

Wedelia chinensis-derived biomass porous carbon as anode material for high performance sodium/potassium ion batteries

Zengwei Pang

Lanzhou University of Technology

Letong Wang

Lanzhou University of Technology

Shenteng Wan

Lanzhou University of Technology

Miaomiao Liu

Lanzhou University of Technology

Xiaohui Niu

Lanzhou University of Technology

Kunjie Wang

wangkj80@163.com

Lanzhou University of Technology

Hongxia Li

Lanzhou University of Technology

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Abstract

Sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) are potential alternatives of lithium-ion batteries (LIBs) due to their high energy density and low cost. Unfortunately, they are difficult to use for large-scale grid energy storage due to the lack of suitable anode materials for sodium/potassium energy storage. Biomass-derived carbon, which is widely available and environmentally friendly, is one of the most promising anode materials for SIBs/PIBs, but the design and regulation of its microstructure is exceptionally complex. By selecting suitable biomass precursors, it is expected that biomass-derived carbon with suitable microstructures can be simply prepared. In this study, *wedelia chinensis* were selected as biomass precursors, and biomass-derived carbon materials with large interfacial spacing, suitable pores and high specific surface area were prepared by a simple one-step pyrolysis method. The material exhibited fast energy storage kinetics when electrochemically tested as an anode and showed different performance advantages in storing sodium/potassium. When tested as an anode for SIBs, it exhibited excellent specific capacity and cycling stability ($380.7 \text{ mA h g}^{-1}$ after 500 cycles at 100 mA g^{-1}); When tested as an anode for PIB, it exhibited excellent rate performance ($128.6 \text{ mA h g}^{-1}$ at 10 A g^{-1}).

1. Introduction

The development and utilization of green energy and renewable resources has received a great deal of attention in the past few decades due to the energy crisis that has ensued from the overexploitation of fossil fuels [1–3]. The practical application of green energy and renewable energy needs to be realized with energy storage technology [4, 5]. Electrochemical energy storage dominates among many energy storage technologies due to its unique advantages of flexibility and reliability [6, 7]. LIBs have played a huge role in electrochemical energy storage since they were commercialized more than 30 years ago [8, 9]. However, low reserve and uneven distribution of lithium resource further hinder their large-scale stationary energy storage. There is an urgent need to find a new energy storage technology as a replacement. The advantages of SIBs and PIBs over LIBs have inspired researchers due to their lower production cost, abundant resources, and similar physicochemical properties to lithium [10–14]. Unfortunately, the large ionic radius of Na^+/K^+ (Na^+ : $1.02 \text{ \AA}$, K^+ : $1.38 \text{ \AA}$) [15] severely hinder the diffusion kinetics, which negatively affects the cycling performance and rate performance of the device [16, 17]. During the charging/discharging process, the repeated embedding/de-embedding of Na^+/K^+ will very easily result in the fragmentation of the anode material, which will lead to the deterioration of the electrochemical reversibility [18, 19]. Therefore, the development of high specific capacity anodes with structural stability and fast energy storage kinetics is the key to solving the problems faced by SIBs/PIBs.

Carbon is gradually becoming the most promising material for industrial applications due to its excellent physical and chemical stability [20], abundant sources and low price [21]. Graphitic carbon has a high theoretical specific capacity (372 mA h g^{-1}) [22] and a layered structure that favors Li^+ embedding [23].

However, due to the mismatch between the lattice structure of graphite and the larger size of Na^+/K^+ , it is difficult for Na^+/K^+ to be embedded in graphite, which hampers the application of graphite anodes in SIBs/PIBs [24, 25].

Amorphous carbon has a large layer spacing and many pores/defects, which are favorable for embedding/de-embedding of Na^+/K^+ ions and accommodating volume changes during cycling [26, 27]. Among them, biomass-derived carbon anodes are receiving extensive attention and a great deal of research due to their advantages of low cost, easy availability, fast regeneration and environmental friendliness [28–30]. However, the fabrication of high-quality biomass-derived carbonaceous materials with suitable pores and specific surface areas (SSA) is usually too cumbersome for large-scale preparation [31, 32]. Therefore, there is an urgent need to find a biomass-derived carbonaceous material that is suitable for industrial preparation. The *Spartina alterniflora* Loiser-derived biomass carbon prepared by Huanyu Wei et al. [33] in a one-step process as an anode material for SIBs maintained a reversible capacity of $141.63 \text{ mAh g}^{-1}$ after 1,000 cycles. Zhenrui Wu et al. [34] investigated the electrochemical performance of lignin-derived biomass carbon when used as anode for PIBs. The reversible specific capacity of lignin-derived biomass carbon in PIBs was 300 mAh g^{-1} at a current density of 0.1 A g^{-1} , and 79% capacity retention was obtained.

Wedelia chinensis is extremely strong in growth and adaptation and is widely distributed in Asia. In this study, *wedelia chinensis* was utilized as a carbon source for direct pyrolysis in order to achieve the goal of large-scale preparation of biomass carbon (Fig. 1). Structural characterization and electrochemical analyses showed that the *wedelia chinensis*-derived porous carbon (WDPC) with appropriate pores and suitable specific surface area can be used as anode materials for NIBs and PIBs, providing good rate performance and high specific capacity. As an anode material in SIBs, WDPC maintains a high reversible specific capacity of $380.7 \text{ mA h g}^{-1}$ after 500 cycles at 100 mA g^{-1} with a capacity retention of 97%. While in PIBs, WDPC also exhibits an excellent rate performance, maintaining a high specific capacity of $128.6 \text{ mA h g}^{-1}$ even at a high current density of 10 A g^{-1} . This low-cost carbon-based material prepared by one-step pyrolysis provides guidance for the development of SIBs and PIBs.

2. Experimental Section

2.1 Preparation of WDPC materials

Collected *wedelia chinensis* were thoroughly washed with deionized water followed by soaking in ethanol for 12 h. After sufficient drying, the pulverized raw material was annealed in a tube furnace at 800°C under argon for 2 h. The obtained sample was denoted as WDPC.

2.2 Material characterization

The structure of the materials was determined by using X-ray diffraction (XRD, X'Pert Pro, Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a sweep speed of $10^\circ \text{ min}^{-1}$. Field emission scanning electron

microscopy (SEM, JSF-6700F, Japan) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan) were used to observe the microscopic morphology of biomass-carbon. The surface composition of the material was determined by Thermo Scientific Escalab 259Xi X-ray spectrometer (XPS). Laser Raman spectroscopy (Raman spectroscopy) was performed using an excitation wavelength of 532 nm (LabRAM HR Evolution Raman spectrometer). Micromeritics ASAP 2020 nitrogen adsorption/desorption tester was used to test the specific surface area and the pore size distribution of the materials.

2.3 Electrochemical measurement

The working electrode of the NIBs was prepared by thoroughly grinding and mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) with a mass ratio of 7:2:1. The above slurry was evenly coated on Cu foils that were dried at 110 °C for 12 h under vacuum. The loading density of active material was about 0.5 ~ 1.0 mg cm⁻². As for PIBs, the binder was sodium carboxymethyl cellulose (CMC), the other operations were the same as above. A series of CR2032 coin-type cells were assembled in a glove box filled with Ar (the content of H₂O and O₂ content < 0.01 ppm). The glass fibers (GF/D, Whatman) was used as separator, fresh sodium or potassium foil severed as counter electrode. The electrolyte was 1 M NaClO₄ in EC-PC (v:v = 1:1) and 0.8 M KFP₆ in EC-DEC (v:v = 1:1), respectively. Galvanostatic charge/discharge (GCD) curves, cycling performance and galvanostatic intermittent titration technique (GITT) tests were performed on a battery test system (LAND CT2001) with a voltage window of 0.01-3 V. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI 760E).

3. Results and Discussion

3.1 Morphology and structural features of materials

Figure 2a-b display the SEM images of the WDPC sample at different magnifications. It can be seen that WDPC is an irregular blocky morphology with abundant pores on the surface. The presence of these pores opens up channels for charge transfer and increases the active sites, which can play a positive role in the electrochemical properties of the material [35, 36]. The HRTEM images show the typical amorphous feature of WDPC. The SEAD pattern does not show the diffraction spots of the crystals, again indicating the amorphous structure of WDPC.

In order to further investigate the structural properties, the material was characterized by XRD (Fig. 3a). It can be seen that the characteristic diffraction peak at 26° corresponding to the (002) crystal plane in the graphite structure becomes broader, weaker and shifts to a lower angle (22°), which indicates a decrease in the degree of crystallinity of the carbon material and an increase in the spacing between the layers [37, 38]. Calculated from Bragg's equation, the (002) crystal plane spacing is found to be 0.376 nm. Larger lattice spacing facilitates rapid insertion and extraction of alkali metal ions to overcome high-energy diffusion barriers [39]. The characteristic diffraction peak at 43° corresponding to the (101) crystal plane almost disappears, further indicating that the carbon material structure tends to be disordered [40, 41].

The Raman spectrum of the WDPC material is shown in Fig. 3b. Two peaks at 1340 and 1595 cm^{-1} correspond to the D and G peaks of the carbon, respectively. The intensity ratio of $I_{\text{D1}}/I_{\text{G}}$ is 0.94, indicating a low degree of graphitization. The specific surface area and pore size distribution of the materials were analyzed using N_2 adsorption/desorption isotherm. As can be seen in Fig. 3c, the high nitrogen adsorption at $P/P_0 < 0.05$ indicates that there is a large amount of micropores in the material. Moreover, there is a smaller H4-type hysteresis loop in the relative pressure interval of $0.45 < P/P_0 < 0.98$, indicating that there is also a certain amount of mesoporous structure in the material (Fig. 3d). The WDPC material has suitable specific surface area and porosity ($374.94 \text{ m}^2 \text{ g}^{-1}$ and $0.26 \text{ cm}^3 \text{ g}^{-1}$). Generally, the high specific surface area and ample pore structure are favorable of the ion transfer and the increase of active sites, which greatly improve the electrochemical performance of the materials. However, it is not conducive to the improvement of the initial Coulombic efficiency (ICE) because of more irreversible parasitic reactions [42]. XPS determines the elemental composition and state on the material surface. Only two elements, carbon and oxygen, were detected in the XPS survey scan. The oxygen content is 9.34%, which indicates that the material structure contains more oxygen-containing functional groups and more defects. In addition, the doping of heteroatoms can improve the wettability of the carbon material and increase the contact between the electrolyte and the electrode [43, 44]. The diffusion and transport distances of ions and electrons are also shortened, which is beneficial for improving the material rate performance [45]. High-resolution C1s and O1s XPS spectra of the WDPC sample are presented in Fig. 3e-f. The high-resolution C1s spectrum can be deconvoluted into three peaks at 284.8, 286, and 288.8 eV, corresponding to C-C, C-O-C, and C-O = C, respectively [46]. Similarly, the O1s spectrum can be decomposed into two peaks (Fig. 3f), which are also assigned to C-O (531.6 eV) and C = O (533.2 eV) in different ratios, respectively [47].

3.2 the electrochemical performance of WDPC as for anode material of NIBs/PIBs

The sodium/potassium ions storage performance of the WDPC electrode is investigated in a half-cell with Na/K metal as the counter electrode. In order to investigate the energy storage behavior of WDPC material, the CV curves were tested at different scan rates within an electrochemical window of 0.01–0.3 V. As shown in Fig. 4a-b, the shape of the CV curves is still remains the same with the increase of scanning speed, and the embedded sodium ion potential is slightly shifted to a higher potential. This fully demonstrates the high reversibility and fast kinetic properties of the electrochemical reaction [48]. Since SIBs and PIBs have the same energy storage mechanism, the CV curves of PIBs is basically similar to that of SIBs. However, the integration area of CV curve in PIBs is slightly smaller than that of SIBs due to the larger radius of K^+ ions, consequently making the intercalation/deintercalation of K^+ into the interfacial layer of the same carbon-based material relatively more difficult. It can also be seen from the CV curves that the intercalation/deintercalation potential of potassium ions in WDPC is significantly higher than sodium ions. Therefore, from the safety point of view, PIBs have higher safety than SIBs [49, 50]. For the SIBs, the initial discharge/charge capacity was $647.9 \text{ mA h g}^{-1}/308.2 \text{ mA h g}^{-1}$ at 0.1 A g^{-1} (Fig. 4c), corresponding to 47.6% of ICE. The ICE is relatively low due to the formation of the solid

electrolyte interface (SEI) layer and the occurrence of irreversible side reactions [51]. Except for the irreversible discharge loss in the first cycle, the GCD curves show slope characteristics without obvious plateau, indicating good electrochemical kinetic behavior of the material [52]. The GCD curves almost overlap in the subsequent cycles, suggesting that the electrochemical processes at the WDPC electrode are highly reversible. The GCD curve of PIBs at 0.1 A g^{-1} is similar to that of SIBs, demonstrating a fast kinetic behavior in PIBs. The poor reproducibility of the GCD curves for PIBs is attributed to the higher reactivity of K^+ and the increased chance of side reactions on the electrode surface, which will cause significant decay of the specific capacity (Fig. 4d) [53]. Therefore, it is particularly important to precisely regulate the microstructure of anode materials in PIBs. SIBs and PIBs are subjected to rate performance tests at different current densities, and the results are shown in Fig. 4e. The discharge specific capacities of WDPC in SIBs are 320.7, 246.4, 191, 147.7, 95.8, 75.7, and 68.4 mA h g^{-1} at current densities of 0.1, 0.2, 0.5, 1, 2, 5, and 10 A g^{-1} . When the current density is restored to 0.1 A g^{-1} , the discharge specific capacity is returned to $331.8 \text{ mA h g}^{-1}$, showing good reversibility and structural tolerance. The electrochemical properties of WDPC in PIBs are slightly different from those of SIBs. The specific capacity is significantly lower than that of SIBs at low current densities. The specific capacity decays more seriously at 0.1 A g^{-1} , which is consistent with that showed by the GCD curves. However, the typical features such as the smaller solvation radius [54], lower solvation energy and fast ion transport properties of potassium ions [55] are beneficial to boost the ion transport kinetic behavior, finally resulting in the superior rate capabilities. Hence, the specific capacity decay in PIBs becomes much slower than SIBs with the increase of the current density. At the high current density of 10 A g^{-1} , as high as $128.6 \text{ mA h g}^{-1}$ of specific capacity still can be achieved by WDPC anode in PIBs, displaying superior rate performance. Figure 4f demonstrates the cycling performance of WDPC in SIBs and PIBs. At a current density of 0.1 A g^{-1} , the WDPC displays a specific capacity of 380.7 mAh g^{-1} with essentially no capacity degradation, and Coulombic efficiency is nearly to 100% after 500 cycles in SIBs system. However, in the PIBs system, the cycling stability is relatively poor and the Coulombic Efficiency floats obviously. This is mainly due to the repeated intercalation/deintercalation of larger potassium ions between the carbon layers of WDPC, leading to a more serious volume change.

In order to reveal the nature of the excellent electrochemical properties of WDPC material, its electrochemical energy storage kinetic behavior was investigated. The CV curves of the WDPC electrodes were tested at different sweep rates. According to the relationship showed in equations (1) and (2), $\log(i)$ versus $\log(v)$ at different voltages are plotted separately, and the b values at different potentials can be obtained from the slopes of the straight lines [56, 57].

$$i = av^b$$

1

$$i = k_1v + k_2v^{1/2}$$

2

As shown in Fig. 5a-b, in both SIB and PIB, the b values are between 0.5 and 1 but not lower than 0.7, indicating that charge storage is contributed by both a surface-driven behavior and a diffusion-controlled process, but the current response is mainly stemmed from the fast surface capacitance controlled process (Fig. 5b). Semi-quantitative calculations based on Eq. (2) show that the charge storage mainly originates from diffusion-controlled processes at low sweep speeds (Fig. 5c-d). As the scan rate increases, the electrolyte ions diffuse at a slower rate and the diffusion-controlled process contributes progressively less to the charge storage (Fig. 5e-f). In particular, the radius of K^+ ion is larger, and the diffusion-controlled process reduces, the contribution to charge storage more significantly (Fig. 5f). The above results demonstrate that WDPC anodic material with abundant pore structure has fast kinetic behaviors, and the ions transfer kinetic behavior dominated by surface capacitance-controlled processes during the charging and discharging processes. The superior kinetic behavior is inextricably linked to the microstructure and composition of the material, such as reasonable pore size distribution, large layer spacing, increased active sites, and heteroatom doping and so on.

The fast diffusion kinetic behavior of the WDPC anode was confirmed in measurements by the constant-current intermittent titration technique (GITT) as shown in Fig. 5a-b. A simplified form of Fick's second law is used to calculate the diffusion coefficient of sodium/potassium ions with the equation as shown in follows [58, 59]:

$$D_{K^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$

3

In the equation, m_B , V_M and M_B are the mass (g), molar volume ($L \text{ mol}^{-1}$) and molar mass ($g \text{ mol}^{-1}$) of the active substance, respectively. A is the geometric contact area between the electrode material and the electrolyte. τ is the constant current pulse time, ΔE_τ is the total transient potential change in time τ due to the application of constant current I , and ΔE_s is the change in the steady state voltage of the cell due to the application of the constant current I . The cell voltage change in time τ is the change in the steady-state voltage of the electrode material. For the WDPC anode materials, the trends of overpotential changes in SIBs and PIBs are basically the same. During the charging process, the overpotential gradually increases. The overpotential during discharge decreases as the degree of discharge increases [60]. According to Fick's second law calculation, D_{Na^+} varies in the range of $4.58 \times 10^{-10} \sim 1.12 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ during charging and discharging, while D_{K^+} varies in the range of $7.12 \times 10^{-11} \sim 5.21 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ (Fig. 6c-d). Apparently, the ion diffusion rate slows down with increasing metal ion radius in the same electrode material, which is also closely related to its ease of embedding into the carbon material interlayer.

4. Conclusion

In this work, with the aim of simple preparation of high-performance carbon anode materials for SIBs/PIBs, biomass-derived carbon materials with suitable specific surface area and rich pore structure were prepared by selecting *wedelia chinensis* as the biomass carbon source. The sodium/potassium storage properties of the material were investigated by GCD and rate performance testing. The relationships between the electrochemical properties of the material and the structure (the lattice spacing, the specific surface area, the pore structure and the surface functional groups) were clarified. The kinetic behavior of the material for energy storage was also deeply investigated. Benefiting from the moderate specific surface area, abundant pore structure and larger interfacial spacing of WDPC, a high reversible specific capacity and a long cycling performance were achieved in both SIBs and PIBs. The WDPC is expected to be a potential anode candidate for the next-generation high-performance SIBs and PIBs.

Declarations

Conflicts of interest

There are no conflicts to declare.

Author Contribution

Kunjie Wang: Conceptualization, project management; Zengwei Pang: Writing the paper, preparing samples, testing statistics; Letong Wang: Investigation; Shenteng Wan: Software, resources; Miaomiao Liu: Validation, formal analysis; Xiaohui Niu: Data organization, supervision; Hongxia Li: Visualization.✉ Writing the paper✉ formal analysis.

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Supporting Information

Supporting Information is available from the author.

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Figures

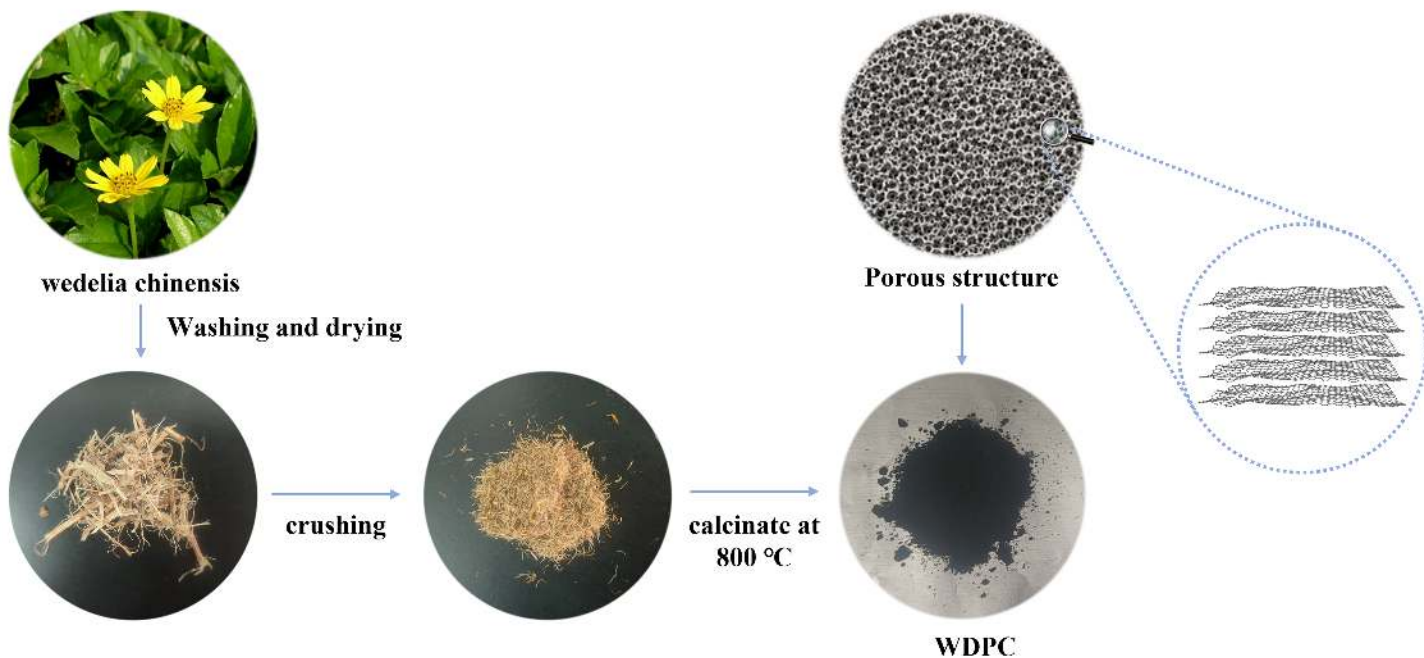


Figure 1

Schematic illustration of the preparation of WDPC

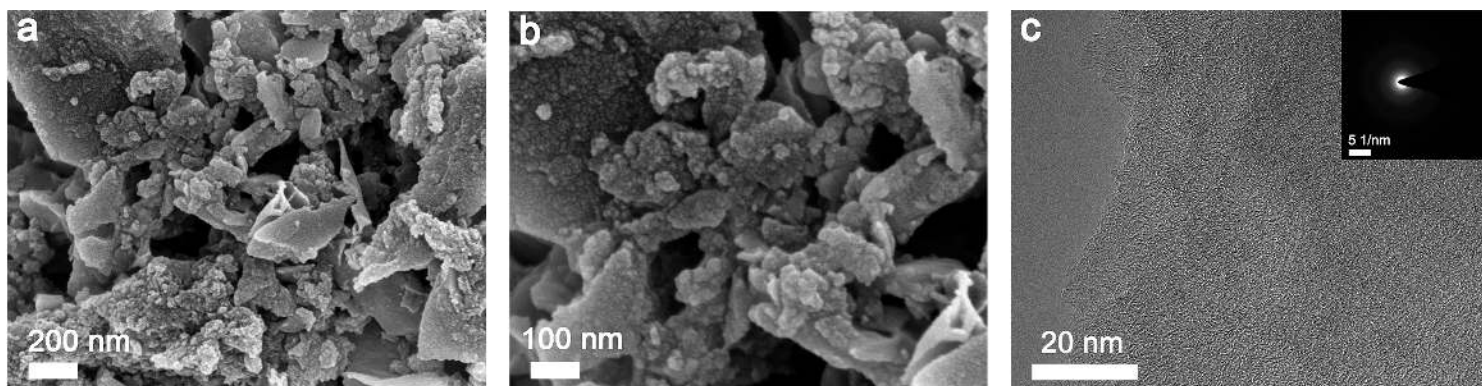


Figure 2

a, b SEM images, **c** HRTEM image and selected area electron diffraction (SEAD) pattern of WDPC sample

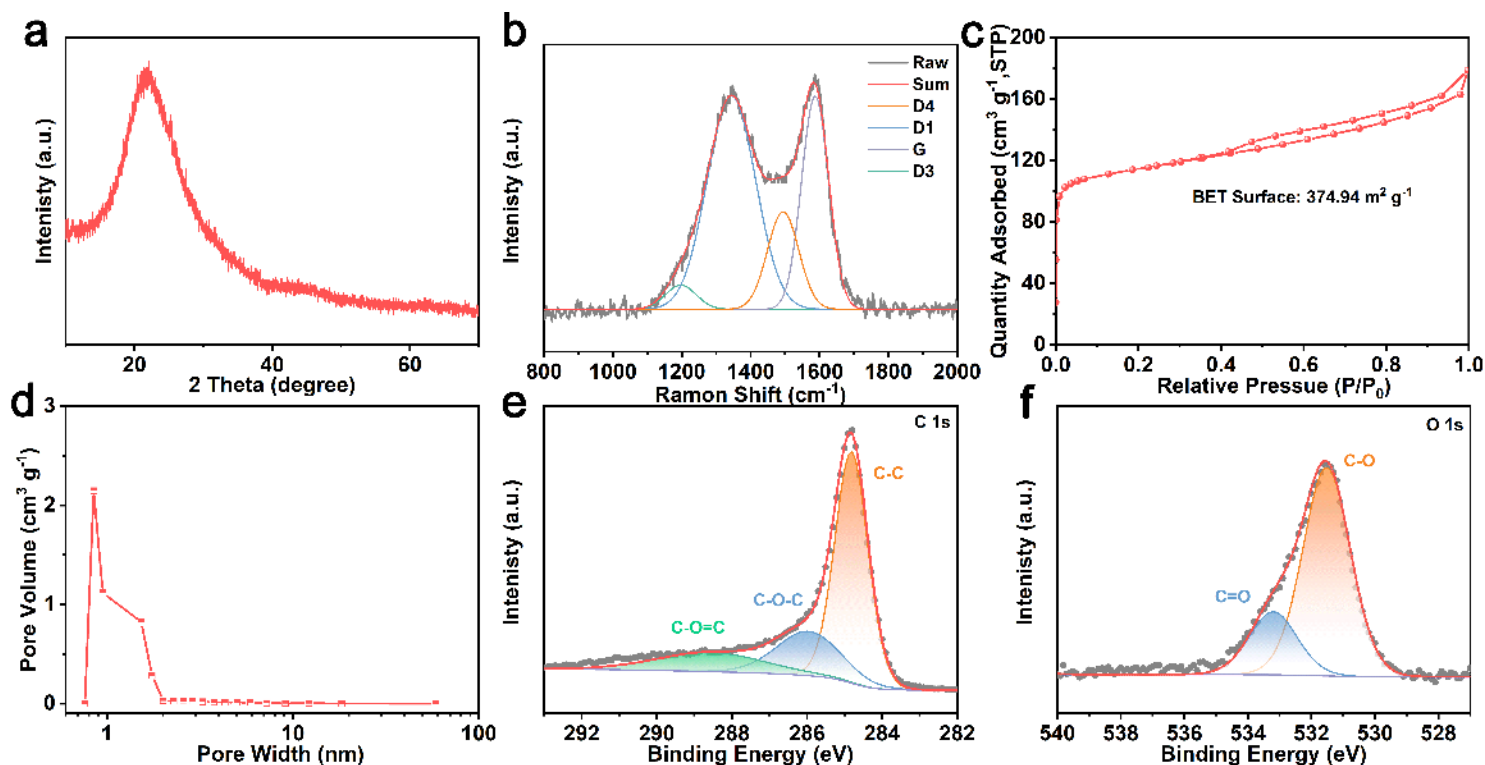


Figure 3

a XRD pattern; **b** Raman spectra; **c** Nitrogen adsorption-desorption isotherms; **d** Pore size distribution plot; **e** C1s; **f** O1s XPS spectra of WDPC sample

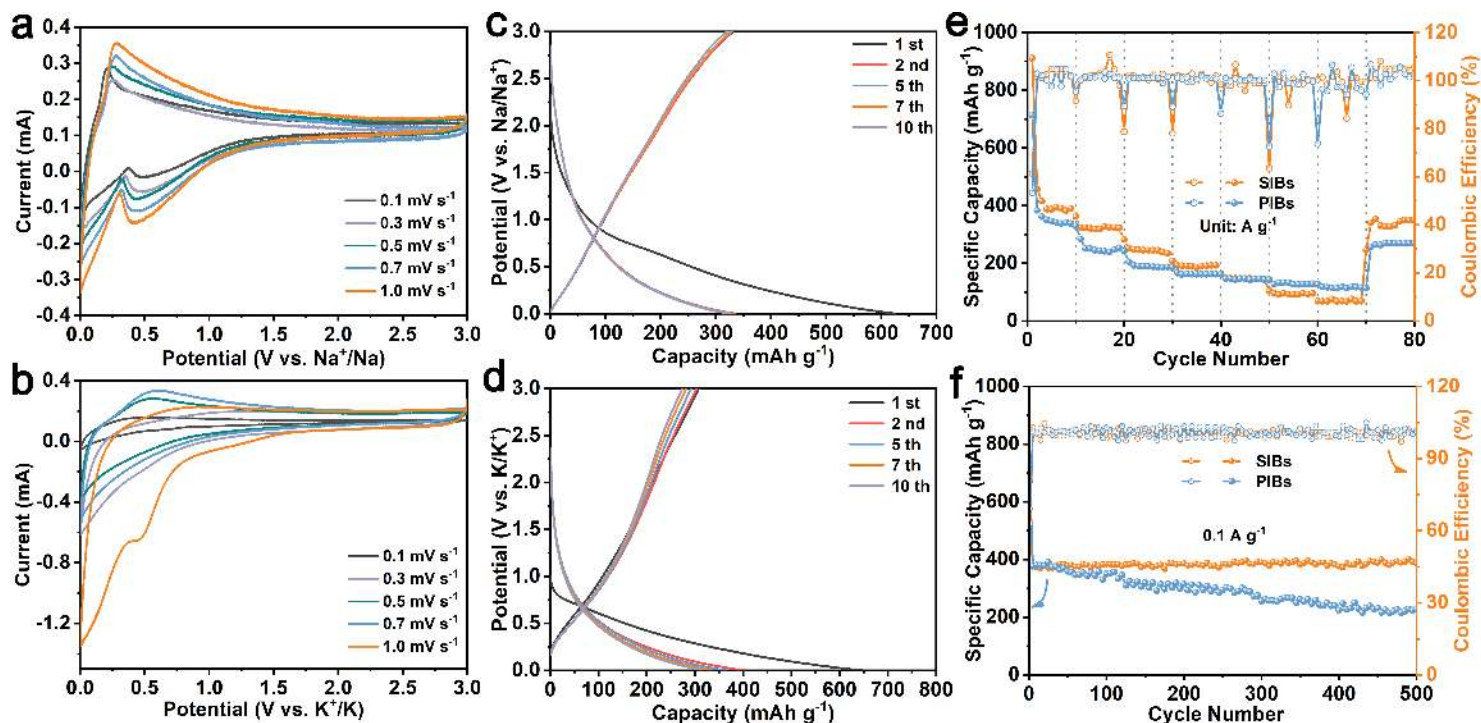


Figure 4

The CV curves under different scan rate in **a** SIBs, **b** PIBs respectively; GCD plots at 0.1 A g⁻¹ of WDPC anode electrode material in **c** SIBs **d** PIBs respectively; **e** Rate capability and **f** cyclic performance at 0.1 A g⁻¹ of WDPC anode electrode material

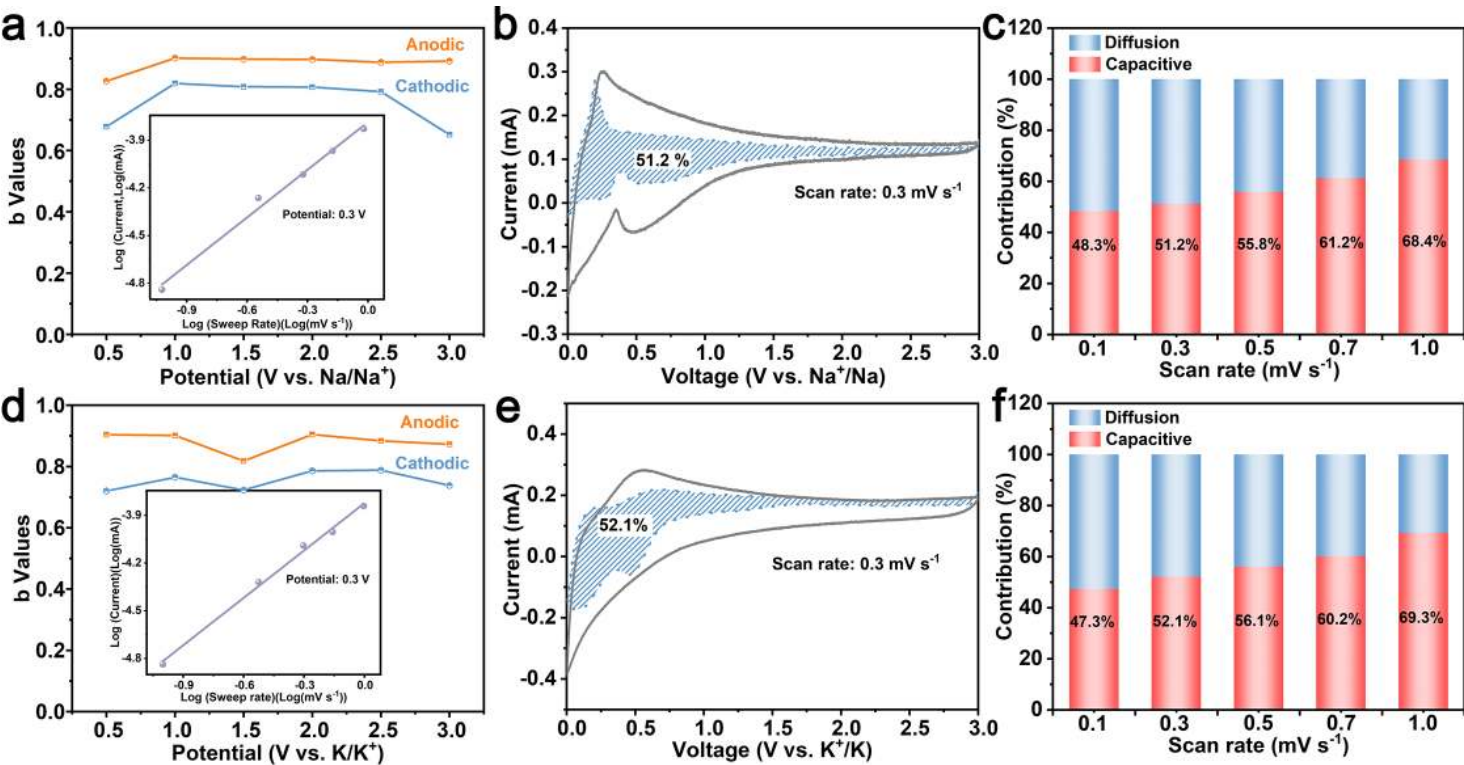


Figure 5

a, b *b* values in SIBs and PIBs respectively; Capacitive contribution ratios **c, d** at scan rate of 0.3 mV s⁻¹ and **e, f** at different scan rate in SIBs and PIBs, respectively

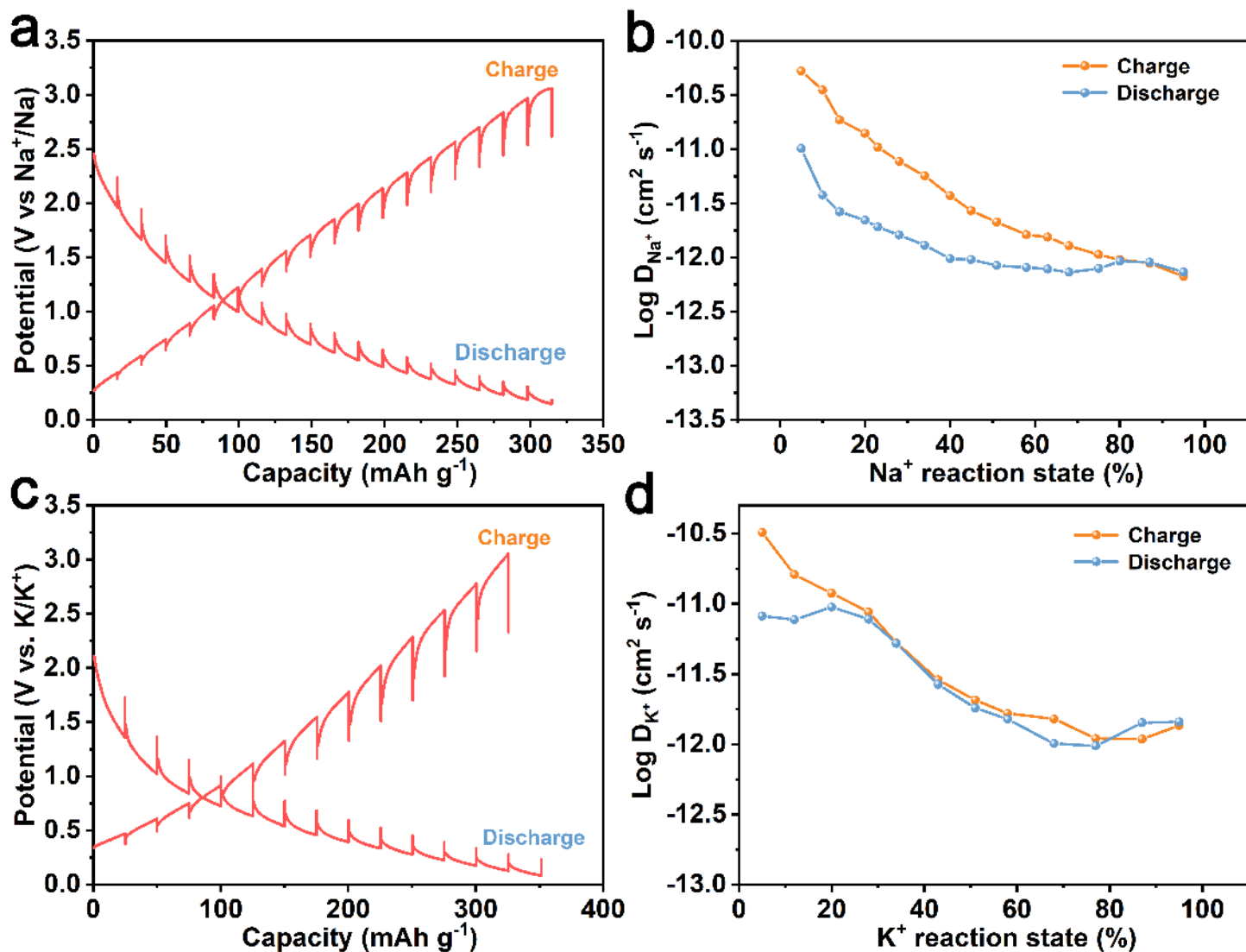


Figure 6

GITT plots in **a, b** SIBs and PIBs, respectively; Ion diffusion coefficients in **c, d** of SIBs and PIBs, separately.