 1d). The average distance between the graphite sheets is about 0.37 nm. Considerable numbers of nanovoids, presumably formed by the gas escape during the pyrolyzation process, are evident in the amorphous regions.

Fig. 2a compares the XRD patterns of the pristine polyaniline, HCNP-800, -1000 and -1150 materials. The pristine PANI exhibits a broad peak around $2\theta = 25^\circ$, indicating an amorphous morphology [23, 28, 29]. All of the carbon products, in contrast, have two broad peaks at 25° and 44° , corresponding to the (002) diffraction of the graphitic layer-by-layer structure and the (101) diffraction of graphite, respectively. Notably, the locations of the (002) peaks for HCNP-800, -1000, -1150 are at 25.39° , 25.03° and 24.34° , respectively, indicating that a slightly negative shift occurs with increasing pyrolysis temperature. According to the positions of the (002) peaks, the spacing between the stacked graphite sheets in HCNP-800, -1000, -1150 are calculated to be 0.350, 0.355 and 0.366 nm, respectively. The value for HCNP-1150 is in good agreement with that from

the HRTEM data in Fig. 1d. At first glance, the increase in the spacing between the graphite sheets with increasing processing temperature may seem unusual, but this may originate from nitrogen atom intercalation in-between the graphite sheets during the pyrolyzation at elevated temperature, as reported by other authors [30, 31] and as schematically shown in Fig. 2b. The elemental analysis demonstrates that the residual contents of nitrogen atoms in the resulting carbon materials gradually decrease with increased processing temperature (Tab. 1), suggesting that nitrogen atoms are removed from the graphite sheets. It is possible that part of the dissociated nitrogen atoms can reside in between the graphite sheets so as to expand their spacings. The presence of nitrogen atoms in-between the graphite layers can be confirmed by XPS measurements. N1s XPS data for the pristine PANI and the pyrolyzed carbon obtained at different temperatures are shown in Fig. 3 and listed in Tab. 1. The N1s peak of the pristine PANI (Fig. 3a) can be deconvoluted into two peaks arising from nitrogen in two different environments. The peak positioned at lower binding energy (399.3 eV) is associated with the uncharged amine sites, while the other peak located at a higher binding energy (400.3 eV) is attributed to imine cationic radicals [32]. The XPS data in the N1s region for the pyrolyzed carbon are different (Fig. 3b, c and d). The spectrum for HCNP-800 splits into two peaks and envelopes the contributions from three components after fitting (Fig. 3b). The peak centered at 398.2 eV may be attributed to pyridinic-nitrogen (N-6) in the phenazine heterocyclic structure formed in the early stage of carbonization. The second peak positioned at 400.8 eV may be assigned to the quaternary (N-Q) nitrogen species doped at the edges of or in-between the graphite layers [33]. The last peak located at the highest binding energy (401.4 eV) implies a more positively charged nitrogen site than

for the imine cationic radicals in pristine PANI (Fig. 3a), which possibly results from the N-O binding in the surface layer due to air exposure [34]. The fitted peak around 398 eV decreases in intensity with an elevation in pyrolysis temperature and disappears completely at 1150 °C, suggesting an enhanced denitrification and graphitization. However, it is possible that a small portion of the nitrogen groups removed from the condensed carbon rings may reside in-between the graphite layers (as shown in Fig. 2b), resulting in increased interlayer distances, as can be corroborated from the remaining strong peak around 401 eV. The shift towards higher binding energy for the peaks assigned to the N-Q (~401 eV) and N-O (~402 eV) binding implies that a slight change in the chemical environment occurs with increased temperature.

Electrochemical impedance spectroscopy (EIS) was performed to understand the Na⁺ cation diffusion properties within HCNP-1150 electrode. Fig. 4a and b show the experimental impedance spectra measured at various potentials during discharge and charge, respectively. These data show that the electrochemical resistance of the electrode tends to decrease with the depth of discharge (Fig. 4a), while it increases with the depth of charge (Fig. 4b). This phenomenon probably arises from the increased electric conductivity of the sodium-carbon material with sodiation process, which facilitates the electrochemical reaction kinetics. Fig. 4c shows a typical Nyquist plot for the HCNP-1150 electrode obtained during charging at 0.11 V. It displays two depressed semicircles in the high and medium frequency regions and a monotonic dependence in the low frequency region. It can be presumed that the semicircles in the high and medium frequency regions are attributed to the surface film resistance between the electrode and

electrolyte and to the charge transfer resistance, respectively, while the linear region corresponds to the Warburg diffusion of Na^+ cations in the bulk carbon.

Fig. 4d shows a linear relationship between the Z' ($-Z''$) and the square root of the frequency ($\omega^{-1/2}$) in the low frequency Warburg region of Fig. 4c. Since the Na^+ cation diffusion coefficient (D_{Na^+}) can be written as [7, 35-37]:

$$D_{\text{Na}^+} = 1/2 \left[\left(\frac{V_m}{FSA_w} \right) \frac{dE}{dx} \right] \quad (1)$$

based upon the EIS response, where V_m is the molar volume of carbon (C_6) ($6 \times 5.75 \text{ cm}^3 \text{ mol}^{-1}$) calculated using the XRD density (2.086 g cm^{-3} ; hexagonal crystal system with lattice vectors $a = 2.45 \text{ \AA}$, $c = 7.32 \text{ \AA}$); F is the Faraday constant ($96,486 \text{ C mol}^{-1}$); S is the contact area between electrolyte and electrode material (approximately taken as the BET surface area of HCNP-1150 equal to $23.5 \text{ m}^2 \text{ g}^{-1}$); A_w is the Warburg coefficient, which was determined as the average values of the slope from the Z' and $-Z''$ vs. $\omega^{-1/2}$ plots (ω is the angular frequency) shown in Fig. 4d; and (dE/dx) is the differential of the galvanostatic titration curve. D_{Na^+} at different OCV values during charge and discharge can be calculated using the Eq. 1 (Fig. 5). D_{Na^+} demonstrates a similar variation with OCV during the Na^+ cation insertion and extraction processes and exhibits a broad peak around 0.6 and 0.1 V followed by sharp decrease below 0.1 V. This $\log D$ vs. E curve at low potential region is very similar to that observed during Li^+ cation diffusion in graphite, [38, 39] suggesting a phase transition process from graphitic carbon to NaC_x structure (that is, forming sodium-graphite intercalation compounds (Na-GICs). The slight increase of D_{Na^+} nearby 0 V is probably due to the highly attractive interactions between the inserted Na ions in the single-phase Na-GICs, similar to Li^+ cation insertion in graphite near 0 V as reported in previous literatures. [32, 40, 41] In the voltage range

of 0–1.0 V, D_{Na^+} is equal to 10^{-13} – 10^{-15} $\text{cm}^2 \text{ s}^{-1}$, which is two orders of magnitude lower than that of D_{Li^+} in graphite (10^{-10} – 10^{-13} $\text{cm}^2 \text{ s}^{-1}$), reflecting, among other factors, the larger diameter of the Na^+ cations.

Fig. 6a displays the initial discharge-charge profiles of the HCNP electrodes. The electrodes were tested in the potential range between 0–1.2 V (vs. Na/Na^+) at a constant current rate of 50 mA g^{-1} (0.2 C). These data demonstrate that the HCNP-800, -1000 and -1150 electrodes have an uptake discharge capacity of 628, 556 and 523 mAh g^{-1} and offer a reversible charge capacity of 230, 266 and 270 mAh g^{-1} , respectively. There is a clear trend of enhanced electrochemical performance of the HCNPs manifested by the decrease in the initial irreversible capacity loss and the increase in the reversible capacity with the elevation in the heat treatment temperature. It should be noted that the improvement is not very significant for the 1000 to 1150 $^{\circ}\text{C}$ temperature range. All of the HCNPs undergo irreversible reactions in the potential range of 1.5–0.4 V (vs. Na/Na^+) giving rise to a notable irreversible capacity loss. Similar to the irreversible reactions which occur for LIB electrodes, this irreversible capacity loss is mainly due to decomposition of the electrolyte components on the active sites on the electrode surface and the formation of a solid-electrolyte interphase (SEI) film on the carbon surface. Furthermore, it can be observed that the discharge curves have two distinct regions: a relatively flat plateau around 0.1 V and a sloping discharge above 0.2 V (Fig. 6a). The plateau at lower potential is attributed to the Na^+ cation insertion-extraction in the interlayers of the graphite sheets similar to that for Li^+ cation insertion-extraction in graphite. The slope in 1.2–0.2 V voltage range may be attributable to charge transfer on the surface of the small graphitic clusters, in other words, to the adsorption of Na^+ ions on

the surficial active sites of the carbon. The charge-discharge curves are in good agreement with those for hollow nanowire shaped carbon reported previously by our group [23]. Another phenomenon that should be noted is that the potential plateau elongates with increasing HCNP carbonization temperature (Fig. 6a), suggesting that an increased fraction of the charge capacity is due to Na^+ cation insertion/extraction between the graphitic sheets. This phenomenon was also observed in pseudographitic carbon nanosheets [25]. As the carbonization temperature increases, the ordered graphitic domains in the carbon will grow, thus providing more Na^+ cation insertion sites. Our previous theoretical simulation of the energy cost for Na^+ cation insertion into carbon indicates that the enlargement of the spacing between the graphitic layers is beneficial for Na^+ cation insertion. Thus, Na^+ cation insertion into the graphitic nanocrystallites is facilitated in HCNP-1150 which has the largest spacing between the graphitic layers. It is noteworthy that the charge cutoff voltage for the HCNP electrode is set to 1.2 V, which means that the capacity achieved is in the optimum voltage range for full SIBs. Therefore, the useful capacity of the HCNP active material is one of the highest reported to date. Although some disordered hard carbon might have high Na storage capacity as reported higher than 300 mAh g^{-1} [42], they display a slop potential curve at a wide potential range up to 3 V similar to the insertion of Li into disordered carbon. In fact, we need anode materials with low average potential to improve the energy density of batteries. So, hard carbons with high graphitic degree and large lattice distance are more practical due to the increased reversible Na storage capacity at the low potential region (Fig 6a).

Fig. 6b shows the CV curves for the HCNP-1150 electrode cycled at a scan rate of 0.1 mV s^{-1} . Two small reduction peaks at 1.1 and 0.5 V (vs. Na/Na^+) appear only in the first

cathodic scan suggesting that irreversible reactions occur. Moreover, a pair of sharp redox peaks in the low potential region is related to the reversible insertion/extraction of Na^+ cations between the graphitic layers, and a pair of weak humps at 0.2–1.0 V are attributed to the charge transfer occurring on the surfaces of the small graphitic clusters. In the subsequent cycles, the CV curves almost overlap, illustrating a high Na^+ cation insertion/extraction reversibility. Interestingly, the shape of the CV curves correlate well with the variation in the Na^+ cation diffusion coefficient shown in Fig. 5, further highlighting the differences in Na^+ cation diffusion mechanism in different voltage regimes.

Fig. 6c shows the cycling performance of the HCNP electrodes at a constant current density of 50 mA g^{-1} . The HCNP-800, -1000 and -1150 electrodes exhibited a capacity loss of 0.56%, 0.17% and 0.05% per cycle, respectively. HCNP-1150 has the highest cyclability, as well as reversible capacity, due to the considerable fraction of crystalline graphite clusters and appropriate interlayer spacing for low-barrier Na^+ cation insertion. Even after 500 cycles, the HCNP-1150 electrode still maintains a high reversible capacity of 207 mAh g^{-1} , corresponding to a 77% capacity retention. However, the low initial coulombic efficiency of 51.6% is still an issue that needs to be addressed prior to practical applications. Although the surface area of HCNP-1150 is 30% smaller than that of our previously reported hollow carbon nanowires [23], the initial coulombic efficiency only shows a 1.2% improvement, indicating other factors, such as the modification of the electrolyte, are responsible for this effect. Nevertheless, after the initial cycle, the coulombic efficiency of the electrode increases to ~96% at the fifth cycle and then to approximately ~99% after 10 cycles.

Fig. 6d displays the cycling rate behavior of the HCNP-1150 electrode. The electrode delivers reversible capacities of 275, 266, 236, 181, 72 and 45 mAh g⁻¹ at a current density of 25 (0.1C), 50 (0.2 C), 125 (0.5 C), 250 (1 C), 1250 (5 C) and 2500 (10 C) mA g⁻¹, respectively. When the rate is reset to 50 mA g⁻¹, the electrode capacity recovers to 260 mAh g⁻¹ (i.e., retains 82% of the original capacity) after 200 cycles, which indicates both a high rate capability and excellent tolerance of the material to rapid Na⁺ cation insertion and extraction. However, the rate capability of the present HCNP-1150 is inferior to that of the hollow carbon nanowires reported previously [23], probably because of slower electron transfer.

Conclusions

Hard carbon nanoparticles were prepared by pyrolyzing a polyaniline precursor. The carbon material obtained at 1150 °C shows an interlayer distance of 0.366 nm between the graphitic layers, sufficient for low-barrier Na⁺ cation insertion and extraction. Such an interlayer distance is attributed to a residual nitrogen atom incorporation in-between the graphitic layers. The Na⁺ cations diffusion variation throughout the insertion/extraction processes in HCNP was first measured, which provides helpful insight into the stepwise Na⁺ cation insertion/extraction phases and rates in hard carbon materials. The HCNP-1150 electrode exhibits a high initial Na⁺ cation storage capacity (270 mAh g⁻¹ at a 50 mA g⁻¹ rate in the voltage range of 0–1.2 V), good cycling stability (77% capacity retention over 500 cycles), and high rate capability (45 mAh g⁻¹ at 2500 mA g⁻¹). Significantly, the work presented here provides a new method for the synthesis of promising anode material for cost-efficient SIBs.

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Table 1 Results of the BET data, elemental compositions and binding energies of N1s component peaks for PANI and HCNPs.

	BET/m ² g ⁻¹	Pore Volume/cc g ⁻¹	Elemental analysis / wt.%			XPS analysis / eV		
			C	N	H	Component 1	Component 2	Component 3
PANI	30.3	0.338	60.07	11.1	5.1	399.3	400.3	--
HCNP-800	18.5	0.156	78.36	1.4	6.6	398.2	400.8	401.4
HCNP-1000	21.0	0.151	82.95	1.2	2.6	398.1	400.9	401.8
HCNP-1150	23.5	0.139	85.60	1.0	1.7	--	401.1	402.3

Figure captions:

Fig. 1 (a, b) SEM images of PANI and HCNP-1150. (c) TEM image of HCNP-1150. (d) High-Resolution TEM (HRTEM) image of HCNP-1150.

Fig. 2 (a) XRD patterns of polyaniline and the HCNPs pyrolyzed at different temperatures. (b) Schematic illustration of the formation and structural characteristics of HCNP.

Fig. 3 N1s XPS spectra of (a) pristine PANI, (b) HCNP-800, (c) HCNP-1000 and (d) HCNP-1150.

Fig. 4 EIS results for HCNP-1150. Nyquist plots at various potentials during (a) discharge and (b) charge. (c) Nyquist plot and fitting curve using the equivalent circuit (inset in Fig. 4c). (d) Z' or $-Z''$ vs. $\omega^{-1/2}$ plot at 0.11 V during charge.

Fig. 5 Logarithm diffusion coefficient ($\log D$) vs. OCV plots at various potentials for HCNP-1150.

Fig. 6 Electrochemical characterization of the HCNPs as anode material for SIBs. (a) First discharge/charge profiles of HCNPs pyrolyzed at different temperatures between 0 and 1.2 V at a current density of 50 mA g^{-1} (0.2 C). (b) CV curves of the HCNP-1150 electrode between 0–2.5 V (vs. Na/Na⁺) at a potential sweep rate of 0.1 mV s^{-1} . (c) Cycling performance of the HCNP electrodes at a current density of 50 mA g^{-1} (0.2 C). (d) Cyclability rate of the HCNP-1150 electrode at different discharge/charge current densities of 25 (0.1 C), 50 (0.2 C), 125 (0.5 C), 250 (1 C), 1250 (5 C) and 2500 (10 C) mAh g⁻¹, respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

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MS Title: Hard Carbon Nanoparticles as High-capacity, High-stability Anodic Materials for Na-ion Batteries

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Graphical Abstract

Hard carbon nanoparticles (HCNPs) synthesized by the pyrolysis of a polyaniline precursor display an optimum electrochemical performance. Particularly, the first measurements of the Na cations diffusion variation throughout the insertion/extraction processes in HCNP provide helpful insight into the stepwise Na cation insertion/extraction phases and rates in hard carbon materials.