



Electrochemical Modification of Methane Plasma-Derived Recovered Carbon by Phosphorus Doping as an Anode Material for Sodium-Ion Batteries

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Abstract: High-capacity and sustainable anode materials are critical for the commercial advancement of sodium-ion batteries (SIBs). In this study, red phosphorus was integrated into a carbon framework using high-energy ball milling to create a phosphorus-doped recovered carbon (PRC) composite. Structural characterization through HRTEM and XRD confirms that phosphorus incorporation induces a significant lattice expansion ($d_{002} = 0.358$ nm), providing widened pathways for sodium-ion (Na^+) transport. Electrochemical evaluations reveal that the PRC anode has an outstanding reversible capacity of 250 mAh/g at 0.1 A/g and sustains around 100 mAh/g at a high current density of 5.0 A/g, significantly outperforming the pristine recovered carbon (55 mAh/g). Kinetic analysis using the Randles-Sevcik equation indicates an order-of-magnitude boost in the diffusion coefficient $3.5 \times 10^{-13} \text{ cm}^2/\text{s}$ compared to the undoped precursor. Furthermore, b -value analysis demonstrates that the superior rate capability is driven by dominant pseudocapacitive charge storage and enhanced structural stability over 200 cycles. These findings underscore the potential of heteroatom-doped recovered carbon as a robust, low-cost platform for high-power density SIBs.

Keywords: Na-ion batteries; anode; phosphorus doping; plasma; recovered carbon

1. Introduction

The expanding global market for renewable energy storage technologies has accelerated the search for low-cost alternatives to lithium-ion batteries. Among the emerging candidates, sodium-ion batteries (SIBs) have attracted significant interest due to the high natural abundance and cost-effectiveness of sodium resources [1,2]. However, the commercial realization of SIBs is fundamentally hindered by the sluggish kinetics and significant volumetric expansion of traditional anode materials during Na^+ intercalation. Hard carbons, while stable, often suffer from limited theoretical capacity and restricted interlayer spacing, which can impede the diffusion of the relatively large sodium ions ($1.02 \text{ \AA}$) [3–6]. Hard carbons (HC) have been recognized as the most attractive anode candidates because of their turbostratic disorder and increased interlayer spacing. Unlike graphite, the “non-graphitizable” nature of HC creates a “house-of-cards” architecture that provides robust mechanical support and internal nanovoids for sodium storage [7–9]. However, pristine hard carbons often suffer from limited theoretical capacity and low electronic conductivity. To overcome these barriers, heteroatom doping, specifically with phosphorus (P) has proven to be a transformative strategy [10,11]. Phosphorus was selected as the dopant because its larger atomic radius relative to carbon can perturb the local carbon framework and modify the interlayer spacing, potentially facilitating Na^+ transport and storage. In addition, phosphorus-containing surface and lattice environments can modify the electronic and defect structure of carbon. Although P-doped hard carbons have been widely investigated, the present work focuses on phosphorus modification of methane plasma-derived recovered carbon using a high-energy ball-milling approach, thereby combining carbon recovery from methane with post-synthetic structural modification [12,13]. In alignment with the goals of a circular economy, the utilization of biomass-derived precursors offers a sustainable and carbon-neutral pathway for HC production. By integrating recycling protocols with precursor modification, it is possible to engineer high-performance anodes that bridge the



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gap between environmental sustainability and electrochemical excellence [14–17]. By integrating recycling protocols with precursor modification, it is possible to engineer high-performance anodes that bridge the gap between environmental sustainability and electrochemical excellence.

Despite these advantages, the sodium-storage behavior of hard carbon remains strongly dependent on its local structural disorder, interlayer spacing, pore architecture, and surface chemistry. Consequently, recent studies have focused on controlling these structural characteristics through heteroatom doping and related carbon-engineering strategies. For instance, Stevens et al. proposed “house of cards” model to describe sodium storage in hard carbons, emphasizing the role of randomly oriented graphene layers and nanopores. Their study revealed that the presence of nanopores is critical for achieving reversible capacities above 300 mAh g⁻¹ [18]. Building on this concept, Samanta et al. investigated nitrogen and sulfur co-doping hard carbons developed at 1200–1600 °C, achieving resulting in an interlayer spacing to 0.41 nm. The optimized sample reported a reversible capacity of ~268 mAh g⁻¹ at 0.25 mA g⁻¹, with improved c-rate due to enhanced electronic conductivity. The initial coulombic efficiency (ICE) was 77.4%, attributed to excessive defect sites and high surface area leading to irreversible Na⁺ consumption. Their results highlighted the trade-off between increased active sites and irreversible capacity loss in heteroatom-doped systems. This underscored the need for controlled doping strategies to balance capacity and efficiency [19]. More recently, Ramireddy et al. demonstrated that high-energy ball milling enables uniform phosphorus incorporation into carbon matrices, avoiding phase segregation commonly observed in vapor-phase methods. Their optimized P-doped carbon exhibited a reversible capacity, attractive stable cyclic performances at the level of 350–400 mAh g⁻¹ with an ICE of 89.9%. These findings demonstrate the effectiveness of ball milling as a scalable approach for heteroatom doping [20]. Liang et al. phosphorus-doped porous hard carbon (HC@PC-P) was synthesized by integrating natural soy lecithin with hard carbon derived from the carbonization of olive kernel biomass. The addition of phosphorus and pore-regulating agents resulted in the formation of numerous mesoporous structures and efficient heteroatom incorporation, which significantly optimized the carbon architecture. The HC@PC-P electrode demonstrated a high reversible capacity of 350 mAh g⁻¹ at 0.1 A g⁻¹ with an ICE of 89.6%, outperforming most reported biomass-derived hard carbons. Furthermore, the optimized HC@PC-P exhibited excellent long-term cycling stability, maintaining 93.9% retained capacity after 1000 cycles at 1 A g⁻¹, indicating enhanced structural robustness and stable electrochemical behavior. This increased performance is due to the synergistic effect of the mesoporous structure and phosphorus doping, that facilitates rapid Na⁺ transport, provides abundant active sites, and enhances reaction kinetics [21]. Liu et al. demonstrated a direct recycling method for hard carbon (HC) from manufacturing waste and end-of-life sodium-ion batteries by combining an ice-stripping process with a minimal-temperature treatment at 300 °C. It was discovered that higher temperatures (above 400 °C) caused structural degradation of graphene layers, resulting in poor electrochemical results. In contrast, HC treated at 300 °C retained its structural integrity and delivered reversible capacity of 243 and 228 mAh g⁻¹ for scrap and EOL samples. That corresponding full cells demonstrated stable cycling, with 86–89% retained capacity after 200 cycles. This study demonstrated that mild recycling conditions are crucial for preserving the sodium storage efficiency of hard carbon [22].

Here, we report the synthesis of a phosphorus-doped recovered carbon (PRC) composite via a high-energy ball-milling process. By leveraging the mechanical attrition of milling, red phosphorus was successfully hybridized into the fine powder of the RC precursor. Comprehensive structural analysis via HRTEM and XRD reveals that P-doping facilitates a strategic expansion of the d₀₀₂ spacing, correlating to an order-of-magnitude increase in the sodium-ion diffusion coefficient. Through a combination of cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) evaluations, we demonstrate that the PRC anode exhibits exceptional rate capability and long-term stability, outperforming pristine RC and many recently reported P-doped carbon hybrids.

2. Experimental

2.1. Sample Preparation

The methane plasma process operates by introducing methane into a high-power plasma torch, where an electric arc generates a high-temperature plasma zone. Within this zone, methane molecules dissociate into carbon radicals that nucleate and aggregate to form carbon black particles, with hydrogen generated as the primary gaseous byproduct [23]. The resulting material is referred to as recovered carbon (RC). To synthesize phosphorus-doped recovered carbon (PRC), the RC was blended with red phosphorus in a 97:3 weight ratio. This mixture was subjected to high-energy planetary ball milling at 400 rpm for 5 h, utilizing a 10-min cooling interval every hour and alternating rotation directions to ensure a homogeneous, chemically hybridized phosphorus-carbon composite.

2.2. Electrode Preparation

The working electrodes were fabricated by casting a multi-component slurry onto a high-purity copper foil current collector. The slurry composition consisted of 70 wt.% active material, 20 wt.% conductive additive (Super-P), and 10 wt.% binder (comprising 6 wt.% CMC and 4 wt.% SBR). To prepare the slurry with a target total solid content of 35 wt.%, the required volume of deionized water (DI water) solvent was calculated accordingly. First, CMC was dissolved in the DI water under stirring for 30 min. Next, Super-P and the active material were added sequentially in batches over approximately 2 h. Finally, SBR was introduced and stirred for 15 min, followed by 10 min of ultrasonic degassing. The resulting homogeneous slurry was uniformly cast onto the copper foil using a 100 μm doctor blade coater. The coated electrodes were dried at 80 °C and subsequently calendered to 70% of their initial thickness to enhance electrode density. Finally, the electrodes were punched into 14 mm diameter discs and vacuum-dried before being transferred to an argon-filled glove box for half-cell assembly.

2.3. Characterization

The phase purity and crystalline architecture of the hard carbon specimens, synthesized across various temperature gradients, were analyzed using X-ray diffraction (XRD, Bruker D2 PHASER, Karlsruhe, Germany) with Cu K α radiation $\lambda = 1.5418 \text{ \AA}$). Complementary structural defect analysis and carbon hybridization states were evaluated via Raman spectroscopy (Horiba iHR550), employing a 532 nm excitation source. The morphological evolution and internal microstructure of the samples were visualized through scanning electron microscopy (SEM; JEOL JSM 7600F) and high-resolution transmission electron microscopy (HR-TEM; JEOL JEM2100). To quantify the surface chemistry and elemental valence configurations, X-ray photoelectron spectroscopy (XPS) was conducted using a JEOL Photoelectron Spectrometer (ESCA, KA1069-10-12-04-03). Furthermore, the textural properties, including specific surface area (SSA) and localized pore size distributions, were determined through N₂ adsorption-desorption isotherms based on Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) computational models.

2.4. Electrochemical Measurements

In this experiment, a series of electrical tests were conducted using CR-2032 coin cell batteries, and the battery components used were manufactured by Ubico. The coin cells were assembled inside an argon-filled glove box, where the oxygen and moisture levels were maintained below 0.5 ppm. The assembly process first places the battery cover facing up, then puts the negative electrode piece, separator film, sodium metal sheet, and spring sheet in order, and the electrolyte part is 1 M NaClO₄ dissolved in PC, and 5% FEC added, and finally puts the battery into the pressing machine to complete the battery assembly.

3. Results and Discussion

Figure 1a presents the XRD patterns of recovered carbon (RC) and phosphorus-doped recovered carbon (PRC), revealing the characteristic broad (002) and (100) diffraction reflections associated with the disordered structure of hard carbon. The (002) reflections of both RC and PRC are located at approximately 25.6° (2 θ), indicating that no pronounced peak shift can be resolved after phosphorus modification. Using Bragg's law, $n\lambda = 2d\sin\theta$, with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), the corresponding XRD-derived d₀₀₂ value is approximately 0.348 nm for both RC and PRC. In comparison, HRTEM measurements give local interlayer spacings of 0.352 nm for RC and 0.358 nm for PRC. The small differences between the XRD- and HRTEM-derived values are reasonable because XRD provides an ensemble-averaged structural parameter, whereas HRTEM measures local lattice spacings. The larger local d-spacing observed for PRC by HRTEM suggests that phosphorus modification may induce localized structural expansion; however, this change is not sufficiently pronounced to produce a clearly resolvable shift in the broad XRD (002) reflection [24].

The structural properties of the PRC samples were examined using Raman spectroscopy with the resulting spectra displayed in Figure 1b. To gain a deeper understanding of the disordered structure, the primary peaks were the graphite G band of carbon and the disordered structure D band. D1, D3, and D4 represent the D band. The D1 band (about 1350 cm⁻¹) was produced by carbon atoms vibrating at the edge of the graphite sheet and by graphite crystal defect, and the D3 band (about 1500 cm⁻¹) came from carbon atoms vibrating and graphite crystal defect and the edge of the graphite sheet. The D4 band was related to the aliphatic component of the carbon macromolecule bound to the aromatic ring [25,26] and the area was calculated according to the integral theorem, and the integral area of D1 was the numerator and the denominator was G, and the integral ratios of PRC and RC were 1.21 and 1.16, respectively. The D/G-related integral area ratio increased from 1.16 for RC to 1.21 for PRC,

indicating a modest increase in defect- or edge-associated carbon environments after phosphorus modification. Such sites may provide additional locations for surface-associated Na^+ storage. However, the Raman ratio alone does not directly quantify electronic conductivity. The improved electrochemical kinetics are more directly supported by the EIS results, where the charge-transfer resistance decreased from 27.27 Ω for RC to 12.9 Ω for PRC. The combined structural and electrochemical results therefore suggest that phosphorus modification alters the defect structure and facilitates charge-transfer kinetics.

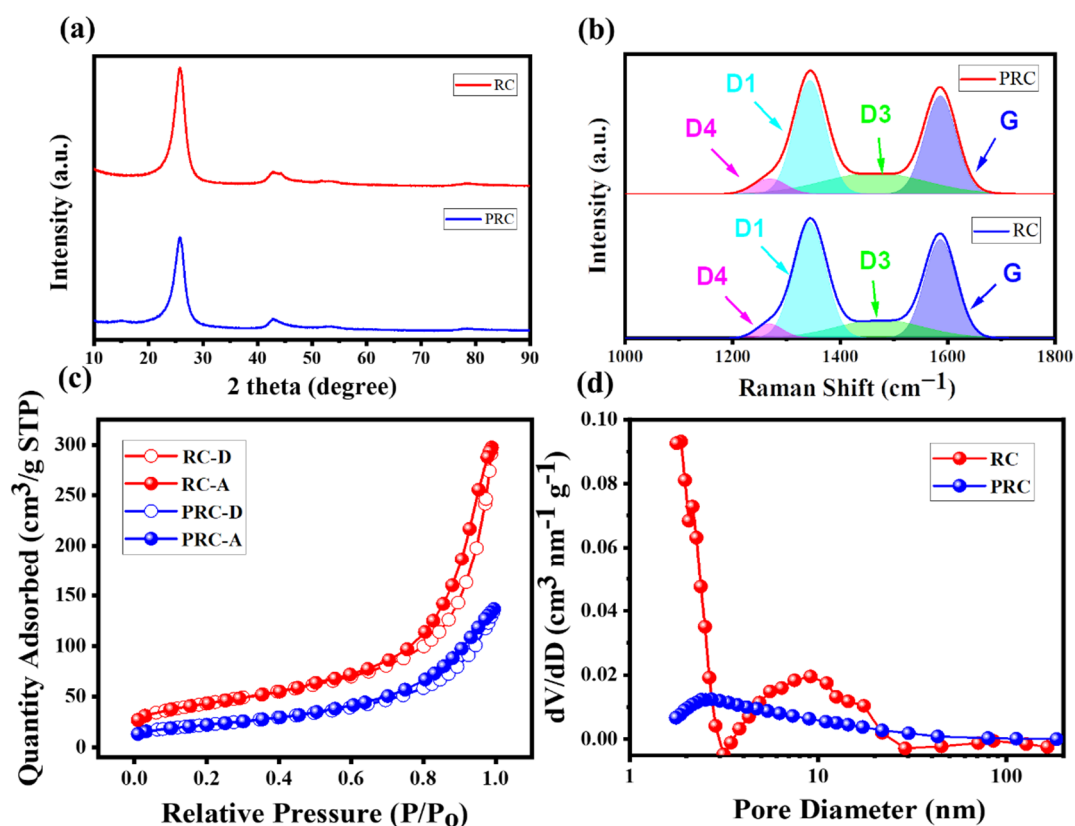


Figure 1. (a) XRD patterns of RC and PRC, (b) Raman spectra of RC and PRC, (c) N_2 adsorption-desorption isotherms of RC and PRC, (d) pore size distribution of RC and PRC.

The specific surface area (SSA) and pore structure properties of RC and PRC were evaluated using nitrogen adsorption/desorption isotherms. As shown in Figure 1c, both samples exhibited characteristics of micropores (Type I) and mesopores (Type IV). Based on the Brunauer-Emmett-Teller (BET) equation, the total SSA of RC was 153 m^2/g , which significantly decreased to 80 m^2/g for PRC. Additionally, non-local density functional theory (NLDFT) calculations were utilized to determine the pore size distributions of the samples. The NLDFT model is based on slit geometry. Figure 1d shows that most of the pores of RC samples are between 1–25 nm, especially in the range of 8–10 nm, so the pores of PRC are distributed between 0.5~1 nm. In addition, the total pore volume decreased from 0.45 cm^3/g in RC to 0.209 cm^3/g in PRC, a change attributed to the inability of N_2 molecules to enter the micropores blocked by phosphorus-containing functional groups [27,28].

X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental composition and surface chemical states of the phosphorus/carbon (P/C) composite. The survey spectrum in Figure 2a confirmed the presence of C 1s, O 1s, P 2s, and P 2p signals. The P 2p spectrum in Figure 2b exhibited two major components centered at 133.1 and 134.2 eV, which are assigned to P–C-containing and oxidized P–O-containing environments, respectively. The lower-binding-energy component is consistent with P–C-containing environments, indicating chemical interaction between phosphorus and the carbon framework, whereas the higher-binding-energy component is associated with oxidized phosphorus species at or near the carbon surface. Because phosphorus-containing surfaces are susceptible to oxidation upon exposure to air, the P–O component may partly originate from surface oxidation during post-synthesis handling and XPS measurement. Therefore, the presence of P–O species does not necessarily indicate that these groups were formed during the ball-milling process. Accordingly, the XPS results provide evidence of phosphorus-containing chemical environments and chemical interaction between phosphorus and the carbon matrix, but the relative contributions of direct P–C bonding and surface P–O-containing species should be interpreted cautiously. The XPS results are therefore considered together with the

XRD, HRTEM, and elemental-mapping results rather than being used alone to establish the complete phosphorus incorporation mechanism. Additionally, the O 1s spectrum in Figure 2c revealed O–P/O–O (531.5 eV) and O–C (532.8 eV) environments, while the high-resolution C 1s spectrum in Figure 2d was deconvoluted into four components, including the dominant C–C component at 284.8 eV, a P–C-related component at 284.3 eV, and C–O and C=O components at 286.2 and 288.5 eV, respectively. These oxygen-containing species are consistent with surface oxygen functionalities [29,30].

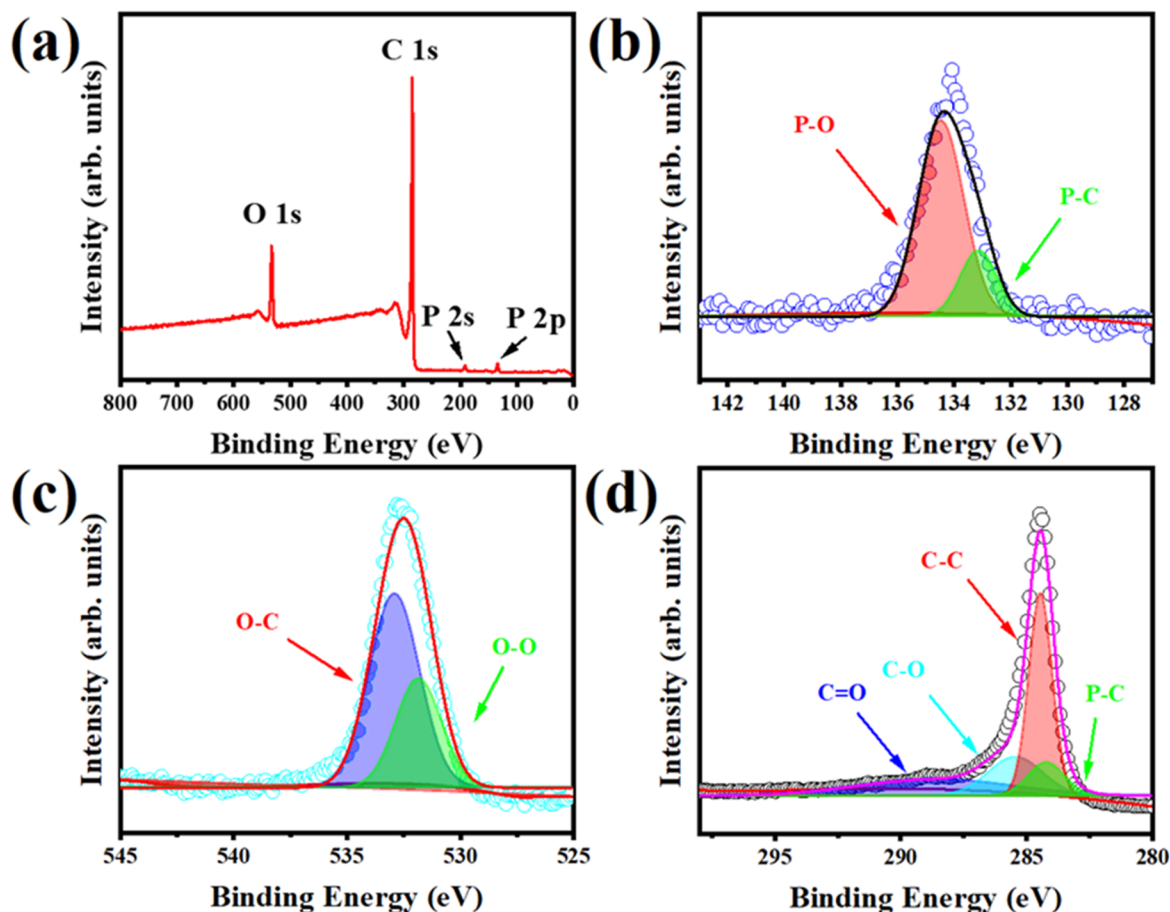


Figure 2. (a) XPS spectra of PRC, (b) P 2p, (c) O 1s, (d) C 1s.

The morphological evolution and surface topographies of the pristine RC and the synthesized PRC composite were characterized via scanning electron microscopy (SEM). As illustrated in Figure 3a, the raw RC precursor exhibited a well-defined architecture consisting of an interwoven network. This structure possessed inherent macroporosity, evidenced by numerous voids and channels that were conducive to accommodating the volumetric expansion of phosphorus during electrochemical cycling. In contrast, the PRC composite in Figure 3b underwent a distinct structural transformation following high-energy ball milling. The initial fibrous morphology was replaced by a compact, granular state with a significantly reduced particle size. This mechanical attrition refines the surface topography, yielding irregularly shaped particles that shorten ion diffusion pathways and potentially enhance rate capability. Because the PRC sample was prepared by high-energy ball milling whereas the pristine RC control was not subjected to the same milling treatment, the individual contributions of mechanical size reduction and phosphorus incorporation cannot be completely separated from the present dataset. Therefore, the observed structural, morphological, and electrochemical changes are discussed as the combined effects of phosphorus modification and mechanical treatment. Figures 3c–e are used to validate chemical homogeneity and elemental mapping. The results showed that carbon (C), phosphorus (P), and oxygen (O) signals were spatially co-localized with high intensity. This uniform overlap confirms that red phosphorus was homogeneously dispersed within the carbon framework rather than existing as isolated agglomerates, signifying the successful synthesis of a robust, chemically uniform phosphorus-carbon hybrid.

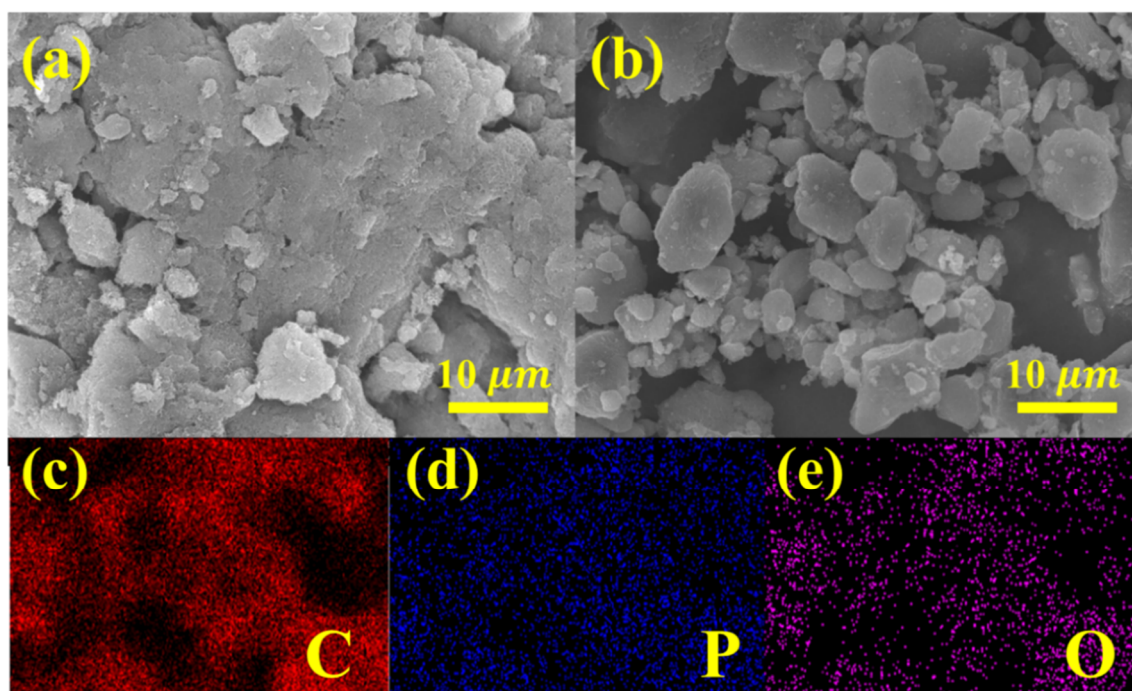


Figure 3. SEM images of (a) RC, (b)PRC, (c–e) PRC EDS mapping.

The internal microstructure and crystalline characteristics of the nanocarbon fibers were further investigated using High-Resolution Transmission Electron Microscopy (HRTEM). The image of the pristine RC shown in Figure 4a revealed a well-defined morphology with a high aspect ratio. Corresponding HRTEM analysis, shown in Figure 4b, exhibited ordered lattice fringes with an interlayer spacing (d_{002}) of 0.352 nm, characteristic of graphitic-like carbon layers. Upon phosphorus incorporation, the PRC composite displayed in Figure 4c maintained its fundamental framework, suggesting that the doping process preserves the structural integrity of the carbon matrix. However, HRTEM analysis of the PRC (Figure 4d) revealed an expanded lattice spacing of 0.358 nm. This expansion was attributed to the incorporation of phosphorus atoms into the carbon lattice, which induced structural distortion and increased the distance between graphene-like layers. This observation aligned with the lower-angle shift observed in XRD patterns, further confirming the successful lattice engineering of the fibers [31]. Moreover, EDS mapping in Figure 4e showed overlapping signals of C, O, and P, confirming that phosphorus species were uniformly distributed without localized clustering or phase separation. This homogeneous dispersion, coupled with the enlarged interlayer spacing, was expected to facilitate rapid ion diffusion and mitigate volume change during electrochemical cycles. Structural characterization confirms that the ball-milling process facilitates the covalent integration of phosphorus atoms into the carbon matrix, rather than simple physical encapsulation. X-ray photoelectron spectroscopy (XPS) identified a distinct P-C bond signal at 133.1 eV, providing evidence of chemical hybridization. Because phosphorus atoms possess a larger covalent radius than carbon, they function as “structural pillars” within the lattice. This was quantitatively confirmed by XRD and HRTEM analysis, which showed a shift to lower diffraction angles and an expansion of the graphitic interlayer spacing (d_{002}) from 0.352 nm to 0.358 nm. This lattice dilation was critical for battery performance as it reduced the energy barrier for sodium-ion (Na^+) intercalation, providing widened “highways” for rapid ion transport.

To study the chemical reaction of RC and PRC as anode materials, cyclic voltammetry (CV) was used for the first three cycles and at different scan rates. First, the first three cycles of the test were performed at a sweep rate of 0.1 mV/s over a voltage range of 0.01 to 3 V (V vs. Na/Na^+), and as can be seen from Figure 5a,d, a wide peak occurred around 0.75–1.5 V during the initial reduction, which was linked to the electrolyte’s decomposition and development of the SEI film on the electrode surface. In addition, near the 0.1 V spike and 0.1–1.5 V The less obvious wide peaks in the V voltage range correspond to the platform area and the slope region in the charge-discharge curve. When the anode material undergoes significant polarization, the potential difference ($\Delta E = E_{\text{pc}} - E_{\text{pa}}$) between the oxidation and reduction peaks increases significantly, as electron and ion transport speeds are slower, requiring greater potential differences to facilitate the reaction process [32]. As shown in Figure 5b,e at different scan rates, PRC showed superior overlap, indicating superior cyclic stability, consistent with the results of impedance

analysis. In addition, Figure 5c,f showed the diffusion coefficients of RC and PRC calculated according to the Randles-Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (1)$$

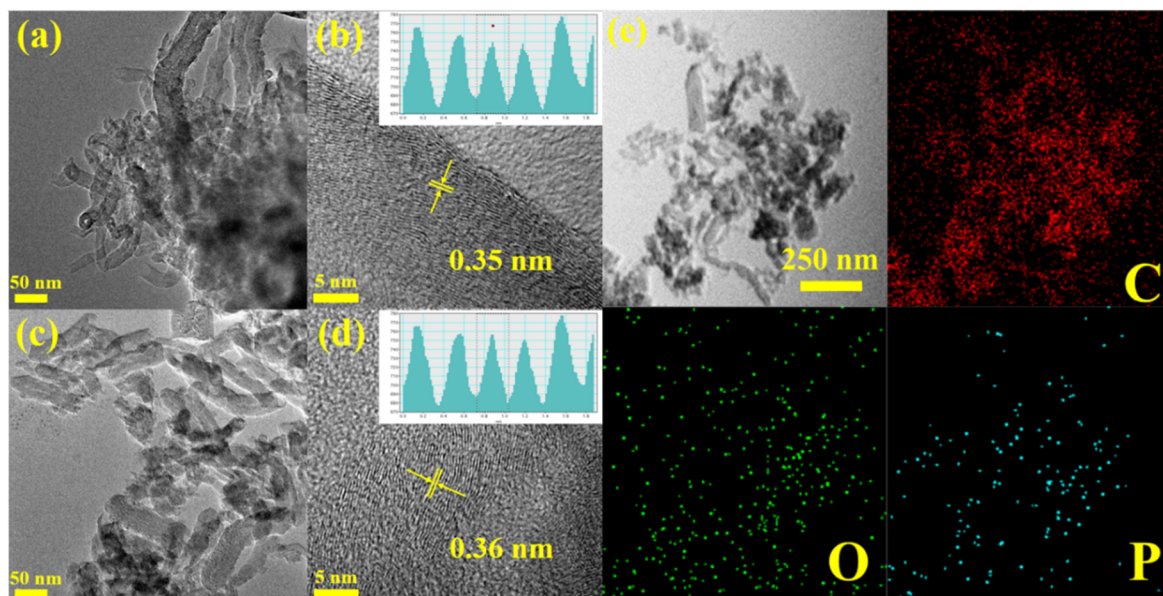


Figure 4. HR-TEM images of (a,b) RC and (c,d) PRC; (e) EDS elemental distribution analysis diagram of PRC.

Among them, I_p stands for current, n for pole piece area, D for sodium ion diffusion coefficient, C for the molar concentration of Na^+ in the negative electrode, and v for scan rate. The diffusion coefficients (D_{Na^+}) of RC and PRC were calculated according to Figure 5b,e, which were $8.8 \times 10^{-10} \text{ cm}^2/\text{s}$ and $2.0 \times 10^{-9} \text{ cm}^2/\text{s}$, respectively. The CV- and EIS-derived diffusion parameters both indicate faster apparent Na^+ transport kinetics for PRC than for RC. However, the absolute values obtained from these methods differ substantially because they are based on different experimental conditions and theoretical assumptions. The CV-derived value should therefore be regarded as an apparent kinetic parameter, particularly because the hard-carbon electrode exhibits a substantial surface-controlled contribution, whereas the EIS-derived value reflects the low-frequency Warburg response under the specific measurement conditions. The obtained results demonstrated that PRC exhibited superior electrochemical performance, particularly in terms of long-term cycling stability and sodium-ion diffusion kinetics. These characteristics were of great importance for enhancing the overall performance of sodium-ion batteries. Therefore, PRC represents a highly promising anode material capable of effectively improving the rate capability and cycling lifespan of sodium-ion batteries [33]:

$$i = av^b \quad (2)$$

$$\log i = \log(a) + b \log(v) \quad (3)$$

In addition, the b value can be calculated by using Equations (2) and (3). A b -value approaching 1 is generally associated with predominantly surface-controlled kinetics, whereas a value approaching 0.5 is commonly associated with diffusion-controlled behavior. In the present study, the near-unity b -values suggest a substantial surface-controlled contribution to the electrochemical response. However, the b -value analysis alone does not establish a specific pseudocapacitive storage mechanism. And the b values of RC and PRC were close to 1, as shown in Figure S1 and the b values of RC and PRC were close to 1, which proved that this reaction kinetics was capacitively controlled [34]. It should be noted that the b -value analysis and EIS measurements probe different aspects of electrode kinetics. A near-unity b -value indicates that the CV current has a substantial surface-controlled contribution, whereas the low-frequency EIS response reflects the impedance associated with ion transport and interfacial processes under a small-amplitude perturbation at a specific electrochemical state. Therefore, a near-unity b -value does not necessarily require an ideal capacitive response in the low-frequency EIS region. These two analyses are consequently interpreted as complementary kinetic measurements rather than as direct confirmation of one another.

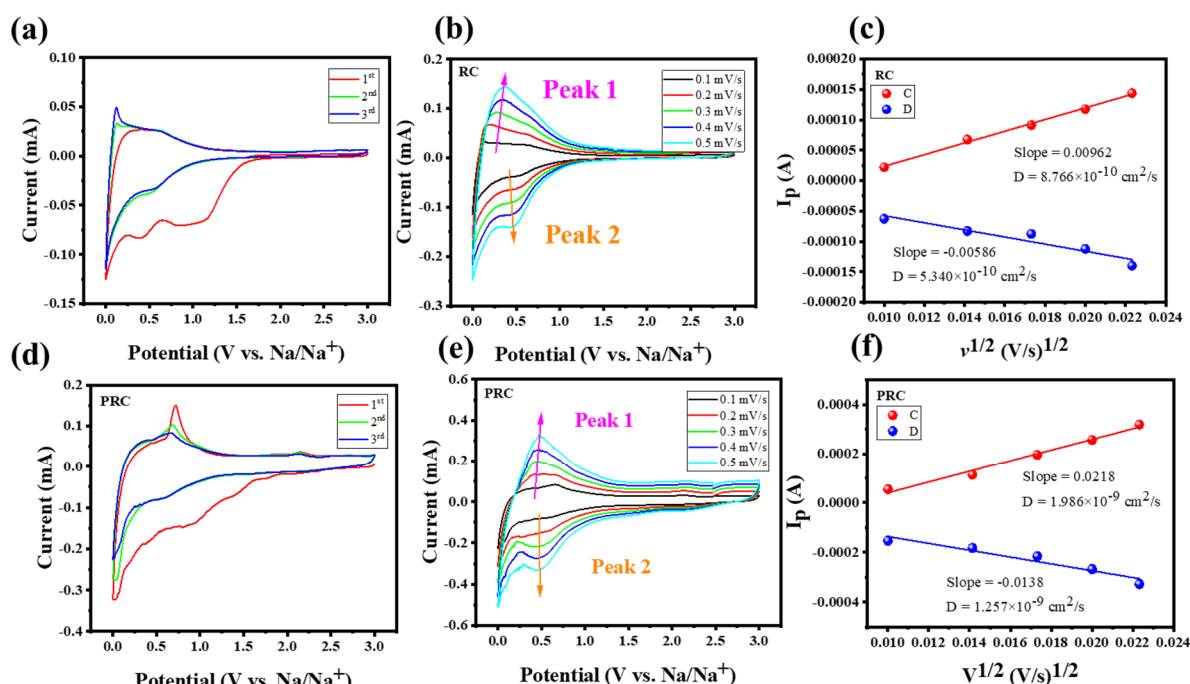


Figure 5. Cyclic voltammograms of (a) RC and (d) PRC for the first three cycles; CV curves at different scan rates for (b) RC and (e) PRC; and corresponding Na^+ diffusion coefficients of (c) RC and (f) PRC.

To further understand the rate performance, the charge-discharge tests were conducted for RC and PRC at different current densities, as shown in Figure 6a, with different current density of 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A/g to perform five cycles of charge-discharge tests, the reversible capacity of RC was 140, 105, 95, 87, 72 and 55 mAh/g, and when the current density was restored to 0.1 A/g, the reversible capacity was 120 mAh/g, while the reversible capacity of PRC was 250, 190, 150, 135, 115 and 100 mAh/g. Conversely, the reversible capacity can be returned to 200 mAh/g when the current density is restored to 0.1 A/g. In addition, the charge-discharge curves at different current densities were compared, as shown in Figure S2, PRC had a smoother curve, higher capacity retention, and less polarization than pristine RC. With a voltage range of 0.01 to 3.0 V, after the first three cycles of charge and discharge activation at 0.1 A/g, and then 200 cycles of long cycle life test at 1.0 A/g, as shown in Figure 6b. After 200 cycles of charge and discharge, the capacity of RC was 52 mAh/g, while the capacity of PRC was 143 mAh/g, and the capacity retention rate was 74.42%, which was much higher than the 58.25% of RC. In Figure 6c, the charge-discharge curves under different cycles can be used to compare the performance of capacity retention. The results indicated that PRC exhibited excellent cyclic stability, and using the charge-discharge curves of different cycles, the slope region and the plateau region of the capacity can be calculated. The slope region represented the adsorption of sodium ions on the surface, and the plateau region was the storage of sodium ions embedded in the crystal lattice of the material. From Figure S3, it can be seen that PRC sodium ions were adsorbed on the surface more than that of RC and sodium ions were embedded in PRC and stored more than that of RC. These results proved that both the adsorption surface and the embedded storage method perform better with PRC. Charge-discharge experiments of RC and PRC for three cycles were performed with a current density of 0.1 A/g to demonstrate the effects of P doping, as illustrated in Figure 6c. The initial coulombic efficiency reflected the irreversible capacity caused by SEI formation and the concurrent consumption of sodium ions. Specifically, the ICEs of RC and PRC were 29.97% and 43.90%, respectively. The charge and discharge curves at the first cycle, the overlap between the second and third cycles, and the PRC's reversible capacity of up to 250 mAh/g are all displayed in Figure S4. The formation of the SEI, which reacted more after the first cycle of activation and slowed down the others, was identified as the reason for the weak peak in the curve between 0.5 and 1.0 V during the discharge. The relatively low ICE values of RC (29.97%) and PRC (43.90%) indicate substantial irreversible Na^+ consumption during the first cycle. This behavior may be associated with electrolyte decomposition and SEI formation on defect-rich carbon surfaces, together with irreversible Na^+ trapping at surface and pore sites. Notably, phosphorus modification substantially reduced the BET surface area from 153 to 80 $\text{m}^2 \text{g}^{-1}$ and the total pore volume from 0.45 to 0.209 $\text{cm}^3 \text{g}^{-1}$. The reduced accessible surface area and pore volume may decrease the extent of electrolyte decomposition and irreversible Na^+ consumption, contributing to the higher ICE of PRC. Nevertheless,

the ICE remains below that desirable for practical full-cell applications. Further improvement could be achieved through optimization of electrolyte/additive chemistry, surface modification, or presodiation strategies [35,36].

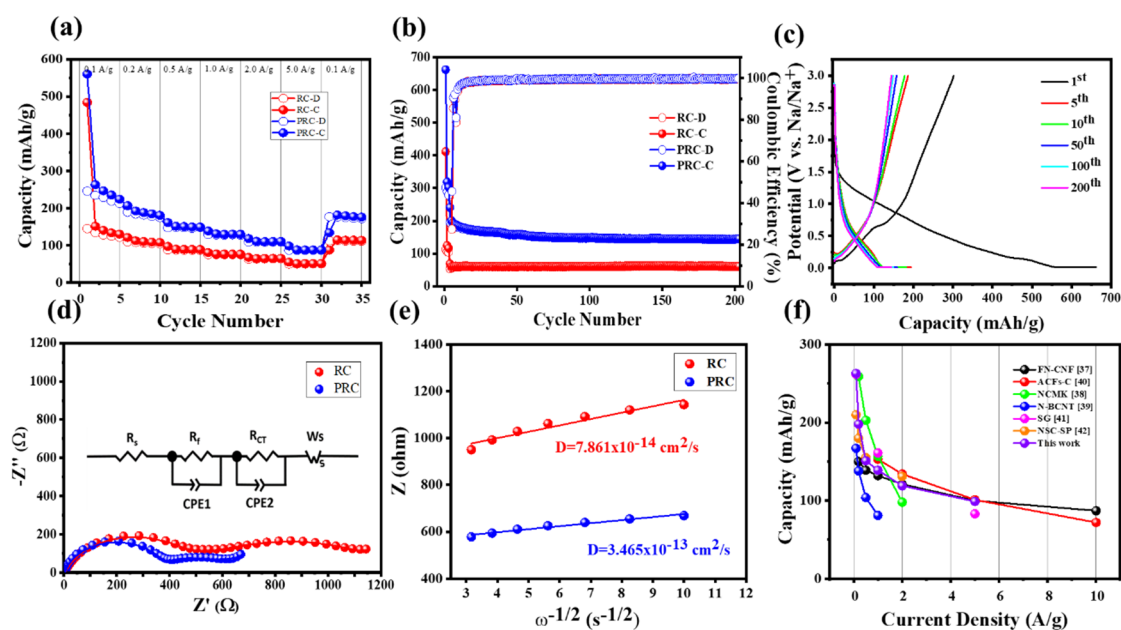


Figure 6. (a) Rate performance of RC and PRC at various current densities, (b) Cycle life tests of RC and PRC for 200 cycle under current density of 1.0 A/g; (c) Charge/discharge curves of PRC at the 1st, 5th, 10th, 50th, 100th, 150th, and 200th cycles (d) Each sample's electrochemical impedance spectrum (equivalent circuit inset) (e) plots of Z' versus $\omega^{-1/2}$ at low-frequency region RC and PRC; (f) Comparison of capacity of different current densities in the reference literature of carbon-doped materials.

The Nyquist plot consists of real and imaginary impedance measured by electrochemical impedance maps, in the high and mid frequency ranges, the semicircular curve is shown in Figure 6d while in the low frequency range it is a slash, and the position on the frequency axis with the y-axis intercept is expressed as ohmic resistance (R_s), which represents resistance caused by the electrodes, electrolytes, and separators of the battery. In the mid-frequency range, the first semicircle represents the impedance (R_{SEI}) of the SEI layer, the second semicircle corresponds to the charge transfer impedance (R_{CT}), and the slash line in the low-frequency range correlates with ion diffusion in the battery.

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma_w^2} \quad (4)$$

Among them, R is the gas constant, T is the temperature, n is the number of electrons per molecule during oxidation, A is the electrode surface area, F is the Faraday constant, C is the sodium ion concentration, σ_w is the Warburg factor, and D is the diffusion coefficient. According to this formula, the smaller the slope in the relationship between impedance and frequency reciprocal square root, the greater the diffusion coefficient. EIS test is performed on each half cell containing the corresponding electrode, and the Nyquist diagram is fitted into the equivalent circuit to obtain the corresponding impedance value, and the specific surface area (SSA) is closely related to the R_{SEI} , so when the SSA is high, the R_{SEI} also tends to increase. After 2.5 cycles, the PRC showed lower impedance than other samples, and the lower SSA contributed to the formation of the SEI layer, while too many macropores could lead to the absorption of too much electrolyte and unwanted side reactions during the electrochemical process. For RC and PRC, the plot of Z' to $\omega^{(-1/2)}$ is calculated from the linear region of the low-frequency region of the Nyquist plot, as shown in Figure 6e, the diffusion coefficients of these samples are 7.9×10^{-14} and 3.5×10^{-13} cm²/s, respectively, as seen in Table S1, the above results indicate that PRC exhibited larger diffusion coefficient, this structural material enhances sodium ion storage by shortening the ion diffusion distance and providing more active sites. Previous works can also be seen that phosphorus-doped carbon materials had a considerable impact on the application of sodium-ion batteries, and the capacity comparison under different current densities can be seen in Figure 6f [37–42]. The improved performance of PRC was primarily attributed to phosphorus doping, which enhances the structural and electrochemical properties of the carbon matrix by increasing active sites, facilitating ion transport, and stabilizing the electrode/electrolyte interface. This accelerated

diffusion, coupled with a reduced charge-transfer resistance (R_{ct}) of only 12.9 Ω , allows the PRC to deliver a high reversible capacity of 250 mAh/g at 0.1 A/g. Furthermore, the PRC demonstrated remarkable structural robustness, maintaining a capacity of 143 mAh/g after 200 cycles at 1.0 A/g, significantly outperforming the undoped recovered carbon. These results indicated that the synergistic effect of lattice expansion and covalent P-C bonding created a stable, high-rate platform for sustainable sodium-ion storage.

4. Conclusions

In summary, this study demonstrated the successful synthesis of a phosphorus-doped recovered carbon (PRC) composite with high-performance sodium-ion batteries. Experimental characterization and electrochemical analysis reveal that the covalent integration of phosphorus atoms expands the graphitic interlayer spacing from 0.352 nm to 0.358 nm, significantly reducing the energy barrier for sodium-ion intercalation. The resulting PRC anode exhibited a superior reversible capacity of 250 mAh/g at 0.1 A/g and remarkable cyclic stability, maintaining 74.42% capacity after 200 cycles at 1.0 A/g. Kinetic studies, including Randles-Sevcik calculations and b -value analysis, confirmed that the enhanced performance originated from a synergistic combination of accelerated ion diffusion 3.5×10^{-13} cm²/s and dominant pseudocapacitive charge storage. By bridging the gap between sustainable precursor recovery and advanced lattice engineering, this work provided a robust strategy for developing low-cost, long-life electrode materials for next-generation large-scale energy storage systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://media.sciltp.com/articles/others/2609281506231370/GEFR-26070059-SI.pdf>, Figure S1: Fitted slope b -value for RC and PRC at different peaks; Figure S2: Charge/discharge curves of RC and PRC at different current densities; Figure S3: Capacity contribution of RC and PRC at different cycles showing slope and plateau region storage; Figure S4: Charge/discharge curves of RC and PRC at the first three cycles under a current density of 0.1 A g⁻¹; Table S1: Equivalent circuit parameters and Na⁺ diffusion coefficient (D_{Na^+}) fitting calculation results from EIS analyses; Table S2: Comparison of phosphorus-containing hard-carbon anodes reported in the literature and PRC.

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