Graphitic Carbon Nanocage as a Stable and High Power Anode for Potassium-Ion Batteries

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As an emerging electrochemical energy storage device, potassium-ion batteries (PIBs) have drawn growing interest due to the resource-abundance and low cost of potassium. Graphite-based materials, as the most common anodes for commercial Li-ion batteries, have a very low capacity when used as an anode for Na-ion batteries, but they show reasonable capacities as anodes for PIBs. The practical application of graphitic materials in PIBs suffers from poor cyclability, however, due to the large interlayer expansion/shrinkage caused by the intercalation/deintercalation of potassium ions. Here, a highly graphitic carbon nanocage (CNC) is reported as a PIBs anode, which exhibits excellent cyclability and superior depotassiation capacity of 175 mAh g$^{-1}$ at 35°C. The potassium storage mechanism in CNC is revealed by cyclic voltammetry as due to redox reactions (intercalation/deintercalation) and double-layer capacitance (surface adsorption/desorption). The present results give new insights into structural design for graphitic anode materials in PIBs and understanding the double-layer capacitance effect in alkali metal ion batteries.

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices and are regarded as the most promising candidates for electric vehicles due to their high energy and power densities.[1] Since large-scale electrical energy storage systems are critical for utilizing intermittent renewable energy, in the foreseeable future, the high cost and the limited nature of lithium resources would hinder further application of LIBs in this field.[2,3] Therefore, secondary metal-ion batteries based on low-cost and resource abundant elements (such as Na,[4–6] Mg,[7] Al,[8] and K[9–11]) are being widely considered. Among these emerging battery technologies, potassium-ion batteries (PIBs) have great advantages as an ideal alternative for LIBs because potassium not only is a low-cost, nontoxic, and resource-abundant element (2.4 wt% potassium in the Earth’s crust), but also has a low redox potential of −2.93 V versus standard hydrogen electrode (SHE) as the K+/K couple, resulting in a high working voltage and high energy density for PIBs with low cost.

To date, alloy-based materials,[12–16] transition-metal oxides/sulfides,[17–19] and MXene-based materials[20–22] have been reported as anode materials for PIBs. Carbon-based anode materials,[23–37] however, are regarded as the most promising ones for large-scale applications. As one advantage for PIBs, graphite, the current commercial anode material for LIBs, can be used as anode for PIBs.[23a,25] Accordingly, PIBs could be well suited to the existing LIB manufacturing technology due to their similar working mechanism and cell structure.[38] Graphitic materials show amazing electrochemical activity when used as anode for PIBs, since their layered structure is available for K+ intercalation to form the stage-one K-graphite intercalation compound (KC₆) with the theoretical capacity of 279 mAh g$^{-1}$.[23a] Moreover, the graphitic materials have a long and stable K+ intercalation/deintercalation plateau above 0.1 V versus K+/K. This low plateau potential not only is suitable for a high working voltage and thus high energy density when coupled with cathode materials,[39] but also avoids the formation of potassium dendrites and the related safety concerns. Nevertheless, the full potassiation of graphite with almost 60% incremental expansion in the interlayer distance would lead to irreversible structural damage due to the larger K+ radius (1.38 Å, almost 1.82 times larger than Li+). Therefore, potassiation/depotassiation of graphite is not highly reversible, even under charge/discharge at low current density. With few reports on graphitic carbon anodes for PIBs,[23–25] this issue is still not effectively solved. Therefore, the main problem for...
graphite as an anode material of PIBs is the severe structural degradation during cycling. Accordingly, designing a highly stable structure to accommodate the expansion in interlayer distance during charge/discharge is urgent for application of graphic materials in PIBs.

In this study, we propose a highly graphitic carbon nanocage (CNC) to meet the requirements on anode materials for PIBs. The cage-like structure could effectively reduce anisotropy due to the concentric arrangement of carbon layers and thus avoid interlayer slipping to ensure structural integrity. Accordingly, the hollow cage-like structure could effectively accommodate the strain relaxation during K⁺ intercalation/deintercalation and thus improve the cyclability. Moreover, the interconnected network structure of CNC is a 3D electrically conducting network that permits fast electron transfer among the different carbon nanocages, thus achieving better electrochemical kinetics to ensure excellent rate performance. Based on the above, CNC exhibits excellent cyclability and a superior deposition capacity of 175 mAh g⁻¹ with high capacity retention of 79% at 35 °C. In addition, the cyclic voltammetry analysis has revealed the hybrid potassium storage mechanism in CNC, i.e., redox reactions (intercalation/deintercalation) and double-layer capacitance (surface adsorption/desorption). The present results give new insights into structural design for graphic anode materials with stable cyclability in PIBs and understanding the hybrid potassium storage mechanism.

The CNC were prepared by high temperature treatment of Ketjen carbon black (EC300J) at 2800 °C under Ar atmosphere (Figure S1, Supporting Information). Since Ketjen carbon black is a commercially available material and the high-temperature treatment of carbonaceous materials is a mature technology, the production of CNC could be easily scaled up. The CNC has the appearance of a string of grapes with interconnected structure in 3D space (Figure 1a), and the integrated structure can be further proved by the high resolution transmission electron microscope (HRTEM) image (Figure 1b). In addition, the CNC has a uniform hollow cage-like morphology (Figure 1c) with an average particle diameter of about 50 nm and a shell thickness of ~5 nm. The interconnected structure could permit fast electron transfer among different nanocages (illustrated schematically in Figure 1d), and the hollow nanocage morphology with thin shells could effectively reduce the ion diffusion length in solid phase, thus achieving better electrochemical kinetics to ensure excellent rate performance. In the X-ray diffraction (XRD) patterns (Figure 1e), the sharp (002) peak indicates the highly graphitic layered structure of CNC, which is critical to ensure its typical graphite-like electrochemical behavior with a low potassium storage potential for PIBs. The Raman spectrum of CNC (Figure 1f) shows a strong G band (1585 cm⁻¹, graphitic structure) and D band (1360 cm⁻¹, defective structure). The integrated intensity ratio of the G band to the D band (I_G/I_D) is as high as 3.96, confirming the highly ordered graphitic structure of CNC, which corresponds to the XRD and HRTEM results. Furthermore, the appearance of the D band reveals the existence of defective sites on the surface of nanocage, suggesting an imperfectly closed cage-like structure for the CNC. Unlike the edge sites in graphite-based materials with open layered structure, those surface defective sites are active sites for ion intercalation/deintercalation.[40] As a reference sample, mesophase graphite (MG) was prepared in our laboratory by polycondensation from coal tar pitch and graphitization at 2800 °C. This widely applied commercial LIBs anode material with high cycling stability has a highly graphitic nature (XRD pattern and Raman spectrum in Figure 1e,f, respectively) with an open-layered structure (Figure S2, Supporting Information).

The potassium intercalation/deintercalation behavior of CNC was investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge. As shown in Figure 2a (CV curves at scan rate of 0.1 mV s⁻¹), potassium ion intercalation/deintercalation in CNC can be clearly observed by the presence of two pairs of redox peaks between 0 and 0.6 V versus K⁺/K, which correspond to the phase transformation phenomenon of K-graphite intercalation compounds (K-GICs) from a dilute stage to a high stage (Stage 1, KC₆) and their backward transformation.[23a,24] A strong reduction peak around 0.7 V can be observed only in the first scan, which is attributed to the formation of solid electrolyte interphase (SEI) due to the decomposition of
electrolyte.[23a] In the following scans, the CV curves are almost overlapping, indicating the excellent electrochemical reversibility of CNC. In the high potential region (0.6–3.0 V versus K⁺/K), the well separated cathodic and anodic segments with rectangular shape in the CV curves of CNC electrode imply significant capacitive potassium storage behavior in comparison with the CV curve of MG electrode (Figure S3a, Supporting Information). Voltage profiles of CNC and MG electrodes at the current density of 0.2 C (1 C = 279 mA g⁻¹) are shown in Figure 2b and Figure S3b (Supporting Information), respectively. The long and stable voltage plateaus above 0.1 V versus K⁺/K help to avoid the formation of potassium dendrites and allow a high working voltage when coupled with a cathode in the full cell system.[9,10] From Figure 2b, several small plateaus corresponded to the different stage phase transformations can be well distinguished, which are consistent with the CV results. In the initial charge–discharge, a large irreversible capacity can be observed, corresponding to the formation of the SEI due to the high surface area of CNC. During the following 50 charge–discharge cycles, the overlapping voltage profiles suggest the excellent cyclability of CNC. In comparison with CNC, the separated voltage profiles of MG (Figure S3b, Supporting Information) indicate fast capacity fading. Moreover, the small voltage hysteresis (Figure S3c, Supporting Information) between the charge and discharge curves of CNC also confirms the far better electrochemical kinetics than that of MG. This improvement of CNC is likely to be due to the large specific surface area (102.7 m² g⁻¹), which provides higher electrochemical activity, and the thin shells of graphitic nanocages, which reduce the ion diffusion distance in the solid phase. The cycling performances of CNC and MG at 0.2 C are shown in Figure 2c. The CNC delivers an initial reversible capacity of 212 mAh g⁻¹ with a Coulombic efficiency of 40%. The reversible capacity of CNC is lower than the theoretical capacity of KC₈, which is ascribed to the presence of crystal defects in CNC, such as turbostratic structure. Since the stage 1 intercalation compounds (such as KC₈ and LiC₆) prefer adjacent carbon layers with “AAAA” stacking arrangement,[23b,c] carbon layers with turbostratic disorder unable shift into the “AAAA” stacking arrangement to form stage 1 intercalation compound[23b] thus
resulting lower capacity of CNC than the theoretical capacity. The low initial Coulombic efficiency of CNC is ascribed to its large surface area, which consumes more electrolyte for the formation of SEI and can potentially be improved by additives in the electrolyte or using pre-potassiation technology. After 100 cycles, CNC still has a reversible capacity of 195 mAh g\(^{-1}\) with a high capacity retention of 92%. After 140 cycles, further cycles can be achieved by replacing potassium metal and adding new electrolyte to the cell due to the potassium metal with high chemical activity consuming limited amount of electrolyte (shown in Figure S4 and see more detailed discussion in the Supporting Information). Although MG has a higher initial reversible capacity of 248 mAh g\(^{-1}\) at 0.2 C, its reversible capacity decreases gradually with cycling. After 50 cycles, only 62% of the initial capacity can be maintained. The fast capacity fading in MG electrode may be ascribed to structural degradation induced by the large expansion in interlayer distance.

In order to reveal the different cyclability of CNC and MG electrodes after 100 cycles at 0.2 C, the electrodes were characterized by HRTEM. As the HRTEM images shown in Figure 2d, the interconnected cage structure of CNC still can be clearly observed, which is essential to ensure stable cyclability. The well-dispersed C, K, F, S, and O elements (Figure 2e) that have come from SEI components revealed the stable nature of the electrode/electrolyte interface during cycling. Moreover, the interlayer spacing in the original CNC and the CNC after 1 cycle was evaluated by selected area electron diffraction (SAED) in Figure S5 in the Supporting Information. The results indicated that the interlayer spacing in CNC was increased to 3.53 from 3.46 Å, suggesting that the few-layer graphitic shell structure can be expanded. After 100 cycles, the interlayer spacing in CNC was 3.54 Å, which is very similar to that of CNC after 1 cycle, demonstrating that the high structure stability of CNC, and the few-layer graphitic shell can reversibly expand/shrink due to potassium intercalation/deintercalation. By comparison, the MG was exfoliated to carbon nanosheets dispersed in amorphous SEI (Figure 2f), indicating severe structural degradation owing to large interlayer change during potassiation/depotassiation. It is well known that the structural degradation would also consume electrolyte and increase the internal resistance, thus leading to cell failure. For reviewing the interfacial features of the carbon electrodes in different cycles and avoiding interference from potassium metal, electrochemical impedance spectroscopy (EIS) was carried out on symmetric cells (see more discussion of symmetric cell EIS in the Supporting Information) after different cycles (Figure S6, Supporting Information). The semicircle in Nyquist plots of fresh cells reflects the intrinsic interface impedance between the carbon particles and the electrolyte, which is related to the electronic resistance of the electrode and the ion adsorption process on surfaces. After cycling, the semicircles became depressed and large, indicating a new interface state due to the formation of the passivated layer. For CNC electrodes (Figure 2g), the diameter of the semicircle increased gradually from the 1st cycle to the 10th cycle, while the Coulombic efficiency increased rapidly to 95% from 40% (Figure 2c), and then remained stable, even after the 30th cycle, suggesting that the SEI layer is stable after initial few cycles of activation. For MG electrodes, however, the diameter of the semicircle keeps growing as cycling continues, indicating that structural degradation has induced the repeated growth of SEI. Thus, we can conclude that there is no significant structural degradation of CNC during cycling, which is consistent with the HRTEM observations (Figure 2d). It is well known that a stable electrode/electrolyte interface is critical for stable electrochemical performance. Since the outer surface of CNC is composed of carbon basal planes, there is no doubt that the formation of a stable electrode/electrolyte interface can be ascribed to its unique cage-like structure. As mentioned above, the excellent cyclability of CNC should be attributed to its cage-like structure, because the cage-like structure could effectively reduce the anisotropy due to the concentric arrangement of carbon layers and thus avoid interlayer slipping to ensure structural integrity. The cage-like structure possesses high chemical and structural stability, as it cannot be exfoliated by Hummers’ method under rigorous conditions. Moreover, the cage-like structure is also a hollow structure. Since hollow structure has been demonstrated to be an attractive structure with excellent electrochemical performance in LIB/sodium ion battery (SIB) electrode materials. The unique hollow structure could effectively accommodate strain relaxation during potassium ion intercalation/deintercalation and thus help to maintain the structural integrity to alleviate capacity fading. The poor cycling performance of MG is ascribed to its open-layered structure, which could not endure the large interlayer changes during potassiation/depotassiation. The structural variations of CNC and MG during potassium storage are schematically illustrated in Figure 2i.

The rate capability between CNC and MG was also compared, as shown in Figure S7 in the Supporting Information. CNC has a reversible capacity of 137, 99, 71, and 56 mAh g\(^{-1}\) at current rates of 0.5 C, 1 C, 2 C, and 3 C, respectively. Even at the high current density of 5 C, the CNC can still deliver a reversible capacity of 40 mAh g\(^{-1}\). Among the reported graphitic materials, CNC has the superior rate performance. In contrast, the capacity of MG quickly dropped to 100 mAh g\(^{-1}\) at 0.5 C and only 30 mAh g\(^{-1}\) at 1 C. Although CNC exhibits much superior rate capability to MG, the capacity drop of CNC at high current rates seems too fast, which is ascribed to the large polarization and impedance in the potassium half-cell (Figure S8, Supporting Information) because potassium metal may not be a good reference electrode (see more comments in the Supporting Information). To further examine the depotassiation capability of CNC and avoid the influence of polarization on potassiation, CNC electrode was potassiated at 0.1 C and depotassiated at different rates. As shown in Figure 3a, CNC can present a large reversible capacity of 175 mAh g\(^{-1}\) at an ultrahigh rate of 35 C, i.e., the capacity retention is as high as 79% of that at 0.1 C (221.5 mAh g\(^{-1}\)). These results indicate that CNC has outstanding high-rate depotassiation capability. As summarized in Table S1 in the Supporting Information, a stable plateau with a capacity contribution of 75% is rarely reported at such a high rate of 35 C. After high rate depotassiation, the CNC electrode was taken out from the cell and characterized by HRTEM. It is clearly observed that CNC still had an interconnected cage structure with no exfoliation (Figure 3c), indicating that there was no structural degradation during high rate depotassiation.
The electrochemical behavior and kinetics of CNC were analyzed by CV techniques to gain further insight. As mentioned above, the CV curves of CNC show two different types of electrochemical behaviors in the low and high potential ranges. In the low potential range, the redox peaks dominated region (Figure S9a, Supporting Information), indicating the typical faradic process, is attributed to the K\(^+\) intercalation/deintercalation reaction. For the high potential range (Figure S9a,b, Supporting Information), the rectangle-shaped region is attributed to the double-layer capacitive behavior, as CNC has a well-developed surface area. This phenomenon has been observed and accepted in both lithium storage (Figure S9c,d, Supporting Information) and sodium storage,[47–51] proving the ubiquity of double-layer capacitance in electrochemical energy storage systems with electrode materials that have a high specific surface area. The CV curves for CNC/K half-cells at various scan rates from 0.01 to 0.5 mV s\(^{-1}\) (Figure 4a) show similar shapes with redox peaks in the low potential region and a rectangular shape in the high potential region, indicating intercalation and double-layer capacitance dominated behaviors, respectively.[52] The capacitive effects were analyzed by the power law relationship between the measured current (\(i\)) and the sweep rate (\(v\)) according to the following equation

\[i = av^n\]  

(1)

where the \(b\)-value can be determined from the slope of the plot of \(\log(i)\) versus \(\log(v)\).[52,53] For \(b = 0.5\), the current is diffusion-controlled, indicating a Faradaic intercalation process; moreover, \(b = 1\) represents a capacitive response because the capacitive current is linearly proportional to the scan rate. As shown in Figure 4b, the \(b\)-values were plotted as a function of potential in the cathodic scan. At potentials higher than 0.7 V, the \(b\)-values are in the range of 0.8–1.0, suggesting that the current is dominated by capacitive behavior. This result also corresponds with the rectangular shape in the CV curves within the high potential range (Figure 4a). In the low potential range of 0–0.5 V, the \(b\)-values are slightly higher than 0.5 within the range of 0.55–0.65. This result indicates that the response current due to double-layer capacitance is independent of the potential, although the current comes primarily from the K\(^+\) intercalation in a Faradaic intercalation dominated process. Therefore, capacitive behavior should exist throughout the reduction. The capacitive characteristics of CNC was also investigated in a CNC symmetric cell. As shown in Figure 4c, the CV curves show a typical rectangular shape even at an ultrahigh scan rate of 50 V s\(^{-1}\), indicating the extraordinary power capability of CNC.[54]

Since the response current from the double-layer capacitance is linearly proportional to the scan rate and exhibits rectangular shape in the CV curve,[52] we assume that the capacitive current is not affected by the Faradic current, so that the double-layer capacitance contribution in potassiation can be quantified based on the current response at high potential. A typical separation of the double-layer capacitance contribution is shown in Figure 4d. Note that the capacitive contribution was considered only in the cathodic process (K\(^+\) intercalation) because the current baseline in the anodic scan is difficult to distinguish. The ratios of double-layer capacitance to the total charge are shown in Figure 4e, the quantitative results indicate that the double-layer capacitance contribution is 12.8% at 0.01 mV s\(^{-1}\), which increases gradually with the scan rate and reaches a value of 22.1% at 0.5 mV s\(^{-1}\). Furthermore, the capacity retention of intercalation reactions drops quickly with scan rate. The capacity retention of double-layer
The diffusion coefficients of CNC and MG were evaluated from the galvanostatic intermittent titration technique (GITT) profiles (Figures S10 and S11, Supporting Information) by Fick’s second law using Equation S1 in the Supporting Information. In potassiation, the diffusion coefficients decrease slowly below 0.25 V and then drop quickly, suggesting that the formation of a high stage intercalation compound might be the kinetics limited step. For depotassiation, the diffusion coefficients with relatively higher values throughout the process reveal the excellent depotassiation capability of CNC, which is consistent with previous electrochemical tests. Moreover, CNC shows lower over-potential and higher diffusion coefficients than MG in both potassiation and depotassiation, suggesting better electrochemical kinetics for CNC than that for MG. The potassium storage mechanism in CNC consists of potassium intercalation with high energy density and surface capacitive adsorption with high power density, which is briefly shown in Figure 4f.

In conclusion, CNC exhibits excellent cyclability and a superior depotassiation capacity of 175 mAh g \(^{-1}\) with high capacity retention of 79% at 35 C. The excellent cyclability and depotassiation capability of CNC are attributed to its unique interconnected cage structure as well as its hybrid potassium storage mechanism. First, the cage-like structure could effectively reduce anisotropy due to the concentric arrangement of carbon layers, and thus avoid interlayer slipping to ensure structural integrity. Moreover, the hollow structure could effectively accommodate strain relaxation during potassium ion intercalation/deintercalation and thus help to maintain the structural integrity. It is well known that maintaining the structural integrity during electrochemical reactions is essential for maintaining stable electrochemical properties. Therefore, the ultrastable cage-like structure is the basis for realizing stable electrochemical reactions. Second, the thin shell of CNC could effectively reduce the K\(^+\) diffusion distance in the solid phase, while the interconnected structure of CNC represents a 3D electrically conducting network that permits fast electron transfer among the different cages, thus achieving better electrochemical kinetics to ensure excellent rate performance. Last but not least, the highly graphitic structure of CNC is essential to ensure the low and stable K\(^+\) intercalation/deintercalation potential, which would be helpful for realizing a high working voltage in K-ion full cells. The hybrid potassium storage mechanism in CNC was revealed by cyclic voltammetry as due to redox reactions (intercalation/deintercalation) and double-layer capacitance (surface adsorption/desorption). The quantified capacitive contributions indicate that the double-layer capacitance effect with high capacity retention is critical for achieving high power capability. As a nonnegligible potassium storage behavior, the double-layer effect also plays an important role in realizing high power performance in CNC electrodes due to the nature of adsorption/desorption. In future research, the ratio between capacitance and intercalation, which offers a combined energy storage with redox reactions (chemical energy storage) and surface adsorption/desorption (physical energy storage), should be optimized to achieve a good balance between the energy density and power density.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

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