Nitrogen-doped porous carbon derived from bimetallic zeolitic imidazolate frameworks for electrochemical Li$^+$/Na$^+$ storage

Shuai Dong · Jiewu Cui · Dongbo Yu · Zhongnan Cao · Cuiping Yu · Yong Zhang · Yucheng Wu

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Abstract

Porous carbon is regarded as one of the most promising anode candidates for Li-ion battery and Na-ion battery, and the specific porous structure and heteroatom doping within porous carbon play a key role in the electrochemical performance. We herein demonstrate a series of nitrogen-doped porous carbon (NPC) by simply carbonizing bimetallic ZnCo-containing zeolitic imidazolate frameworks (ZnCo-ZIFs). The nitrogen content, specific surface area, and microstructure of prepared NPCs are balanced by adjusting the Zn$^{2+}$/Co$^{2+}$ molar ratio of ZnCo-ZIFs and carbonization process parameters. The optimized NPC derived from ZnCo-ZIFs delivers high specific capacity of 876.5 and 352.6 mA h g$^{-1}$ for Li$^+$ storage at 0.1 and 5 A g$^{-1}$, respectively. After repeating 500 cycles at a high current density of 1 A g$^{-1}$, it almost has no capacity loss. In addition, the electrode also shows a great promise for Na$^+$ storage. The excellent electrochemical Li$^+$/Na$^+$ storage performances could be attributed to the hierarchical porous structure, large specific surface area, and relatively high N-doping content.

Keywords Bimetallic zeolitic imidazolate frameworks · Nitrogen-doped porous carbon · Li-ion battery · Na-ion battery

Introduction

Li-ion batteries (LIBs) and Na-ion batteries (SIBs) are considered as promising representatives of a secondary battery system, which are widely applied in smart grids, portable electronics, and electrical vehicles [1, 2]. It is well known that the property of electrode materials is crucial to the electrochemical performance of batteries. Among the applied electrode materials, transition metal oxides, tin, silicon, and red phosphorus with high theoretical specific capacity are common anode materials for LIBs [3–11]. However, during the ion intercalation, these electrodes usually suffer from severe volume expansion and voltage lag, leading to massive irreversible capacity loss and poor stability, and thus hampering their practical application seriously [12, 13]. Different from LIBs, SIBs have much more sluggish electrochemical kinetics than LIBs, and the larger radius of Na$^+$ ions results in more rapid capacity fading and structural degradation, which sets higher demands on the electrodes [14–17]. For example, commercial graphite is available for LIBs but no longer suitable for SIBs, because the interplanar spacing of graphite (~0.34 nm) is smaller than the critical minimum spacing of 0.37 nm required for good Na$^+$ insertion properties [18]. Instead, porous carbon has been attracted more attention, which not only owns good electronic conductivity and stability, but also improves ion diffusion and volumetric strain [19–23]. In addition, rational pore distribution, high electrical conductivity, and heteroatom doping play positive roles in electrochemical performances [24–28]. Therefore, nanoporous carbon with optimized porous structure and heteroatom doping is expected to show more promise for electrochemical energy storage.

As a new type of porous crystal materials, metal–organic frameworks (MOFs), assembled by the coordination bonds between organic ligands and inorganic metal ions/clusters,
have developed rapidly in recent years [29–31]. Due to the unique structural characteristics, high porosity, and specific surface area, MOFs and their derived materials emerged as outstanding candidates in energy storage, gas separation, and nanoreactor, etc. [32–37]. Particularly, ZIFs such as ZIF-8 and ZIF-67 have been extensively studied for energy applications. Benefiting from the N-containing imidazole rings within ZIFs, the nanoporous carbon derived from ZIFs can be self-doped by N heteroatoms after a simple carbonization process [38]. At a properly controlled carbonization temperature, nitrogen-doped porous carbon (NPC) derived from Zn-containing ZIF-8 can basically inherit the pore structure of the initial precursor, demonstrating large surface area and high N-doping content, whereas the amorphous nature of ZIF-8-derived NPC causes low electrical conductivity, greatly suppressing the rate performance [33, 39]. By contrast, the reduced metal Co particles during carbonization of ZIF-67 have a strong catalytic effect of graphitization and even facilitate the formation of CNTs [40], while the enhancement of electrical conductivity is actually at the cost of surface area and N-doping content, which also hampers the electrochemical storage performances. In view of this, a core–shell hybrid structure is designed to combine advantages of both ZIF-8-derived and ZIF-67-derived NPCs [33, 41], but the synthesis of such core–shell hybrids requires stepwise procedures. Apart from the construction of core–shell hybrids, bimetallic ZnCo-ZIFs are used as unprecedented templates [42, 43]. The agglomeration of Co nanoparticles can be effectively inhibited; as a result, NPCs derived from ZnCo-ZIF inherit both merits of carbon independently from ZIF-8 and ZIF-67, and the features such as surface area, graphitization, and N-doping content can be well balanced. More importantly, the synthesis procedure of ZnCo-ZIF is very simple, and the Zn/Co molar ratio can be easily adjusted.

To this end, here in this work, we employ bimetallic ZnCo-ZIFs to prepare nanoporous carbon for the anodes of LIBs and SIBs. By optimizing the Zn/Co molar ratio and carbonization temperature, the resulting NPC achieves desirable properties including high surface area and favorable porous structure as well as high N-doping content, which endows with ample active sites, accessible electron transfer, and ion diffusion, and thus exhibits excellent Li⁺/Na⁺ storage performances.

**Experimental section**

**Material preparation**

Zinc acetate dehydrate (Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O), 2-methylimidazole (2-MeIM), cobalt acetate tetrahydrate (Co(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O), ethanol, and other chemicals and raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were of analytical reagent grade and used directly without further purification.

**Synthesis of ZIF-8 and ZIF-67 polyhedra**

ZIF-8 polyhedra were prepared by the previously reported procedure with some modifications. A total of 0.53 g of Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O was dissolved in 6 ml of deionized water, and 1.97 g of 2-methylimidazole (2-MeIM) was dissolved in 30 ml of deionized water. The two solutions were mixed together and kept at 5 °C in a refrigerator for 24 h. The formed white powders were washed with deionized water and ethanol for several times, collected through centrifugation, and dried at 80 °C in an oven overnight. A similar procedure was applied for the preparation of purple powders of ZIF-67 polyhedra, expect that Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O was replaced by Co(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O.

**Synthesis of ZnCo-ZIF polyhedra**

The synthesis of ZnCo-ZIF polyhedra with different Zn/Co molar ratios (denoted as xZn\textsubscript{y}Co-ZIF, where x\% and y\% were the percentages of Zn and Co, respectively) was similar to that of ZIF-8, taking the synthesis of 80Zn20Co-ZIF for example. The mixture of 0.42 g of Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O and 0.12 g of Co(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O was dissolved in 6 ml of deionized water, and 1.97 g of 2-MeIM was dissolved in 30 ml of deionized water. The two solutions were mixed and kept at 5 °C in a refrigerator for 24 h. The formed light purple powders were washed with deionized water and ethanol for several times, collected through centrifugation, and dried at 80 °C. It was worth noting that the total molar amount of Zn(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O and Co(CH\textsubscript{3}COO)\textsubscript{2}·2H\textsubscript{2}O was fixed to be 2.4 mmol.

**Preparation of NPC polyhedra**

Typically, the prepared ZnCo-ZIF was calcinated at different temperatures (600, 700, 800, or 900 °C) under Ar atmosphere for 2 h with a heating rate of 5 °C min\textsuperscript{-1}. Subsequently, the obtained black powders were added into a diluted HNO\textsubscript{3} solution for 24 h at 80 °C to remove Zn and Co species. Finally, the samples were dried at 80 °C overnight and denoted as NPC(xZn\textsubscript{y}Co)-T, where T represents the carbonization temperature.

**Material characterization**

The phase of the samples was tested by X-ray diffraction (XRD, D/MAX2500 V, Rigaku, Japan) equipped with Cu-Kα radiation (0.15418 nm) at 40 kV and 40 mA. The
morbidity and structure of the samples were observed by field emission scanning electron microscope (FESEM, SU8020, Hitachi, Japan), field emission transmission electron microscope (FETEM, JEM-2100F, JEOL, Japan), energy dispersive spectroscopy (EDS, Inca, Oxford, UK), and Raman spectra (LabRAM HR Evolution, HORIBA JOBIN YVON). The state of the elements was characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo, US). The thermal gravimetric analysis (TGA) was operated by a simultaneous thermal analyzer (STA449F3, Netzsch, Germany). The specific surface area and pore size distribution of the samples were calculated by Brunauer–Emmett–Teller (BET) method with a gas sorption surface area and pore size analyzer (Quadrasorb-EVO).

Electrochemical measurements

The electrochemical behavior of NPCs was studied using CR2032 half coin cells with lithium foil or sodium foil as the counter electrode. The electrode paste was prepared by mixing active materials (NPCs, 80 wt.%), conductive carbon black (10 wt.%), and polyvinylidene fluoride (PVDF, 10 wt.%) in N-methylpyrrolidone. Then, the slurry was blade casted onto copper foil uniformly and dried at 60 °C for 12 h in a vacuum oven. The mass loading of NPC was about 1 mg cm⁻², and the electrode thickness was determined as ~25 μm by the SEM detection (Fig. S1). The electrolyte used for LIBs was LiPF₆ (1.0 M) in a mixture of ethylene carbonate and diethyl carbonate (1:1 vol%), and the electrolyte used for SIBs was NaClO₄ (1.0 M) in a mixture of ethylene carbonate and propylene carbonate (1:1 vol%). Whatman GF/D membrane was used as the separator. The coin cells were assembled in an argon-filled glove box with moisture and the oxygen content below 1 ppm. Galvanostatic charge and discharge (GCD) tests and rate capability were measured by a multichannel battery testing system (LANHE, CT-2001A) with a potential range between 0.01 and 3 V, measured by a high-temperature evaporation, giving rise to micro-/mesopores within NPCs [42, 43].

The XPS spectra of NPC(40Zn-60Co)-T are recorded in Fig. S7. Figure S7b–e show the high-resolution C 1 s XPS spectra of NPC(40Zn-60Co)-T; the peaks centered at 284.8, 285.8, and 288.5 eV correspond to the C–C bond of sp² carbon, C=O, and C-N functional groups, respectively [27], and the small peak at 291.7 eV can be ascribed to the C–N bond at high temperatures. The XPS spectra (Fig. S8) can be fitted into three peaks including pyridinic N (398.6 ± 0.1 eV), pyrrolic N (399.9 ± 0.1 eV), and nitrogen N (400.7 ± 0.4 eV) [45, 46]. The detailed N content values are summarized in Fig. S8e and Table S1. In the N doping, it can be seen that NPC(40Zn-60Co)-600 °C has 10.74% of N-doping content, which is higher than 9.77% for NPC(40Zn-60Co)-700 °C, 5.90% for NPC(40Zn-60Co)-800 °C, and 4.90% for NPC(40Zn-60Co)-900 °C. Obviously, the increase of annealing temperature leads to the decrease of nitrogen content in carbon materials, which can be attributed to the breakage of the C-N bond at high temperatures. The N doping can endow more active sites for higher specific capacity and facilitate charge transfer for better rate capacity [46]. In addition, the proportion of graphitic N in the total nitrogen content also increases from 14.3 to 47.5% with the increase of temperature, resulting from the transformation of pyrrolic N and pyridinic N into graphitic N [47]. Furthermore, the specific surface area and porous structure are evaluated by N₂ adsorption–desorption analysis (Fig. S9). NPC(40Zn-60Co)-600 °C, NPC(40Zn-60Co)-700 °C, NPC(40Zn-60Co)-800 °C, and NPC(40Zn-60Co)-900 °C have 313.0, 259.4, 363.1, and 411.0 m² g⁻¹.
of specific surface area, respectively. With the increasing temperature from 600 – 900 °C, the graphitization process is accelerated, leading to decreasing surface area; meanwhile, more CNTs are gradually produced which contributes additional surface area. Therefore, we can see NPC(40Zn-60Co)-700 °C has the lowest surface area.

**Fig. 1** Schematic illustration for the fabrication of NPCs derived from ZIFs

**Fig. 2** SEM (a), TEM (b), and EDS mapping (c) images of 20Zn80Co-ZIF
area. Interestingly, all samples demonstrate a kind of hierarchically porous structure, which would play an important role on the Li+/Na+ storage performance, since micropores can supply numerous electroactive sites for high capacity, and mesopores can boost the ion transfer for superior rate performance [48].

Apart from calcination temperature, the influence of the Zn/Co molar ratio was also investigated. As displayed in Figs. S6a, S10, and 3a, the amount of CNTs increased with the increasing Co content, and there were less or even no CNTs grown on the surface of NPC(100Zn)-600 °C and NPC(80Zn-20Co)-600 °C. That is because the more Co content caused the agglomeration of Co clusters which boosted the catalytic effect on graphitization of carbon [49]. The TEM and HRTEM images in Fig. 3b–d further confirm the existence of CNTs, and still a bit of Co nanoparticles enwrapped by CNTs were retained after acid etching. The residual Co nanoparticles should be removed as many as possible, because they would contribute no capacity to the final capacity. Moreover, C and N elements were uniformly distributed in NPC(20Zn-80Co)-600 °C (Fig. 3e), indicating the successful self-doping of heteroatom N.

In the XRD patterns of NPC(xZn-yCo)-600 °C (Fig. 4a), the two peaks located at ~26° and 44° could be assigned to C(002) and Co(111) planes, respectively. It is seen that the peak at ~44° is not observed for NPC(100Zn)-600 °C, while another new peak located at ~22° emerges, suggesting the formation of amorphous carbon [50]. The existence of amorphous carbon is originated from no Co nanoparticles generated during the carbonization process, which retards the graphitization of amorphous carbon [51]. In the Raman spectra (Fig. 4b), all the samples display two distinct peaks at 1353 and 1590 cm\(^{-1}\), which correspond to the disordered carbon (D band) and the ordered graphitized carbon (G band), respectively. The intensity ratio of D band and G band (\(I_D/I_G\)) reveals the crystal defects and graphitization degree of carbon materials. With the increase of Co/Zn molar ratio, \(I_D/I_G\) value decreases from 1.08 to 0.98,
indicating the enhancement of graphitization degree of NPCs [44]. Figure S11 shows the XPS spectra of NPC(xZn-yCo)-600 °C. Similar to NPC(40Zn-60Co)-T, the high-resolution C 1 s XPS spectra of NPC(xZn-yCo)-600 °C are fitted into C–C, C=O, C-N, and π-π bonds (Fig. S11b–f), and the high-resolution N 1 s spectra are fitted into pyridinic N, pyrrolic N, and graphitic N (Figs. 4c and S12). The total N-doping content gradually rises with the increasing Zn/Co molar ratio (Fig. 4d and Table S2), because the produced metal Co nanoparticles cause the fracture of the C-N bond, which shows the similar effect as high temperature. Note that pyrrolic N and pyridinic N can not only absorb Li+/Na+ ions to afford additional capacity, but also promote the ion diffusion for rate performance; in addition, graphitic N can enhance the electronic conductivity [25, 52]. The specific surface area values of NPC(100Zn)-600 °C, NPC(80Zn-20Co)-600 °C, NPC(60Zn-40Co)-600 °C, NPC(20Zn-80Co)-600 °C, and NPC(100Co)-600 °C are determined as 16.9, 21.1, 193.5, 313.0, and 352.8 m² g⁻¹, respectively (Fig. S13). We can see Zn-rich, NPC(100Zn)-600 °C, and NPC(80Zn-20Co)-600 °C show very low specific surface area, which is caused by their poor catalytic capability to the formation of carbon [53].

The electrochemical properties of NPC(xZn-yCo)-T for Li⁺ storage were investigated by CV and GCD techniques in the potential range of 0.01–3.0 V vs. Li⁺/Li. Figure 5a shows the initial three CV curves of NPC(20Zn-80Co)-600 °C at a scan rate of 0.1 mV s⁻¹, an obvious peak appears around 0.6 V at the 1st cycle, which is due to the formation of solid-electrolyte-interphase (SEI) film, and the peak near 0 V results from the insertion of Li⁺ ions into the porous carbon [54]. The 2nd and 3rd cycles almost overlap each other, indicating the excellent electrochemical reversibility of NPC(20Zn-80Co)-600 °C. Figure 5b shows CV curves of NPC(20Zn-80Co)-600 °C at different scan rates. The electrochemical reaction kinetics can be evaluated according to the following equations [55]:

\[
i = av^b
\]

log \(i = b \log v + \log a\)  \(\quad (2)\)

where \(i\) and \(v\) are the response current and scan rate, respectively, and \(a\) and \(b\) are adjustable constants where the \(b\) value could be determined from the slope of log \(i\) versus log \(v\) curve from Eq. (2). If \(b=0.5\), the reaction is subjected to diffusion-control behavior, while if \(b=1\), the kinetics is controlled by capacitive behavior [56]. Herein, the \(b\) values at different potentials range from 0.5 to 1 (Fig. 5c), suggesting the co-existence of diffusion-control and capacitive processes. In addition, the total capacity could also be divided into a diffusion-control part (\(k_1v^{1/2}\)) and a capacitive part (\(k_2v\)) at a fixed potential (\(V\)) according to the following equations [57]:
It can be seen that the capacitive contribution increases from 52.3 at 0.1 mV s\(^{-1}\) to 83.2% at 2 mV s\(^{-1}\), and the capacitive behavior thus dominates the total capacity (Fig. 5d), implying the superior rate performance of NPC(20Zn-80Co)-600 °C. Figure 5e shows the typical GCD curves of NPC(20Zn-80Co)-600 °C at the current density of 0.1 A g\(^{-1}\) for the first fifty cycles. The initial charging and discharging specific capacity of NPC(20Zn-80Co)-600 °C are 804.2 and 1251.9 mA h g\(^{-1}\) with the coulombic efficiency (CE) of 64.2%, and the CE value increases to ~93.2% at the 2nd cycle and maintains >98% at the following cycles. The capacity loss is actually originated from the irreversible processes such as decomposition of electrolyte and the formation of SEI film [58].

The influence of calcination temperature and Zn/Co molar ratio on the rate capability is investigated. NPC(40Zn-60Co)-600 °C delivers 786.0, 736.9, 634.9, 521.8, 401.1, and 254.1 mA h g\(^{-1}\) at current density of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g\(^{-1}\), respectively (Fig. S14). When the current density returns to 0.1 A g\(^{-1}\), a capacity as high as 783.6 mA h g\(^{-1}\) still can be achieved. NPC(40Zn-60Co)-600 °C shows the better performance than NPC(40Zn-60Co)-700 °C, NPC(40Zn-60Co)-800 °C, and NPC(40Zn-60Co)-900 °C, which can be attributed to its higher N-doping content that offers more active sites and facilitates more feasible ion diffusion. In addition, NPC(20Zn-80Co)-600 °C exhibits

\[ i(V) = k_1 v^{1/2} + k_2 v \]  
\[ i(V)/v^{1/2} = k_1 + k_2 v^{1/2} \]  

Fig. 5 Li\(^+\) storage performance: initial three CV plots of NPC(20Zn-80Co)-600 °C at 0.1 mV s\(^{-1}\) (a); CV curves of NPC(20Zn-80Co)-600 °C at different scan rates (b); relationship between the logarithm current and scan rate of NPC(20Zn-80Co)-600 °C (c); contribution ratio of diffusion-control and capacitive processes at different scan rate (d); initial fifty GCD curves of NPC(20Zn-80Co)-600 °C at a current density of 100 mA g\(^{-1}\) (e); rate capability of NPC(xZn-yCo)-600 °C (f); cycling stability of NPC(20Zn-80Co)-600 °C at 0.1 A g\(^{-1}\) after 100 cycles (g) and at 1 A g\(^{-1}\) after 500 cycles (h); and Nyquist plots of NPC(xZn-yCo)-600 °C (i).
reversible capacity of 876.5, 768.9, 664.7, 570.7, 480.9, and 352.6 mA h g\(^{-1}\) at current density of 0.1, 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\), respectively (Fig. 5f), which are higher than other NPC(xZn-yCo)-600 °C. When the current density is back to 0.1 A g\(^{-1}\), NPC(20Zn-80Co)-600 °C gains a capacity of 857.9 mA h g\(^{-1}\). It is observed that at high current densities of 2 and 5 A g\(^{-1}\), the capacity of NPC(20Zn-80Co)-600 °C decreases, by reason of the increasing internal diffusion resistance within the electrodes during the Li\(^+\) ion insertion/extraction process [59]. Since the solid nature of NPC(20Zn-80Co)-600 °C significantly retards the Li\(^+\) ion diffusion and diminishes the efficient utilization of active material, its three-dimensional particle shape also lowers the possibility of forming continuous and long-range charge transfer pathway; therefore, in our future, it would be of significance to tailor ZnCo-ZIFs with well-designed architectures such as hollow or one-dimensional structures [60].

Figure 5g, h show the cycling performance of NPC(20Zn-80Co)-600 °C at a low current density of 0.1 A g\(^{-1}\) and a high current density of 1 A g\(^{-1}\), respectively. NPC(20Zn-80Co)-600 °C could retain 99.8% of initial specific capacity after 500 cycles at 1 A g\(^{-1}\), indicating the excellent long-term stability. The charge transfer kinetics of the NPC(xZn-yCo)-600 °C are further investigated by EIS (Fig. 5i). Each Nyquist plot consists of a semicircle in the high-frequency region and an approximate oblique line in the low-frequency region, corresponding to the charge transfer resistance (\(R_{ct}\)) and Warburg impedance (\(Z_w\)), respectively [61]. NPC(20Zn-80Co)-600 °C has the minimum \(R_{ct}\) compared to other NPCs, which gives the reason of its superior rate capacity. Compared to commercial graphite, NPC(20Zn-80Co)-600 °C exhibits much better capability for Li\(^+\) storage, because its larger specific surface area and N-doping content afford more active sites for higher specific capacity, the desired pore-size distribution enables a short-ion diffusion path for more accessible charge transfer, and the porous structure is capable to accommodate more volumetric strain for long-term cycling stability [46, 62]. Encouragingly, the Li\(^+\) storage performance of as-prepared NPC(20Zn-80Co)-600 °C is also competitive with other reported porous carbon-based materials (Table S3).

In the meantime, NPC-(20Zn-80Co)-600 °C is also applied for electrochemical Na\(^+\) storage. Figure 6a shows the initial three CV curves at a scan rate of 0.1 mV s\(^{-1}\); the first irreversible reduction peak around 0.6 V in the CV curve is mainly caused by the formation of SEI film [63], and the peak located around 0 V suggests the sodium ion insertion into NPC(20Zn-80Co)-600 °C [18]. In addition, the CV curves almost overlapped with each other in the second and third cycles, indicating that NPC(20Zn-80Co)-600 °C electrode materials have good cycling performance in the process of Na\(^+\) intercalation/de-intercalation. In addition, a rectangular area can be observed in a potential range of 1.5–3 V, suggesting a capacitive behavior [64]. Figure 6b

![Figure 6](image_url)
illustrates the CV curves of NPC(20Zn-80Co)-600 °C at different scan rates ranging from 0.1 to 2.0 mV s⁻¹ with the similar shape, revealing its high reversibility and good repeatability in the electrochemical reactions. Similar to the similar shape, revealing its high reversibility and good cycling behavior (Fig. S15a). As demonstrated in Fig. 6c, the capacitive behavior accounts for more than half of the total capacity, ranging from 53.9 (at 0.1 mV s⁻¹) to 83.2% (at 2.0 mV s⁻¹).

Figure 6d illustrates the first fifty GCD curves of NPC(20Zn-80Co)-600 °C at a current density of 0.02 A g⁻¹; the initial discharging and charging specific capacity is 43.3%, which gradually increases to 98.4% at the 20th cycle and 98.9% at the 50th cycle, suggesting the good cycling stability of NPC(20Zn-80Co)-600 °C at a current density of 0.02 A g⁻¹. In comparison with NPC(20Zn-80Co)-700 °C, NPC(20Zn-80Co)-800 °C, and NPC(20Zn-80Co)-900 °C, NPC(20Zn-80Co)-600 °C exhibits the better rate performance, which can be attributed to the more feasible charge transfer as demonstrated in Fig. S15b. The electrode still achieves a capacity of 218.0 mA h g⁻¹ after 450 cycles at 0.05 A g⁻¹ (Fig. S15c); at a high current density of 1 A g⁻¹, a reversible specific capacity of 117.8 mA h g⁻¹ could be retained after 1000 cycles (Fig. 6f). The relatively intact polyhedral shape after repeating cycles also reveals the good cycling stability of NPC(20Zn-80Co)-600 °C (Fig. S16), as the porous structure can accommodate large volumetric variation during the insertion/extraction process of Li⁺/Na⁺ ions. Furthermore, the excellent rate and cycling performance of NPC(20Zn-80Co)-600 °C is also comparable with other reported porous carbon-based materials (Table S4).

Conclusions

In summary, a series of NPCs have been successfully synthesized by simply carbonizing Zn-Co-ZIFs in Ar atmosphere. It is found that both the Co/Zn molar ratio and carbonization temperature play crucial roles in N-doping content, specific surface area, and graphitization degree of the final NPCs. The formation of CNTs endowed with additional surface area, resulting from the catalytic function of Co nanoparticles produced in the carbonization process. Meanwhile, the high Co/Zn molar ratio enables more Co nanoparticles which shows the similar effect as high temperature, and the Co nanoparticles accelerate the fracture of the C–N bond and graphitization process, leading to enhanced graphitization degree and decreased N-doping content. Because NPC(20Zn-80Co)-600 °C integrated desired pore-size distribution with high specific surface area and N-doping content, which can afford plentiful active sites, enable accessible charge transfer, and accommodate volumetric strain, the electrode finally exhibits excellent electrochemical performances for Li⁺/Na⁺ storage. The as-prepared NPCs are expected to be promising alternatives for the application in energy storage and other related fields.

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Declarations

Competing interests The authors declare no competing interests.

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