

A bamboo-carbon-coated separator with biomimetic ion channels for high-loading sodium metal anodes

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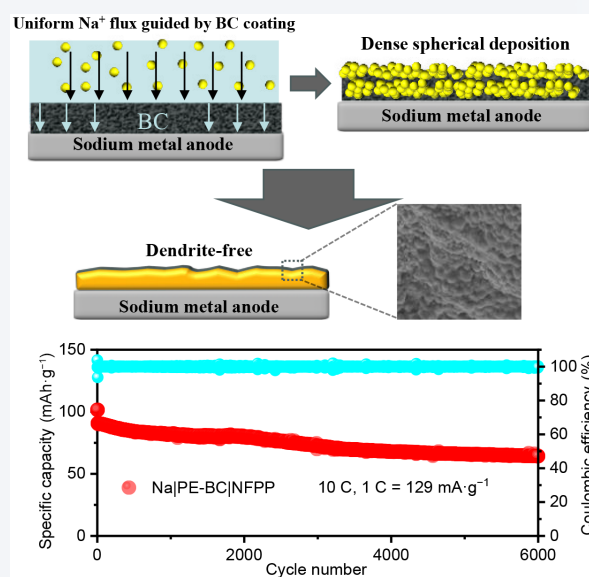
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Cite this article: *Nano Research*, 2026, 19, 94909133. <https://doi.org/10.26599/NR.2026.94909133>

ABSTRACT: Sodium, due to its abundance in the Earth's crust (2.74%), is 421 times that of lithium (0.0065%), making sodium-metal batteries (SMBs) a promising supplement to lithium-based systems. The intrinsic properties of sodium metal, including kinetic and thermodynamic instabilities during plating and stripping, however, lead to dendrite growth, internal shorts, and serious safety issues. In this work, a functional polyethylene (PE) based separator decorated with a uniform layer of bamboo carbon (BC) is prepared using a simple blade casting method. Compared with the pristine PE separator, the BC-modified separator shows better electrolyte wettability and uniform biomimetic channels. The coated BC promotes uniform sodium-ion flux and even sodium deposition, effectively suppressing dendrite formation and greatly enhancing cycling stability. The BC-modified PE separator mitigates the tip effect at sodium metal defects, enabling stable performance of symmetric cells. In electrochemical tests, sodium symmetric cells with this separator operated stably for over 450 h at $0.5 \text{ mA} \cdot \text{cm}^{-2}$ and $0.5 \text{ mAh} \cdot \text{cm}^{-2}$. Moreover, Na|PE-BC|sodium iron pyrophosphate phosphate (NFPP) full cells retained over 98% capacity after 1000 cycles at 1 C ($1 \text{ C} = 129 \text{ mA} \cdot \text{g}^{-1}$), over 90% after 2000 cycles at 5 C, and over 70% after 6000 cycles at a high rate of 10 C. Even with a high cathode loading of $7.1 \text{ mg} \cdot \text{cm}^{-2}$, the full cells maintained 90% capacity for more than 300 cycles. This work offers a simple and effective modification of commercial PE separators using renewable, low-cost bamboo carbon, providing a practical and sustainable route toward highly stable, high-loading sodium-metal batteries.

KEYWORDS: sodium metal anodes, separator modification, bamboo carbon, long-term cycle, high loading



1 Introduction

With the growing depletion and pollution of fossil fuels like coal and petroleum, renewable sources, such as wind and solar, are being widely pursued. However, their intermittent nature hinders reliable grid integration, creating a pressing need for large-scale energy storage technologies. Concurrently, the rapid electrification of transportation demands high-efficiency energy storage

systems [1–3]. Lithium-ion batteries, with their high energy density ($150\text{--}250 \text{ Wh} \cdot \text{kg}^{-1}$), currently dominate the market [4–8]. However, the scarcity and uneven global distribution of lithium resources have positioned sodium-based batteries-leveraging sodium's abundance and low cost-as a critical complement to lithium technologies, ensuring energy security [9–13].

Sodium-metal batteries (SMBs), with their high theoretical specific capacity ($1166 \text{ mAh} \cdot \text{g}^{-1}$), are particularly promising. Yet, their practical application is hindered by dendrite growth during operation, leading to low Coulombic efficiency (CE) [14–16]. Addressing this challenge necessitates the development of compatible separators [17, 18]. Commercial polyolefin separators (e.g., polypropylene (PP) and PE) used in lithium-ion batteries are

Received: May 29, 2026; Revised: July 23, 2026

Accepted: August 19, 2026

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unsuitable for SMBs, as they fail to suppress dendrite formation, resulting in dendrite penetration, short circuits, and battery failure [19–23]. While inorganic glass fiber (GF/D) separators are commonly used in lab-scale SMBs, their brittleness compromises manufacturing efficiency, and their excessive thickness, high electrolyte absorption, and micrometer-scale pores limit energy density and safety by inadequately inhibiting sodium dendrite growth [24–27]. Current research focuses on hybrid organic–inorganic composite separators to overcome these limitations [28–30]. Kim et al. [31] deposited a thin SiO_2 layer onto a porous PE separator via chemical vapor deposition. The SiO_2 -modified separator delivered higher voltage stability than glass fiber and substantially enhanced thermal stability (up to 140 °C) relative to pristine PE. Zhou et al. [32] successfully prepared a polydopamine (PDA)@ mAl_2O_3 -PE (the “m” means “modified”) composite separator by coating the surface of polyethylene (PE) modified with a PDA solution with 3-aminopropyltriethoxysilane-modified $\alpha\text{-Al}_2\text{O}_3$. The optimized separator exhibited enhanced thermal stability relative to pristine polyethylene, but its dimensional stability remained limited, with shrinkage occurring at around 150 °C.

Zeng et al. [33] reported a composite separator in which natural halloysite nanotubes (HNTs) were uniformly coated onto both sides of a PP separator using a polyvinylidene fluoride (PVDF)/poly(vinyl alcohol) (PVA) mixed slurry via the spin-coating method. A sodium metal battery was assembled using metallic sodium as the anode and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) as the cathode; its electrochemical performance was evaluated in comparison with a bare PP separator. It demonstrated that a symmetric cell using the HNTs@PP separator could cycle stably for over 900 h at 0.5 $\text{mA}\cdot\text{cm}^{-2}$. After 900 cycles at 500 $\text{mA}\cdot\text{g}^{-1}$, the full cell retained 87% of its capacity after the cycling test, and the separator exhibited markedly enhanced thermal stability and electrolyte wettability compared to pristine PP. Cheng et al. [34] reported a composite separator in which ZnMoO_4 ceramic nanoparticles were mixed with a polyvinylpyrrolidone (PVP) binder and coated onto one side of a PE separator. A half-cell was assembled using hard carbon as the negative electrode and metallic sodium as the positive electrode, and its electrochemical performance was benchmarked against glass fiber and pristine PE separators. The PVP/ ZnMoO_4 @PE separator showed no thermal shrinkage after 30 min at 180 °C (pure PE shrank by 52%), the electrolyte contact angle decreased from 63° to 9°, and the ionic conductivity was significantly improved. The assembled half-cell performed better than the glass fiber separator, whereas the pure PE separator could not function properly in sodium batteries. Li et al. [35] reported a composite separator in which the NASICON-type fast ion conductor $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) was mixed with PVDF and coated onto the surface of a PP separator. Button cells and pouch cells were assembled using metallic sodium as the anode and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as the cathode. Their electrochemical performance was tested and compared with that of pure PP separators and glass fiber separators. This NZSP@PP separator exhibits a contact angle of only approximately 6° in carbonate electrolyte and thermal shrinkage of only 8% at 170 °C (compared to 43% for pure PP). In a symmetric cell, it cycled stably for 1000 h at 0.5 $\text{mA}\cdot\text{cm}^{-2}$.

In this work, we designed a reactive PE-based separator to enhance sodium-metal battery performance. The coated bamboo carbon (BC) was processed via delignification and hemicellulose removal, followed by carbonization at 500 °C to synthesize

microporous carbon. This carbon layer ($\sim 17.5\ \mu\text{m}$) was coated onto a PE separator, improving electrolyte wettability, guiding Na deposition, and suppressing dendrite growth. The Na||Na symmetric cell demonstrated stable cycling for 450 h at 0.5 $\text{mA}\cdot\text{cm}^{-2}$ /0.5 $\text{mAh}\cdot\text{cm}^{-2}$ in carbonate-based electrolyte, with an overpotential below 300 mV. For Na||sodium iron pyrophosphate phosphate (NFPP) full cells, capacity retention exceeded 98% after 1000 cycles at 1 C (1 C = 129 $\text{mA}\cdot\text{g}^{-1}$), 90% after 2000 cycles at 5 C, and 70% after 6000 cycles at 10 C. Notably, under high cathode loading (7.1 $\text{mg}\cdot\text{cm}^{-2}$), the full cell retained 90% capacity after 300 cycles. This work presents a scalable and sustainable approach to engineer high-performance SMB separators using renewable bamboo-derived carbon, advancing the development of safe and energy-dense sodium-metal batteries.

2 Experimental

2.1 Pretreatment and purification of bamboo powders

A three-neck flask was charged with 50 g of bamboo powders, and enough anhydrous ethanol was added to completely submerge the material. The mixture was stirred continuously for 6 h under reflux at 80 °C in a water bath. After the reaction, the mixture was vacuum-filtered, and the filter cake was washed with fresh anhydrous ethanol. The solid was then dried in an oven at 105 °C for 3 h to obtain pre-purified bamboo powder.

The ethanol-washed bamboo powder was transferred into a three-neck flask, followed by the sequential addition of 500 mL of deionized water, 6.6 mL of glacial acetic acid (CH_3COOH), and 3.3 g of sodium chlorite (NaClO_2). The mixture was shaken to achieve uniform mixing. The flask was then heated in a 75 °C water bath for 1 h, with intermittent manual swirling to ensure a thorough reaction. After 1 h, another equal portion of glacial acetic acid (6.6 mL) and sodium chlorite (3.3 g) was added, and the heating and shaking procedure was repeated. This “addition heating” cycle was carried out a total of three times. After the reaction, the mixture was filtered under vacuum and the resulting solid was rinsed with copious deionized water until the washings reached a neutral pH. Finally, the obtained solid was dried in an oven at 105 °C for 6 h to constant weight, yielding the acid-treated bamboo powder.

The acid-treated bamboo powder was divided equally into two portions, each placed in a 500 mL beaker. To each portion was added a pre-prepared mixed solution containing 5 wt.% NaOH and 1 wt.% urea. The mixture was stirred continuously at 30 °C for 30 min. After the reaction, each mixture was vacuum filtered, and the filter cake was rinsed thoroughly with deionized water until the filtrate reached neutrality. The two batches of solid were then combined and dried in an oven at 105 °C for 6 h to constant weight, yielding the purified bamboo fiber material.

The purified bamboo fiber was placed in a tube furnace and carbonized under a continuous flow of argon/hydrogen mixed gas (5 vol.% H_2). We heated the precursor to 500 °C at a ramp of 5 °C $\cdot\text{min}^{-1}$ and held at this temperature for 2 h. The sample was allowed to cool spontaneously to room temperature under the protective atmosphere, and the resulting product was collected as BC.

2.2 Separation of slurry and coating of separator

The as-prepared BC powder and PVDF binder were combined in

N-methyl-2-pyrrolidone (NMP) at a BC-to-PVDF mass ratio of 8:2, and the mixture was loaded into a ball mill jar for homogenization. The mixture was ball-milled at 320 rpm for 4 h to form a homogeneous slurry. The slurry was then uniformly blade-coated onto a commercial PE separator. After coating, the separator was vacuum-dried at 80 °C for 8 h to eliminate all residual NMP. Circular discs (19 mm in diameter) were then punched from the dried separator and designated as PE-BC for cell assembly.

2.3 Preparation of NFPP cathode material

PVDF powder was first dissolved in NMP to yield a 5 wt.% solution. NFPP, Super P, and the PVDF solution were then combined at a mass ratio of 8:1:1 (NFPP:Super P:PVDF). After adding additional NMP, the mixture was ball-milled at 240 rpm for 4 h to form a homogeneous and viscous slurry. The homogeneous slurry was uniformly cast onto an aluminum foil current collector. The electrode was subsequently dried under vacuum at 80 °C for 12 h to eliminate all residual NMP. Circular discs with a diameter of 12 mm were then punched from the dried electrode for cell assembly.

2.4 Materials characterization

The prepared BC powder was subjected to Fourier-transform infrared spectroscopy (FTIR, VERTEX 80V) and Raman spectroscopy (Raman, DXR532) to characterize the carbon microstructure, and the degree of disorder and defect density in the BC were quantitatively evaluated using the I_D/I_G ratio, where I_D and I_G were the integrated intensities of the D and G bands, respectively. Scanning electron microscopy (SEM, Regulus 8100) was used to characterize the surface morphology of the powder. To determine the electrical conductivity of the BC powder, the powder was loaded into a solid-state battery mold and pressed under a constant pressure of 5 t. The electronic conductivity was determined from cyclic voltammetry (CV) data collected in the potential range of −0.1 to 0.1 V, using the following equations

$$R = \frac{U}{I} \quad (1)$$

$$\sigma_e = \frac{L}{RS} \quad (2)$$

where U was the applied voltage, I was the corresponding current, σ_e was the electronic conductivity, L was the thickness of the BC laminate, S was the effective electrode area, and R was the resistance obtained from impedance measurements.

X-ray diffraction (XRD 3 kW/SmartLab) was employed to examine the crystal structure of the PE-BC separator, while the surface morphology and thickness of the PE-BC were characterized via scanning electron microscopy. The electrolyte wettability was characterized by static contact angle measurements performed on a droplet shape analysis system (SDC-80S). A Thermo Scientific K-Alpha spectrometer fitted with a monochromatic Al K α excitation source ($h\nu = 1486.6$ eV) was employed for all X-ray photoelectron spectroscopy (XPS) characterization. During the test, the beam spot size was set to 400 μm , and the vacuum in the analysis chamber was better than 5.0×10^{-7} mbar. The instrument operating voltage was 12 kV, the filament current was 6 mA, the electron emission angle was 60°, and the work function was 4.2 eV. Depth profiling was performed using an argon ion gun with an etching energy of 2000 eV and an etching current intensity of mid. The typical

etching rate, calibrated using a Ta₂O₅ standard sample, was approximately 0.30 nm·s^{−1}. The flood gun was kept on throughout the test to neutralize the charge.

2.5 Electrochemical characterization

All battery performance tests were conducted using CR2025 button cells. A sodium metal sheet (Canrd Technology Co., Ltd., Guangdong, China, 450 μm thick) was used as the anode, and NFPP as the cathode, with an areal loading of approximately 1 mg·cm^{−2}. The electrolyte employed was a commercial 1.0 M NaPF₆ dissolved in a 1:1 (v/v) blend of ethylene carbonate (EC) and dimethyl carbonate (DMC), with the addition of 5% fluoroethylene carbonate (FEC, purchased from Canrd Technology). An argon-filled glove box was used for assembling the cells and preparing the electrolytes. The H₂O and O₂ concentrations inside the box were continuously controlled to remain under 0.1 ppm. Constant-current charge–discharge cycling and rate performance tests were conducted on a NEWARE testing system, and electrochemical impedance spectroscopy (EIS) was performed on a CHI 660E workstation over a frequency range of 0.01 Hz to 100 kHz.

3 Results and discussion

As schematically illustrated in Fig. 1, the pristine PE separator suffers from an uneven Na⁺ flux distribution across its surface, which readily triggers the tip effect. Sodium ions preferentially nucleate at high-curvature protrusions and evolve into needle-like dendrites. With increasing deposition capacity, these dendrites propagate continuously and eventually pierce through the separator, causing internal short-circuiting. In stark contrast, the PE-BC separator constructs uniform ion-transport channels through the hierarchical porous structure of the BC coating. Simultaneously, the abundant oxygen-containing functional groups (C=O/C–O) on the coating surface serve as sodiophilic sites, effectively lowering the sodium nucleation overpotential. Under this dual regulation of ion channels and sodiophilic sites, Na⁺ ions distribute uniformly across the separator/anode interface and deposit smoothly as spheroidal grains. This spherical, dendrite-free morphology eliminates the tip effect and substantially enhances the safety and cycling stability of the cell.

To investigate the constituent components of BC, we first performed infrared and Raman spectroscopy tests (Figs. 2(a) and 2(b)). FTIR spectroscopy was employed to investigate the surface chemistry of BC (Fig. 2(a)). The broad absorption band near 3430 cm^{−1} arises from O–H stretching vibrations of hydroxyl groups and adsorbed water [36], indicating that the surface exhibits significant hydrogen bonding and strong hydrophilicity. Within the 3000–2800 cm^{−1} range (C–H stretching vibrations), we observed two weak but discernible peaks at 2920 and 2852 cm^{−1}, assigned to the asymmetric stretching of –CH₂ and the symmetric stretching of –CH₃ groups [37]. This confirms the retention of aliphatic carbon chains from incomplete carbonization at 500 °C.

It is worth noting that the fingerprint region (1800–900 cm^{−1}) reveals a rich array of oxygen-containing functional groups. The prominent peak at approximately 1620 cm^{−1} can be attributed to the stretching vibration of conjugated C=O groups and/or the skeletal C=C vibrations of the aromatic carbon framework, both of which are typically observed in partially carbonized biomass and are often difficult to deconvolve unambiguously [38, 39], which are commonly found in partially carbonized biomass. The band at

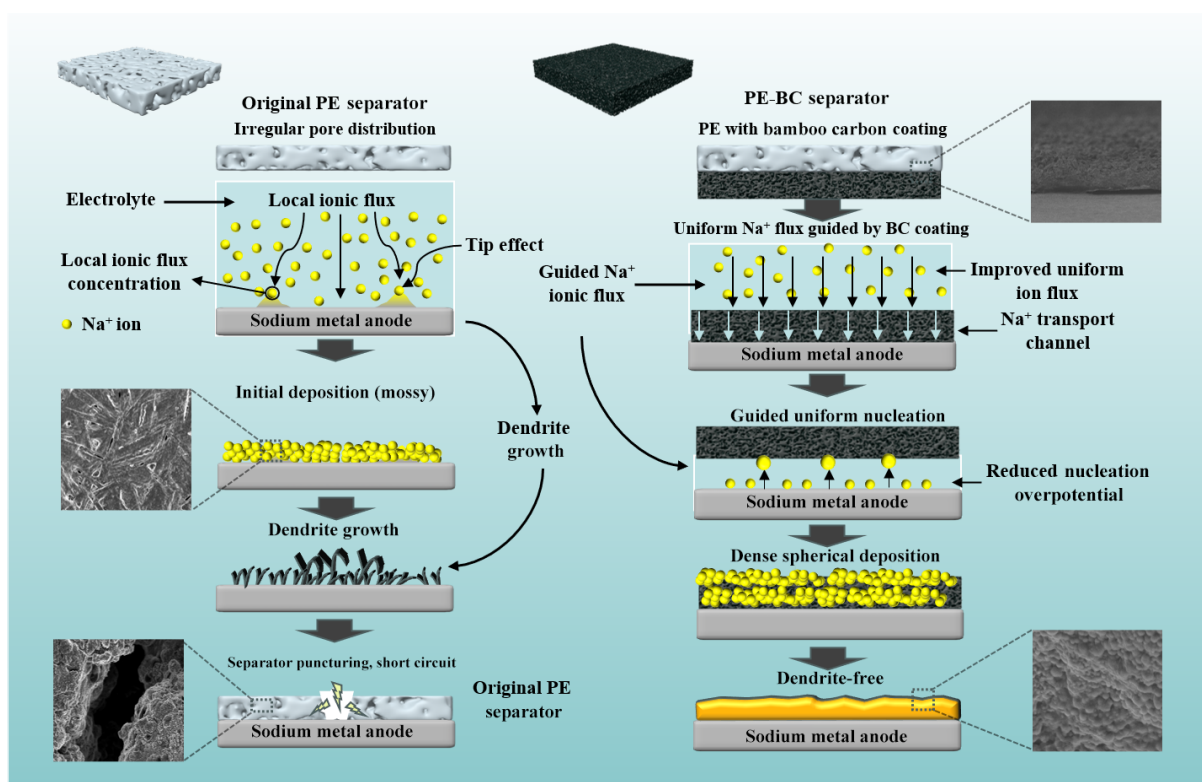


Figure 1 Schematic diagram of the cycling process using a PE separator and a PE-BC separator.

approximately 1380 cm^{-1} is ascribed to $-\text{CH}_3$ bending or the symmetric stretching of COO^- groups [37]. More importantly, the strong, broad absorption band spanning the $1300\text{--}1000\text{ cm}^{-1}$ range is primarily attributed to the C–O stretching vibrations of various functional groups. The complexity of this absorption band indicates that the chemical environment of the oxygen atoms is highly heterogeneous. These spectral features indicate that BC possesses a carbon framework decorated with a high density of residual oxygen-containing functional groups. It is anticipated that these functional groups serve as active sites for sodium ion adsorption, thereby promoting an increase in adsorption capacity.

The local carbon microstructure of BC was characterized by Raman spectroscopy. As shown in Fig. 2(b), the spectrum displays two broad and overlapping bands, which are characteristic of highly disordered carbonaceous materials. The first-order Raman features are dominated by the D band (defect-induced band) centered at approximately 1345 cm^{-1} and the G band (graphitic band) located at around 1590 cm^{-1} . The D band is attributed to the breathing mode of aromatic sp^2 carbon, which becomes Raman-active only in the presence of lattice imperfections, while the G band corresponds to the in-plane stretching vibration of sp^2 carbon atoms [40–42].

Quantitative spectral analysis reveals that BC exhibits highly amorphous properties. The D band is unusually broad, with an intensity comparable to that of the G band, resulting in a low-resolution doublet. Peak deconvolution using a Lorentzian function yielded an integrated intensity ratio of $I_D/I_G = 1.05$. This high I_D/I_G value clearly indicates that the carbon framework possesses an extremely high structural defect density, very small lateral grain sizes in the pseudographite domains, and a low degree of graphitization—all of which are consistent with a carbonization temperature as low as $500\text{ }^\circ\text{C}$. Collectively, the Raman spectra indicate that BC possesses a highly defective, predominantly

amorphous carbon framework. It is anticipated that this defect-rich microstructure will provide abundant Na^+ adsorption sites via surface-controlled capacitive mechanisms, thereby forming a dominant declining capacity region in the constant-current charge–discharge curves.

To investigate the microstructure of the PE-BC separator, we performed morphological and phase analyses. The crystal structures of the pristine PE separator and the PE-BC separator were compared using XRD. As shown in Fig. 2(c), both samples exhibited identical diffraction patterns, with two sharp characteristic peaks at $2\theta = 21.4^\circ$ and 24.1° , corresponding to the (110) and (200) reflections of orthorhombic polyethylene crystals, respectively [43]. No additional diffraction peaks attributable to the bamboo carbon coating were detected. This result confirms that the coating is X-ray amorphous, as bamboo carbon prepared at $500\text{ }^\circ\text{C}$ is inherently amorphous. The XRD pattern of the BC powder (Fig. S1 in the Electronic Supplementary Material (ESM)) displays a broad (002) peak at approximately 24° , characteristic of turbostratic carbon with a low graphitization degree. Several sharp peaks are also observed, which are attributed to naturally occurring inorganic salts (ash) from the bamboo precursor, a common feature in low-temperature biomass-derived carbons. These residues are present as minor inclusions, and their potential influence on the electrochemical behavior is discussed in the ESM. Furthermore, the coating is extremely thin, and when attached to a highly crystalline polyethylene substrate, its total mass is far below the detection limit of conventional XRD. These results confirm that the bamboo carbon coating does not alter the crystal structure of the polyethylene membrane matrix.

The surface SEM image of the BC powder presented in Fig. 2(d) reveals that the BC powder contains a small number of pores. The cross-sectional SEM image in Fig. 2(e) shows that the bamboo

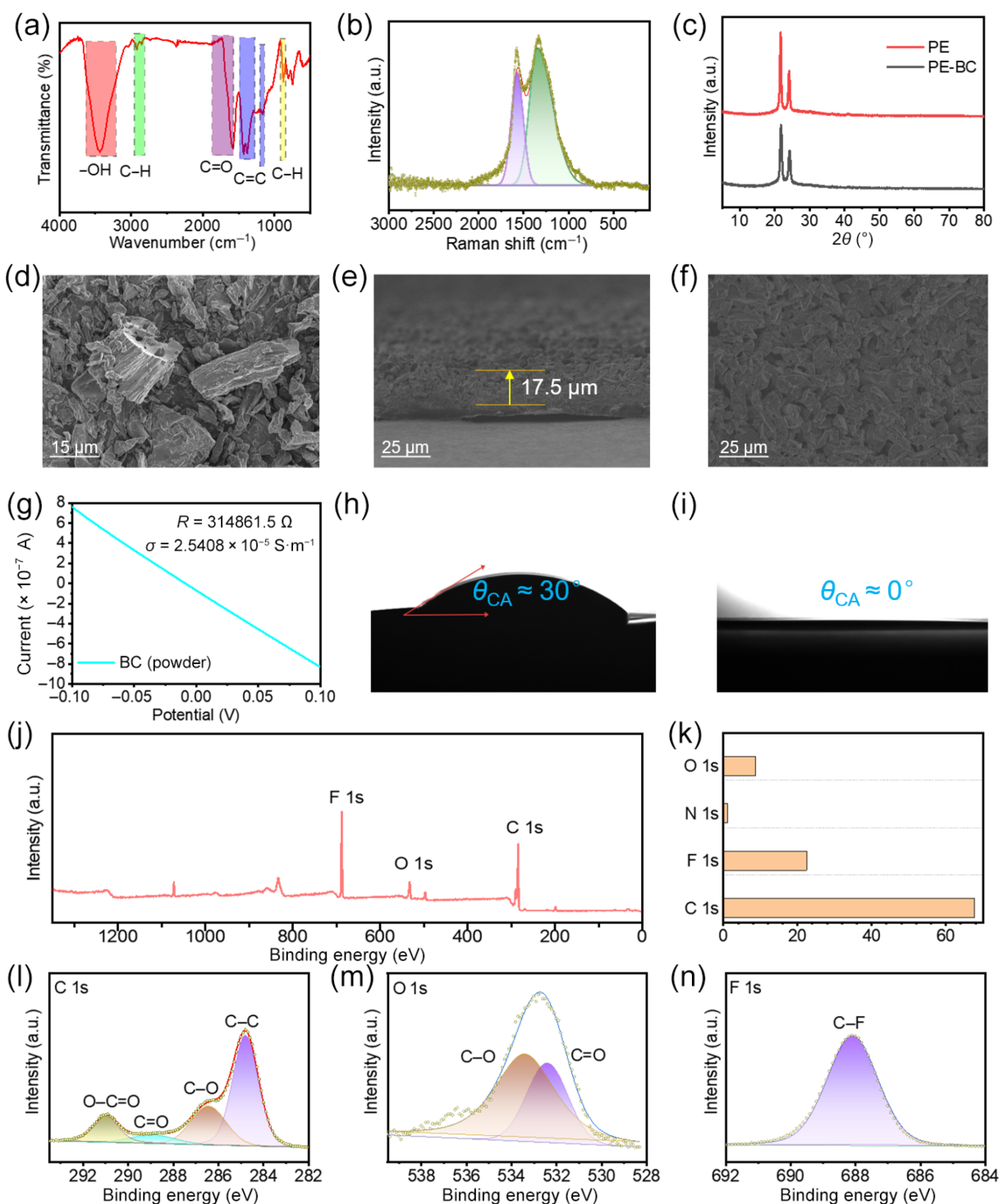


Figure 2 (a) FTIR spectrum of BC powder. (b) Raman spectrum of BC powder. (c) XRD patterns of PE separator and PE BC separator. (d) Top-view SEM image of BC powder. (e) Cross-sectional SEM image of PE BC separator. (f) Surface SEM image of PE BC separator. (g) Electronic conductivity of BC powder; contact angle measurements of electrolyte: (h) PE and (i) PE BC. (j) XPS survey spectrum of the PE BC separator. (k) Corresponding atomic percentages. (l)–(n) XPS spectra of the PE BC separator.

carbon powder is uniformly coated onto the surface of the PE separator, forming a continuous, dense layer approximately 17.5 μm thick. Compared to the PE separator, the top-view SEM image in Fig. 2(f) indicates that the micropores originally present on the PE separator surface have been covered by the BC layer. The coated surface is compact, and the BC itself possesses a microporous structure, which facilitates electrolyte wettability and

ionic transport. As shown in Fig. 2(g), the BC powder exhibits very low electronic conductivity, behaving as a near-insulating semiconductor, thereby effectively blocking direct electronic contact between the anode and cathode. The separator-electrolyte affinity directly influences the interfacial impedance and cycling stability of the battery. We measured the contact angles of PE and PE-BC separators in the electrolyte (Figs. 2(h) and 2(i)). In the electrolyte

(1 M NaPF₆ in EC:diethyl carbonate (DEC) = 1:1 with 5% FEC), the contact angle of the PE membrane was approximately 30°, whereas that of the PE-BC membrane was close to 0°, indicating complete wetting. These results demonstrate that the hydrophilic porous BC coating significantly enhances the membrane's wetting ability toward the electrolyte, thus facilitating the formation of a uniform electrode/electrolyte interface with low interfacial impedance.

The surface chemical composition and bonding configuration of the PE-BC separator were investigated using XPS (Figs. 2(j)–2(n)). The full spectrum of PE-BC (Fig. 2(j)) confirmed that carbon, oxygen, and fluorine are the major elements, with a notably strong O 1s peak (approximately 532 eV). Quantitative analysis indicates that the oxygen content of PE-BC is 8.61 at.% (Fig. 2(k)). Analysis of the high-resolution C 1s spectrum of PE-BC (Fig. 2(l)) allows for the resolution of the bonding environments of individual carbon atoms. The prominent peak at 284.8 eV is attributed to sp²/sp³ C–C/C=C bonds [44, 45]. That is, a graphite carbon framework. The shoulder peak at approximately 286.4 eV corresponds to single C–O bonds (such as hydroxyl or ether groups), while the weaker but distinct peak at 288.9 eV is attributed to carbonyl (C=O) or carboxyl (O=C–O) functional groups; the prominent peak at 291 eV is attributed to C–F bonds. The significant intensity of these carbon–oxygen components quantitatively confirms (Fig. 2(m)) that the carbon lattice of PE-BC is heavily decorated with oxygen-containing functional groups, which is consistent with its incomplete carbonization at such a low temperature. The O 1s spectrum (Fig. 2(m)) provides further insight into the nature of these oxygen-containing groups. Fitting the asymmetric O 1s

envelope curve yielded two major components: a peak at approximately 531.8 eV attributed to the C=O group and a peak at approximately 533.0 eV attributed to the C–O group. Overall, XPS analysis indicates that the surface of PE-BC is enriched with oxygen functional groups, primarily C=O and C–O groups. This chemically heterogeneous surface is a direct result of the limited carbonization temperature (500 °C), which is insufficient to eliminate these thermally unstable functional groups. Although such functional groups provide abundant sodium adsorption sites, thereby contributing to high-rate capacity. The test results were consistent with expectations: The sample was a PVDF-coated bamboo carbon composite (Fig. 2(n)), with uniform PVDF distribution, bamboo carbon retaining a moderate amount of oxygen-containing functional groups, and no significant impurities on the surface.

To investigate the deposition and stripping behavior of sodium metal on different separators, we first assembled a Na||Na symmetric cell and performed EIS measurements (Fig. 3(a)). The results of the equivalent circuit fitting showed that both the bulk resistance (R_b) and charge transfer resistance (R_{ct}) of the PE-BC separator cell were significantly lower than those of the cell using a PE separator, indicating superior ionic conductivity and faster interfacial reaction kinetics. The critical current density (CCD) test (Figs. 3(b) and 3(c)) confirms the stability of the cell under high current conditions. At a deposition capacity of 0.25 mAh·cm^{−2}, the cell employing the PE-BC separator can withstand a current density as high as 7 mA·cm^{−2} without short-circuiting.

The nucleation overpotential was determined from the initial

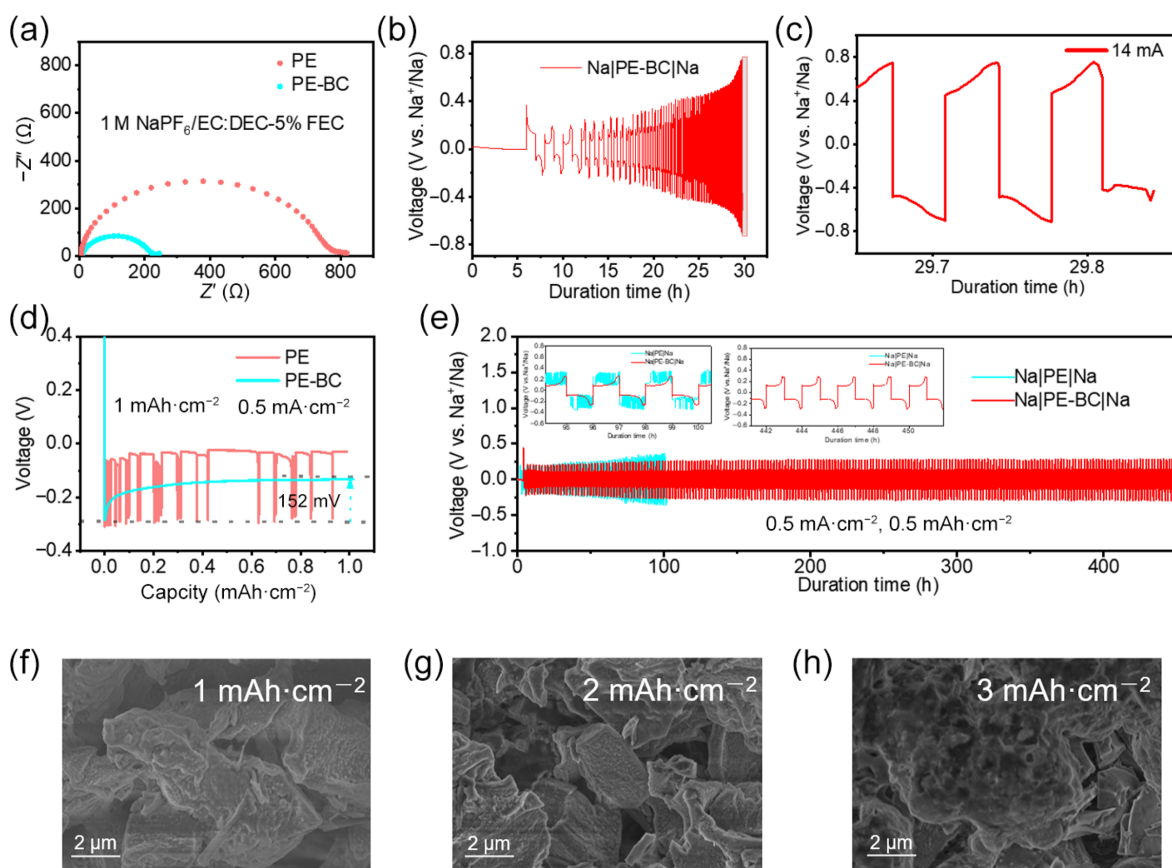


Figure 3 (a) EIS spectra of cells with PE and PE-BC separators. (b) CCD measurement of the cell using the PE-BC separator and (c) a magnified view. (d) Voltage–capacity curves of half-cells with different separators during sodium nucleation. (e) Long-term cycling performance of Na||Na symmetric cells assembled with different separators. ((f)–(h)) Top-view SEM images of sodium surfaces deposited with different capacities on the PE-BC separator.

galvanostatic plating curve at $0.5 \text{ mA}\cdot\text{cm}^{-2}$, defined as the difference between the sharp voltage minimum at the onset of Na nucleation and the subsequent stable plating voltage, following the methodology described by Pei et al. [46]. The nucleation overpotential analysis in Fig. 3(d) demonstrates that the cell with the PE-BC separator exhibits a significantly lower sodium nucleation overpotential of approximately 152 mV. In contrast, the cell with the pristine PE separator failed to operate properly from the very beginning, confirming that the BC coating provides abundant sodiophilic sites that effectively lower the nucleation barrier. In long-term cycling tests at $0.5 \text{ mA}\cdot\text{cm}^{-2}$ and $0.5 \text{ mAh}\cdot\text{cm}^{-2}$ (Fig. 3(e)), the symmetric cell with the PE-BC separator delivers stable operation for over 450 h, with the overpotential remaining consistently below 300 mV. By contrast, the cell assembled with the pristine PE separator experienced severe voltage fluctuations under the same conditions and failed to operate stably. To further evaluate the rate tolerance of the PE-BC separator, we tested symmetric cells under conditions of $1 \text{ mA}\cdot\text{cm}^{-2}$ and $1 \text{ mAh}\cdot\text{cm}^{-2}$ (Fig. S2 in the ESM). The Na||Na symmetric cell using the PE-BC separator could cycle stably for over 150 h, with a smooth and stable overpotential. In contrast, the cell using a pure PE separator exhibited severe voltage fluctuations and rapidly failed. These results indicate that even at higher current densities, the BC coating effectively suppresses dendrite growth, which is fully consistent with the low nucleation overpotential (152 mV) and high critical current density ($7 \text{ mA}\cdot\text{cm}^{-2}$) described earlier.

Cross-sectional SEM images show that the BC coating has a uniform thickness of approximately $17.5 \mu\text{m}$, corresponding to a surface mass loading of $0.9 \text{ mg}\cdot\text{cm}^{-2}$ and an apparent density of approximately $0.51 \text{ g}\cdot\text{cm}^{-3}$. To further explore the potential for reducing the coating mass, a thinner BC coating was also prepared, with a thickness of approximately $9 \mu\text{m}$ and a corresponding areal mass loading of $0.5 \text{ mg}\cdot\text{cm}^{-2}$. A symmetric Na||Na cell assembled using this thinner coating also exhibited stable cycling performance (Fig. S3 in the ESM), indicating that the BC coating can be optimized to reduce its mass contribution without compromising its ability to suppress dendrite growth. Even for the thicker coating, the mass of the BC accounted for only $\sim 12.7\%$ of the high-loading NFPP cathode ($7.1 \text{ mg}\cdot\text{cm}^{-2}$), indicating that the BC coating has a negligible impact on the overall mass energy density. This lightweight characteristic, combined with the multifunctional advantages of the hierarchical porous structure and sodium-affinity functional groups, highlights the practical feasibility of the BC coating strategy in sodium-metal batteries. At the same time, the BC coating itself as low-temperature carbonized biomass carbon may contribute a small amount of additional capacity during the cycling process. The areal density of the BC coating is approximately $0.9 \text{ mg}\cdot\text{cm}^{-2}$. Based on the typical specific capacity of low-temperature biomass hard carbon in the slope region ($200\text{--}300 \text{ mAh}\cdot\text{g}^{-1}$), the maximum possible areal capacity contributed by the BC coating is $0.18\text{--}0.27 \text{ mAh}\cdot\text{cm}^{-2}$. In contrast, the $450 \mu\text{m}$ thick sodium metal anode used in this study has an areal capacity exceeding $50 \text{ mAh}\cdot\text{cm}^{-2}$. Therefore, the BC coating accounts for less than 0.5% of the capacity relative to the sodium metal anode, and its contribution to the total battery capacity is negligible. Furthermore, the primary function of the BC coating is to serve as an interface modification layer-homogenizing Na^+ flux, providing sodium-affinity nucleation sites, and suppressing dendrite growth—rather than acting as a second active electrode.

SEM characterization of the sodium anode at different

deposition capacities (Figs. 3(f)–3(h)) provides a clear insight into its deposition mechanism. For sodium deposits obtained using a PE-BC separator at a capacity of $1 \text{ mAh}\cdot\text{cm}^{-2}$, sodium particles nucleate as isolated hemispherical nuclei with smooth surfaces. As the capacity increased to 2 and $3 \text{ mAh}\cdot\text{cm}^{-2}$, these nuclei evolved into dense, compact films composed of spherically shaped grains of uniform size, with no dendritic features or needle-like protrusions observed. This spherical, non-dendritic morphology minimizes the electrolyte-accessible surface area, thereby suppressing parasitic side reactions and promoting highly reversible sodium deposition and stripping. These results demonstrate that the bamboo-derived carbon layer is rich in oxygen-containing functional groups, which render the separator surface highly sodiophilic. These polar nucleation sites homogenize the Na^+ flux across the interface and lower the nucleation overpotential, thereby promoting uniform nucleation and lateral growth rather than vertical dendritic propagation. Furthermore, the carbon coating mechanically shields the concentration gradients on the anode surface, further contributing to a uniform ion distribution. The morphological evolution presented in the SEM images provides compelling visual evidence that the BC coating functions as an effective interfacial regulator, capable of guiding dendrite-free sodium deposition and thereby enabling long-term stable operation of the sodium metal anode.

To quantitatively reveal the influence of deposition capacity on sodium morphology, a statistical analysis of sodium particle size was performed based on the SEM images (over 25 particles randomly selected for each condition) (Fig. S4 in the ESM). At a low capacity of $1 \text{ mAh}\cdot\text{cm}^{-2}$, the sodium deposits appear as uniformly distributed spherical particles with an average diameter of approximately $0.09 \mu\text{m}$ and a narrow size distribution, indicating uniform initial nucleation induced by the BC coating. When the capacity increases to $2 \text{ mAh}\cdot\text{cm}^{-2}$, the sodium spheres grow uniformly to an average diameter of $0.18 \mu\text{m}$ while retaining their intact spherical morphology. Upon further increasing the capacity to $3 \text{ mAh}\cdot\text{cm}^{-2}$, severe volume expansion induces concentrated internal stress, leading to structural fragmentation and pulverization of the spheres into porous layered debris with an equivalent size of approximately $0.27 \mu\text{m}$ but lacking regular geometric boundaries. This evolutionary trend from uniform spherical growth at lower capacities to structural collapse at higher capacities demonstrates that the sodiophilic sites on the BC coating effectively guide uniform sodium nucleation and lateral growth under moderate deposition conditions. However, the mechanical stability of the sodium deposit deteriorates sharply at high areal capacities, which likely represents a key failure mechanism limiting long-term cycling stability.

To verify the contribution of oxygen-containing functional groups to high-rate stability at the kinetic level, we conducted variable-scan-rate CV tests over a scan rate range of $0.5\text{--}1.25 \text{ mV}\cdot\text{s}^{-1}$ (Fig. S5 in the ESM). As shown in Fig. S5(a) in the ESM, the CV curves at different scan rates all exhibit symmetrical, rectangular-like profiles within the slope voltage range of $2\text{--}3.6 \text{ V}$, and the redox peak current gradually increases with increasing scan rate. To further quantify the kinetic characteristics of charge storage, we used the power-law relationship $i = av^b$ (where i is the peak current, v is the scan rate, a is a proportionality constant, and b is the kinetic parameter reflecting the charge-storage mechanism) to calculate the b values for the anode oxidation peak (O peak) and the cathode reduction peak (R peak). As shown in Fig. S5(b) in the ESM, the b

value for the O peak is approximately 0.85, close to 1.0, indicating that the desodiation process ($\text{C-O-Na} \rightarrow \text{C=O} + \text{Na}^+ + \text{e}^-$) is primarily governed by surface capacitive behavior and proceeds extremely rapidly. The b value of the R peak is approximately 0.64, falling between 0.5 and 1.0, suggesting that the sodium insertion process ($\text{C=O} + \text{Na}^+ + \text{e}^- \rightarrow \text{C-O-Na}$) is jointly dominated by capacitance and diffusion— Na^+ must first diffuse from the electrolyte to the C=O site for charge transfer to occur, resulting in a certain degree of diffusion limitation. Nevertheless, the b value of the R peak remains significantly higher than the 0.5 typical of purely diffusion-controlled processes, confirming that pseudocapacitance plays a crucial role throughout the entire redox process. The Dunn method ($i(V) = k_1v + k_2v^{1/2}$, where V is the given potential, and k_1 and k_2 are the coefficients associated with the capacitive and diffusion-controlled contributions, respectively) was used to further quantitatively separate the capacitive and diffusion contributions.

As shown in Fig. S5(c) in the ESM, at a scan rate of $1.0 \text{ mV}\cdot\text{s}^{-1}$, the capacitive contribution accounted for approximately 78% of the total capacity. As the scan rate increased from 0.5 to $1.25 \text{ mV}\cdot\text{s}^{-1}$, the proportion of the capacitive contribution rose steadily from 62% to 83%. This trend clearly indicates that, under faster charging and discharging conditions, the surface pseudocapacitive reaction gradually becomes the dominant charge storage mechanism. The above kinetic analysis directly confirms that the abundant C=O/C-O functional groups on the BC coating surface provide a significant pseudocapacitive contribution through rapid, reversible surface redox reactions ($\text{C=O} + \text{Na}^+ + \text{e}^- \leftrightarrow \text{C-O-Na}$), thereby explaining, from a kinetic perspective, the excellent rate performance and long-term cycling stability of the PE-BC separator.

After cycling, a solid electrolyte interphase (SEI) formed on the sodium foil. Its chemical composition and depth distribution were subsequently probed by XPS depth profiling. Figure 4(a) compares the total spectra before and after etching (10 nm etching). The as-received surface exhibited strong C 1s, O 1s, and F 1s signals, indicating the presence of a thick SEI layer formed by the decomposition of the electrolyte. After etching, the relative intensity of the C 1s signal decreased significantly, while the intensity of the Na 1s peak increased, suggesting that surface organics had been removed and the underlying sodium metal was exposed. Quantitative analysis (Fig. 4(b)) shows that the atomic percentage of carbon decreased from 26.32% to 23.84% after etching, while the atomic percentage of sodium increased from 29.84% to 33.90%. Notably, the fluorine content remained at a relatively high level ($15.36\% \rightarrow 13.62\%$), indicating the continued presence of sodium fluoride (NaF) species within the internal SEI. The oxygen content remained relatively stable ($\sim 27\%$), suggesting that inorganic oxides or carbonates were still present even after etching. Trace amounts of nitrogen ($\sim 0.56\%$) and sulfur ($\sim 1.0\%$) were also detected, likely originating from residual electrolyte additives or decomposition products.

The high-resolution XPS spectra were deconvoluted to determine the chemical states of key elements. The C 1s spectrum of the as-received surface (Fig. 4(c)) can be fitted to five components: C-C/C-H (284.8 eV), C-O (286.3 eV), C=O (288.0 eV), CO_3^{2-} (289.5 eV), and $-\text{CF}_2-$ (292 eV). After etching, the C-O intensity decreased, the C=O bond intensity increased slightly, and the residual carbonate peak remained, indicating that inorganic carbonate species are embedded within the SEI (Fig. 4(d)). The O

1s spectrum of the as-received surface (Fig. 4(e)) shows a main peak at 532.0 eV (from C-O/C=O in organic matter) and a shoulder at 531.5 eV (Na-O/Na-CO_3). After etching, the peak at 531.5 eV became dominant, confirming the enrichment of Na_2O and/or Na_2CO_3 within the SEI.

The F 1s spectra (Fig. 4(f)) are dominated primarily by a single peak at 688.5 eV (C-F). The persistence of the Na-F signal after etching indicates that NaF is a robust, insoluble component that remains tightly bound to the Na metal. The Na 1s spectra (Fig. 4(g)) shift slightly from 1071.5 eV (unetched) to 1071.2 eV (after etching), corresponding to the transition from sodium compounds (NaF and Na_2CO_3) to metallic Na. Collectively, these deep-section XPS results reveal a two-layer SEI structure: The outer layer is rich in organic compounds (C-O, C=O, and $-\text{CH}_2-$) and can be easily removed by etching; the inner layer is primarily inorganic, consisting of NaF, Na_2O , and Na_2CO_3 . It is known that a stable, NaF-rich inner layer promotes the uniform distribution of Na^+ flux and suppresses dendrite growth (Fig. 4(h)), which explains the excellent cycling stability exhibited by the modified sodium anodes in this study.

To further characterize the chemical composition of BC, energy-dispersive X-ray spectroscopy (EDS) analysis was performed (Fig. S6 in the ESM). The EDS mapping image (Fig. S6(a) in the ESM) confirms that BC powder is primarily composed of carbon and oxygen, with an oxygen content of approximately 11.57 wt.%, consistent with the XPS O 1s result (8.61 at.%). The carbon elemental map (Fig. S6(b) in the ESM) and oxygen elemental map (Fig. S6(c) in the ESM) reveal a homogeneous distribution of oxygen across the carbon matrix without noticeable localized aggregation. This uniform dispersion of oxygen functional groups is essential for providing evenly distributed sodiophilic nucleation sites across the entire separator surface. It is worth noting that EDS probes the bulk composition at the micrometer scale, whereas XPS is sensitive to the top 5–10 nm of the surface. The consistent detection of abundant oxygen by both techniques demonstrates that the oxygen-containing functional groups are present not only on the outermost surface but also throughout the bulk of the BC particles. The selection of 500 °C as the carbonization temperature was carefully considered and reflects a balance between two conflicting factors. Raman spectroscopy analysis indicates that BC carbonized at 500 °C exhibits a high I_D/I_G ratio of 1.05, which is characteristic of a highly defective, eddy-current-like carbon framework. Meanwhile, XPS analysis confirmed the substantial retention of C=O/C-O functional groups (8.61 at.% oxygen). According to previous studies on biomass carbonization, lower temperatures ($< 400^\circ\text{C}$) result in incomplete carbonization and poor structural integrity, while higher temperatures ($> 700^\circ\text{C}$) lead to the extensive removal of oxygen functional groups, which serve as key sodium-binding sites. Therefore, the 500 °C condition falls within the optimal temperature window (450–550 °C), allowing for the maintenance of a stable carbon framework while retaining a high density of surface oxygen functional groups, which is consistent with trends reported for various biomass precursors [47].

To evaluate the performance of the PE-BC separator in a practical battery system, the Na|PE-BC|NFPP full cell was assembled using NFPP as the cathode and sodium metal as the anode. The rate performance test (Fig. 5(a)) demonstrates that the cell can discharge stably at various rates ranging from 0.5 to 10 C. As the rate increases, the discharge capacity gradually decreases from $100.57 \text{ mAh}\cdot\text{g}^{-1}$ at 0.5 C to $81.78 \text{ mAh}\cdot\text{g}^{-1}$ at 10 C. When the rate is switched back to 0.5 C, the capacity recovers to

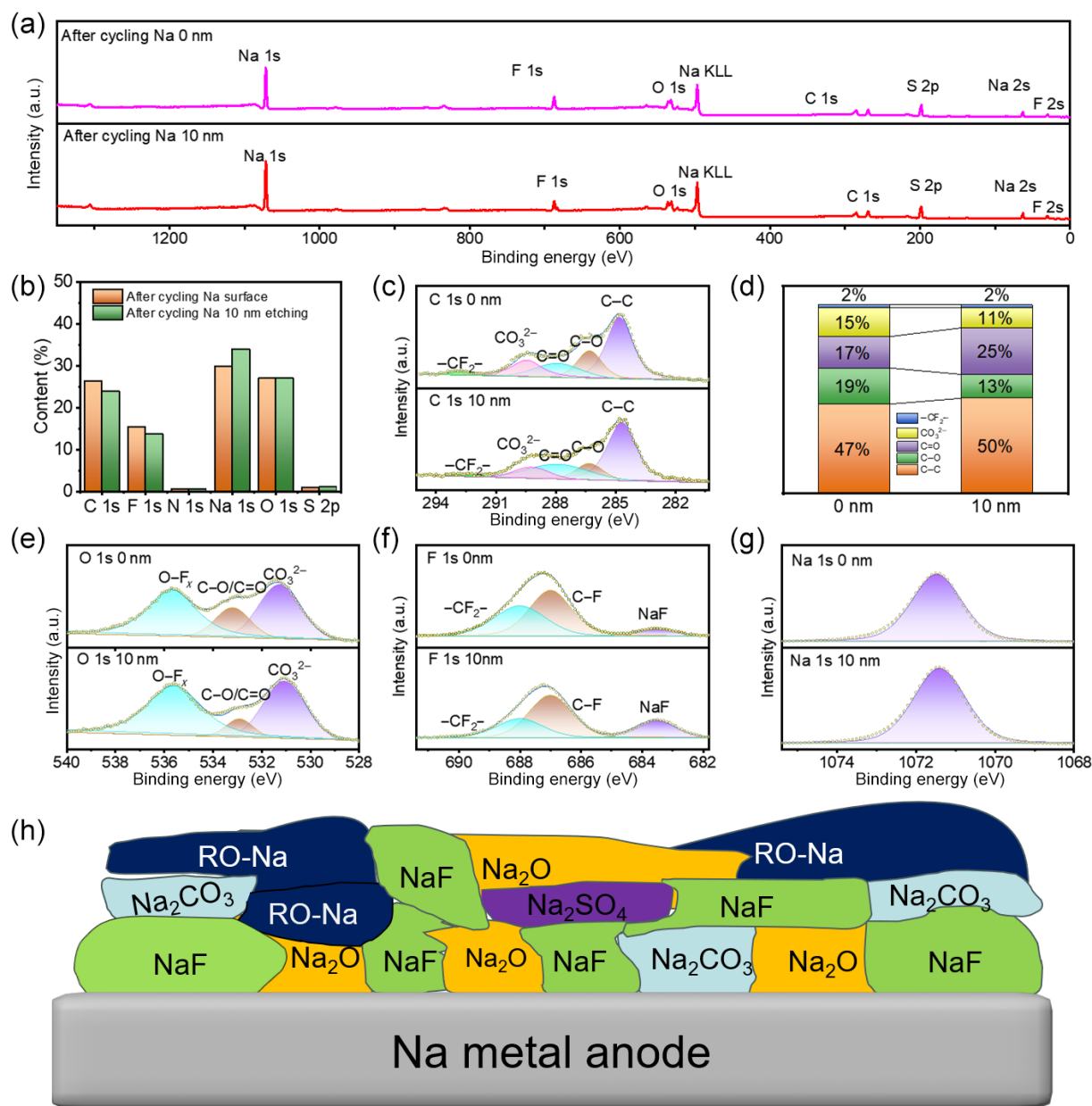


Figure 4 (a) XPS survey spectra of the Na metal SEI in a Na|PE-BC|Na cell at different etch depths. (b) Comparison of component contents before and after etching. (c) C 1s spectra and (d) the corresponding fractions of each component. (e) O 1s spectra. (f) F 1s spectra. (g) Na 1s spectra. (h) Schematic illustration of the SEI composition.

99.98 mAh·g⁻¹, corresponding to a high retention of 99.41%, demonstrating excellent kinetic reversibility. The Na|PE-BC|NFPP full cell demonstrated even better long-term cycling stability (Figs. 5(b)–5(d)). At a 1 C rate, the cell exhibited an initial capacity of 99.20 mAh·g⁻¹ and retained 97.62 mAh·g⁻¹ over 1000 cycle, corresponded to a capacity retention of 98.41%; at a 5 C rate, the cell exhibited an initial capacity of 96.15 mAh·g⁻¹ and retained 90.52 mAh·g⁻¹ over 2000 cycle, corresponded to a capacity retention of 90.94%; at a 10 C rate, the cell exhibited an initial capacity of 90.52 mAh·g⁻¹ and retained 64.22 mAh·g⁻¹ over 6000 cycle, corresponded to a capacity retention of 70.95%. In contrast, the Na|PE|NFPP full cell assembled using a pure PE separator could not operate stably under either 1 or 5 C conditions.

In contrast, the Na|PE|NFPP full cell assembled using a pure PE separator could not operate stably under either 1 or 5 C conditions.

To further evaluate its commercialization potential, a thick electrode with a high active material loading of 7.1 mg·cm⁻² was prepared and assembled into a full cell. This high-loading cell delivers an initial capacity of 92.96 mAh·g⁻¹ at 1 C and cycles stably for over 300 cycles, with the capacity retention remaining at 90% (Fig. 5(e)). The galvanostatic charge–discharge (GCD) curves recorded at different rates for the Na|PE-BC|NFPP full cell are depicted in Figs. 5(f)–5(h). All curves exhibit a distinct reduction plateau in the 2.6–2.8 V range, and this plateau remains highly stable throughout cycling, indicating that the electrode reactions are highly reversible.

To compare the electrochemical performance of PE-BC separators with current state-of-the-art technologies, this paper presents a comprehensive comparison of recently reported modification strategies for sodium-metal battery separators. As

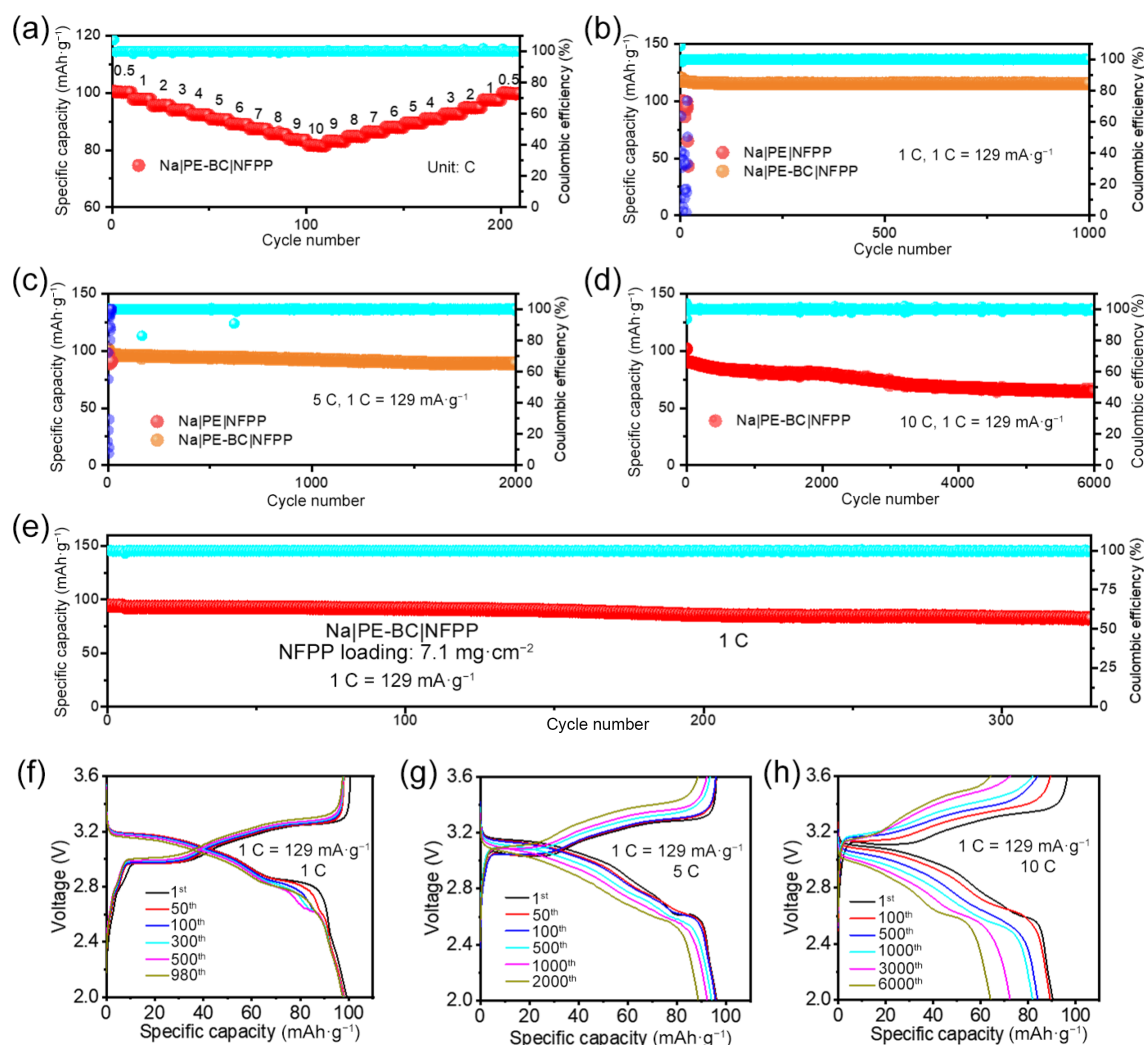


Figure 5 Electrochemical evaluation of Na||NFPP full cells. (a) Rate capability at various C rates. ((b) and (c)) Cycling stability at 1 and 5 C for cells assembled with different separators. (d) Long-term cycling stability of the cell using the PE-BC separator at 10 C. (e) Cycling performance of the PE-BC separator cell at a high NFPP areal loading of $7.1 \text{ mg}\cdot\text{cm}^{-2}$. ((f)–(h)) GCD profiles of the full cells at different C rates.

shown in Fig. S7 in the ESM, the full-cell capacity retention and cycle life of the PE-BC separator are presented side-by-side with corresponding data from representative separators in recent literature (including inorganic ceramic coatings, clay mineral coatings, NASICON-type conductive layers, and other carbon-based coatings). The PE-BC separator (marked with a red asterisk) is located in the upper-right region of the figure, indicating that it possesses both high capacity retention and an exceptionally long cycle life. Specifically, a Na||NFPP full cell using the PE-BC separator achieved a capacity retention of 98.41% after 1000 cycles at a 1 C rate, outperforming most systems reported at comparable rates. Even at a high rate of 10 C, it maintained a capacity retention rate of 70.95% after 6000 cycles—a combination of high-rate performance and long-term durability that has rarely been achieved by previously reported separators. This comprehensive comparison highlights the competitive advantage of the bamboo-derived carbon coating strategy, which integrates sodium-affinity functional groups, a hierarchical porous structure, and a sustainable biomass source into a single separator platform [33, 35, 48–53].

To investigate the origin of this reduction platform/peak, we ruled out the influence of the cathode material. XRD patterns (Fig. 6(a)) of the NFPP cathode after 50 cycles revealed no

significant changes in its phase composition compared to that before cycling. We then performed SEM analysis on the sodium anodes after cycling (Figs. 6(b)–6(d)) and found that the sodium anode surface using the PE separator exhibited numerous cracks and flocculent dendrites, whereas the sodium anode surface using the PE-BC separator was dense (Figs. 6(e)–6(g)), with a large number of BC porous structures embedded with sodium spheres visible; sodium was uniformly deposited within them, and no dendrites were formed. This confirms that the characteristic reduction peak in the GCD curve originates from the reversible reaction between sodium and the microporous carbon on the PE BC separator surface. This process facilitates the development of a stabilized electrode/electrolyte interface, thereby further enhancing the capacity retention rate. These results fully demonstrate that the PE-BC separator can effectively regulate sodium deposition and suppress dendrite formation in high-load batteries under conditions close to practical application, indicating excellent feasibility for practical use.

4 Conclusions

To tackle the dendrite problem in sodium metal batteries, this work takes an innovative approach: converting renewable bamboo

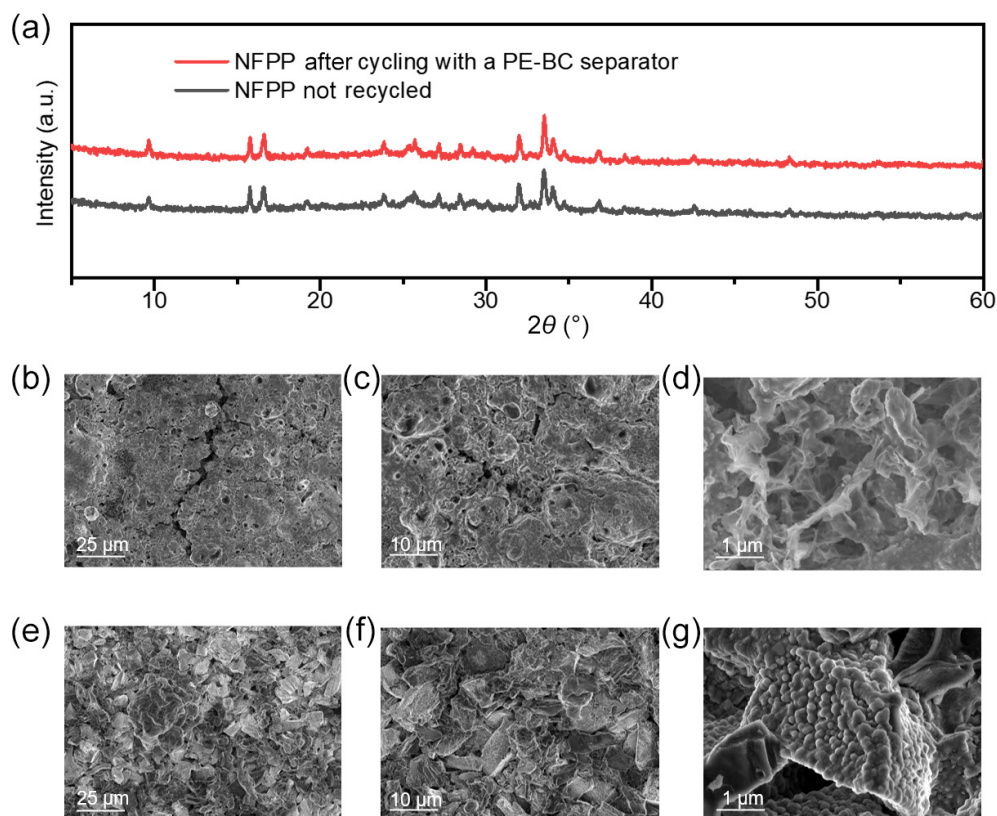


Figure 6 (a) XRD patterns comparing a fresh NFPP electrode and one taken from a full cell after 50 cycles. ((b)–(d)) SEM images of sodium anode surfaces after 50 cycles in a Na|PE|Na full cell. ((e)–(g)) SEM images of sodium anode surfaces after 50 cycles in a Na|PE-BC|Na full cell.

powder into porous BC through carbonization, then coating it onto a commercial PE separator to form an organic–inorganic composite separator (PE-BC). As a result of its excellent electrolyte wettability (contact angle = 0°) and uniform microporous structure, the PE BC separator effectively guides uniform sodium deposition, transforming dendritic growth into dense sodium spheres. Consequently, the Na||Na symmetric cell using the PE BC separator exhibited stable operation for more than 450 h at a current density of $0.5 \text{ mA}\cdot\text{cm}^{-2}$. More impressively, Na|PE-BC|NFPP full cells retain over 98% of their capacity after 1000 cycles at 1 C, and even with a high cathode loading of $7.1 \text{ mg}\cdot\text{cm}^{-2}$ they still deliver more than 300 stable cycles. This work offers a low-cost and high-efficiency separator modification strategy for developing safe, long-lasting, and practical sodium metal batteries.

Electronic Supplementary Material: Supplementary material (XRD patterns, Na||Na symmetric cell cycling, sodium sphere size statistics, EDS elemental mapping, variable scan rate CV, and literature comparison) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909133>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was financially supported by the Basic Research Program

of Jiangsu (No. BK20251880) and the Young Elite Scientists Sponsorship Program of the Jiangsu Association for Science and Technology (No. JSTJ-2025-089). The authors would like to thank Prof. Wenchao Zhao from Nanjing Forestry University for his insightful discussions and valuable suggestions on the experimental design.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

D. C. J. contributed to data curation, validation, writing manuscript, and experimental design. W. W. D. contributed to data curation, project administration, validation, and experimental design. Q. L. Z. contributed to project administration, writing manuscript, and experimental design. Q. Y. G. contributed to data curation, validation, and writing manuscript. Q. N. contributed to project administration and validation. W. J. Z. contributed to data curation and experimental design. C. Y. L. contributed to project administration and writing manuscript. B. W. contributed to data curation and validation. Q. Q. Z. contributed to project administration and funding acquisition. Y. D. W. contributed to writing manuscript and experimental design. X. H. contributed to project administration, funding acquisition, writing manuscript, supervision, and conceptualization. All the authors have approved the final manuscript.

Use of AI statement

None.

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