Carbon-based anode materials for potassium-ion batteries: From material, mechanism to performance

Jinhui Zhou | Shaojun Guo

School of Materials Science & Engineering, Peking University, Beijing, China

Correspondence
Shaojun Guo, School of Materials Science & Engineering, Peking University, Beijing 100871, China.
Email: guosj@pku.edu.cn

Funding information
National Key R&D Program of China, Grant/Award Number: 2017YFA0206701; National Science Fund for Distinguished Young Scholars, Grant/Award Number: 52025133; Tencent Foundation through the XPLORER PRIZE; Beijing Natural Science Foundation, Grant/Award Number: JQ18005; National Natural Science Foundation of China, Grant/Award Number: 22002003

Abstract
Potassium-ion batteries (PIBs) show great potential in the application of large-scale energy storage devices due to the comparable high operating voltage with lithium-ion batteries and lower cost. Carbon-based materials are promising candidates as anodes for PIBs, for their low cost, high abundance, nontoxicity, environmental benignity, and sustainability. In this review, we will first discuss the potassium storage mechanisms of graphitic and defective carbon materials and carbon-based composites with various compositions and microstructures to comprehensively understand the potassium storage behavior. Then, several strategies based on heteroatoms doping, unique nanostructure design, and introduction of the conductive matrix to form composites are proposed to optimize the carbon-based materials and achieve high performance for PIBs. Finally, we conclude the existing challenges and perspectives for further development of carbon-based materials, which is believed to promote the practical application of PIBs in the future.

Keywords
carbon-based anode materials, heteroatoms doping, potassium-ion batteries, storage mechanism

1 | INTRODUCTION

To ensure the sustainability of energy development, exploring high-performance lithium-ion batteries (LIBs) is vital for energy storage due to the intermittency of green environmental solar and wind sources. However, the barren and geographic maldistribution of lithium resource in the Earth’s crust (17 ppm, mainly in Chile, Argentina, and Bolivia) and its high cost seriously hamper its application in large-scale electric power devices where low cost, long cycle life, high energy density, and fast charge-discharge capability should be met. In this regard, sodium and potassium, in the same main group with Li element in the elemental table with similar physico-chemical properties, have attracted extensive attention for their abundant distribution in the Earth’s crust (23000 ppm for Na, and 15000 ppm for K, Figure 1A, the diameter for each circle represents log (abundance)) and low cost.

Nevertheless, the energy density of sodium-ion batteries (SIBs) cannot reach a relatively high level of LIBs because the low operating voltage of SIBs results from the high standard reduction potential of Na/Na+ couple (−2.71 V vs. standard hydrogen electrode [SHE]), which further restricts its application to practical production. Fortunately, the fact that the standard reduction potential of K/K+ couple (−2.92 V vs. SHE) is low and very close to Li/Li+ couple (−3.04 V vs. SHE) makes it possible for PIBs
to obtain high-energy density (Figure 1B). Meanwhile, it is found that the redox potential of the K/K+ couple (−2.88 V vs. saturated calomel electrode [SCE]) is lower than those of Na/Na+ couple (−2.56 V vs. SCE) and Li/Li+ couple (−2.79 V vs. SCE) in propylene carbonate (PC) solvent, which further brings about the higher energy density of PIBs in nonaqueous electrolytes than those of LIBs and SIBs.11 Meantime, low cost, high abundance, and high ionic conductivity in electrolytes arouse the enthusiasm of PIBs’ research. K element is one of the most natural common resources. Additionally, unlike lithium, potassium cannot form the alloy with metal aluminum at low potential, so the aluminum foil can replace the copper foil as the current collector for anodes in PIBs, which can lower the battery weight and reduce the price.12,13 As shown in Figure 1C, although potassium ion has the biggest ion radius (1.38 Å) compared to lithium (0.68 Å) and sodium (0.97 Å) ions, its Stocks radius in PC solvents is the smallest (3.6 Å) as compared with lithium ion (4.8 Å) and sodium ion (4.6 Å), which is the result of its weakest Lewis acidity. Thus, potassium salts have higher ionic conductivity in PC solvents.13 Moreover, the first principles of molecular dynamics simulations have shown that larger K ions have more disordered and flexible solvation structures than Li ions, leading to three times higher diffusion coefficient of K ions than that of Li ions.14 Based on the abovementioned factors, PIBs show great potential in high-energy density, high rate performance, and long cycle stability of the batteries when compared to LIBs and SIBs, and are promising in the application of large-scale electric power devices.

Similar to LIBs and SIBs, PIBs consist of an anode, nonaqueous electrolyte, and cathode, exhibiting a rocking-chair working mechanism, as schematically demonstrated in Figure 1D (graphite as anode, layered oxide as cathode, and KPF6 in EC/DEC as electrolyte). During the charging process, K ions can extract from the cathode, travel across the electrolyte, and then intercalate into the anode. The reverse direction occurs in the discharge process with the electron moving in the external circuit to generate electric energy. To gain a high-energy density of PIBs, both high cell potential and high cell capacity are the key points, which highly depend on the electrode materials, especially anodes. Different from the laboratory counter/reference electrode studies of half-cell, the particularly reactive K metal, acting as a commercial anode, may cause severe safety issues. In this regard, searching for suitable K-host anode materials for PIBs is a top priority.

Graphite, as the commercial anode material for LIBs, was found to be a suitable host material for the electrochemical intercalation of K+ in 2015.15,16 After that, a large amount of carbon-based materials with composition and nanostructure design have been investigated as anodes for PIBs, such as graphite, graphene, hard carbon, heteroatoms doping carbon, and carbon-based composites (with alloying materials, metal sulfates/selenides, etc.). The carbon-based materials show great advantages in abundance, nontoxicity, and great flexibility of

FIGURE 1 (A) Comparison of the abundance of Li, Na, and K resources with the diameter of each circle represents log (abundance, ppm). (B) Comparison of the standard reduction potential of different couples in a different situation. (C) Comparison of the ion radius and Stokes radius of Li, Na, and K. (D) Schematic illustration of the working mechanism of potassium-ion batteries.
crystallinity and composition. Till now, various strategies are applied to improve the reaction kinetics and cycle stability of the host materials limited by the large radius of potassium ions, and the improved carbon-based materials as anodes show great potential in the application for high-performance PIBs with considerable capacity, high rate capability, and excellent cycle stability. In this review, the mechanisms of carbon-based materials for PIBs, including intercalation, adsorption, and capacitive mechanism are summarized. Then, we review the strategies to optimize the carbon-based materials for PIBs based on heteroatoms doping, unique nanostructure design, and introduction of the conductive matrix to form composites (Figure 2). Finally, the existing issues and challenges to be addressed, and perspectives for further development of high-performance PIBs are proposed to indicate the direction for potassium-ion batteries (PIBs) toward potential commercialization.

2 | GRAPHITIC CARBON FOR POTASSIUM-ION BATTERIES

Graphite, as a commercial anode material for LIBs, was proved to be a suitable host material for K\(^+\) to intercalate/extract between the graphitic interlayer reversely. Unlike pure graphite’s failure in SIBs,\(^{17,19}\) K\(^+\) storage behavior in graphite is similar to that in LIBs, showing an intercalation mechanism. Generally, graphite consists of many sp\(^2\) hybridized carbon layers with a certain interlayer distance (0.336 nm). Appropriate guest species like ions, atoms, and molecules can diffuse into the interlayer and form the intercalation compounds, whose physicochemical properties can be tuned by the guest species and concentrations.\(^{20-22}\)

Actually, the Stage-I K-graphite intercalation compounds (GICs) KC\(_8\), synthesized via potassium vapor transport or immersing and solvating graphite and potassium metal in a nonaqueous solution, was discovered as the first alkali metal GIC in 1932.\(^{23}\) Afterward, Van der Waals density functional theory (DFT) calculations revealed that the enthalpy of formation of KC\(_8\) was found to be \(-27.5\) kJ/mol, more negative than that of LiC\(_6\) (\(-16.4\) kJ/mol), illustrating K\(^+\) could intercalate into the graphitic interlayer of graphite easily to generate K-GICs.\(^{24}\) However, NaC\(_6\) and NaC\(_8\) were unstable with positive enthalpies of formation (+20.8 and +19.9 kJ/mol, respectively). It is believed that the reason for unstable Na-GICs is that the graphite would be stressed when Na ions intercalate into it.\(^{25}\)

Intercalation of potassium ions into graphite anode for PIBs was studied by many researchers. In 2015, potassium ions were first reported to intercalate into graphite electrochemically, and ex-situ X-ray diffraction (XRD) measurements for selected states of charge in the first cycle were conducted to reveal its potassium storage mechanism.\(^{15}\) In the first charge process, graphite got a considerable capacity of 273 mA h/g, being almost consistent with the theoretical value of 279 mA h/g (corresponding to the formation of KC\(_8\)), and a relatively high initial Coulombic efficiency (ICE, 54.7%; Figure 3A). However, unsatisfactory cycle stability with the rapid fade of capacity was observed in Figure 3B, mainly due to the huge volume expansion after the intercalation of large potassium ions. Ex-situ XRD results showed that with the potassium ions intercalating into graphite, phase transitions of different stages of GICs were detected (Figures 3C and 3D). The stage-III K-GIC KC\(_{36}\) was first detected between 0.3 and 0.2 V, followed by the appearance of the stage-II K-GIC KC\(_{24}\), and finally, the pure-phase stage-I K-GIC KC\(_8\) was observed after discharged to 0.01 V, showing the stage change of graphite–stage III KC\(_{36}\)—stage II KC\(_{24}\)—stage I KC\(_8\) (Figure 3E). In the following depottassiation process, the stage-I K-GIC KC\(_8\) experienced the opposite phase transformation to finally get pure-phase graphite (although a lower degree of crystallinity), indicating the highly reversible intercalation/extraction process. Another work reported by Luo et al.\(^{16}\) presented a different staging mechanism (graphite-stage III KC\(_{24}\)—stage II KC\(_{16}\)—stage I KC\(_8\)) confirmed by the coincidence of DFT calculations and experimental results. In-situ XRD measurements of K metal/graphite cell were also investigated to reveal the phase transformation in the potassium ion intercalation process, and similar results that graphite first changed to stage-III KC\(_{36}\) and finally...
transformed to stage-I KC₈, but without the appearance of stage-II KC₂₄ were demonstrated. Since these different intermediate phase transformations were discovered in the same system, more in-depth investigations with advanced characterization techniques like in-situ spectroscopy or electron microscopy technologies should be developed to establish an accurate intercalation staging transformation mechanism.

Whatever, based on the fact that the final full-discharged product was the stage-I K-GIC KC₈, a huge volume expansion (~61%) of graphite was revealed by calculations, six times larger than that in Li/graphite cell, leading to rapid capacity fading especially in the first several cycles and eventually a battery failure after long-cycle potassiation/depotassiation process. In addition, larger ion radius makes it a little more difficult for K⁺ than Li⁺ to insert in the graphite with limited interlayer spacing (0.34 nm), causing poorer rate performance of graphite anode material in PIBs. One of the most effective strategies to improve the rate performance and release the volume expansion is to enlarge the graphic interlayer distance. Commercial expanded graphite (EG)
with extended interlayer spacing (0.387 nm) reported by Jian et al. was used as anode for PIBs, which exhibited excellent electrochemical performance with the same intercalation mechanism (Figures 4A and 4B).\textsuperscript{28} Benefiting from the enlarged interlayer spacings for boosting the ion diffusion coefficient during the charge/discharge process and accelerating the insertion/extraction process of potassium ions, EG electrode material shows the capacities of 263, 242, 219, 205, and 175 mA h/g at the current density of 10, 20, 50, 100, and 200 mA/g, respectively (Figure 4C), much better than that of commercial graphite (CG). The cycle stability of EG was also significantly improved, remaining a reversible capacity of 228 mA h/g with capacity retention of 105.07% after 200 cycles, while the reversible capacity of CG anode decreased from 169 to 61 mA h/g (retention 36.09%) after the same cycles (Figure 4D). Such a great increase in cycling stability is ascribed to the fact that the expanded interlayer spacings can buffer the volume expansion of EG anode material in the continuous potassiation/depotassiation process. Similarly, an increased rate capacity was found in the activated carbon being activated from the graphite, accounting for the fact that the K\textsuperscript{+} diffusion coefficient in activated carbon was up to \(\sim 7\) times larger than that in the unactivated graphite based on the calculations of cyclic voltammetry (CV) analysis results.\textsuperscript{29} In addition,
electrolytes and binders were also investigated to be relevant to the improvement of ICE and cycle performance of graphite anode in PIBs. 

In general, the intercalation mechanism of graphitic carbon anode for PIBs was experimentally proved to be similar to that in LIBs. Potassium ions intercalate into the graphic interlayer via staging mechanism until occupying the neighboring graphite layers to form stage-I K-GIC KC₈, where the voltage plateau is 0.3 V below, leading to high operating potential in full cells. Meanwhile, by enlarging the interlayer spacings of graphite and regulating the electrolytes or binders, the rate capability and cycle stability of graphitic carbon materials could be improved to some extent. Thus, 4 V class PIBs based on graphitic carbon materials are promising to be realized with more systematic and in-depth investigations.

3 | DEFECTIVE CARBON FOR POTASSIUM-ION BATTERIES

Generally, carbon materials could be divided into two parts, graphitic carbon and defective carbon, which depends on the graphitic degree or defective degree. Unlike graphitic carbon, defective carbon has many forms, usually differently in compositions and microstructures, which can lead to different mechanisms and performance for potassium storage. Direct evidence for defective carbons is the value of \( I_D/I_G \) from the Raman spectrum, where D band is assigned to \( \text{A}_{1g} \) vibration mode of sp² carbon rings caused by the defects, and G band is assigned to \( \text{E}_{2g} \) vibration mode of sp² carbon atoms. The broaden (002) peak of defective carbons in the XRD pattern is also ascribed to the amorphous and defective properties. Usually, inherent carbon defects are inevitable and exist in many forms according to the second law of thermodynamics. The most common inherent defects are edges, vacancies or pores, and topological Stone-Wales defects. The introduction of the former two defects has been experimentally implemented via physical strategies (plasma or ball milling) and chemical methods (reduction or etching). In addition, extrinsic defects are another vital type of carbon defects, usually induced by heteroatom doping like N, S, P, F, and so on. Compared with graphitic carbon, defective carbon materials show great diversity in composition and microstructure, which could enhance the electronic conductivity, regulate the electronic structures, and improve the reaction kinetics of carbon skeleton. Moreover, all of these have an influence on the potassium storage mechanism.

3.1 | Effects of defects on carbon materials

For the storage of potassium ions in defective carbon materials, generally, three storage mechanisms are involved, including intercalation mechanism, adsorption mechanism, and capacitive mechanism. There are at least two mechanisms that play a role in the storage process of defective carbon, and the different mechanisms usually have a synergistic effect to maximize the electrochemical performance of PIBs.

The intercalation mechanism is the basic mechanism for carbon materials, and the capacity of carbon materials is highly limited by the quantity of K ions that can be intercalated into the interlayer to occupy the reactive sites. Increasing reactive sites like defects in graphitic interlayer and edges, as an effective way to improve the limited capacity determined by the full-discharged product of graphite KC₈, have attracted extensive research attention. Actually, the adsorption mechanism mainly works in the materials that contain a large number of active sites, such as edges of graphitic layers, vacancy defects, and heteroatoms (N, S, P, F, etc.) on the surface. The electronic states of these active sites are altered to be reactive as compared to the pristine carbon crystalline structure, that is to say, potassium ions prefer to adsorb in these sites to provide extra capacity for PIBs. Meanwhile, the active defective sites usually could promote the reaction kinetics with big spaces to accommodate the large potassium ions, resulting in improved rate capacity and cycle performance. Through rationally regulating and optimizing the quality and quantity of active sites, the K storage properties like reactive kinetics and capacity could be significantly enhanced. Additionally, unlike the intercalation mechanism (diffusion-controlled faradic intercalation process), intercalation/extraction or adsorption/desorption of potassium ions could also occur at the surface or near-surface defects and nano-voids of carbon nanomaterials, which is regarded as the capacitive mechanism of potassium storage. Generally, CV measurements at different scan rates are used to describe the capacitive behavior of specified materials. The power-law relationship between the current \( i \) and scan rate \( v \) shows \( i = av^b \), where the value of parameter \( b \) can be determined by plotting \( \log(i) \) versus \( \log(v) \) from the obtained CV curves. A calculated value of 0.5 for \( b \) corresponds to an ideal diffusion-controlled process, while a calculated value of 1.0 refers to a capacitive-controlled process. Undoubtedly, a calculated value between 0.5 and 1.0 of \( b \) demonstrates a mixed diffusion-controlled and capacitive-controlled process. Moreover, the capacitive contribution for potassium storage can be separated from diffusion-controlled contribution based on Dunn’s method. The capacitive mechanism results in an extra capacitive contribution, including pseudocapacitance and double layer...
capacitance, to the overall capacity of batteries. For carbon materials, it mainly occurs in those being downsized to the nanoscale with high specific surface areas. Moreover, the reaction kinetics of potassium ions storage with the capacitive mechanism could be improved a lot, leading to the enhanced rate performance, which is promising to boost the fast charge/discharge capability of PIBs. In short, constructing a unique carbon nanostructure, enlarging the graphitic interlayer spacing, and introducing heteroatoms are three aspects of strategy for increasing the density of defects and optimizing carbon materials for high-performance PIBs anodes.

3.2 Hard and soft carbons with intrinsic defects

As mentioned before, inherent carbon defects are inevitable. However, the inherent defects generated in graphitic materials only by thermodynamic factors are very limited. Various strategies, such as chemical reduction, can introduce more edges and vacancies or pores into the carbon skeleton controllably.

Hard carbon materials are one of the typical representatives with such defects. Different from graphitic carbon with long-range ordered stacked graphitic structure, hard carbon materials consist of short-range ordered partial graphitic stacking with nanovoids due to the disorder in the c direction, thus usually showing an amorphous structure. In recent years, many researchers have reported the application of hard carbon materials for PIBs, including MOF-derived hard carbons, polymer-derived hard carbons, and biomass-derived hard carbons. The edges and voids of hard carbon could provide additional storage sites for the adsorption of potassium ions, thereby improving the capacity of carbon materials in PIBs. The cellulose-derived carbons deliver a reversible capacity of 290 mA h/g due to the cross-linkage introduced by pre-heating and transformed voids and pores via high-temperature pyrolysis. Kamiyama et al. synthesized hard carbons by heat-treating macroporous phenolic resin for PIBs anodes. Through the heating treatment under different temperatures, reversible capacity for PIBs increased from 295 to 336 mA h/g for the successful extra K storage in the macroporous structures. Our group reported an amorphous ordered mesoporous carbon (OMC) as anode for PIBs prepared through a typical template method as illustrated in Figure 5A. After removing the silica template, the mesoporous structure and short-ordered properties were retained with high specific surface area, which was revealed by the results of Raman spectrum, high-resolution transmission electron microscope (HRTEM) and corresponding selected electron area diffraction, and the nitrogen adsorption–desorption isotherm and pore size distribution of OMC (Figure 5B-D). All these results point out that there are a large number of edges and defects existing in OMC anode. Thus, additional K ions adsorbed on the active sites of edges and defects in OMC contributed to part of the overall capacity. The reversible capacity of OMC based on the adsorption-intercalation mechanism in the first depotassiation process was 307.4 mA h/g at 50 mA/g, higher than the theoretical value of graphite indeed. In addition, the enlarged interlayer spacing in short range made it more flexible to the deformation of carbon layers, leading to good structural stability in the continuous potassiation and depotassiation process. Thus, a high reversible capacity of 146.5 mA h/g was obtained over 1000 cycles with a capacity decay of only 0.03% per cycle (Figure 5F). However, the poor flexibility of crystalline and degree of graphitization in hard carbon materials limited the electronic conductivity of hard carbon, leading to limited rate performance for PIBs.

Soft carbon is another representative of defective carbon materials whose degree of graphitization is between graphite and hard carbon. Meanwhile, the crystallinity and lattice spacing of soft carbon are highly tunable by controlling the graphitization temperature, which is also the key factor during the synthesis. The soft carbon could be transformed to a higher degree of graphitization as the temperature increases to enhance the electronic conductivity. Liu et al. synthesized the pitch-derived soft carbon under different temperatures (800, 1200, and 1500 °C), and it was found that the soft carbon with a moderate degree of graphitization (under 1200 °C, denoted as SC-1200) with suitable lattice spacing and defect density showed the highest capacity. Although in-depth structure-performance relationship has not been revealed in the work, in-situ XRD measurements were applied to monitor the structural change of SC-1200 during the K⁺ insertion/deinsertion process and were compared to that of graphite (Figure 6). Unlike the staging mechanism of graphite, the (002) peak of SC-1200 gradually shifted from 25.57° to 16.55° during the intercalation process, revealing a gradual change in the carbon lattice, which is universal for the defective carbon materials even in LIBs or SIBs. In addition, the rate performance of SC-1200 was better when compared to hard carbon via a heat treatment under the same temperature (denoted HC-1200). The reason is not mentioned in the study, but might be ascribed to the enhanced and better conductivity than HC-1200 due to its graphitizable property. The enhancement of conductivity can accelerate the ion and electron transportation and improve the reaction kinetics, finally leading to the excellent rate capability. Moreover, by integrating the advantages of soft carbon in high-capability rate and of hard carbon in long cycling stability, hard-soft composites applied in PIBs exhibited highly amenable performance with both high rate capability and stable long-term cycling.
FIGURE 5  (A) Schematic diagram of the preparation of OMC. (B) Raman spectrum, (C) HRTEM image and the corresponding SEAD pattern (inset), and (D) N₂ adsorption-desorption isotherm curve and pore size distribution (inset) of OMC material. (E) Cycle stability at a current density of 1000 mA/g of OMC sample for PIBs. HRTEM, high-resolution transmission electron microscope; OMC, ordered mesoporous carbon; PIBs, potassium-ion batteries; SEAD, selected electron area diffraction. Reproduced with permission: Copyright 2018, Wiley-VCH

FIGURE 6  The in-situ XRD patterns of (A) graphite and (B) SC-1200 sample with the corresponding discharge/charge curves on the right. XRD, X-ray diffraction. Reproduced with permission: Copyright 2020, Wiley-VCH
3.3 Heteroatom-doped carbon materials

Apart from the intrinsic defects occurring in some soft carbons and hard carbons, heteroatom doping is an effective way to introduce extrinsic defects for carbon materials (Figure 7). Moreover, the introduction of heteroatoms, such as N, F, P, S, and O could change the mechanism of potassium storage behavior to some extent, which is ascribed to the perturbation of electron distribution of the graphitic structure of carbon skeleton by heteroatoms, whose electron affinity and electronegativity are different from the ordered sp2 hybridized carbon atoms. Doping of heteroatoms could improve the conductivity and increase the density of adsorption sites by altering the localized electronic state, increase the interlayer distance by the larger radius heteroatoms and their repulsion effect, accelerate ion and electron transportation, and promote the charge-transfer process by adjusting the surface wettability. These, in turn, are believed to improve the capacity, rate performance, and long cycle stability of PIBs.

Graphene, with a monolayer or few layers of sp2 hybridized carbon atoms arrangement, was found to be an ideal host material for alkali metal ions due to its more exposed surfaces than graphite. However, pure graphene materials seem to be unsatisfactory in electrochemical performance with moderate capacity and poor cycle stability mainly due to its poor adsorption ability.49 Thus, graphene is thought to be an existing model to investigate the effects of doping heteroatoms.

3.3.1 O-doped carbon materials

Reduced graphene oxide (RGO) synthesized by a modified Hummer’s method was reported to be applied as anode for PIBs.16 RGO, a template of O-doped graphene material, has rich oxygenous groups in the surface introduced by the oxidation of graphite. It showed a first charge capacity of 222 mA h/g, higher than that of graphite, which was attributed to the rich functional groups in the surface. Unluckily, on the other hand, these surface groups lowered the electronic conductivity of RGO, causing poorer rate capability than graphite. O-rich carbon nanofiber (CNF-O) prepared by oxygen-plasma treatment for carbon nanofiber (CNF) was reported as an anode for PIBs.50 The CNF-O material showed lower ICE but higher Coulombic efficiency in later cycles compared to CNF, demonstrating that the introduction of the O element might increase the irreversible capacity loss due to surface oxygen reactivity, but be beneficial to the formation of K2CO3 species for forming a superior solid electrolyte interface (SEI) layer. However, the poor performance rate of CNF-O was also revealed due to the poor electronic conductivity after O doping in this study. In addition, O doping was proved by Yang et al. to be beneficial for improving the wettability by the hydrophilic groups (C-OH, C-O, etc.) to reduce the inert surface area and providing plenty of active sites for K storage.51 By the way, since many organic precursors contain oxygen elements, the O-doped carbon materials could also be easily synthesized by heat treatment of such precursors.

3.3.2 N-doped carbon materials

Nitrogen is the most studied doping element for carbon materials. The electronic conductivity, reaction activity, and wettability of the carbon skeleton could be increased through the introduction of N dopant. Moreover, nitrogen doping in carbon materials is relatively easy to be realized due to the fact that many precursor substances contain nitrogen elements, such as imidazole-based MOFs and some biomass materials.52-54 Heat treatment under NH3 atmosphere is another effective method to induce N dopant. N-doped few-layer graphene (N-FLG) materials were reported to possess an enhanced capacity exceeding 350 mA h/g, comparable to anode capacity in commercial LIBs.55,56 It is acknowledged that the electronegativity of nitrogen (3.04) is higher than carbon (2.55), which might have a significant influence on the electronic characteristics of the graphene, and then increase the interaction between the graphene structure and potassium ions, thereby leading to additional potassium storage capacity. Keith et al. also prepared the defective undoped few-layer graphene (d-FLG) with sp3 carbon defects but no N doping as reference sample to verify that where the additional capacity was produced.55 Surprisingly, the results show that N-FLG has the highest
capacity, while d-FLG has the lowest one even lower than that of FLG, which strongly verified that the N-doping sites, but not C defects, were the source of improved capacities in N-FLG with an adsorption mechanism. The in-situ Raman analysis of FLG and N-FLG demonstrated a similar staging process but different mechanisms in the range of 0.4–0.8 V, elucidating the role of N-doping was providing storage sites distributed in the carbon matrix for potassium ions without disruption of the formation of stage-IK-GIC, different from that the sp$^2$ carbon defects might impede the formation of GIC. These findings could also account for different storage behaviors of defective carbon materials from graphitic carbons that will be discussed later.

Generally, the dopant nitrogen has three different configurations, including pyridinic (N-6), pyrrolic (N-5), and graphitic nitrogen (N-Q). The N-5 and N-6 atoms located on the edge of the honeycomb-like lattice have been found to possess higher reactive activity than the N-Q atom just replacing the carbon in the pristine lattice, owing to the fact that they can introduce more defects and create more active sites for potassium ion storage, of which the pyridinic nitrogen (N-6) is the most reactive. Motivated by this, many high pyridinic N-doped carbons were reported and applied as an anode to achieve higher performance for PIBs recently.$^{52,57,58}$ The potassium storage performance of an ultrahigh pyrrolic/pyridinic-N doped necklace-like hollow carbon (NHC) was investigated in a recent work of our group.$^{59}$ A series of N-doped hollow carbon materials with different N content and distribution were synthesized by controlling the ratio of electrospinning precursors and the subsequent heat treatment atmosphere and temperature (Figure 8A-C). A high content of N (10.71 at%) after balancing the graphitic degree and an ultrahigh pyrrolic/pyridinic-N doping (22.0% and 64.0%, respectively) was achieved in the sample NHC$_2$-NH$_3$/Ar (Figure 8D). The material showed the best rate performance in all the NHC materials under different current densities, where reversible capacities of 277.8, 266.1, 260.9, 242.6, 224.3, and 204.8 mAh/g were obtained at 50, 100, 200, 500, 1000, and 2000 mAh/g, respectively. Excitedly, the reversible capacity could retain 262.6 mAh/g when the current density was reset to 50 mA/g (Figure 8E). After 1600 cycles at 1000 mA/g, the reversible capacity was maintained to 161.3 mAh/g, demonstrating its long cycle stability (Figure 8F). Furthermore, DFT calculations revealed that the pyrrolic N and pyridinic-N had more negative relative adsorption energy ($AE_a$) than graphitic N, suggesting stronger K-adsorption in the pyrrolic and pyridinic N doped structure. And such excellent rate capability and long-term cycle stability were mainly due to the enhancement of electronic conductivity by the high doping proportion of N element and ultrahigh pyrrolic/pyridinic N doping.

3.3.3 | S-doped carbon materials

Different from the adsorption mechanism of potassium ions to nitrogen dopants, sulfur doping was reported to be electrochemically active for potassium ions. Meanwhile, the larger radius of S atom is effective for the enlargement of the graphitic interlayer spacing, which is beneficial for the intercalation/deintercalation of potassium ions to facilitate the reaction kinetics. Thus, S is a significant dopant for carbon materials that promote the K storage behavior with enhanced capacity and better rate capability. The potassium storage behavior of sulfur-doped RGO (S-RGO) sponges was studied by Li et al.$^{60}$ S-RGO-600 sample with a high S doping content (10.17 wt%) was prepared after the heat treatment of RGO under 600°C in S steam. When applied as an anode in PIBs, the S-RGO-600 sample possessed a high reversible capacity of 456 mAh/g in the first depotassiation process and remained 361 mAh/g after 50 cycles. Ex-situ X-ray photoelectron spectroscopy (XPS) measurements of S-RGO-600 proved that C–S bonds could react with K to form C–S–K bonds, which exhibited a higher K-ion storage capacity compared with carbon (KC$_8$), leading to an increased capacity for PIBs. An ultrahigh S doping content of 38 wt% was achieved by an in situ sulfurization process and the corresponding reversible depotassiation capacity was 581 mAh/g, more than double the known intercalation capacity of graphite with K (279 mAh/g).$^{61}$ Similar S-doping content of 12.9 at% (~32.0 wt%) was achieved by a pre-introduction of S element into the polymer salt, which demonstrated almost the same capacity of 582 mAh/g. However, it was emphasized that the “free” state S, which is not chemically bound to the carbon, should be avoided especially in the situation of high-content S doping, S in “free” state might form K$_2$S$_n$ (5 ≤ n ≤ 6) polysulfide with K whose voltage platform is about 2.2 V, which was deleterious for extended cycling. Furthermore, DFT calculations revealed that K$^+$ is favorable to adsorb in the S sites (7.2%) with smaller volume expansion of the structure than C sites (10.6%), which was also the source of the outstanding rate capability and cycle stability.$^{63}$

3.3.4 | P-doped carbon materials

The reason for electrochemical performance improvement of phosphorus-doped carbon materials is similar to those of N-doped and S-doped ones. The phosphoric acid treatment with a subsequent high-temperature
calcination process of the precursors is a common strategy for P-doping. In addition, direct heat treatment of precursor (carbon source) and P2O5 or NaH2PO4 (dopant source) and solution plasma process could also induce P dopant.

P-doped graphene synthesized by mixing as-prepared GO and the phosphorous precursor and the subsequent heat treatment was applied as anode for PIBs. It delivered a reversible capacity of 566.6 mA h/g at 50 mA/g, mainly due to the fact that lots of vacancies and defects were generated and were beneficial for potassium-ion storage. Meanwhile, the enhanced electronic conductivity after P doping fastens the reaction kinetics, accounting for the better rate performance.
The electrochemical performance of P-doped hard carbon (3.47 at% P dopants) synthesized by crosslinking phosphoric acid and epoxy resin followed by annealing at 700°C was also investigated by Qian et al.\(^{65}\) It delivered higher capacity and longer cycle life than that without P dopants. In situ Raman and in-situ NMR measurements in LIBs revealed that the P–O and P–C bonds could enhance the adsorption to alkali metal ions, and P–C bond could participate in electrochemical redox reaction by forming the Li,P,C\(_4\) for high capacity and excellent rate performance. And further solid-state NMR demonstrated a similar mechanism and regularity for potassium ion storage. Thus, it was evident that more electroactive sites and affinity to potassium caused by P–O and P–C bonds in the P-doped sample led to its elevated electrochemical performance.

### 3.3.5 | F-doped carbon materials

Different from the above doping element, when fluorine, the most electronegative element, is covalently attached to the sp\(^2\) hybridized carbon skeleton to form the C–F bond, the hybridization state of C would be converted from sp\(^2\) to sp\(^3\), inducing local deformation of the graphitic lattice and creating high structural disorder. Meanwhile, the electronic structure of the local carbon skeleton would have a significant change in the potassium storage behavior. The F dopants are usually successfully doped into carbon skeleton by direct heat treatment of F-containing precursors, such as polyvinylidene fluoride (PVDF) and poly-tetrafluoroethylene (PTFE), or posttreatment of HF etching.\(^{71,72}\) NH\(_4\)F, through mixing with the carbon sources and further pyrolyzing the mixture under inert atmosphere, was also found to be an effective F dopant.\(^{73}\)

F-doped few-layer graphene foam (FFGF), synthesized by a high-temperature solid-state reaction of PVDF, was investigated as anode for PIBs and delivered a high reversible capacity of 355.6 mA h/g at 50 mA/g and an attractive rate capability.\(^{74}\) The fluorine-surface modification was believed to improve the pore affinity to the electrolyte and increase the graphitic interlayer spacing of graphene, achieving excellent rate performance especially in the high-speed electrochemical reaction. F element was successfully doped into porous carbon nanopolyhedra by HF etching and second annealing procedure of Zr-based MOF-derived composites along with the removal of ZrO\(_2\).\(^{72}\) Even if the doping content of F was only 0.13 at%, the electronic structure of carbon was influenced significantly to facilitate the adsorption of alkali metal ions. Thus, the as-prepared sample delivered a high reversible specific capacity of 405 mA h/g at 0.1 A/g and preeminent long cycle stability (218 mA h/g after 2000 cycles at 1 A/g with approximately 92% capacity retention). The DFT calculations revealed that the calculated \(\Delta E_s\) of F-doped material was \(-2.12\) eV, suggesting its enhancement of the K-adsorption ability. Interestingly, the value of \(\Delta E_s\) gradually decreased but maintained negative with the increase of the adsorption number of K atoms, suggesting a highly stable reaction of K storage in F-doping sites. Further calculations based on Bader charge analysis showed that K atoms donated 2.885 electrons to porous carbon with F doping, thus resulting in an enhanced capacity.

### 3.3.6 | B-doped carbon materials

B-doping graphene was also investigated by DFT calculations as a promising anode for PIBs.\(^{75}\) The B-doped graphene with B\(_4\)C\(_{28}\) structure (doping concentration of 12.5 at%) was studied to be metallic with good electronic conductivity and possess a large specific capacity of 546 mA h/g with the maximum eight K\(^+\) adsorptions to graphene layer to form K\(_8\)B\(_4\)C\(_{28}\), although without further experimental investigations of this structure. However, B-doped porous carbon materials were successfully synthesized by a liquid-state template method using B\(_2\)O\(_3\) as dopant and the elevated specific capacity of carbon materials after B doping was verified.\(^{76}\)

### 3.3.7 | Dual-doped carbon materials

The function of different heteroatom doping in carbon and effects on K-storage behavior discussed above are summarized in Table 1. Apart from mono-atom doping, dual-doped carbon materials have also been extensively investigated for energy storage devices. The dual doping for carbon materials usually has a synergistic effect of the two dopant elements for promoting the electrochemical performance of PIBs. Till now, dual doping carbon materials have been intensively reported to be used in PIBs with excellent performance, such as N/O dual doping, N/S dual doping, P/N dual doping, F/O dual doping materials, and so on.\(^{53,64,70,72,77-79}\) NH\(_4\)HB\(_4\)O\(_7\)·3H\(_2\)O was used as a dopant to generate B\(_2\)O\(_3\) and NH\(_3\) in the heat treatment to simultaneously introduce the doping of B and N atoms in the porous carbons (BN-PC, Figure 9A).\(^{76}\) The HRTEM image (Figure 9B) showed several sp\(^3\) defective carbon areas in the continuous sp\(^2\) graphitic carbon conductive network. Based on the results of XPS spectra, the possible formation process of C-N-B bonds in BN-PC was proposed by the model in Figure 9C, where the N element was first doped to the carbon skeleton, and the dopant B atom bonded to the N atom and carbon.
TABLE 1 The summarizing on the function of heteroatom doping in carbon and their effects on K storage behavior

| Heteroatom | Function in carbon skeleton | Effects on K storage behavior |
|------------|-----------------------------|------------------------------|
| O          | Lower the electronic conductivity | Worsen rate capability |
| N          | Increase reaction activity (N-6 > N-5 > N-Q) | Additional K storage sites |
| S          | Enlarge the interlayer spacing | Facilitate the reaction kinetics |
| P          | Enhance electronic conductivity | Enhanced reaction kinetics |
| F          | High structural disorder (the most electronegative element) | Facilitate the adsorption of K |
| B          | Improve the pore affinity to the electrolyte | Enhanced reaction kinetics |
|           | Increase the graphitic interlayer spacing | Highly stable reaction of K storage |
|           | Improve the electronic conductivity | Enhanced reaction kinetics |

skeleton. After B/N dual-doping, BN-PC delivered a higher reversible capacity of 462.5 mA h/g at a current density of 0.05 A/g, much higher than undoped (PC, 86.5 mA h/g), mono B-doped (B-PC, 201.8 mA h/g), and mono N-doped (N-PC, 371.3 mA h/g) porous carbon materials. It was revealed that the formed B–N–C bonds occupied the micropores in the carbon network and improved its order and integrality, eventually leading to higher electronic conductivity of BN-PC. The synergistic effect of electron-deficient B and electron-rich N not only balanced sp³ defective carbon clusters and sp² graphitic carbon domains but also provided the conductive carbon networks to facilitate the charge-transfer process, achieving a balance between high conductivity and high activity of BN-PC. The electrical conductivity of BN-PC was tested to be 47 S/m, much higher than those of N-PC and B-PC samples (<10 S/m), which was confirmed by the lowest $R_{ct}$ value of the BN-PC anode in the electrochemical impedance spectroscopy (EIS) of PIBs (Figure 9D). The enhanced reaction kinetics resulting from the superior electronic conductivity finally led to the outstanding rate performance (Figure 9E) and ultra-long cycle stability (Figure 9F, a reversible capacity of 144.4 mA h/g after 15,000 cycles at 5 A/g). The synergistic effect of P/N co-doping was investigated by He et al. through the use of P-doped N-rich honeycomb-like carbon (PNHC) for potassium storage. It was found that P-doping could modify the electronic structure and induce more open edge sites to increase the formation of pyridinic N of the carbon framework, which greatly promoted the reactivity of interfacial K⁺ adsorption reactions, leading to the excellent electrochemical performance of PNHC materials. Remarkably, the ICE of PNHC materials in the potassiation/depotassiation process was improved significantly with further P doping mainly due to the decreased defective sites that contributed to the irreversible capacity. A similar configuration of N/P dual doping was conducted by Chen et al. in their recently reported work. The N/P dual-doped hollow porous bowl-like carbon (N/P-HPCB) with the 5.85% N and 4.25% P contents showed a high reversible capacity of 531 mA h/g with the highest ICE compared to the undoped and N-doped samples. It was believed that the high pyridinic/pyrrolic-N contents after P doping could suppress the irreversible capacity from the electrolyte decomposition and SEI formation. Generally, defects are the active sites for potassium storage, but not all defects are devoted to the reversible capacity. Therefore, further control in the formation of effective defects for reversible potassium storage will be vital to achieving high-performance carbon anode materials for PIBs.

3.4 Nanostructured carbon materials

As summarized above, a majority of carbon materials were synthesized by the heat treatment of the carbonaceous framework. As the temperature rises in the annealing process, non-carbonaceous elements will evaporate, and only a small amount of them will remain on the carbon skeleton in the form of doped elements. Thus, with the evaporation of these elements on the pristine framework, a new skeleton with many defects such as vacancies and pores will generate, leading to large specific surface areas of defective carbon materials.
It is worth noting that rich active defect sites and large specific areas could induce an extra capacitive contribution due to the intercalation/extraction or adsorption/desorption of potassium ions that occur at the surface or near-surface defects and nano-voids of carbon nanomaterials. Moreover, the reaction kinetics of the potassium storage at the surface or near-surface is faster than that of intercalation for its shortened ion and electron transportation pathway, thereby resulting in enhanced rate capability of PIBs.

Based on this, some unique carbon nanostructures, such as ultrathin wrinkled nanosheets, hierarchical porous structure, and hollow structure are designed to further achieve high-performance PIBs. In the paper of Liu et al., wrinkled envelope-like carbon nanosheets annealed from glucose (N-CNS) with a template method possessed a high
Brunauer–Emmett–Teller (BET) surface of 674 m²/g. When applied as an anode in PIBs, the N-CNS sample showed the reversible capacity of 367 mA h/g at 50 mA/g in the first depotassiation and good reversibility in the following cycles (Figure 10A). The charge capacities of N-CNS were 361, 273, 271, 246, 189, 178, and 168 mA h/g at current densities of 50, 100, 200, 500, 1000, 1500, and 2000 mA/g, respectively, and when the current rate was set back to 200 mA/g, the charge capacity retained 227 mA h/g, demonstrating high rate performance (Figure 10B). The capacitive contribution of the materials for K⁺ storage was investigated by CV measurements at the sweep rates between 0.2 and 1.2 mV/s (Figure 10C-F). The b values revealed mixed diffusion-controlled intercalation and capacitive reactions for potassium storage. The proportions of capacity contribution at different scan rates exhibited an increased capacitive contribution with the scan rate increasing. Remarkably, the capacitive-controlled contributions were calculated to be 55% and 78% at scan rates of 0.2 and 1.2 mV/s, respectively, indicating that the capacity especially at high scan rates was mainly from the adsorptive-controlled capacitive mechanism, which was also the reason for the outstanding rate performance of N-CNS. However, it should be noted that not all induced defects of nanostructured carbon materials would be devoted to the capacitive-controlled process, and some of them might be irreversible adsorption sites for potassium ions and would not participate in the following charge/discharge process as mentioned before, which leads to a low ICE. Therefore, besides dual-doping, further investigations should be focused on how to distinguish the defects acting as irreversible adsorption sites from the useful defects and how to convert them to the effective or to avoid their formation.

3.5 | Synergistic effect of multiple defects in carbon materials

The defective carbon materials show much higher potassium storage capacity (almost greater than 220 mA h/g and even up to 580 mA h/g), more excellent rate performance, and longer cycle stability than that of graphitic carbon materials mainly due to the following reasons: (1) the enlargement of the graphitic interlayer spacing of (002) facilitates the intercalation/deintercalation of large potassium ions and provides more space to buffer the volume expansion resulting from the large radius of K⁺; (2) the unique carbon nanostructures with large specific

FIGURE 10 (A) Charge/discharge profiles of N-CNS anode at 50 mA/g. (B) Rate performance of N-CNS at current densities from 50 to 2000 mA/g. (C) CV curves at scan rates from 0.2 to 1.2 mV/s. (D) Capacitive contributions and diffusion-controlled contributions to capacities at various scan rates. Capacitive contributions at (E) 0.2 and (F) 1.2 mV/s for potassium ions storage. CV, cyclic voltammetry. Reproduced with permission: Copyright 2018, Wiley-VCH.
surface areas shorten the ion and electron transportation pathway and provide more active sites for K⁺ adsorption; (3) heteroatoms doping alters the electronic structure of carbon skeleton and creates abundant defects, thus, more active sites are provided for potassium ion storage. In the recently reported work of our group, a three-dimensional (3D) carbon framework constructed by N/S co-doped graphene nanosheets (CFM-S₃₀NG) with expanded interlayer spacing was successfully synthesized by combining the above three advantages.⁸⁵ The as-prepared sample exhibited a 3D hierarchical porous carbon nano-framework structure assembled by ultrathin graphene nanosheets (Figure 11A). After further sulfur doping, the structural morphology of the CFM-S₃₀NG sample was maintained and the interlayer spacing was expanded to 0.448 nm with the successful doping of the N and S element (Figure 11B-D). Meanwhile, abundant edge defects introduced by N/S co-doping served as active sites for potassium storage. Thus, the CFM-S₃₀NG sample delivered a high reversible capacity of 348.2 mA h/g and showed the best cycle stability and rate performance as compared with the undoped/mono-doped samples (Figures 11E and 11F). In addition, the proportions of capacity contribution at different scan rates were calculated, indicating the existing adsorptive-controlled process, especially at high scan rates (Figure 11G). Thus, the mixed intercalation, adsorption, and capacitive mechanism were devoted to the storage of potassium ions due to the synergistic effect of unique carbon nanostructure, enlarged graphitic interlayer spacing, and heteroatoms doping, eventually leading to optimized electrochemical performance of PIBs.

**FIGURE 11** (A) TEM image of 3D porous carbon nano-framework structure and SEM image in the inset. (B) TEM and (C) HRTEM images of as-prepared CFM-S₃₀NG. (D) HAADF-STEM image and EDS mapping of as-prepared CFM-S₃₀NG. Comparison of (E) cycle stability at 100 mA/g and (F) rate capability of different samples. (G) Contribution ratios of the capacitive capacity of CFM-S₃₀NG at scan rates from 0.1 to 1.2 mV/s. EDS, energy dispersive X-ray spectrometry; HRTEM, high-resolution transmission electron microscope; HAADF-STEM, high-angle annular dark field scanning transmission electron microscopy. Reproduced with permission: Copyright 2020, American Chemical Society⁸⁵
CARBON-BASED COMPOSITE MATERIALS FOR POTASSIUM-ION BATTERIES

Although great success has been achieved in optimizing carbon materials for high-performance PIBs, the limited capacity of the carbon material itself still hampers its development in high-energy-density devices mainly due to the low theoretical capacity of graphite and low tap density of defective carbon materials. Therefore, searching materials with high theoretical capacity and high tap density is significant for the development of high-energy-density PIBs. To date, researchers have made great efforts on alloying materials and intercalation-conversion materials with relatively high theoretical capacity. However, these two categories of materials undergo huge volumetric change during the potassiation/depotassiation process due to the large radius of K⁺ and their corresponding K⁺ storage mechanism, leading to structural collapse of materials and battery failure with poor cycle performance. Designing a unique nanostructure and introducing a conductive carbon framework (hollow spheres, porous carbon, carbon coating, etc.) for these materials is the most common strategy to improve cycle stability. Generally, unique nanostructures could also be introduced to carbon-based composite materials in various routes, such as electrospray-assisted strategy, ball milling, carbon coating, and hydrothermal method, and in-situ MOF-derived method.

4.1 Carbon-based alloying materials

Alloying materials have been extensively studied as anodes for PIBs with an alloying/dealloying mechanism during the potassiation/depotassiation process, such as Sn-based, Sb-based, Pb-based, and Ge-based materials. The theoretical capacity of these materials depends on the final alloying composition, so does the magnitude of volume changes. Generally, alloying materials suffer from huge volume expansion due to their inherent structural limitations, leading to electrochemical performance deterioration resulting from structural collapse and the loose connection with the current collector in the repeated alloying/dealloying process. By compositing with a carbon matrix with large spaces, the structural damage resulting from volume expansion could be efficiently avoided to some extent, and the reaction kinetics could be improved at the same time.

Sn nanoparticles homogeneously embedded in 3D hierarchically porous carbon shells with a NaCl template were investigated as PIBs anodes. By controlling the calcination temperature, the size and distribution of Sn nanoparticles and the electronic conductivity of carbon achieved a balance, finally resulting in high performance of the Sn/C composites in PIBs.

Phosphorus (P) shows great potential as anode for PIBs with a high theoretical specific capacity (2595 mAh/g), but severe capacity decay caused by huge volume expansion and poor electronic conductivity in the charge/discharge process impede its development. After anchoring red P nanoparticles on a 3D porous carbon nanosheet framework (red P@CN composite) with a particle size of 10–20 nm, the reversible depotassiation capacity based on the mass of phosphorus was 715.2 mA h/g, much higher than the bare red P anode (244.6 mA h/g). Meanwhile, the cycle stability (retained capacity of 427.4 mA h/g over 40 cycles at 100 mA/g) and rate performance were remarkably enhanced. The similar regularity and conclusion were revealed in the investigation of red P/C anode materials. The potassium ion storage behavior of Sn₄P₃/C and Se₃P₄/C composite materials was investigated after alloying with Sn and Se for the sake of further improving the electronic conductivity of P-based materials. Actually, similar to K-S batteries, Se could also alloy with K to provide the capacity, denoted as K-Se batteries with moderate operating voltage. After binding the Se anode into supported carbon nanosheets, the rate performance and cycle stability could be significantly improved.

Huang et al. recently reported the Sb-based yolk-shell nanofibers (Sb@CNFs) synthesized by a MOFs-engaged electrospinning strategy and further reduction treatment (Figure 12A) as anode for PIBs and conducted in-situ TEM characterizations to reveal the effect of the yolk-shell structure. As shown in Figure 12B, Sb bulk material suffered from rapid capacity decay (43 mA h/g after 200 cycles), especially in the first several cycles, which probably resulted from the collapse of Sb bulk during the alloying/dealloying processes. Notably, the Sb@CNFs sample exhibited outstanding cycling stability with a high capacity of 338 mA h/g at 200 mA/g after 200 cycles, demonstrating much higher reversibility than bulk Sb material. In-situ TEM characterizations were conducted in real-time to further investigate the effect of the yolk-shell structure in the potassiation/depotassiation process (Figure 12C-F). Sb nanoparticles gradually grew larger and finally filled the internal void spaces in the carbon shell as the reaction time increased in the potassiation process. And in the subsequent depotassiation process, volume shrinkage of carbon shell and reduced size of Sb nanoparticles were observed. These real-time observations verified the high structural stability of the yolk-shell Sb@C structure, which was responsible for the stable cycling performance of Sb@CNFs in PIBs.
extent and improve the reaction kinetics, the low loading of alloying materials on carbon will sacrifice their reversible capacity. In addition, the volume change still occurs in the inner of the alloying materials, causing low CE and poor reaction reversibility in PIBs.

4.2 Carbon-based intercalation-conversion materials

Intercalation-conversion materials mainly consist of transition metal compounds, which mainly include oxides, sulfates, selenides, and tellurides with the
reaction of $M_{a}X_{b} + (b\cdot n) K \leftrightarrow K_{b}M_{a}X_{b} \leftrightarrow aM + bK_{n}X$ for PIBs. $M$ denotes the transition metal like Fe, Co, Ni, Mo, Re, and so on, $X$ denotes the anion (O, S, Se, Te, etc.), and $n$ is the oxidation state of $X$. Some of transition metal compounds might only show the intercalation process without the conversion process, which could be much more stable during the cycling. For the intercalation-conversion materials, although some of them, especially sulfates and selenides, possess the layered structure, huge volume expansion still occurs due to the large radius of potassium ions and the chemical transformation in conversion process. Metallic graphene-like VSe$_2$ ultrathin nanosheets, applied as anode for PIBs, delivered a high reversible capacity of 366 mA h/g at 100 mA/g based on the intercalation-conversion mechanism and showed long-term cyclability (87.3% capacity retention over 500 cycles at 2000 mA/g) due to the ultrathin morphology.\textsuperscript{114} Although benefit from the two-dimensional ultrathin structure, the cyclability of VSe$_2$ for PIBs is not good enough compared with similar materials in LIBs and SIBs.\textsuperscript{115}

Furthermore, by combining the high capacity anode materials with a conductive carbon buffer framework, the carbon-based composite materials could make a balance of high-specific capacity and long cycle life and are promising to achieve high energy density PIBs. Pistachio-shuck-like MoSe$_2$/C core/shell nanostructure (PMC) synthesized by a colloidal method with controlled reaction time was reported by our group as an advanced anode for boosting the performance of PIBs.\textsuperscript{116} The PMC consisted of a core of a few layers of MoSe$_2$ with expanded interlayer spacing (0.85 nm) to facilitate K$^+$ intercalation/deintercalation and a thin amorphous carbon as the shell confining the MoSe$_2$ core from structural collapse during cycling (Figures 13A and 13B). To be specific, the flexible carbon matrix can buffer the volume expansion to maintain the structural integrity of active material in the continuous charge/discharge process, and meanwhile improve the electronic conductivity to facilitate ion and electron diffusion, thus promoting the reaction kinetics, as shown in Figure 13C. The PMC sample showed a high capacity of 322 mA h/g at 0.2 A/g over 100 cycles (Figure 13D). When compared with the short reaction time nanospheres (NS) and the broken nanosheets (BPS) with longer reaction time, the PMC sample showed the best cycle stability and rate capacity (Figures 13E and 13F). Moreover, a capacity of 226 mA h/g over 1000 cycles was remained at the high current density of 1.0 A/g, demonstrating the long-term cycle stability of PMC.

Different from the particle morphology of the alloying materials, the morphology of intercalation-conversion materials could be various like nanosheets, nanorods, nanowires, and other shapes. Thus, the extensive unique structures of carbon-based intercalation-conversion composite materials were proposed to better play the buffering role of the carbon skeleton and better
utilize the reactivity of active materials, such as N/P co-doped porous carbon sheets/CoP hybrids,117 sandwich-like MoS2@SnO2@C,122 and so on. Yolk-shell FeS2@C structure on graphene matrix, applied as anode for PIBs, delivered a high reversible charge capacity of 451 mA h/g.88 The charge capacity retained 308 mA h/g after 100 cycles and 270 mA h/g even after 1000 cycles, demonstrating the best cycling stability compared to that of G@FeS2@C, G@FeS2, and FeS2 anodes. The excellent electrochemical performance should be ascribed to the synergistic effect of the yolk-shell structure (provide interior void space), carbon coating (protective from collapse), and the graphene matrix (fasten the transport of electrons and ions).

Yao et al.121 reported a compact MoS2/graphene tightened by a densifying strategy for potassium storage. It delivered a high reversible capacity of 505 mA h/g after the initial 5 cycles and stable cycle performance with a capacity retention of 75.2% over 800 cycles at a current density of 1 A/g. It was worth noting that the electrode thickness of compact MoS2/graphene was less than that of a freeze-dried MoS2 sample with the same mass loading. Thus, a higher volumetric capacity of 467 mA h/cm3 at 0.1 A/g was achieved for compact MoS2/graphene, about 1.5 times that of the MoS2 electrode. That is to say, the carbon-based composites also show great potential in realizing relatively high volumetric energy density despite the light carbon matrix with low tap density.

Particularly, when the transition metals of the transition metal compounds could be alloyed with K metal, such as Sb and Sn whose alloying mechanisms were discussed in the previous section, a following alloying process of transition metal and K metal would occur after the intercalation-conversion process to provide extra capacity. However, the problem is that they often suffer from severer transformation, leading to much poorer cycle ability.121,124,127 One typical example is that bare Sb2S3 nanowires showed a high capacity of near 500 mA h/g based on the intercalation-conversion and alloying mechanism, but poor rate capacity and cycle stability due to the severe structural deformation during the charge/discharge process, revealed by in situ TEM at the atomic scale.121 Interestingly, the electrochemical performance of Sb2S3 nanowires could be dramatically improved after carbon coating, attributed to the enhanced K+ transport kinetics caused by high electronic conductivity and high ionic conductivity, and the good mechanical strength of Sb2S3/C core/shell structure, verified by in situ TEM results.

5 | CONCLUSION AND PERSPECTIVE

Developing high-performance energy storage and conversion devices is vital for the sustainability of energy development. PIBs show great advantages for the abundance and low cost of potassium resources in the application of large-scale electric power devices based on the experience of LIBs whose development was limited by the barren lithium resources. Searching suitable K-host anode materials is significant for PIBs to gain a high energy density with both high cell potential and high cell capacity. Carbon materials stand out for the relatively low potential versus K/K+ couple and meanwhile possess good conductivity. This review focuses on the recent researches and the strategies for the improvement of carbon-based materials as anodes for high-performance PIBs. Graphite, as the commercial anode for LIBs, applied as anodes in PIBs delivers a moderate capacity with relatively low intercalation potential, but with unsatisfactory cycle stability due to the structural collapse originating from the large radius of K+. After modification by some strategies, the potassium storage behavior changes and the electrochemical performance of PIBs is improved a lot. To be specific, the edges, pores, and vacancies introduced by heat treatment in hard carbons and soft carbons could increase the K+ adsorption, thereby providing additional capacity. Heteroatoms doping could not only alter the electronic structure of the carbon skeleton to enhance the ion diffusion and electron transfer but also create new defective sites and then enlarge the interlayer spacing for further K+ storage. Through designing a unique nanostructure for carbon framework, the increased defect density and specific surface area bring out the additional capacitive-controlled for carbon materials, showing mixed diffusion-controlled intercalation and capacitive mechanism. The experimental results show that the optimized carbon materials with the above strategies deliver higher capacity, better rate capability, and longer cycle stability. Moreover, many researches show great success in carbon-based composites by combining non-carbonaceous anode materials with conductive carbon matrix as buffer materials. With the balance of high capacity of alloying materials or intercalation-conversion materials and the cycle stability and enhanced reaction kinetics improved by carbon matrix, the carbon-based composites show great potential in the application of PIBs. The electrochemical performance, including the reversible capacity, rate capability, and cycle stability of recently reported carbon-based materials have been summarized and illustrated in Figure 14 and Table 2.
To promote the further practical application of carbon-based materials in PIBs, some specific challenges are listed as follows:

First, numerous studies have verified that the defects (including edges, pores, vacancies, and heteroatoms doping) in carbon skeleton could improve the electrochemical performance toward potassium ion storage in terms of specific capacity and rate capability. However, not all induced defects in carbon materials are devoted to reversible capacity. Some of them might be irreversible adsorption sites for potassium ions or electrolytes and would not participate in the following potassiation/depotassiation process, leading to low initial Coulombic efficiency (ICE) of PIBs and seriously hampering the high capacity. Excessively high concentration of defects will hamper the long cyclability of carbon materials to some extent, so controlling an appropriate concentration of defects in carbon materials is extremely important to improve the ICE and the cycle stability. Therefore, it is significant to optimize the synthetic strategies so that the defect sites could be constructed accurately and controllably in carbon materials. Additionally, new characterization methods should be developed to monitor the synthesis process of defect sites in real-time.

Second, it was found to be a common phenomenon in the many researches that the defective carbon materials with various defect sites show an inconspicuous voltage plateau during the potassiation/depotassiation process, different from the obvious plateau in the K-graphite battery system, leading to low initial Coulombic efficiency (ICE) of PIBs and seriously hampering the high capacity. Excessively high concentration of defects will hamper the long cyclability of carbon materials to some extent, so controlling an appropriate concentration of defects in carbon materials is extremely important to improve the ICE and the cycle stability. Therefore, it is significant to optimize the synthetic strategies so that the defect sites could be constructed accurately and controllably in carbon materials. Additionally, new characterization methods should be developed to monitor the synthesis process of defect sites in real-time.

Third, although low ICE is common in the defective carbon materials influenced by irreversible adsorption sites, it was found in the early report that graphite also suffered from low ICE, which could be improved by the use of different electrolytes and binders. Further investigations also verified that the use of different electrolytes and binders could improve the ICE of carbon-based materials to some extent. For example, it was proved that the KFSI could efficiently suppress the growth of potassium dendrites and avoid excessive side reactions, leading to a high ICE. At the same time, a binder with better coatability for the electrode could enable a more uniform coating layer and reduce the formation of SEI film, which not only improves the ICE but also enhance the cycle stability of the electrode materials. More important, it is proved that appropriate electrolytes could promote the formation of a stable SEI layer and avoid the decomposition of electrolyte solvent, which is also effective for the enhancement of long cycle stability. However, the related investigation of electrolytes and binders toward high-performance PIBs is still in the early stage. More in-depth and systematic investigations, including the optimization of electrolytes and binders, selection of additives for electrolytes, and the analysis of the formed SEI should be studied to achieve high-performance PIBs.

Last but not the least, to achieve practical application and commercialization of the carbon-based materials, it is necessary to study the full cell fabrication and the corresponding performance. However, full cell fabrication
needs clear reaction mechanisms and accurate matching of carbon-based anodes with the corresponding cathodes, which is an obstacle for carbon-based materials with relatively low ICE (less than 60%). Even so, full cells based on carbon-based materials with potassium Prussian blue, PTCDA, and so on as cathode have been investigated in reported work with moderate capacity and energy density, which even could lighten light-emitting diode. However, the energy output and long cycle stability cannot be satisfied for the practical application. More efforts should be dedicated to the study of the full cell fabrication, as well as the further optimization of carbon-based materials and the corresponding cathodes.

In conclusion, carbon-based materials have been extensively studied and the electrochemical performance has been improved by various strategies in recent years. The specific existing challenges and the perspectives for further investigations have been summarized. It is believed that through further optimization based on the above strategies, carbon-based materials may promote the practical PIBs application in the future.

**ACKNOWLEDGMENTS**

This study was financially supported by the National Key R&D Program of China (Grant no. 2017YFA0206701), the National Science Fund for Distinguished Young
Scholars (Grant no. 52025133), the Tencent Foundation through the XPLORER PRIZE, Beijing Natural Science Foundation (Grant no. JQ18005), and the National Natural Science Foundation of China (Grant no. 22002003).

CONFLICT OF INTERESTS
The authors declare that there are no conflict of interests.

ORCID
Shaojun Guo https://orcid.org/0000-0003-4427-6837

REFERENCES
1. Dunn B, Kamath H, Tarascon J-M. Electrical energy storage for the grid: a battery of choices. Science. 2011;334:928-935.
2. Larcher D, Tarascon JM. Towards greener and more sustainable batteries for electrical energy storage. Nat Chem. 2015;7:19-29.
3. Chu S, Cui Y, Liu N. The path towards sustainable energy. Nat Mater. 2017;16:16-22.
4. Liu K, Liu Y, Lin D, Pei A, Cui Y. Materials for lithium-ion battery safety. Sci Adv. 2018;4:eaaas9820.
5. Zeng X, Li M, Abd El‐Rahman M, et al. Commercialization of lithium battery technologies for electric vehicles. Adv Energy Mater. 2019;9:1900161.
6. Barandiarán J. Lithium and development imaginaries in Chile, Argentina and Bolivia. World Dev. 2019;113:381-391.
7. Hirsh HS, Li Y, Tan DHS, Zhang M, Zhao E, Meng YS. Sodium-ion batteries paving the way for grid energy storage. Adv Energy Mater. 2020;10:2001274.
8. Li M, Lu J, Ji X, et al. Design strategies for nonaqueous multivalent-ion and monovalent-ion battery anodes. Nat Rev Mater. 2020;5:276-294.
9. Pramudita JC, Peterson VK, Kimpton JA, Sharma N. Potassium-ion intercalation in graphite within a potassium-ion battery examined using in situ X-ray diffraction. Powder Differ. 2017;32:S43-S48.
10. Hou H, Qiu X, Wei W, Zhang Y, Ji X. Carbon anode materials for advanced sodium-ion batteries. Adv Energy Mater. 2017;7:1602898.
11. Ge P, Fouletier M. Electrochemical intercalation of sodium in graphite. Solid State Ion. 1988;28-30:1172-1175.
12. Kovtyukhova NI, Wang Y, Berkdemir A, et al. Non-oxidative intercalation and exfoliation of graphite by Brønsted acids. Nat Chem. 2014;6:957-963.
13. Chekhova GN, Pinakov DV, Shubin YV, et al. Room temperature synthesis of fluorinated graphite intercalation compounds with low fluorine loading of host matrix. J Fluorine Chem. 2020;232:109482.
14. Makotchenko VG, Nazarov AS, Yakovlev II. Dicarbon fluoride intercalation compounds as new molecular containers of volatile compounds. Dokl Chem. 2001;380:252-254.
15. Schlee E, Wellmann M. Notiz über die Herstellung eines Lindemanglases für Kapillaren zwecks Aufnahme von luftempfindlichen Substanzen mit langwelliger Röntgenstrahlung. Z Kristallogr Cryst Mater. 1932;83:148-149.
36. Yi S, Qin X, Liang C, et al. Insights into KMnO₄ etched N-rich carbon nanotubes as advanced electrocatalysts for Zn-air batteries. *Appl Catal B.* 2020;264:118537.

37. Jiang H, Gu J, Zheng X, et al. Defect-rich and ultrathin N doped carbon nanosheets as advanced trifunctional metal-free electrocatalysts for the ORR, OER and HER. *Energy Environ Sci.* 2019;12:322-333.

38. Zhao G, Yu D, Zhang H, et al. Sulphur-doped carbon nanosheets derived from biomass as high-performance anode materials for sodium-ion batteries. *Nanoscale*. 2020;67:104219.

39. Shi R, Xie L, Chen G, et al. 3D well-ordered porous phosphorus doped carbon as an anode for sodium storage: structure design, experimental and computational insights. *J Mater Chem A.* 2019;7:11400-11407.

40. Yuan Y, Chen Z, Yu H, et al. Heteroatom-doped carbon-based materials for lithium and sodium ion batteries. *Energy Storage Mater.* 2020;32:65-90.

41. Wang J, Polleux J, Lim J, Dunn B. Pseudocapacitive contributions to electrochemical energy storage in TiO₂ (anatase) nanoparticles. *J Phys Chem C.* 2007;111:14925-14931.

42. Yamamoto H, Muratsubaki S, Kubota K, et al. Synthesizing higher-capacity hard carbons from cellulose for Na- and K-ion batteries. *J Mater Chem A.* 2018;6:16844-16848.

43. Kamiyama A, Kubota K, Nakano T, et al. High-capacity hard carbon synthesized from macroporous phenolic resin for sodium-ion and potassium-ion battery. *ACS Appl Energy Mater.* 2020;3:135-140.

44. Wang W, Zhou J, Wang Z, et al. Short-range order in mesoporous carbon boosts potassium-ion battery performance. *Adv Energy Mater.* 2018;8:1701648.

45. Liu Y, Lu Y-X, Xu Y-S, et al. Pitch-derived soft carbon as stable anode material for potassium ion batteries. *Adv Mater.* 2020;32:2000505.

46. Qiu S, Xiao L, Sushko ML, et al. Manipulating adsorption-insertion mechanisms in nanostructured carbon materials for high-efficiency sodium ion storage. *Adv Energy Mater.* 2017;7:1700403.

47. Jin Q, Wang K, Feng P, Zhang Z, Cheng S, Jiang K. Surface-dominated storage of heteroatoms-doping hard carbon for sodium-ion batteries. *Energy Storage Mater.* 2020;27:43-50.

48. Jian Z, Hwang S, Li Z, et al. Hard-soft composite carbon as a long-cycling and high-rate anode for potassium-ion batteries. *Adv Funct Mater.* 2017;27:1700324.

49. Share K, Cohn AP, Carter RE, Pint CL. Mechanism of potassium ion intercalation staging in few layered graphene from in situ Raman spectroscopy. *Nanoscale.* 2016;8:16435-16439.

50. Adams RA, Syu J-M, Zhao Y, Lo C-T, Varma A, Pol VG. Binder-free N- and O-rich carbon nanofiber anodes for long cycle life K-ion batteries. *ACS Appl Mater Interfaces.* 2017;9:17872-17881.

51. Yang J, Ju Z, Jiang Y, et al. Enhanced capacity and rate capability of nitrogen/oxygen dual-doped hard carbon in capacitive potassium-ion storage. *Adv Mater.* 2018;30:1700104.

52. Li Y, Yang C, Zheng F, et al. High pyridine N-doped porous carbon derived from metal–organic frameworks for boosting potassium-ion storage. *J Mater Chem A.* 2016;6:17959-17966.

53. Xu F, Zhai Y, Zhang E, et al. Ultrastable surface-dominated pseudocapacitive potassium storage enabled by edge-enriched N-doped porous carbon nanosheets. *Angew Chem Int Ed.* 2020;59:19460-19467.

54. Chen J, Zhang H, Hu J, et al. Nitrogen-rich hard carbon as a highly durable anode for high-power potassium-ion batteries. *Energy Storage Mater.* 2017;8:161-168.

55. Share K, Cohn AP, Carter R, Rogers B, Pint CL. Role of nitrogen-doped graphene for improved high-capacity potassium ion battery anodes. *ACS Nano.* 2016;10:9738-9744.

56. Ju Z, Li P, Ma G, Xing Z, Zhuang Q, Qian Y. Few layer nitrogen-doped graphene with highly reversible potassium storage. *Energy Storage Mater.* 2018;11:38-46.

57. Xu Y, Zhang C, Zhou M, et al. Highly nitrogen doped carbon nanofibers with superior rate capability and cyclability for potassium ion batteries. *Nat Commun.* 2018;9:1720.

58. Sun Y, Zhang Y, Xing Z, Wei D, Ju Z, Zhuang Q. A hollow neuronal carbon skeleton with ultrahigh pyridinic N content as a self-supporting potassium-ion battery anode. *Sustain Energy Fuels.* 2020;4:1216-1224.

59. Yang W, Zhou J, Wang S, et al. Freestanding film made by necklace-like N-doped hollow carbon with hierarchical pores for high-performance potassium-ion storage. *Energy Environ Sci.* 2019;12:1605-1612.

60. Li J, Qin W, Xie J, et al. Sulphur-doped reduced graphene oxide sponges as high-performance free-standing anodes for K-ion storage. *Nano Energy.* 2018;53:415-424.

61. Ding J, Zhang H, Zhou H, et al. Sulfur-grafted hollow carbon spheres for potassium-ion battery anodes. *Adv Mater.* 2019;31:1900429.

62. Tao L, Yang Y, Wang H, et al. Sulfur-nitrogen rich carbon as stable high capacity potassium ion battery anode: performance and storage mechanisms. *Energy Storage Mater.* 2020;27:212-225.

63. Chen M, Wang W, Liang X, et al. Sulfur/oxygen codoped porous hard carbon microspheres for high-performance potassium-ion batteries. *Adv Energy Mater.* 2018;8:1800171.

64. Gong J, Zhao G, Feng J, et al. Controllable phosphorylation strategy for free-standing phosphorus/nitrogen co-functionalized porous carbon monoliths as high-performance potassium ion battery anodes. *ACS Nano.* 2020;14:14057-14069.

65. Qian Y, Jiang S, Li Y, et al. In situ revealing the electroactivity of P-O and P-C bonds in hard carbon for high-capacity and long-life Li/K-ion batteries. *Adv Energy Mater.* 2019;9:1901676.

66. Alvin S, Chandra C, Kim J. Extended plateau capacity of phosphorus-doped hard carbon used as an anode in Na- and K-ion batteries. *Chem Eng J.* 2020;391:123576.

67. Hou H, Shao L, Zhang Y, Zou G, Chen J, Ji X. Large-area carbon nanosheets doped with phosphorus: a high-performance anode material for sodium-ion batteries. *Adv Sci.* 2017;4:1600243.

68. Zhou Y, Jia Z, Shi L, et al. Pressure difference-induced synthesis of P-doped carbon nanobowls for high-performance supercapacitors. *Chem Eng J.* 2020;385:123858.

69. Kim D-Y, Li OL, Kang J. Novel synthesis of highly phosphorus-doped carbon as an ultrahigh-rate anode for sodium ion batteries. *Carbon.* 2020;168:448-457.

70. Ma G, Huang K, Ma J-S, Ju Z, Xing Z, Zhuang Q-C. Phosphorus and oxygen dual-doped graphene as superior anode
material for room-temperature potassium-ion batteries. J Mater Chem A. 2017;5:7854-7861.

71. Liu Y, Li Q, Guo X, et al. A highly efficient metal-free electrocatalyst of F-doped porous carbon toward N₂ electro-reduction. Adv Mater. 2020;32:1907690.

72. Lu J, Wang C, Yu H, et al. Oxygen/fluorine dual-doped porous carbon nanopolyhedra enabled ultrafast and highly stable potassium storage. Adv Funct Mater. 2019;29:1906126.

73. Sun X, Zhang Y, Song P, et al. Fluorine-dispersed ultrathin MoS₂ nanosheets inside hollow carbon skeleton: toward fast potassium storage by constructing spacious “Houses” for K ions. Adv Funct Mater. 2020;30:1908755.

74. Huang K, Xing Z, Wang L, et al. Direct synthesis of 3D hierarchically porous carbon/Sn composites via in situ generated NaCl crystals as templates for potassium-ion batteries. J Mater Chem A. 2018;6:434-442.

75. Gong S, Wang Q. Boron-doped graphene as a promising anode material for potassium-ion batteries with a large capacity, high rate performance, and good cycling stability. J Phys Chem C. 2017;121:24418-24424.

76. Feng W, Feng N, Liu W, et al. Liquid-state templates for constructing B, N, Co-doping porous carbons with a boosting of potassium-ion storage performance. Adv Energy Mater. 2020;11:2003215.

77. Ruan J, Zhao Y, Luo S, et al. Fast and stable potassium-ion storage achieved by in situ molecular self-assembling N/O dual-doped carbon network. Energy Storage Mater. 2019;23:46-54.

78. Cui RC, Xu B, Dong HJ, Yang CC, Jiang Q. N/O dual-doped environment-friendly hard carbon as advanced anode for potassium-ion batteries. Adv Sci. 2020;7:1902547.

79. Ge L, Chen Y, Yan C, et al. A large scalable and low-cost sulfur/nitrogen dual-doped hard carbon as the negative electrode material for high-performance potassium-ion batteries. Adv Energy Mater. 2019;9:1901379.

80. He H, Huang D, Tang Y, et al. Tuning nitrogen species in three-dimensional porous carbon via phosphorus doping for ultra-fast potassium storage. Nano Energy. 2019;57:728-736.

81. Chen J, Cheng Y, Zhang Q, et al. Designing and understanding the superior potassium storage performance of nitrogen/phosphorus Co-doped hollow porous bowl-like carbon anodes. Adv Funct Mater. 2021;31:2007158.

82. Liu L, Chen Y, Xie Y, Tao P, Li Q, Yan C. Understanding of the ultrastable K-ion storage of carbonaceous anode. Adv Funct Mater. 2018;28:1801989.

83. Zhang H, Luo C, He H, et al. Nano-size porous carbon spheres as a high-capacity anode with high initial coulombic efficiency for potassium-ion batteries. Nanoscale Horiz. 2020;5:895-903.

84. Zhang Z, Jia B, Liu L, et al. Hollow multihole carbon bowls: a stress-release structure design for high-stability and high-volumetric-capacity potassium-ion batteries. ACS Nano. 2019;13:11363-11371.

85. Yang W, Zhou J, Wang S, et al. A three-dimensional carbon framework constructed by N/S Co-doped graphene nanosheets with expanded interlayer spacing facilitates potassium ion storage. ACS Energy Lett. 2020;5:1653-1661.

86. Ge X, Liu S, Qiao M, et al. Enabling superior electrochemical properties for highly efficient potassium storage by impregnating ultrafine Sb nanocrystals within nanochannel-containing carbon nanofibers. Angew Chem. 2019;131:14720-14725.

87. Sultana I, Ramíreddy T, Rahman MM, Chen Y, Glushenkov AM. Tin-based composite anodes for potassium-ion batteries. Chem Commun. 2016;52:9279-9282.

88. Zhao Y, Zhu J, Ong SH, et al. High-rate and ultralong cycle-life potassium ion batteries Enabled by in situ engineering of yolk–shell FeS₂@C structure on graphene matrix. Adv Energy Mater. 2018;8:1802565.

89. Cui Y, Liu W, Feng W, et al. Controlled design of well-dispersed ultrathin MoS₂ nanosheets inside hollow carbon skeleton: toward fast potassium storage by constructing spacious “Houses” for K ions. Adv Funct Mater. 2020;30:1908755.

90. Huang K, Xing Z, Wang L, et al. Direct synthesis of 3D hierarchically porous carbon/Sn composites via in situ generated NaCl crystals as templates for potassium-ion batteries. J Mater Chem A. 2018;6:434-442.

91. He Y, Wang L, Dong C, et al. In-situ rooting ZnSe/N-doped hollow carbon architectures as high-rate and long-life anode materials for half/full sodium-ion and potassium-ion batteries. Energy Storage Mater. 2019;23:35-45.

92. Zhang H, Xing Z, Hu Z, et al. Sn-based submicron-particles encapsulated in porous reduced graphene oxide network: advanced anodes for high-rate and long life potassium-ion batteries. Appl Mater. Today. 2019;15:58-66.

93. Li C, Bi AT, Chen HL, et al. Rational design of porous Sn nanospheres/N-doped carbon nanofibers as an ultra-stable potassium-ion battery anode material. J Mater Chem A. 2021;9:5740-5750.

94. Zheng J, Yang Y, Fan X, et al. Extremely stable antimony–carbon composite anodes for potassium-ion batteries. Energy Environ Sci. 2019;12:615-623.

95. Huang H, Wang J, Yang X, et al. Unveiling the advances of nanostructure design for alloy-type potassium-ion battery anodes via in situ TEM. Angew Chem. 2020;132:14612-14618.

96. Zhang W, Pang WK, Sencadas V, Guo Z. Understanding high-energy-density Sn₅P₈ anodes for potassium-ion batteries. Joule. 2018;2:1534-1547.

97. Xiong P, Bai P, Tu S, et al. Red phosphorus nanoparticle@3D interconnected carbon nanosheet framework composite for potassium-ion battery anodes. Small. 2018;14:1802140.

98. Chang WC, Wu JH, Chen KT, Tuan HY. Red phosphorus potassium-ion battery anodes. Adv Sci. 2019;6:1801354.

99. Louiza LC, Moncoutur L, Senez V, Si and Ge-based anode materials for Li-, Na-, and K-ion batteries: a perspective from structure to electrochemical mechanism. Small. 2020;16:1905260.

100. Yang Q, Wang Z, Xi W, He G. Tailoring nanoporous structures of Ge anodes for stable potassium-ion batteries. Electrochem Commun. 2019;101:68-72.

101. Wu Y, Hu S, Xu R, et al. Boosting potassium-ion battery performance by encapsulating red phosphorus in free-standing nitrogen-doped porous hollow carbon nanofibers. Nano Lett. 2019;19:1351-1358.

102. Li B, He Z, Zhao J, Liu W, Feng Y, Song J. Advanced Sn₅P₈@C anode with exceptional cycling life for high performance potassium-ion batteries. Small. 2020;16:1906595.

103. Huang H, Luo X, Yao Y, et al. Binding Se into nitrogen-doped porous carbon nanosheets for high-performance potassium storage. InfoMat. 2021;3:421-431.

104. Liu C, Luo S, Huang H, Zhai Y, Wang Z. Direct growth of MoO3 reduced graphene oxide hollow sphere composites as advanced
anode materials for potassium-ion batteries. *ChemSusChem*. 2019;12:873-880.

105. Shimizu M, Yatsuzuka R, Koya T, Yamakami T, Arai S. Tin oxides as a negative electrode material for potassium-ion batteries. *ACS Appl Energy Mater*. 2018;1:6865-6870.

106. Li Y, Zhang Q, Yuan Y, et al. Surface amorphization of vanadium dioxide (B) for K-ion battery. *Adv Energy Mater*. 2020;10:2000717.

107. Wu M, Yang J, Ng DH, Ma J. Rhenium diselenide anchored on reduced graphene oxide as anode with cyclic stability for potassium-ion battery. *Phys Status Solidi RRL*. 2019;13:1900329.

108. Jia B, Yu Q, Zhao Y, et al. Bamboo-like hollow tubes with MoS2/N-doped-C interfaces boost potassium storage. *Adv Funct Mater*. 2018;28:1803409.

109. Yang L, Hong W, Zhang Y, et al. Hierarchical NiS2 modified with bifunctional carbon for enhanced potassium-ion storage. *Adv Funct Mater*. 2019;29:1903454.

110. Lin H, Li M, Yang X, et al. Nanosheets-assembled CuSe crystal pillar as a stable and high-power anode for sodium and potassium-ion batteries. *Adv Energy Mater*. 2019;9:1900323.

111. Yuan J, Liu W, Zhang X, et al. MOF derived ZnSe–FeSe2/RGO nanocomposites with enhanced sodium/potassium storage. *J Power Sources*. 2020;455:227937.

112. Park GD, Kang YC. Conversion reaction mechanism for yolk-shell-structured iron telluride-C nanospheres and exploration of their electrochemical performance as an anode material for potassium-ion batteries. *Small Methods*. 2020;4:2000556.

113. Wu Z, Liang G, Pang WK, et al. Coupling topological insulator SnSb2Te4 nanodots with highly doped graphene for high-rate energy storage. *Adv Mater*. 2020;32:1905632.

114. Yang C, Feng J, Lv F, et al. Metallic graphene-like VSe2 ultrathin nanosheets: superior potassium-ion storage and their working mechanism. *Adv Mater*. 2018;30:1800036.

115. Ming F, Liang H, Lei Y, Zhang W, Alshareef HN. Solution synthesis of VSe2 nanosheets and their alkali metal ion storage performance. *Nano Energy*. 2018;53:11-16.

116. Wang W, Jiang B, Qian C, et al. Pistachio-shock-like MoSe2/C core/shell nanostructures for high-performance potassium-ion storage. *Adv Mater*. 2018;30:1801812.

117. Bai J, Xi B, Mao H, et al. One-step construction of NiP-codoped porous carbon sheets/CoP hybrids with enhanced lithium and potassium storage. *Adv Mater*. 2018;30:1802310.

118. Du Y, Weng W, Zhang Z, et al. Candied-haws-like architecture consisting of FeS2@C core–shell particles for efficient potassium storage. *ACS Mater Lett*. 2021;3:356-363.

119. Ma G, Xu X, Feng Z, et al. Carbon-coated mesoporous CoS4 nanoparticles on reduced graphene oxide as a long-life and high-rate anode material for potassium-ion batteries. *Nano Res*. 2020;13:802-809.

120. Yang F, Gao H, Hao J, et al. Yolk–shell structured FeP@C nanoboxes as advanced anode materials for rechargeable lithium-/potassium-ion batteries. *Adv Funct Mater*. 2019;29:1808291.

121. Cheng Y, Yao Z, Zhang Q, et al. In situ atomic-scale observation of reversible potassium storage in Sb2S3@carbon nanowire anodes. *Adv Funct Mater*. 2020;30:2005417.

122. Chen Z, Yin D, Zhang M. Sandwich-like MoS2@SnO2@C with high capacity and stability for sodium/potassium ion batteries. *Small*. 2018;14:1703818.

123. Yao K, Xu Z, Ma M, Li J, Lu F, Huang J. Densified metallic MoS2/graphene enabling fast potassium-ion storage with superior gravimetric and volumetric capacities. *Adv Funct Mater*. 2020;30:2001484.

124. Fang L, Xu J, Sun S, et al. Few-layered tin sulfide nanosheets supported on reduced graphene oxide as a high-performance anode for potassium-ion batteries. *Small*. 2019;15:2004806.

125. Liu H, He Y, Cao K, et al. Stimulating the reversibility of Sb2S3 anode for high-Performance potassium-ion batteries. *Small*. 2021;17:2008133.

126. Sheng B, Wang L, Huang H, et al. Boosting potassium storage by integration advantageous of defect engineering and spatial confinement: a case study of Sb2Se3. *Small*. 2020;16:2005272.

127. Sun Q, Li D, Dai L, Liang Z, Ci L. Structural engineering of SnS2 encapsulated in carbon nanoboxes for high-performance sodium/potassium-ion batteries anodes. *Small*. 2020;16:2005023.

**AUTHOR BIOGRAPHIES**

**Jinhui Zhou** is currently a graduate student under the supervision of Prof. Shaojun Guo at the School of Materials Science & Engineering, Peking University. She received her B.Eng. in Materials Science & Engineering from Peking University. Her research interests include fundamental electrochemistry and advanced materials related to ion batteries in energy storage and conversion.

**Shaojun Guo** is a full professor with tenure in the School of Materials Science and Engineering, Peking University, and a Fellow of the Royal Society of Chemistry. He is renowned for his leadership in nano/sub-nano/atomic materials for catalysis and energy applications. He has made outstanding contribution to the interdisciplinary field of materials chemistry for energy electrocatalysis. He has published > 150 papers in top journals as corresponding author, including 19 in Nature, Science, and Nature/Science/Cell sister journals (h-index = 111 and 40,000 citations). He is one of World’s Highly Cited Researchers from 2014 to 2020, and World Top 2% of Scientist (Stanford University).

**How to cite this article:** Zhou J, Guo S. Carbon-based anode materials for potassium-ion batteries: From material, mechanism to performance. *SmartMat*. 2021;2:176-201. https://doi.org/10.1002/smm2.1042