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Boron Carbide and Composites in Advanced Energy Storage: Research Progress and Prospects

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Abstract

Boron carbide (B4C) and its composite materials demonstrate versatile applicability in energy storage technologies, particularly within new energy battery systems. This review systematically examines recent advances in their battery applications. Commencing with an analysis of B4C's distinctive physicochemical properties, crystal structure, and synthesis methodologies, we critically evaluate its implementation in lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), lithium-sulfur (Li-S) batteries, and fuel cells. The discussion substantiates how B4C-based materials augment critical battery performance metrics. Finally, development challenges and future research trajectories are outlined. We anticipate that through targeted performance optimization, innovative processing techniques, advanced interface engineering, and cross-disciplinary integration, B4C composites will unlock broader applications in next-generation energy storage systems.

Keywords: *Boron carbide(B4C); Composite materials; Advanced energy storage; New energy batteries; Application advances*

1 Introduction

The urgent global demand for sustainable energy solutions has propelled technological innovation in advanced energy storage systems to critical significance. Among emerging materials, boron carbide (B4C) and its composites have garnered substantial research interest owing to their exceptional properties, including ultra-high hardness (≈30 GPa), elevated melting point (＞2400℃), low density (2.52 g/cm^3), superior chemical inertness, and notable neutron absorption capacity[1-3]. As a semiconductor with demonstrated thermoelectric potential [4], B4C is now transitioning from traditional applications toward advanced electrochemical energy storage, revealing compelling capabilities[5].

Although research on B4C in battery technologies remains developmental, its foundational merits—exceptional chemical resistance, structural stability, tunable electrical conductivity, catalytic activity, and favorable mass density[6]—have been preliminarily validated in lithium-ion batteries (LIBs)[7] and fuel cells[8]. These attributes position B4C as a promising candidate to address core challenges in contemporary energy storage, such as limited cycle stability, constrained energy density, safety concerns, and cost inefficiencies[9,10].

Despite notable progress, critical scientific questions and technical barriers persist in the application of B4C composites. Deeper exploration of their electrochemical roles promises not only to extend functional boundaries but also to overcome existing bottlenecks in energy storage technology, thereby accelerating the development of efficient, stable, and sustainable systems. Consequently, a systematic review of B4C-based materials in new energy batteries, coupled with critical assessment of their capabilities and limitations, carries significant implications for next-generation battery innovation.

2 Overview of Boron Carbide and Its Composite Materials

2.1 Structure and properties of boron carbide

Boron carbide (B4C), with the chemical formula B4C, exhibits a broad homogeneity range (B4C-B5-10C). Its crystal structure belongs to the rhombohedral system (space group D3d5-R$\bar{3}$m), with lattice parameters *a* = 0.519 nm, *c* = 1.212 nm, and α = 66.3° [11] (Figure 1). At the atomic level, it consists of B_{12} icosahedra interconnected by linear C-B-C chains[12-14]. This unique

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configuration confers exceptional properties including high hardness and high melting point.

The chemical bonds exhibit strong covalent character, with high B-C bond energy, rendering the structure stable under high temperatures, high pressures, and chemical corrosion. Furthermore, boron carbide demonstrates semiconducting behavior (electrical conductivity σ ≈ 100 S/cm), good electrical conductivity, and catalytic activity[6]. Collectively, these properties underpin its diverse applications across multiple fields.

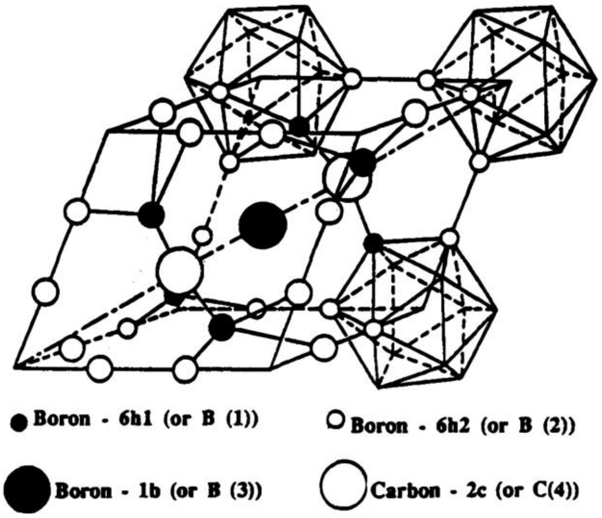

Figure 1 Rhombohedral crystalline structure of boron carbide[11]

2.2 Overview of boron carbide preparation methods

Boron carbide (B4C) is synthesized through diverse methods, with carbothermal reduction being the most prevalent industrial process. This technique involves reacting stoichiometric mixtures of boric oxide (B2O3) and carbon sources (e.g., coke, graphite) in electric furnaces at 2000～2500 ℃, following the reaction: 2B2O3+7C→B4C+6CO↑. Valued for its mature technology and cost-effectiveness, it remains the preferred method for large-scale production[15]. Self-propagating high-temperature synthesis (SHS) utilizes exothermic reactions between boron and carbon powders, where compacted powder mixtures are ignited locally to propagate rapid combustion waves that yield B4C. While SHS offers advantages of rapid kinetics and low energy consumption, it faces challenges in controlling product purity and particle size[16]. Emerging techniques include mechanochemical synthesis, which employs mechanical forces to induce chemical reactions[17], and sol-gel processing that achieves atomic-level mixing through colloidal precursors to produce high-purity nanoscale B4C powders[18,19]. However, these advanced methods are currently confined to laboratory-scale optimization due to cost constraints limiting industrial adoption. Comparative characteristics of common B4C synthesis methods—including principles, process parameters, and key features—are systematically summarized in Table 1.

Table 1 Common Synthesis Methods and Characteristics of Boron Carbide

Synthesis Method	Principle	Process Parameters	Key Features	Development Stage
CarbonThermal Reduction	B_2O_3 reacts with carbon sources (coke, graphite, etc.) to produce B_4C and carbon monoxide.	In an electric furnace at high temperatures (2000 ℃ to 2500 ℃), the reaction is: $2B_2O_3+7C \rightarrow B_4C+6CO\uparrow$	Mature technology and relatively low cost	The preferred choice for large-scale industrial production
Self-propagating High-temperature Synthesis (SHS)	Maintain the reaction using the exothermic chemical reaction of the reactants themselves. Mix boron powder and carbon powder, press into a block, and ignite one end. Once ignited, the reaction will spread on its own.	Self-sustaining propagation upon ignition	he reaction is fast, energy consumption is low, but it is difficult to control the purity and particle size of the product.	Control difficulties exist in practical applications.
Mechanochemical	Chemical reactions are induced via mechanical force.		Currently in the laboratory research optimization phase, with relatively high costs.	Laboratory stage, not yet widely used
Sol-gel	Atomic-level mixing is achieved via the sol-gel process		High-purity, nanoscale boron carbide powder can be prepared, but it is currently in the laboratory research and optimization stage and is relatively expensive.	Laboratory stage, not yet widely used

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2.3 Analysis of application potential for boron carbide and its composites

The distinctive properties of boron carbide (B4C) and its composites have demonstrated significant value in traditional applications. Notable examples include B4C /Al composites utilized in aerospace thermal management components and electronic packaging[20], as well as ceramic-matrix composites (e.g., B4C /SiC). Silicon carbide (SiC) ceramics inherently exhibit exceptional high-temperature resistance and oxidation stability[21], when composited with B4C, these materials achieve further enhanced thermal capabilities, maintaining high strength and hardness above 1500℃—critical for ultra-high-temperature thermal protection systems and extreme-environment components in nuclear reactors. Advancing research into material characteristics has progressively revealed their burgeoning potential in emerging fields, with particular emphasis on applications within new energy batteries.

The development of new energy batteries faces critical challenges including limited cycle life, constrained energy density, and safety concerns. Boron carbide addresses these issues through its high chemical stability, favorable electrical conductivity, exceptional catalytic activity, and robust structural stability—offering novel material-based solutions. These properties demonstrate significant compatibility across lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), lithium-sulfur (Li-S) batteries, and fuel cells, positioning B4C-based materials as a prominent research focus in electrochemical energy storage.

3 Research on Applications of Boron Carbide and Its Composites in New Energy Batteries

3.1 Lithium-ion batteries

In lithium-ion batteries (LIBs), boron carbide (B4C) and its composites demonstrate distinctive advantages. Pure B4C exhibits lithium-ion storage potential owing to its unique crystal structure and electronic properties[22]. Research confirms that in lithiated boron carbide crystals, Li ions occupy interstitial sites above or below linear C-B-C chains, forming reversible ionic bonding interactions with boron and carbon atoms[23].

Chen et al.[24] proposed an innovative composite structure featuring boron carbide (B4C) as a conductive rigid skeleton supporting silicon. Micron-sized Si (1～5 μm) and B4C (1～7 μm) powders were initially blended in controlled ratios (Figure 2-a), followed by high-energy ball milling (HEBM). During this process, the high-Mohs-hardness B4C particles functioned as nano/micro-milling media, effectively fragmenting Si into sub-10 nm particles while simultaneously reducing their own size to 100～300 nm. These in-situ generated nano-Si particles became intimately anchored onto B4C surfaces, forming Si-coated B4C core-shell structures (Si/ B4C) (Figure 2-b). Subsequent planetary ball milling (PBM) of Si/ B4C with graphite induced mechanical exfoliation and uniform encapsulation of the composites by graphite layers, yielding a final triple-layered core-shell-shell architecture (Si/ B4C /graphite, SBG) (Figure 2-c). The outer few-layer graphene coating substantially enhanced electrical conductivity and structural stability while facilitating stable solid electrolyte interphase (SEI) formation. The optimized SBG433 anode (Si: B4C:graphite= 4:3:3) delivered exceptional performance: 94% capacity retention after 100 cycles at 0.3 C and a specific capacity of ≈822 mAh/g based on total electrode mass (including binder and conductive additives), underscoring the critical role of synergistic material-structure co-design strategies in developing high-performance lithium-ion batteries.

Boron carbide (B4C) plays a pivotal role in designing high-capacity anodes for lithium-ion batteries (LIBs) due to its unique mechanical and electrochemical properties. Su et al.[25] innovatively engineered a hierarchical SnS_2/ B4C @OUCNTs composite anode, demonstrating a tripartite synergistic mechanism of B4C involving mechanical buffering, electrical enhancement, and interfacial stabilization. This composite—synthesized via chemical vapor deposition and solvothermal methods—features open-ended carbon nanotubes (OUCNTs) as a conductive skeleton with B4C nanoparticles as an interfacial buffer. Experiments revealed that B4C's ultrahigh hardness (Mohs 9.3～9.5) and elastic modulus (～450 GPa) effectively dissipate lithiation-induced stress in SnS_2, reducing electrode volume expansion by 55%. Its semiconducting behavior (σ ≈ 100 S/cm) synergizes with OUCNTs to construct a 3D conductive network, decreasing interfacial charge-transfer resistance by 67% and enabling a reversible capacity of 620 mAh/g at 5 A/g. Theoretical calculations further revealed charge redistribution (adsorption energy $\Delta E_{ads} \approx$ -2.1 eV) at B4C - SnS_2 heterointerfaces,optimizing Li ion adsorption sites and reducing diffusion barriers by 46% (0.28 eV → 0.15 eV). Additionally, B4C 's chemical inertness inhibits direct SnS_2-electrolyte contact, suppressing polysulfide dissolution and uncontrolled SEI growth, thereby elevating coulombic efficiency to 99.3% with ＞85% capacity retention after 200 cycles. This work validates B4C 's multifunctional coupling effects and establishes a "rigidity-flexibility integration" strategy for developing high-energy-density (＞500 Wh/kg) LIBs with extended cycling (＞500 cycles), extendable to other volume-sensitive anodes (e.g., metal oxides/alloys) through heterointerface engineering for substantial practical implementation.

However, pure boron carbide (B4C) faces limitations as an electrode material, including suboptimal electrical conductivity and restricted Li ion diffusion kinetics. To address these constraints, researchers have integrated B4C with diverse materials, yielding significant performance enhancements in LIBs. For instance, B4C -graphene composites leverage graphene's exceptional electrical properties—boosting composite conductivity by several orders of magnitude—while its 2D flexible architecture buffers volume changes during cycling, mitigating electrode pulverization and delamination to enhance structural integrity. Tan et al.[26] systematically investigated B4C ceramics modified with graphene nanoplatelets (GNPs) and Ti_3AlC_2 sintering additives via spark plasma sintering. Using 0～5 vol% GNPs alongside in-situ formed TiB_2 conductive phases (derived from Ti_3AlC_2 decomposition), they fabricated dense B4C composites with superior electrical/thermal conductivity and mechanical properties. The study revealed that GNPs establish long-range conductive pathways via ultrahigh in-plane carrier mobility (～10^5 cm^2/V·s), while TiB_2 particles act as localized "conductive nodes" at interfaces-synergistically elevating bulk conductivity by 4～6 orders of magnitude with a percolation threshold of 1～2 vol%. This breakthrough overcame B4C's intrinsic insulating nature, enabling its first demonstrated electro-discharge machining (EDM) capability. Conductive atomic force microscopy (C-AFM) confirmed continuous conductive networks formed by GNPs/ TiB_2, effectively reducing grain boundary barriers and optimizing charge carrier transport.

Ding et al.[27] systematically elucidated the mechanistic role of boron carbide monolayers (BCx) as lithium-ion battery anodes through integrated first-principles calculations and experimental validation. Their study revealed that interconnected BC5 hexatomic ring networks provide optimal Li ion migration pathways, with unique charge redistribution characteristics reducing the Li ion diffusion barrier to 0.25 eV—significantly lower than graphite's 0.3～0.5 eV—thereby substantially enhancing ionic transport kinetics. Experimentally, BC3/TiN composites demonstrated exceptional rate capability, maintaining a specific capacity of 1,120 mAh/g at 10C with 98.7% Coulombic efficiency. The B-B interatomic distance within BCx monolayers exhibits positive correlation with theoretical capacity; when expanded to 2.8 Å, Li ions engage in multilayer intercalation, enabling a theoretical capacity of 2,600 mAh/g (≈ 7× graphite's capacity). Synthesized BC5 monolayers delivered an initial discharge capacity of 1,850 mAh/g at 0.1C while retaining ＞85% capacity after 500 cycles.

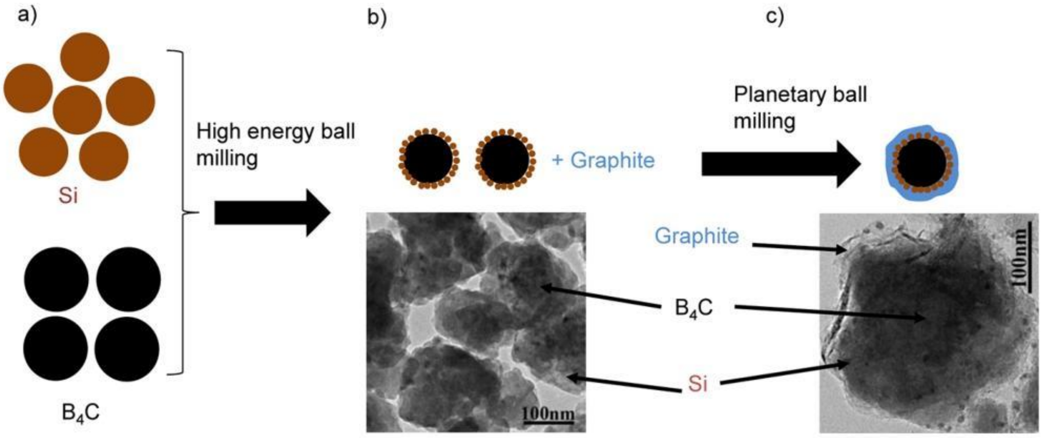

Figure 2 Schematic diagram of the synthesis process of conductive-rigid-skeleton-supported Si with TEM images for the intermediate product of Si/ B4C and the final SBG product. (a) Starting materials of micron-sized B4C and Si. (b) Schematic diagram of the Si/B4C core-shell structure and TEM image. (c) Schematic diagram of the SBG structure and TEM image[24]

3.2 Sodium-ion batteries

In sodium-ion battery (SIB) systems, boron carbide (B4C) and its composites demonstrate significant compatibility. SIBs, leveraging abundant sodium resources and low cost, represent promising contenders for large-scale energy storage. Compared to Li ion (radius ≈0.076 nm), Na ion exhibits a larger ionic radius (≈0.102 nm), necessitating electrode materials with more expansive and stable ion diffusion pathways. B4C's unique crystal structure addresses this requirement through interstitial sites within its 3D framework that facilitate Na ion transport.

Hussain et al. [28] employed density functional theory (DFT) calculations to investigate 3D-B6 C6 porous crystals, revealing metallic behavior with delocalized electrons along B-C-bonded porous channels that confer exceptional electrical conductivity.

Crucially, During the charging and discharging process of sodium-ion batteries, electrode materials also face the problem of volume expansion and contraction. The high structural stability of boron carbide can effectively suppress material pulverization and peeling caused by volume changes, maintain the integrity of the electrode, and ensure the cycle life of the battery. In addition, the good chemical stability of boron carbide allows it to adapt to the electrolyte system of sodium-ion batteries, making it unlikely to undergo side reactions with the electrolyte, reducing internal self-discharge of the battery, and improving the overall performance of the battery.

Zhang et al. [29] synthesized VSe_2/B4C@HCG composites via high-energy ball milling, anchoring VSe_2 and B4C nanoparticles onto highly conductive graphene (HCG). B4C's high hardness suppressed VSe_2 aggregation and volume deformation while synergizing with graphene to enhance charge transfer kinetics (Figure 3). The composite delivered 407.5 mAh/g after 450 cycles (98.5% Coulombic efficiency) and maintained 251.6 mAh/g after 1000 cycles, with significantly superior rate capability versus controls. This work demonstrates B4C's dual role in physical confinement and structural scaffolding to alleviate volume changes, providing new design principles for high-performance SIB anodes.

Sun et al. [30] fabricated a flexible binder-free anode for sodium-ion batteries (SIBs) through high-energy ball milling and free-standing processing, producing B4C /Sn/acetylene black@reduced graphene oxide (B4C /Sn/AB@rGO) films. Their study revealed B4C's multifunctional roles: as a high-hardness conductor, it structurally supports Sn particles while refining micron-sized Sn into nanoscale domains during milling, shortening electron pathways and enhancing overall conductivity. Synergistically with rGO, B4C forms a robust framework buffering Sn's extreme volume changes (～520%) during cycling, suppressing particle aggregation and electrode pulverization to extend cycle life. AB encapsulates B4C /Sn, accelerating electrolyte infiltration and stabilizing solid electrolyte interphase (SEI) formation, while rGO interconnects components as an "electrical nexus" to establish efficient electron transport networks and improve reaction kinetics. The composite delivered 393.4 mAh/g at 0.1 A/g, retained 155.5 mAh/g after 500 cycles at 1 A/g, and maintained 201.5 mAh/g over 50 cycles in full cells at 0.1 A/g, validating B4C's efficacy in optimizing electrode architecture and electrochemical performance.

3.3 Lithium-sulfur batteries

Lithium-sulfur batteries (Li-S) have emerged as a promising candidate for next-generation energy storage technology due to their high theoretical energy density (2567 Wh/kg) and low cost [31-33]. However, they face core challenges such as polysulfide shuttling, slow reaction kinetics, and sulfur volume expansion [34-35]. Boron carbide enhances the cycling stability, rate performance, and energy density of lithium-sulfur batteries through chemical adsorption, catalytic activity, and structural synergy.

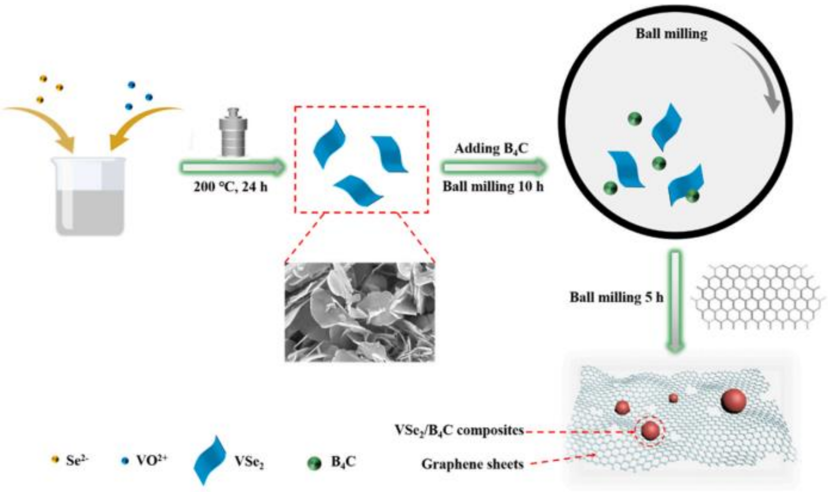

Figure 3 Schematic preparation of the synthesis of VSe2/B_4C@HCG[29]

Song et al. [36] designed a flexible self-supporting lithium-sulfur battery cathode BC-NWs@ACT/S/rGO (Figure 4-b), using B4C nanowires as a rigid skeleton combined with porous active cotton textile (ACT) and reduced graphene oxide (rGO), effectively addressing the issues of polysulfide shuttling and volume expansion. B4C nanowires provide mechanical support due to their high hardness and chemical stability, while the porous structure enhances sulfur loading capacity and suppresses volume expansion. Their interaction with polysulfides reduces the diffusion coefficient, and experiments and simulations confirm the suppression of the shuttle effect. B4C and rGO synergistically form a conductive network, with rGO acting as an adaptive protective layer to buffer sulfur volume changes—molecular dynamics simulations (Figure 4-a) illustrate the atomic configuration of the BC-NWs/S/graphene cylindrical structure during charge-discharge cycles. This cathode exhibits outstanding performance: over 1,000 cycles at 1.5 mA/cm^2, with a capacity decay rate of 0.056% per cycle, an initial discharge capacity of 963 mAh/g, and an increased capacity of 1,395 mAh/g after 50 cycles, demonstrating exceptional rate performance; The assembled flexible battery remains stable under both normal and bent conditions, successfully illuminating an LED, laying the foundation for the development of high-performance flexible energy storage devices.

Luo et al. [37] used a catalyst-assisted process to grow B4C nanowires in situ on the surface of carbon nanofibers (CNF), constructing a self-supporting bifunctional cathode substrate (B4C@CNF), which significantly improved the performance of lithium-sulfur batteries. B4C nanowires form strong chemical adsorption with polysulfides via S-B and S-C bonds, with a binding energy as high as 12.51 eV (Figure 5-b), far exceeding the 1.18 eV of traditional carbon materials, effectively suppressing polysulfide dissolution and shuttling (Figure 5-a). Theoretical calculations show that different B4C crystal faces exhibit distinct adsorption mechanisms (Figure 5-d), and the adsorption process is accompanied by significant electron transfer (Figure 5-e); Bader charge analysis of S atoms further indicates that the charge changes of S atoms after adsorption are correlated with the binding energy (Figure 5-c). Additionally, the catalytic effect of B4C accelerates the redox reaction of polysulfides, increasing the lithium ion diffusion coefficient to 1.3×10^{-7} cm^2/s, thereby improving rate performance. B4C@CNF achieves high sulfur loading (10.3 mg/cm^2) and content (70 wt%) without requiring additional current collectors or binders. Experimental results show that the battery maintains an 80% capacity retention rate after 500 cycles at 1C and exhibits a reversible capacity of 304 mAh/g at 4C; High-sulfur-load batteries achieve an areal capacity of 9 mAh/cm^2, with a capacity retention rate of 82%～95% after 100 cycles; soft-pack batteries with a sulfur load of 200 mg exhibit a capacity of 625 mAh/g and an energy efficiency of 90% after 50 cycles. This design offers new insights for the practical application of high-energy-density lithium-sulfur batteries.

Zhang et al. [38] used a catalyst-assisted process to grow B4C nanoparticles in situ on the surface of activated cotton fibers (ACF), constructing a bifunctional cathode substrate (B4C-ACF), and prepared S/B4C-ACF electrodes by loading sulfur via melt diffusion. Combining SEM, TEM, XRD, XPS, and electrochemical testing (CV, rate performance, cycling stability, EIS), they systematically investigated the adsorption capacity of B4C for polysulfides, its catalytic activity, and the synergistic structural effects. The study revealed that B4C nanoparticles strongly chemically adsorb polysulfides via surface B-S and C-S bonds, inhibiting their dissolution and shuttle effects. Experimental and theoretical calculations confirmed that their adsorption capacity significantly outperforms that of pure ACF substrates. Additionally, B4C's high conductivity and active sites accelerate the conversion reaction of polysulfides, reducing overpotential (from 300 mV to 180 mV) and enhancing lithium ion diffusion efficiency, enabling the battery to maintain a reversible capacity of 928 mAh/g even at a 3C rate. The ACF network provides a rapid electronic transport pathway, while B4C nanoparticles enhance mechanical stability and mitigate sulfur volume expansion, collectively achieving high sulfur loading (3.0 mg/cm^2) and excellent cycling stability. Electrochemical testing shows that the battery achieves an initial capacity of 1415 mAh/g at 0.1C and a reversible capacity of 928 mAh/g at 3C, with significantly superior rate performance compared to the control group (S/ACF). After 3000 cycles at 1C, the capacity decay rate is only 0.012% per cycle, with a coulombic efficiency as high as 99.24%, demonstrating ultra-long cycle life. XPS and Raman analysis indicate that B4C forms B-S and C-S bonds with polysulfides, suppressing the shuttle effect and promoting reaction kinetics; EIS shows that the charge transfer resistance of the B4C-ACF electrode is significantly reduced, confirming its efficient charge transport capability. This study successfully addresses the polysulfide shuttle and reaction kinetics issues in Li-S batteries through the design of a B4C-ACF dual-functional substrate. The chemical adsorption, catalytic activity, and synergistic interaction of boron carbide with ACF significantly enhance the battery's cycle stability, rate performance, and energy density, providing a new strategy for the development of long-life, high-energy-density Li-S batteries.

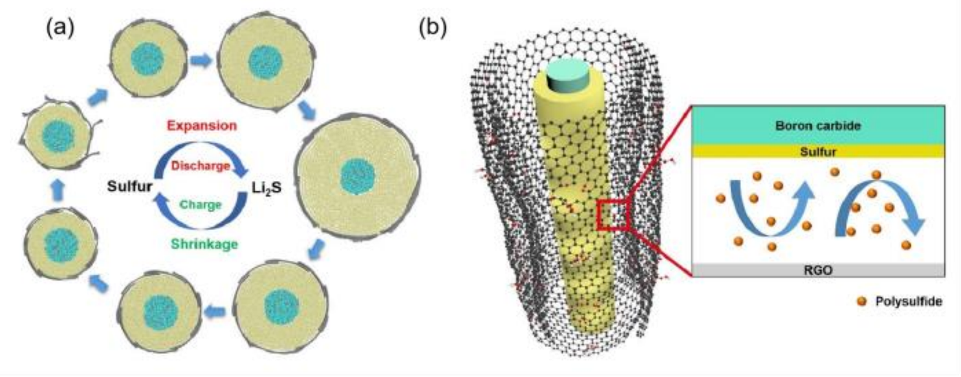

Figure 4 (a)MD snapshots of the atomic configurations representing a cross-section of the BC-NWs/S/graphene cylindrical structure in a cycle of charge/discharge process.(b)Schematic illustration of a representative volume element of BC-NWs@ACT/S/rGO electrode[36]

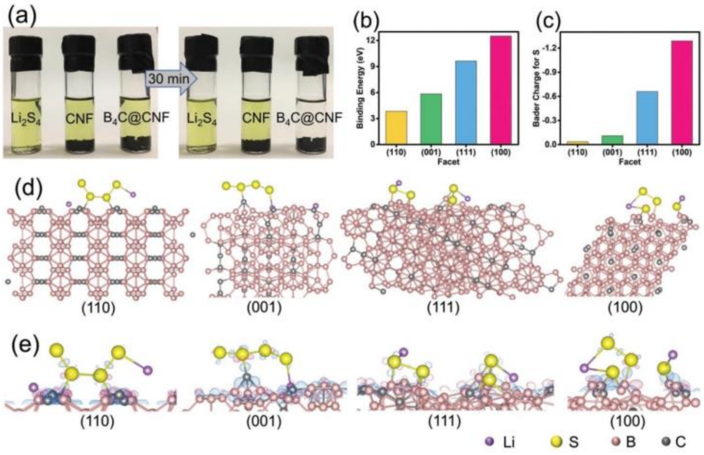

Figure 5 (a) Digital photos of polysulfide adsorption tests.(b) Binding energy and (c) Bader charge for S atoms regarding different B4C@CNF facets.(d) Binding geometry and (e) electron charge transfer when Li2S4 adsorbs on different B4C facets[37]

3.4 Fuel cells

In the research and application of fuel cells, the selection of materials is of critical importance. Boron carbide (B4C) is a highly stable covalent compound. Due to its chemical stability, it is an ideal material for use as a catalyst support, enhancing the catalyst's activity, stability, and resistance to poisoning [39]. Its exceptional high-temperature resistance, high electrical conductivity, excellent chemical stability, high hydrophilicity, and rich surface chemical properties make it a promising candidate material in the field of fuel cells [40]. Zhu et al. [41] conducted a systematic review of the application progress of superhard carbides such as diamond, silicon carbide (SiC), and boron carbide (B4C) in fuel cell catalysis, exploring the advantages of boron carbide as a carrier material and related research findings. Research indicates that boron carbide, with its high chemical stability, conductivity, and surface activity conferred by its strong covalent bond structure, is an ideal alternative to traditional carbon carriers.

Grubb et al. [42] conducted innovative research on fuel cell electrocatalyst supports, using B4C as the platinum-based catalyst support material. They prepared Pt/B4C composite catalysts via chemical adsorption and systematically evaluated their performance in hydrocarbon fuel cells using BET specific surface area testing and in situ electron microscopy analysis. The study demonstrated that the boron-doped carbon carrier significantly enhances platinum's catalytic activity. At 150℃ in phosphoric acid electrolyte, the Pt/B4C anode achieved an electro-oxidation current density of 5 mA/mgPt for propane, which is 9 times higher than that of mechanically mixed platinum black catalysts (0.6 mA/mgPt). Additionally, under the same surface coverage, the Pt/B4C composite catalyst demonstrated superior sintering resistance compared to graphite carriers. Experimental data show that the boron-doped carbon carrier optimizes metal-carrier interactions, increasing the actual active area utilization of platinum by 2.7 times (9.3 vs. 3.5 μA/cm²), while retaining the inherent corrosion resistance and oxidation stability of boron-doped carbon. This study is the first to confirm the feasibility of boron-doped carbon as a fuel cell electrocatalyst carrier, providing a new approach to reducing precious metal usage and enhancing electrode stability.

Meibuhr et al. [43] conducted a systematic study on the performance and mechanism of boron carbide (B4C) as a cathode catalyst in alkaline fuel cells. The study involved preparing porous nickel-based electrodes by mixing boron carbide with polytetrafluoroethylene (Teflon) and conducting polarization tests in a 45% KOH electrolyte. The experimental results showed that the boron carbide electrode exhibited stable oxygen reduction catalytic activity at a current density of 50 mA/cm^2, with its polarization behavior showing no significant correlation with the catalyst loading. However, after long-term operation, the performance of low-loading electrodes deteriorated more rapidly. After removing impurities via an acid/alkali cleaning process, the electrode polarization resistance decreased by approximately 30%, and performance remained stable during a 150-hour test, validating the critical role of impurity control in enhancing catalyst stability. Research indicates that boron carbide's high electrical conductivity (electron conductor), corrosion resistance, and resistance to electrochemical oxidation make it a potential low-cost cathode material. However, its catalytic activity remains lower than that of precious metal catalysts. Comprehensive analysis suggests that boron carbide is more suitable as a catalyst support material. By optimizing the surface properties and impurity content of the support, the long-term stability and economic viability of fuel cell cathodes can be significantly enhanced.

Mu et al. [44] prepared platinum-based catalysts (Pt-RGO/B4C) loaded with nano-boron carbide (B4C)-intercalated reduced graphene oxide (RGO) using the ethylene glycol reduction method, and investigated their performance and stability in the oxygen reduction reaction (ORR) of proton exchange membrane fuel cells (PEMFCs). The study demonstrated that B4C nanoceramic intercalation effectively suppresses graphene agglomeration and wrinkling, forming a highly ordered sandwich structure that enables uniform dispersion and full exposure of Pt nanoparticles, significantly enhancing the catalyst's electrochemical active surface area (ECSA) and mass activity. Experimental data show that the ECSA of Pt-RGO/B4C reaches 121 m^2/g, representing a 55% and 92% increase compared to Pt/RGO (78 m^2/g) and commercial Pt/C (63 m^2/g), respectively (Figure 6-a). Its ORR mass activity is 185 A/gPt, which is 1.8 times that of Pt/RGO and 2.9 times that of Pt/C (Figure 6-b). After 10,000 accelerated durability tests, Pt-RGO/B4C retained 45.2% of its initial ECSA, significantly outperforming Pt/RGO (29.7%) and Pt/C (23.4%) (Figure 6-c). The team revealed that B4C intercalation restricts the migration and agglomeration of Pt nanoparticles through steric hindrance effects, enhances the conductivity and chemical stability of graphene, and significantly improves the catalyst's corrosion resistance and long-term stability.

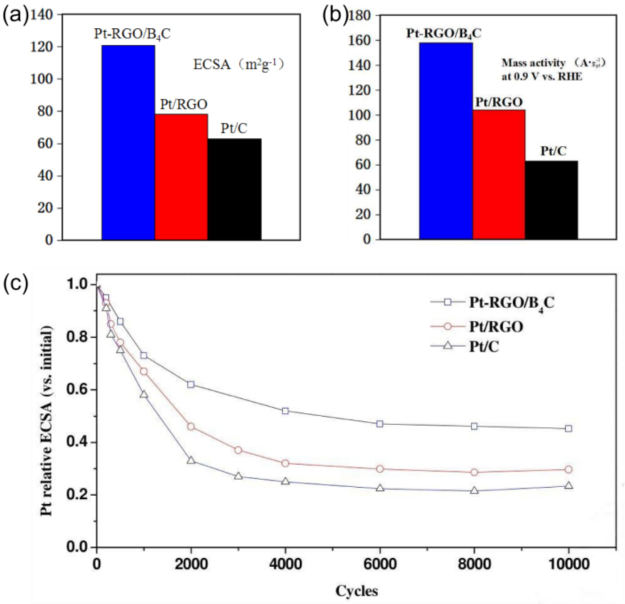

Figure 6 (a)ECSA of Pt-RGO/SiC, Pt/RGO and commercial Pt/C catalysts.(b)mass activities at +0.9 V vs. RHE in 0.1M HClO4 solution.(c)ECSA decay as a function of the number of potential cycles

4 Conclusions and Future Perspectives

4.1 Conclusions

This review establishes that boron carbide (B4C) and its composites exhibit significant potential in mitigating critical challenges across new energy battery systems, leveraging their structural rigidity, chemical robustness, tunable semiconductivity, and surface reactivity. Key advancements include:

In lithium-ion batteries (LIBs), B4C functions as a robust framework or interfacial buffer (e.g., Si/B4C/graphite systems), effectively constraining volume expansion in high-capacity anodes while enhancing electron/ion transport, thereby synergistically improving specific capacity and cyclability.

For sodium-ion batteries (SIBs), its three-dimensional architecture provides stabilized Na$^+$ diffusion pathways (e.g., VSe2/B4C@HCG), physically mitigating electrode pulverization.

In lithium-sulfur (Li-S) batteries, B4C chemically anchors polysulfides via B-S/C-S bonding and catalyzes their conversion (e.g., BC-NWs@ACT/S/rGO), substantially suppressing shuttle effects and reinforcing cathode integrity.

Within fuel cells, as a Pt-catalyst support (e.g., Pt-RGO/B4C), its corrosion resistance and surface properties optimize catalytic dispersion and oxygen reduction reaction stability.

Nevertheless, persistent challenges include high nanomaterial synthesis costs, insufficient intrinsic ionic conductivity, and unresolved interfacial reaction mechanisms.

4.2 Future perspectives

To advance B4C composites in energy storage, four strategic research priorities are proposed:

(1) Performance Optimization: Elucidate structure-property relationships through integrated computational-experimental approaches to precisely engineer materials for enhanced ionic transport, volume-change accommodation, and polysulfide entrapment, ultimately boosting energy density, longevity, and safety.

(2) Process Innovation: Develop scalable, energy-efficient synthesis routes for nanostructured B4C (nanowires, nanosheets, porous architectures). Innovate one-step/in situ fabrication of composite electrodes to streamline manufacturing, reduce costs, and improve interfacial cohesion.

(3) Advanced Interface Engineering: Decipher interfacial interaction mechanisms to design novel modification strategies, thereby minimizing interfacial resistance, stabilizing electrode-electrolyte interfaces, and suppressing parasitic reactions during cycling.

(4) Cross-Disciplinary Integration: Foster convergence of materials science, electrochemistry, and characterization physics. Employ atomic-scale analytical techniques to unravel reaction mechanisms while adapting methodologies from adjacent fields to catalyze innovation in battery technology.

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