Plasma-Doped Carbon-Based Anode Materials in Potassium Ion Batteries: A Review of Current and Future Prospects

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Abstract. With the increasing demand for energy, finding clean, efficient, and renewable energy storage solutions is a crucial focus in today's world. In this context, potassium-ion batteries have garnered widespread research and attention as an essential solution to address environmental pollution and future energy challenges. This paper focuses on one of the key components of potassium-ion batteries - the anode materials, with a special emphasis on plasma-doped carbon-based anode materials. Initially, the significance of carbon-based anode materials in ion batteries is introduced. Subsequently, a detailed exploration is conducted on the diverse applications of plasma-doped carbon-based anode materials in lithium-ion, sodium-ion, and potassium-ion batteries. These materials demonstrate excellent electrochemical performance, significantly improving the energy density, cycle life, and stability of the batteries. Looking ahead, we will additionally discuss the optimization of synthesis methods, further enhancement of electrochemical properties, and the prospective development of large-scale production techniques. Finally, the study underscores the potential of plasma-doped carbon-based anode materials to emerge as a new trend in the field of future energy storage, making a substantial contribution to advancing sustainable energy storage technologies.

Keywords: potassium ion batteries, plasma doping, carbon-based anode materials, review

1. Introduction

Unlimited solar, wind, and hydro energy sources represent some of the most promising solutions to both the current energy crisis and the ongoing issue of environmental pollution.[1,2] Nevertheless, their intermittent operation necessitates high-performance energy storage technologies. Advanced electrochemical energy storage devices, such as secondary batteries and supercapacitors, have been thoroughly researched and are viewed as promising prospects.[3,4] As the sustainable development of large-scale energy storage lithium-ion batteries (LIBs) is constrained by the limited resource and uneven distribution of lithium,[5,6] potassium-ion batteries (PIBs) with abundant reserves of potassium and low cost are potential contenders for new rechargeable batteries. PIBs can be a potential solution to regulate electrochemical energy storage (EES) and electrochemical energy conversion (EEC),[7] and have been the subject of increasing research, as shown in Fig. 1.

Potassium-ion batteries (PIBs) have some notable advantages over their competitor sodium-ion batteries (SIBs). One significant advantage is that the potassium ion has a more negative standard electrode potential (vs. SHE) than sodium. Specifically, the standard electrode potential of K+/K is 2.93 V, while that of Na+/Na is 2.71 V. This value is very close to the Li/Li+ voltage (-3.04 V, vs. SHE), which guarantees a higher operating voltage and higher energy density for PIBs.[8,9] High-performance anode materials are the key to the development of potassium ion batteries (PIBs), carbon materials, transition metal oxides, alloy materials, and other composites that have received extensive attention as anode materials for PIBs.[10] Carbon materials, such as graphite, soft carbon, hard carbon, reduced graphene oxide, and expanded graphite, are the most interesting anode materials due to their sustainability and low cost which makes them great candidates for commercial anode materials. For example, the electrochemical embedding of K+ in graphite is now confirmed, although K+ has a larger Shannon's ionic radius (1.38 Å) than Na+ (1.02 Å) and Li+ (0.76 Å) and Na+ cannot be reversibly embedded without prior graphite swelling or cosolvent molecules.[11,12] The smaller Stoke radius of K+ binding to solvated ions in comparison to Li+ and Na+ implies that it possesses

the greatest ionic mobility and conductivity, at least with respect to the solvent propylene carbonate (PC).[13]

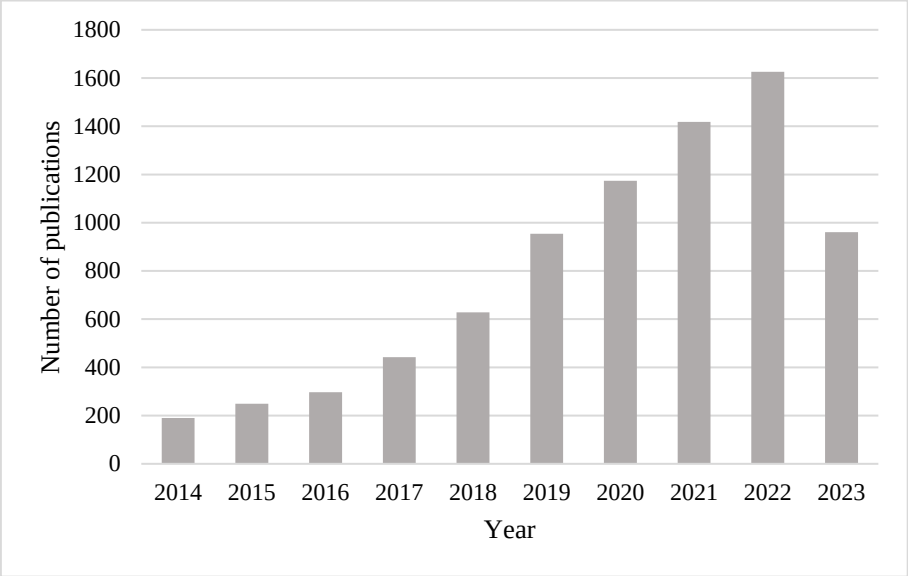


Fig. 1 The number of yearly publications from 2014 to 2023 with the topic of "potassium ion batteries" in Web of Science in Sep. 2023

In 2015, Ji's team disclosed a binary intercalation approach involving potassium ions in negative graphite electrodes through electrochemical processes.[14] The findings demonstrated that potassium ions could ingress the graphite electrode interlayers to create intercalation compounds in a carbonate electrolyte system and enable the retrievable separation of potassium ions from the graphite sheet interlayers upon charging. However, the graphite anode exhibits low cycling stability, leading to rapid capacity decay and poor rate performance in potassium ion batteries.[15] This situation prompts researchers to not only focus on solving the defects of the graphite anode itself but also conduct research and development on various other anode materials suitable for potassium ion batteries, including different carbon materials (carbon nanotubes, carbon microspheres, graphene, and so on) and carbon-containing composites.[16] Fig. 2 illustrates the aforementioned materials.

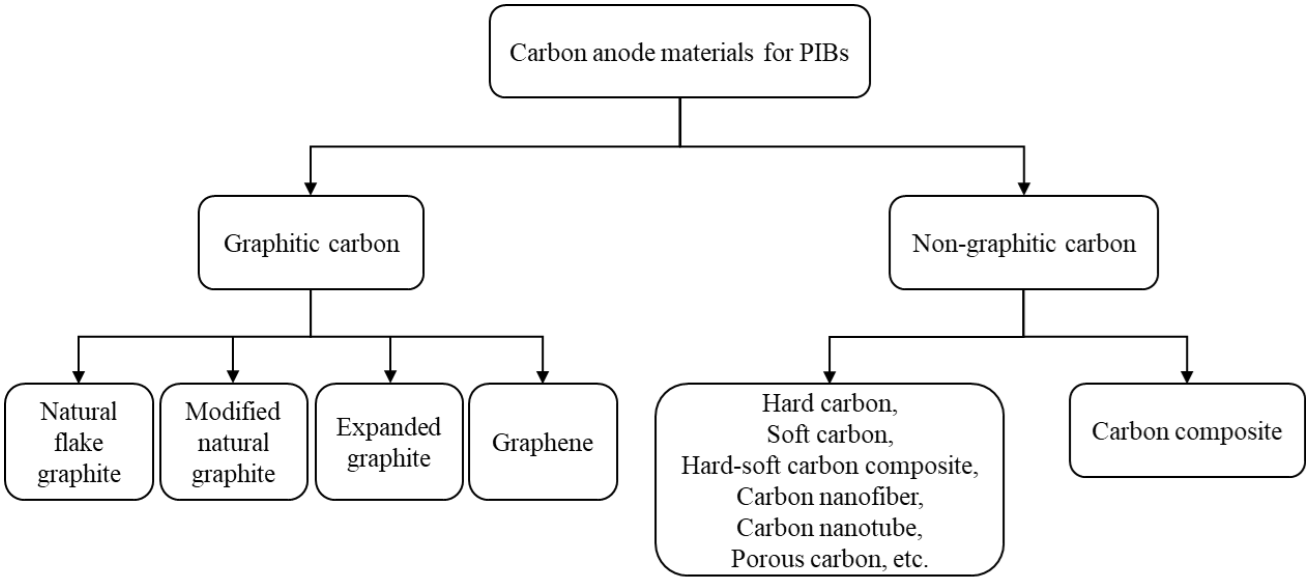


Fig. 2 The carbon anode materials for PIBs

However, the small lattice spacing and inherent surface passivation of carbon-based materials are suboptimal for the storage and transmission of K+.[17] Also, the stability of the solid electrolyte interface (SEI) during the charging and discharging operation must be considered.[18]

Changes in chemical composition and structure can lead to significant alterations in the redox activity of electrochemical materials.[19] Consequently, heteroatom doping has emerged as one of the most crucial strategies for elevating the performance of potassium electrochemical carbon-based anode materials.[20,21] Presently, diverse chemical and physical doping methods have been formulated. Compared to the typical liquid-phase chemical doping method, plasma doping uses a high-energy field to produce high-energy atoms, molecules, and ions, which are then implanted into the parent material. This method boasts high efficiency, wide applicability, flexible control, eco-friendliness, and other advantages, making it a rapidly developing application for electrode material processing. Fig. 3 shows the process of plasma generation and surface functionalization over substrates.

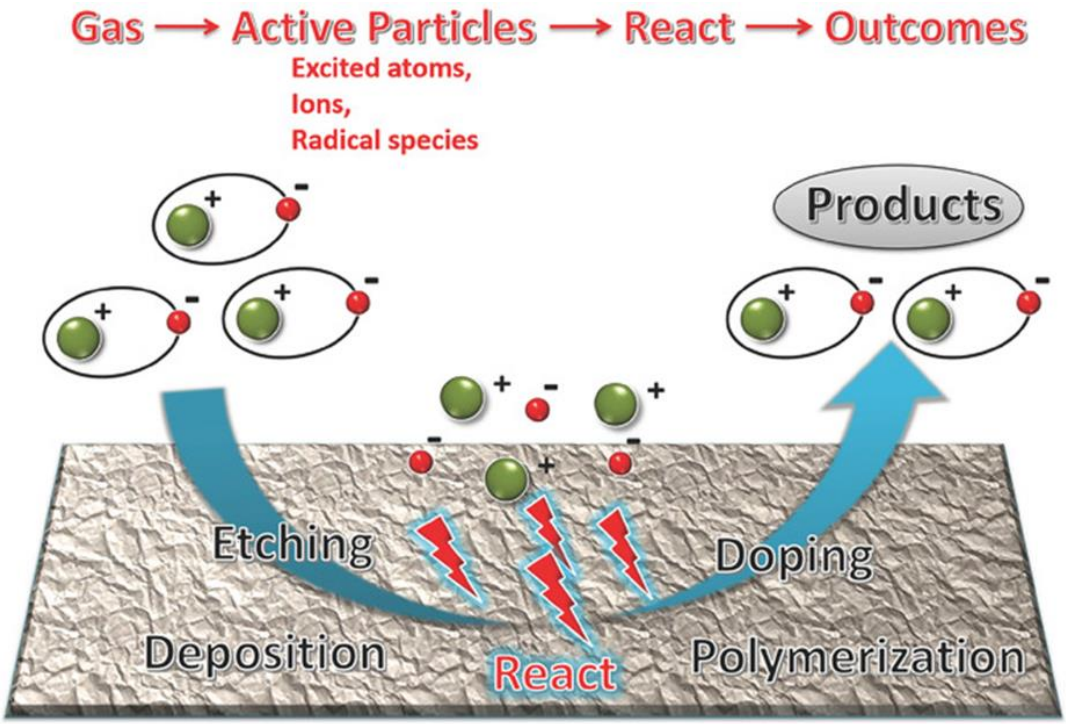


Fig. 3 The process of plasma generation and surface functionalization over substrates.]22]

2. Research status of plasma-doped carbon-based anode materials in alkali metal ion batteries (AMIBs)

2.1. Brief introduction of plasma doping

Plasma technology proves to be a powerful instrument for fabricating and altering low-dimensional nanomaterials, plentiful and reactive species that occur in plasma have a significant impact on accelerating chemical reactions.[23] Plasma technology has been effectively used in the field of electrochemical energy conversion and storage.[24] Doped non-metallic elements (e.g., N, O, S, P, B, F, etc.), metallic elements (Mg, Ti, Fe, Al, Ni, Cu, etc.), and dual/triple elements (e.g., N-S, N-P, N-S-P) have been widely used to modulate the materials of EES devices.[25,26] Fig. 4 shows a diagram of the types of plasma doping in different phases of matter. When energetic particles of the plasma interact with the material surface via momentum transfer, the activated surface atoms/molecules can overcome weak intermolecular forces, such as van der Waals forces or hydrogen bonds.20] Doped elemental particles can be injected into the framework of the substrate material to realize the doping effect, e.g. nitrogen plasma is widely used to dope N atoms into nanomaterials such as graphene, carbon nanotubes (CNTs) and reduced graphene oxide.[27-29] Compared to in-situ growth, plasma doping allows the host doping to be in a highly activated state with high efficiency.[20] Fig. 5 shows a schematic illustration of the plasma doping process.

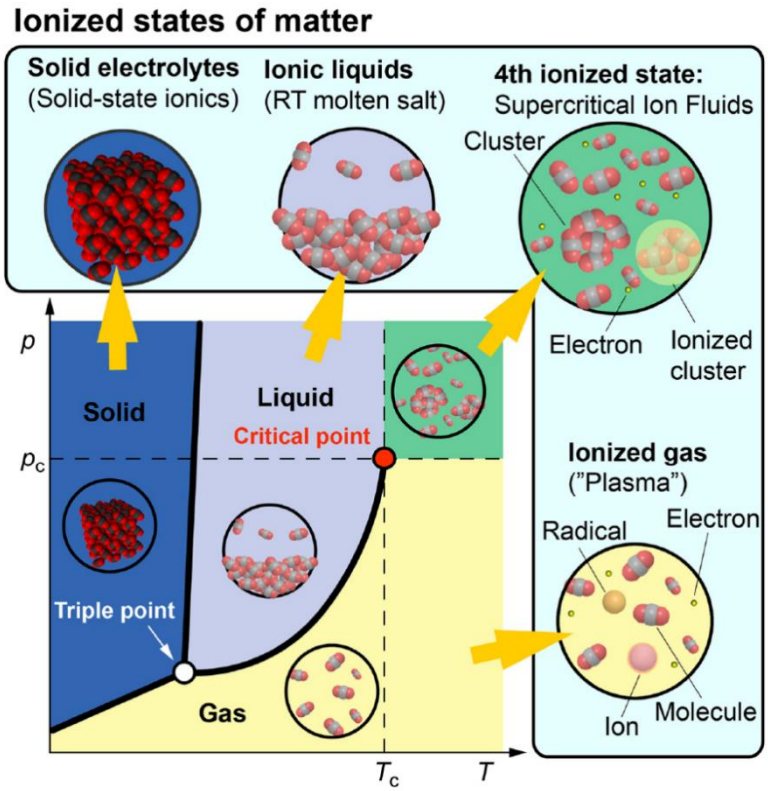


Fig. 4 Diagram of plasma doping in different phases of matter.[30]

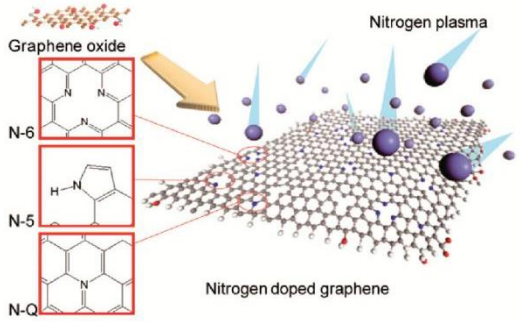


Fig. 5 A schematic illustration of the plasma doping process.[31]

2.2. Lithium ion batteries and sodium ion batteries

Plasma-doped carbon anode materials for lithium-ion batteries were initially reported by Arenst Andreas Arie et al. in 2012. According to their CV results, plasma thermal evaporation-prepared thin films of phosphorus-doped C60 (P:C60) on silicon particles support that P:C60 films are a suitable option as a coating material in anode stages.[32] Dou et al. plasma-treated the prepared graphene composites stretcher-loaded with Co9S8 nanoparticles using NH3 as a gas source, which formed a partial etching on the surface of graphene and Co9S8 nanoparticles, as well as doped N into the composites.[33] Jun Kang et al. prepared Li-doped carbon with high levels of Li doping (~4 wt%) in an organic solvent by dissolving Li precursors.[34] The concept of their plasma process is depicted in Fig. 6. This Li-C design demonstrates outstanding electrochemical capabilities, including high cycling and reversible capacity, whilst also highlighting its potential for use in high-performance LIBs. At a rate of 1C, the material's average reversible capacity is three times greater than that of commercial graphite and it maintains stable cycling performance for over 300 cycles, significantly improving the storage performance of pure lithium carbon. More relevant studies are listed in Table 1.

As sodium-ion batteries (SIBs) have been widely studied, plasma-doped carbon anode materials have been increasingly used in SIBs. Lin et al. utilized a nanocomposite of N-TiO2/CNTs as anode

materials for sodium ion batteries. After 200 cycles, the N-TiO2/CNTs electrode exhibited a specific capacity 1.45 times higher than the TiO2/CNTs electrode at a current density of 50 mA g-1. The study shows that N-TiO2/CNTs is more effective in SIBs due to the enhanced kinetics resulting from nitrogen-doping and the amorphous feature.[35] Xie et al. utilized an O2-plasma treatment method to enhance the wetting behavior of hard carbon (HC) microspheres.[36] This was achieved by introducing oxygen functional groups such as carbonyl and hydroxyl groups. These groups improved the ion diffusion coefficient and provided more sites for Na+ storage. Additionally, the interfacial oxygen groups displayed less chemical activity towards the electrolyte, preventing its decomposition. The strong interaction between the ether or carbonyl groups and the SEI film resulted in a stable performance. This, in turn, led to better ion/charge transport, a more stable cycle performance, and faster charge/discharge under higher current densities. As a result, a higher capacity of 325mA h/g was achieved compared to the pristine HC, which had a capacity of only 225mA h/g. More relevant studies are listed in Table 1.

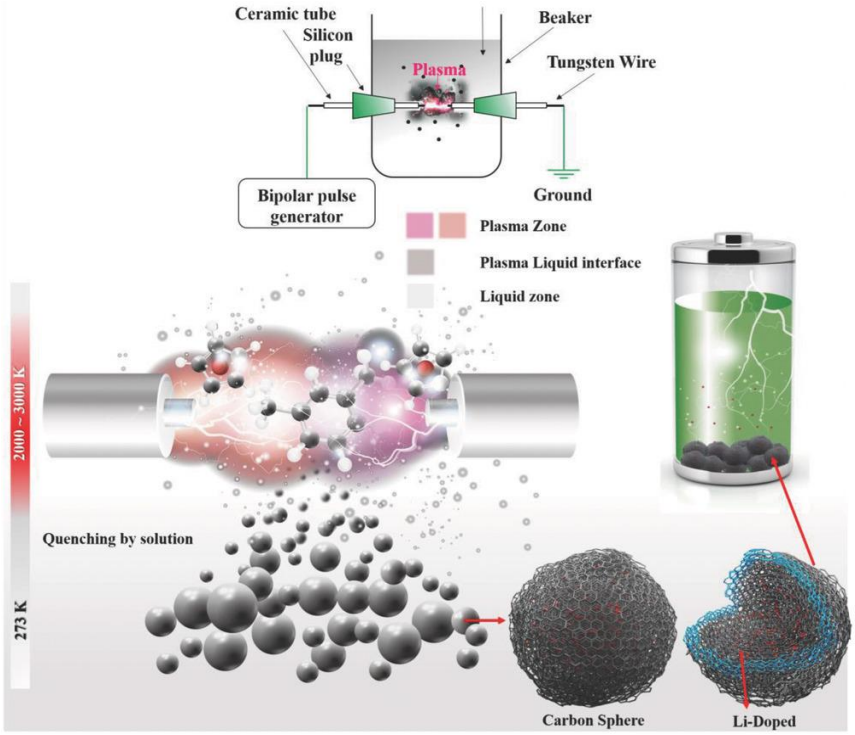


Fig. 6. Schematics illustrating the concept of anode material and the solution plasma process.[34]

2.3. Potassium ion batteries

In recent years, researchers have done a lot of work on optimizing the structure and electrochemical properties of carbon anodes for potassium ion batteries, however, their doping modification based on plasma technology is a relatively new field among them. Adams, R. A. et al successfully prepared nitrogen-doped carbon nanofibers with oxygen-rich functional groups using oxygen plasma treatment of PIBs.[37] Jiang et al. developed a low-temperature Ar plasma-enhanced chemical vapor deposition (PECVD) strategy to synthesize N/S double-doped graphite hollow structures (NSGs) for PIBs.[38] The NSG has hollow structures that make it structurally stable, allowing for the expansion and contraction of graphitic layers during charging and discharging. As a result, the NSG has excellent potassium storage performance, with a favorable rate capability (around 100 mAh g-1 at 5 A g-1) and outstanding cyclic stability (capacity retention rate of 90.2% at 5 A g-1 after 5000 cycles). Li et al. created a film of integrative graphitic carbon network without any interface.[39] They enlarged the film's lattice space and added some defects through a process involving plasma-enhanced etching and S-doping. The anodes produced a high reversible capacity of 408 mAh g−1 at a rate of 20 mA g−1. They also showed ultra-high rate and long-term cyclability,

with a clear discharge plateau. For example, the capacity was maintained at approximately 91.1 mAh g−1 at 5 A g−1, retaining about 60% after 10,000 cycles. More relevant studies are listed in Table 1. Table 2 shows a comparison of electrochemical properties of different plasma-treated carbon anode materials for PIBs.

Table 1. Research of plasma-doped carbon-based anode materials in alkali metal ion batteries (AMIBs)

Devices	Materials	Type of Plasma	Effects	Ref.
LIBs	P:C_{60}/ Si	plasma thermal evaporation	P doping	[32]
	B-C	plasma arc torch, Ar-C_2H_2-B_2H_6	B doping	[40]
	$Li_4Ti_5O_{12}$/carbon	RF plasma, Ar-N_2	N doping	[41]
	Li-C	solution plasma	Li doping	[34]
	N-CNTs/graphene composites	RF plasma, Ar-N_2	N doping	[42]
	MnS@C nanocomposites	DC arc-discharge plasma	Carbon coating	[43]
	Al_2O_3/N-doped CNTs/graphene	RF plasma, Ar-N_2	N doping	[44]
	Co_3O_4/N-doped CNTs/graphene	RF plasma, Ar-N_2	N doping	[45]
	Soft carbon	tornado-type atmospheric pressure plasma jet (APPJ) system	Introduce oxygen functional groups/N doping	[46]
	N-doped Si/C	Glow plasma, N_2-H_2	N doping	[24]
	Hard carbon	RF plasma, O_2	Introduce oxygen functional groups	[36]
	N-TiO 2/CNTs	Glow plasma, N_2-H_2	N doping	[35]
	Hierarchical graphene@SnS	RF plasma, CH_4	Carbon coating	[47]
	Fe_2O_3/Fe_3O_4/N-doped graphene	Microwave plasma, Ar-H_2	Synthesis/N doping	[48]
SIBs	$CoMoSe_4$@carbon cloth	Glow plasma, N_2-H_2	Plasma-assisted selenization	[49]
	N-doped carbon-coated TiO_2	Glow plasma, Ar-H_2	Introduce Oxygen Vacancies (OVs) /N doping	[50]
	semi-ionic C-F bonds functionalized NCNFs	Microwave plasma, CF_4	Introduce semi-ionic C-F bonds	[51]
	S/P dual-doped carbon nanospheres	solution plasma	S/P dual doping	[52]
	Graphene-armored TiO_2 NTs	RF plasma, CH_4	Carbon coating	[53]
	Se-P-C amorphous composites	Glow plasma, Ar	Synthesis	[54]
PIBs	N/S dual-doped graphitic	Glow plasma, Ar	N/S dual-doping	[38]
	N-doped carbon nanofiber	RF plasma, O_2	Introduce oxygen functional groups	[37]
	S/O co-doped graphitic	RF plasma, Ar/H_2S	S/O co-doping	[39]
	B/O dual-doped carbon particles	Glow plasma, Ar	B/O dual-doping	[55]

Table 2. Comparison of electrochemical properties of different plasma-treated carbon anode materials for PIBs

Materials	Capacity (mAh g-1)	Rate performance	First CE (%)	Capacity retention	Voltage window (V)	Ref.
Graphene-armored TiO2 NTs	332 mAh g^{-1} At 0.05 A g^{-1}	120 mAh g^{-1} at 2 A g	≈80	76% after 3000 cycles (5A g^{-1})	0.01-3	[53]
Se-P-C amorphous composites	634 mA h g^{-1} at 0.05 A g^{-1}	248.6 mA h g^{-1} at 1 A g^{-1}	41.74	25.2% after 120 cycles (1 A g^{-1})	0.01-3	[54]
N/S dual-doped graphitic	220 mAh g^{-1} at 0.5A g^{-1}	≈100 mAh g^{-1} at 20 A g^{-1}	≈95	90.2% after 5000 cycles (5 A g^{-1})	0.01-3	[38]
N-doped carbon nanofiber	230 mAh g^{-1} at C/10 rate	110 mAh g^{-1} at 10C rate	95	≈80% after 300 cycles (1C)	0.01-3	[37]
S/O co-doped graphitic	408 mAh g^{-1} at 20mA g^{-1}	91.1 mA h g^{-1} at 5 A g^{-1}	22.4	≈60% after 10,000 cycles (5 A g^{-1})	0.01-3	[39]
B/O dual-doped carbon particles	426.5 mAh g^{-1} at 0.1 A g^{-1}	166.5 mAh g^{-1} at 5 A g^{-1}	22.5	58% after 200 cycles (0.5A g^{-1})	0.01-3	[55]

3. Future outlooks of plasma-doped carbon-based anode materials in potassium ion batteries

Plasma-doped carbon-based anode materials offer many potential advantages, such as high conductivity, good electrochemical activity, and chemical stability. These materials can improve the energy density, cycle life and charge/discharge efficiency of PIBs. By controlling the plasma doping process, the electronic structure and electrochemical properties of the materials can be tuned to further optimize the performance of PIBs.

However, plasma-doped carbon-based anode materials for PIBs are still in the research and development stage. Despite some progress being made, there are still some challenges, such as the optimization of material synthesis methods, the improvement of performance stability, and the development of large-scale preparation techniques.

Here are the prospective aspects of these materials:

Enhanced Battery Performance and Energy Density:

Plasma-doped carbon-based anode materials significantly augment the conductivity and electrochemical activity of PIBs, thereby elevating the energy storage capacity and cycle life of the batteries. Future research should focus on further optimizing material structures and properties to achieve higher energy storage density and prolonged cycling stability.

Exploration of Novel Synthesis Methods and Processes:

Future investigations should concentrate on developing efficient and scalable synthesis methods and processes to ensure the stability and consistency of plasma-doped carbon-based anode materials. This may encompass innovative material synthesis technologies, improved carbonization processes, as well as innovations in self-assembly and nanomaterial fabrication.

Advancing Environmental Sustainability:

Research and application of carbon-based anode materials align with environmental and sustainable development principles, often utilizing cost-effective and abundant carbon sources, contributing to cost reduction while minimizing dependence on finite resources.

Extension of Applications to Other Energy Storage Domains:

Beyond PIBs, research on plasma-doped carbon-based anode materials may extend to other energy storage domains such as SIBs, lithium-sulfur batteries, and supercapacitors, offering novel solutions for a variety of energy storage technologies.

Achieving Commercialization and Industrialization:

With continued research and maturing technologies, plasma-doped carbon-based anode materials are poised to progressively transition from the laboratory to the market. Collaborations and investments will drive these materials towards commercialization and industrial-scale production to meet the escalating demands of energy storage.

In conclusion, plasma-doped carbon-based anode materials hold immense promise in PIBs and other energy storage domains. They are anticipated to make significant contributions to the advancement of sustainable energy storage technologies.

4. Summary

In summary, this comprehensive review discussed carbon-based anode materials in PIBs, focusing on the integration of plasma-doping techniques to enhance their electrochemical performance. Initially, an overview of carbon-based anode materials for PIBs was provided, emphasizing their significance in advancing potassium-ion battery technology.

Subsequently, attention was shifted towards the potential of plasma-doped carbon-based anode materials across a spectrum of alkali metal ion-based battery systems, including LIBs and SIBs. The versatile application of plasma-doping in these contexts was elucidated, underlining its role in addressing the challenges and optimizing the performance of diverse battery technologies.

Looking ahead, the future prospects of plasma-doped carbon-based anode materials were contemplated, envisioning their trajectory towards improved synthesis methodologies, enhanced electrochemical properties, and sustainable, scalable production. Anticipated expansions into other energy storage domains and the imperative drive towards commercialization were highlighted as pivotal areas of development.

In conclusion, the integration of plasma-doping techniques with carbon-based anode materials presents a promising avenue to revolutionize potassium-ion batteries and potentially shape the landscape of energy storage technologies. Through continuous research, innovation, and collaboration, these advancements are poised to contribute significantly to sustainable energy solutions and address the burgeoning global demand for efficient energy storage systems.

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