Replacing “Alkyl” with “Aryl” for inducing accessible channels to closed pores as plateau-dominated sodium-ion battery anode

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Abstract
Hard carbons are promising anodes for sodium-ion batteries. However, there is still considerable controversy regarding the sodium storage behaviors in hard carbons, which are mainly attributed to the varied precursors, confused pyrolysis mechanism, and different characterization methods. Herein, benefiting from the flexible molecular structure of polymers, a series of hard carbons with carefully tuned microstructures are fabricated by adjusting the ratio of aryl and alkyl groups in the epoxy resins. The results of dynamic mechanical analysis, in situ Fourier transform infrared spectra, and synchronous thermal gravimetric-infrared spectrum-gas chromatography/mass spectrometry reveal that replacing the alkyl with aryl groups in the resin can enhance the crosslink density, inhibit the degradation and rearrangement process, and further lead to a more disordered microstructure. In addition, it is suggested that accessible channels provided by sufficiently wide interlayer spacing are necessary for closed pore filling. The optimized anode delivers a high capacity of 375 mAh/g in half cell with an initial Coulombic efficiency of 80.61%, and an energy density of 252 Wh/kg is attained in full cell. Finally, a reliable relationship among precursor–pyrolysis mechanism–structure–performance is established, and the sodium storage mechanism of “adsorption–insertion–pore filling” is well proved.

KEYWORDS
aryl, epoxy, hard carbons, mechanism, sodium ion batteries
1 | INTRODUCTION

Developing next-generation energy storage systems with high effectiveness and sustainability is critically important to meet the increasing demand of global energy. As lithium-ion batteries (LIBs), the successfully established technology, which has already been applied in portable electronics and electric vehicles, is not suitable for large-scale energy storage owing to the limited reserves and uneven distribution of lithium sources. In contrast, sodium-ion batteries (SIBs) with similar chemistry to lithium, high natural abundance, and low processing costs, are considered to be the sustainable and effective substitutes of LIBs in the application of large-scale energy storage. However, lacking of suitable anode materials remains to be a significant limitation for developing state-of-the-art SIBs. It is well known that the widely used graphite anode of LIBs is unsuitable for SIBs in a conventional ester electrolyte, as it is difficult for Na\(^{+}\) ions to intercalate into graphite layers to form stable compounds. Fortunately, hard carbons consist of turbostratic nanocrystallites can deliver a high capacity of around 300 mAh/g with a low operation potential, which are demonstrated to be the potential candidates of graphite in SIBs anodes. However, although much efforts have been devoted to enhance the capacity and explore the energy storage mechanism, the sodium storage mechanism of hard carbons remains a controversy.

Hard carbons can provide sodium storage capacity at defects and functional groups, in pores, and between graphene layers. In addition, the typical charge− discharge profiles of hard carbons mainly consist of two parts including a sloping region at the potential above 0.1 V and a plateau region at the potential below 0.1 V. In 2000, Stevens and Dahn first proposed the “insertion−adsorption” model to explain the sodium storage behaviors, and they supposed that the plateau region was attributed to the micropores filling of Na\(^{+}\) ions, this model was further supported by Komaba with the help of the ex-situ X-ray diffraction (XRD) and Raman techniques. But this model cannot explain the phenomenon that the capacity from plateau region increases with a high pyrolysis temperature, during which the number of pores is decreased. Until 2012, Cao et al. proposed a completely opposite model of “adsorption−insertion” to give a reason. It was pointed out that Na\(^{+}\) ions intercalated into the graphitized carbon layers at the low potential, and a minimum interlayer spacing of 0.37 nm was demanded for the intercalation process. Meanwhile, in situ XRD patterns, ex-situ sodium solid state nuclear magnetic resonance, and many other advanced techniques have been employed to verify this model. It was proved that the graphite layers were expanded during sodiation at the plateau region, and all the stored sodium was in the form of ions. However, the pore filling process is overlooked in the “adsorption−insertion” model. Several works have reported that Na\(^{+}\) ions became more metallic during the low potential, and the existence of quasi-metallic sodium was proved. Therefore, models including “adsorption−pore filling” and “adsorption−insertion−pore filling” were proposed to explain these phenomena more reasonably. Accordingly, there is still considerable debate on the sodium storage behaviors at different potentials.

In addition to the influence of testing instruments and methods, one important reason for this confusion is that the precursors for hard carbons vary in different works, and sometimes their compositions are complicated. This phenomenon further results in the unclear pyrolysis process and the diversity of the carbon microstructure, which increases the difficulty of unifying the mechanism. It is well known that the composition and crosslink density of precursors have a great influence on the microstructure of carbon materials. For instance, adjusting these parameters of pitch by using oxygen, Mg(NO\(_3\))\(_2\), the terminals of MXene, or phenolic resin can regulate its pyrolysis process, further leading to a highly disordered structure of pitch-derived carbon. The hard-carbon-like microstructure endows these pitch-derived carbons with a long discharging plateau. But the crosslink density and detailed pyrolysis information is still hard to identify. As another example, both the hydrothermal glucose and the cellulose can be seen as polymerized products of glucose, but their bonding methods are different. In comparison to cellulose, hydrothermal glucose own a higher crosslink density. The stacked glucose molecules may lead to hard carbons with large numbers of closed pores. Thus, the pore filling process for sodium storage is more obvious in this kind of carbons. On the other hand, the chain molecules of cellulose are arranged in order. Although molecules will bond to each other to form a crosslinked intermediate state during pyrolysis, the internal pores are less. These discrepancies are common in other precursors including phenolic resin, polyacrylonitrile, lignin, biomass materials, etc. Therefore, linking the molecular structure, crosslink density, and pyrolysis mechanism of the precursor with the microstructure of the carbon material is very important for the analysis of the sodium storage mechanism in hard carbons.

In this work, a series of carbon materials with carefully tuned microstructure were fabricated by adjusting the molecular structure of epoxy resins. The pyrolysis mechanism of alkyl- and aryl-rich epoxy resins is investigated by using in-situ Fourier transform infrared (FT-IR) spectra and TG-IR-GC/MS. It is found that replacing alkyl with aryl groups can enhance the crosslink
density, inhibit the degradation and rearrangement process, and further lead to a more disordered microstructure. In addition, the optimized carbon anode delivers a reversible capacity of 375 mAh/g at a current density of 20 mA/g, with an initial Coulombic efficiency of 80.61%. And an energy density of 252 Wh/kg is exhibited based on the total mass of active materials on anode and cathode, indicating its practical application prospect. Furthermore, based on the detailed analysis of structural parameters, electrochemical performance, kinetic process, and ex-situ tests, a reliable relationship among precursor–pyrolysis mechanism–structure–performance is established. And the “adsorption-insertion-pore filling” model of sodium storage is further proved. As a consequence, constructing hard carbons with abundant closed pores as well as accessible channels is necessary for high performance anodes.

2 | RESULTS AND DISCUSSION

A schematic illustration of the curing process is demonstrated in Figure 1A. In general, each amidogen of the curing agent can open two epoxy rings to form a tertiary amine and two alkanols, leading to a crosslinked structure of the resins. By adjusting the categories of the curing agent, the rigidity, cross-linking degree, and thermal stability of the resins can be well controlled. In this case, a series of cured epoxy resins were prepared by using the hybrid curing agents of 1,12-diaminododecane (DAD) and 4,4’-diaminodiphenylmethane (DDM), and the products were labeled as PDDx (where x referred to the content of DDM in ten parts of hybrid curing agents). As shown in FT-IR spectra of the cured resins in Supporting information Figure S1, the peaks at around 3400, 1250, and 1100 cm⁻¹ are attributed to the groups of –OH, Ar–O–C, and C–N, respectively. While the characteristic peaks of epoxy ring at around 914 cm⁻¹ disappeared in all the spectra, indicating that all the epoxy rings are opened and linked with the curing agents. Further, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were conducted to explore the difference of cured resins in thermal and thermomechanical properties. It could be seen from the DSC curves that the glass transition temperature (Tg) of the resins rises with an increased DDM content (Supporting information Figure S2). The reason is that rigid groups may hinder the movement of the segments, and higher temperature is demanded to overcome the kinetic energy barrier for the resins with larger amount of rigid groups. As a result, the aryl-rich resin of PDD10 exhibits the highest Tg of 179.8°C among all the samples. The Tg of the resins calculated from the loss factor (tanδ) of DMA confirms the increased rigidity of the samples (Figure 1B). Besides, the crosslink density (Vc) of polymer systems can be calculated based on the rubber elasticity theory, which could be represented as follow:

\[ E_r = 3V_cRT_r, \]

where \( E_r \), \( R \), and \( T_r \) correspond to the storage modulus of the rubber platform, universal gas constant (8.314 J/mol/K), and the absolute temperature, respectively. Accordingly, the crosslink density of the resins is quantized, which increases gradually from 1670 mol/m³ of PDD0 to 3291 mol/m³ of PDD10 (Figure 1C). Therefore, the rigidity and crosslink density of the polymer could be fine adjusted by tuning the molecular structure, which would further affect its thermal stability and pyrolysis behaviors (Supporting information Table S1). The thermal stability of PDDx was studied using thermal gravimetric analysis (TGA) under the atmosphere of N₂. As shown in Figure 1D, all the samples are stable before 300°C and show a certain decomposition at the range of 350–500°C during pyrolysis. With the largest amount of aryl groups, PDD10 owns the highest char yield among the samples. According to the derivative thermogravimetry (DTG) curves (Figure 1E), the pyrolysis temperature with the maximum degradation rate of the sample shifts to a high value with increasing the aryl content. Besides, there are obviously two peaks on the DTG curve of PDD0, while the peak at around 466°C fades away after decreasing the alkyl content. This phenomenon indicates that aryl-rich structure endows the resin a high thermostability, while resins with high alkyl content may suffer from an extra degradation process, resulting in a low char yield. Meanwhile, extra structural rearrangement process would happen, which may have an impact on the graphitized structure of the material.

To explore the influence of aryl and alkyl on the pyrolytic behavior of the resins. In-situ FT-IR and TG-IR-GC/MS tests were carried out to analyze the evolution of functional groups and decomposition products of the polymers during the pyrolysis process. As shown in the In-situ FT-IR spectra (Figure 2A, B), the characteristic absorption peaks are unchanged below 330°C, indicating that the resins are stable in this condition, which is consistent with the result of TGA. Further elevating the temperature to 350°C, the decreased intensity of the characteristic absorption peaks at around 2900, 1500, 1250, and 1100 cm⁻¹, demonstrate that the C−H, aromatic ring, Ar−O−C, and C–N are degrading gradually. Moreover, compared with PDD0, the composition of PDD10 starts to change at a higher temperature, confirming the better thermal stability of PDD10. It is worth noting that PDD0 owns several C−H groups even at the high temperature of 450°C, while this kind of group is nearly disappeared in PDD10. On the contrary, more aromatic structure is maintained in the skeleton of PDD10. This discrepancy
is resulting from their molecular structure, which would further affect the microstructure of the derived hard carbons. In addition, it could be found that both the PDD0 and PDD10 release large amount of gaseous-phased products during pyrolysis (Figure 2C, D). This process begins at around 350°C, while the temperature for the highest absorbance peak intensity of the released products are 382 and 394°C for PDD0 and PDD10, respectively, indicating the maximum degradation rate of PDD0 and PDD10 appears at such temperatures. After that, all the peaks are disappeared gradually, but the intensity of the absorbance peak at the wavenumber of around 3000 cm⁻¹ for PDD0 rises again at around 470°C after a short descent. This phenomenon demonstrates that an extra degradation process is occurred and more hydrocarbons compounds are released, which is in good accordance with the results of TGA. More detailed information is attained by resolving the volcanic plots, of which results are shown in Supporting information Figure S3. Based on the absorption spectra of the samples at certain temperatures, it could be found that these gaseous products mainly consist of phenolic compounds (3650 cm⁻¹), hydrocarbons (2800–3200 cm⁻¹), aromatic compounds (1500 cm⁻¹), ethers (1250, 1180 cm⁻¹), and amine compounds (1100 cm⁻¹). Meanwhile, most of the gaseous products released from PDD0 are similar to that of PDD10, but it cannot be ignored that PDD0 releases more hydrocarbons than PDD10 among the whole pyrolysis process. In addition, the unique absorbance peak at
1480 cm$^{-1}$ appears in the spectra of PDD0, indicating that long-chain alkanes ($-(\text{CH}_2)_n-$) are released during pyrolysis. As the temperature increased up more than 550 °C, nearly all the absorbance peaks are disappeared, suggesting that the pyrolysis process is complete.

To further distinguish the gaseous products and explore the pyrolysis mechanism, GC/MS test was performed. Figure 2E shows the total ion chromatograms of PDD0 and PDD10, while the corresponding compounds are listed alongside. It can be found that the major pyrolysis components of PDD10 are aromatic compounds, including phenol (peak 1'), benzofuran (peak 2'), phenyl acetate (peak 5'), $N,N$-dimethyl-benzenamine (peak 8'), etc. While in the case of PDD0, products like decane (peak 2), 1-undecylamine (peak 6), dodecane (peak 12), and other long chain hydrocarbons are also observed. Therefore, on the basis of the results from DSC, DMA, TGA, in-situ FT-IR, and TG-IR-GC/MS, it can be concluded that aryl groups can enhance the crosslink density and thermal stability of the resins; the gaseous products of aryl-rich resins during pyrolysis are aromatic compounds with short molecular chains, which is beneficial for the retention of carbon skeleton. As for alkyl-rich resins, the unstable alkyl chains are easy to break and a two-step degradation process is happened during pyrolysis, resulting in a severely damaged carbon skeleton, so that obvious structural rearrangement will take place during carbonization.

Subsequently, hard carbons labeled as PDDx-15 were prepared by carbonizing the cured resins (PDDx) under 1500°C. The morphology and microstructure of the products were observed by scanning electron microscopy and high resolution transmission electron microscopy (HRTEM). As shown in Supporting information Figure S4, all the samples show similar irregular blocks on the micron-scale. However, the inner morphology of these samples are totally different (Figure 3). The HRTEM
images demonstrate that the samples present turbostratic microstructures, and the microcrystalline structure of these carbon materials evolves from an ordered state to a highly disordered state with increasing aryl group content in the precursors. To be specific, PDD0-15 presents a more ordered microstructure with a large number of graphite ribbons compared to other samples. These ribbons consist of well-stacked carbon layers with the average interlayer spacing of 0.354 nm. In addition, closed pores with large diameters are generated from the stacked ribbons. As the alkyl content of the precursors decreases, the graphite ribbons inside the carbons become smaller. Besides, the layer of the stacked carbon is reduced, accompanied by the emersion of closed pores with smaller diameters. The average interlayer spacing of the carbon layers increases from 0.354 nm for PDD0-15 to 0.367, 0.371, 0.373, 0.375, and 0.390 nm for PDD2-15, PDD4-15, PDD6-15, PDD8-15, and PDD10-15, respectively. PDD10-15 derived from the resin with the lowest content of alkyl group shows a highly disordered structure, and disordered carbon lattice stripes as well as small nanopores are found in its HRTEM image, rather than ordered graphite ribbons. Such gradually evolved microstructure may lead to different sodium storage behaviors of these samples.

The microstructure and components of the carbon materials were further investigated by XRD, Raman spectroscopy, small angle X-ray scattering (SAXS), N$_2$ adsorption and desorption isotherms, and X-ray photoelectron spectroscopy (XPS). As shown in Figure 4A, all the samples show two broad peaks at around 24° and 43°, which represent the (002) and (101) planes of graphite, respectively, indicating the amorphous features of these carbon materials. It is worth noting that the (002) peak becomes wider and shifts to a lower angle gradually from PDD0-15 to PDD10-15, indicating the decreased degree of order and increased interlayer spacing for the materials (Figure 4B). In addition, average lateral extension ($L_a$) and stack height ($L_c$) of the pseudographitic segments were estimated using the Scherrer equation and listed in Supporting information Table S2. As can be seen, the $L_a$ and $L_c$ values decrease gradually from PDD0-15 to PDD10-15. The $L_c$ value varies in the range of 1.15–1.50 nm, while the $L_a$ value for PDD0-15 and PDD10-15 are 5.07 and 3.25 nm, respectively. Therefore, more alkyl groups can facilitate the orientation of basal planes and induce the formation of graphite crystallite with larger width. This phenomenon is consistent with the HRTEM observations. Similarly, the Raman spectra of all the samples show two peaks at around 1350 and 1580 cm$^{-1}$ (Supporting information Figure S5), corresponding to the disordered carbon band (D-band) and graphitic band (G-band), respectively. The integrated intensity ratio of D-band to G-band ($I_D/I_G$) can be used to determine the ordered degree of carbon materials, where the value increases from 1.08 for PDD0-15 to 1.26 for PDD10-15, indicating a more disordered structure is formed in PDD10-15 (Figure 4B). Furthermore, SAXS technique was conducted to provide more information about the closed pores of the samples (Figure 4C). All the SAXS patterns exhibit shoulder-shaped scattering at the vector scope of 0.1–0.3 Å$^{-1}$, indicating the
existence of nanopores in the carbon matrix. These patterns are almost overlapped with each other, but the peak intensity at around 0.1 Å$^{-1}$ shows a slight elevation from PDD10-15 to PDD0-15, indicating the closed pore volumes of the samples are similar, while the radius of the closed pores is larger in alkyl-rich resin-derived carbons.

The surface and porosity parameters of the samples were also probed by nitrogen adsorption–desorption measurements. It could be found that all the samples exhibit type-II adsorption–desorption isotherms with low adsorption volume during the whole process, indicating small surface areas of the samples (Supporting information Figure S6A). The Brunauer–Emmett–Teller-specific surface of all the samples are calculated to be around 60–70 m$^2$/g. Such low surface area is benefit for carbon materials to attain a high initial columbic efficiency (ICE). 48,53 Then, calculations based on the DFT method is applied to reveal the pore size distribution of the carbon materials, and the pores with the diameters of around 3–8 nm are found in the materials, which are generated from the released gaseous products during pyrolysis (Supporting information Figure S6B). Furthermore, the pore structures of the samples were investigated by the CO$_2$ adsorption–desorption measurement,54,55 of which results are shown in Supporting information Figure S6C. All the samples show similar adsorption–desorption isotherms with the low CO$_2$ adsorption volume less than 10 cm$^3$/g, confirming that there are very few micropores inside the samples. Meanwhile, the corresponding pore size distribution in Supporting information Figure S6D indicates the presence of pores with diameters of 0.6–0.9 nm in the samples, but the pore volume is low. This result is in well agreement with that from the N$_2$ adsorption–desorption measurements. Accordingly, transforming the alkyl groups of the precursors to aryl groups will not greatly affect the open porous structure of carbon materials, while the diameter of inner closed pores will become smaller.

Figure 4D shows the results of XPS analysis for the carbon materials. It is demonstrated that the nitrogen atoms in all the samples have been eliminated after a high temperature pyrolysis process, and these carbon materials are composed of carbon and oxygen. The oxygen content of the samples are similar with the value of around 3.8 at.%. In addition, the result of the deconvolution of C1s XPS spectrum for PDD10 is shown in Figure 4E. Five peaks at around 284.8, 285.4, 286.8, 287.6, and 289.8 eV can be seen and are corresponded to the carbon species of sp$^2$ C, sp$^3$ C, C–O, C = O, and O = C=O, respectively. Besides, sp$^2$ C and sp$^3$ C are the main species, which are the constituents of carbon layers. 56–58 The deconvolution of C1s XPS spectra for other samples are shown in Supporting
FIGURE 5 Charge/discharge profiles at 20 mA/g of (A) PDD0-15, (B) PDD2-15, (C) PDD4-15, (D) PDD6-15, (E) PDD8-15, (F) PDD10-15. (G) The capacity contributed from the sloping and plateau regions of PDDx-15 samples. (H) Cycling performance of PDDx-15 samples at a current density of 100 mA/g.

Information Figure S7. It could be found that the number of sp² C for carbon materials gradually decreases from PDD0-15 to PDD10-15 (Figure 4F), confirming that the graphitization degree of carbons decreases with increasing the aryl content of the precursors (Supporting information Table S2). In brief, it is proved that replacing alkyl groups with aryl groups will inhibit the two-step degradation process, reduce the release of long-chain alkyl, and increase the carbon residue for the precursors. This condition will further result in carbon materials with high degree of disorder, large interlayer spacing, and small closed pores.

To evaluate the sodium storage performance and further investigate the energy storage behavior of the carbon materials, 2032 coin-type cells were assembled and measured under the potential of 0.01–3.0 V. The galvanostatic charge–discharge (GC) profiles of the carbons are shown in Figure 5A–F. It can be observed that all the materials exhibit a typical charge–discharge profiles of hard carbons, consisting of both sloping (>0.1 V) and plateau regions (<0.1 V). PDD10-15 delivers the highest specific capacities of 355 and 440 mAh/g among the as-obtained carbon materials during the initial charge–discharge cycle, corresponding to an ICE of 80.61%. This irreversible capacity is mainly attributed to the decomposition of electrolytes and further formation of solid-state electrolyte interface (SEI) films. The nearly overlapped GC profiles after the initial cycle demonstrate that the charge–discharge process is highly reversible. Meanwhile, the reversible capacity and ICE of all the samples are listed in Supporting information Table S3. It can be found that there is no significant difference in ICE among the samples, and the value of which ranges from 77.89 to 80.92%. The reason is that
the elemental composition, defect concentration, and surface area of the samples are similar, resulting in the same electrochemical reactions occurred on the electrode surface during charge and discharge. So that the difference in capacity of the materials is mainly related to their graphitized structure. This phenomenon is conducive to further analyze the sodium storage behaviors of the samples. It can be seen that the specific capacity contributed from sloping region is similar with a slightly upshift among the samples, while the capacity below 0.1 V for the samples gradually increases from 117.7 mAh/g for PDD0-15 to 243.5 mAh/g for PDD10-15 (Figure 5G). Correspondingly, Supporting information Figure S8 displays the CV curves of the samples at the scan rate of 0.1 mV/s. It can be found that all the CV curves show a regular evolution. The irreversible small reduction peak at around 0.5 V is attributed to the formation of SEI films. While the sharp redox peak at 0.1 V is resulting from the intercalation and extraction of Na$^{+}$ ions between carbon layers. In addition, this redox peak becomes sharper from PDD0-15 to PDD10-15, indicating a more obvious Na$^{+}$ ions diffusion process inside the PDD10-15 electrode.

Furthermore, to assess their cycling stability, the samples wereycled at a current density of 100 mA/g, of which result is shown in Figure 5H. As a result, the capacity of PDD10-15 remains to be 235 mAh/g after 200 cycles, corresponding to a capacity retention of 81%, while PDD0-15 shows a lower specific capacity (84 mAh/g) but a higher capacity retention (89%). The reason is that less Na$^{+}$ ions can insert into the carbon layers, resulting in the enhanced structural stability of PDD0-15. The rate capability of the carbon materials was conducted at various current densities from 20 to 1000 mA/g. As shown in Figure 6A, PDD10-15 delivers the best rate capability among the samples with the capacities of 375, 329, 283, 255, and 146 mAh/g at the current densities of 20, 40, 80, 100, and 200 mA/g, respectively. But the specific capacity is only 52 mAh/g at 1000 mA/g (Supporting Information Table S3). Figure 6B presents the charge–discharge profiles of PDD10-15 at different current densities. It could be found that at low current densities (<200 mA/g), all the profiles consist of a plateau region and a sloping region. The plateau region shows a significant decay when the current density increases from 100 to 200 mA/g, while it is disappeared with a current density over 400 mA/g, and only a sloping region could be seen in this condition. Therefore, the sodium storage behavior during the sloping region is mainly attributed to Na$^{+}$ ions adsorption on surface and defects with a fast kinetics, while the insertion and pores filling process with a lower kinetics happens at the plateau region. In addition, PDD10-15 exhibits higher sloping capacity at any current than that of PDD0-15, this could be attributed to the lower graphitization degree and higher defect content of PDD10-15 than that of PDD0-15 (Figure 6C).

The reaction kinetics analysis based on the CV curves was conducted to further explore the sodium storage mechanism of PDD10-15 and PDD0-15. Figure 6D, E displays the CV curves of PDD10-15 and PDD0-15 tested at the scan rates from 0.1 to 1.0 mV/s. The scan rate (v) and the corresponding peak current (i) obey the power law relationship of $i = av^b$, $61,62$ which can be used to demonstrate the capacity contributions from diffusion-controlled and surface-controlled process. In briefly, the $v$ can be calculated from the log(i)–log(v) plot, where $b = 1.0$ indicates a fully surface-controlled sodium storage process and $b = 0.5$ indicates a diffusion-controlled reaction. The $b$ values at 0.05/0.5 V for PDD10-15 are 0.45 and 0.81, while they are 0.67 and 0.82 for PDD0-15 (Figure 6F), indicating that the diffusion-controlled process is more dominated in PDD10-15 than PDD0-15 at low potential. Besides, sodium storage behaviors of PDD0-15 and PDD10-15 at the sloping region are mainly controlled by the surface pseudo-adsorption process. These two processes were further quantified using the formula of $i(V) = k_1v^{1/2} + k_2v^{1/2}$, $63–65$ where $k_1$ and $k_2v^{1/2}$ refers to the surface-controlled and diffusion-controlled capacity, respectively. And the fitting plots are listed in Supporting information Figures S9 and S10. It can be seen that the proportion of diffusion-controlled capacity is 67.8% for PDD10-15 at 0.1 mV/s (Figure 6G), which is higher than that of 56.1% for PDD0-15 (Supporting Information Figure S10G), proving that more Na$^{+}$ ions are stored in the bulk phase of PDD10-15 through diffusion. This phenomenon is consistent with the fact that PDD10-15 delivers a larger plateau capacity than that of PDD0-15 at low current density. In addition, the proportion of diffusion-controlled capacity decreases as the scan rate increases, but its value for PDD10-15 is higher than for PDD0-15 at any rates except 1.0 mV/s, confirming that PDD10-15 is more suitable for Na$^{+}$ ions insertion. The similar proportion for PDD10-15 and PDD0-15 at 1.0 mV/s indicates that the Na$^{+}$ ions diffusion process is hindered at high scan rate, causing that Na$^{+}$ ions can only be adsorbed on the surface and near-surface of the electrodes.

Subsequently, galvanostatic intermittent titration technique measurements were conducted to further analyze the sodium storage behaviors of the samples (Supporting Information Figure S11). $49,66,67$ As shown in Figure 6H, the Na$^{+}$ ions diffusion coefficients ($D_{Na^{+}}$) of the samples are calculated to be with the order of $10^{-9}$ cm$^2$/s, which diminish slowly before 0.1 V during sodiation, and an obvious fall appears in the potential range of 0.1–0.05 V, resulting in the minimum value at around 0.05 V. Then, a slight elevation emerges below the potential of 0.05 V. This phenomenon indicates that the sodiation process can be designated into three regions. The faster reaction in the
Figure 6 (A) Rate performance of PDDx-15 samples at various current densities from 20 to 1000 mA/g. (B) Charge or discharge profiles of PDD0-15 at various current densities. (C) Charge or discharge profiles of PDD0-15 and PDD10-15 at the current densities of 20 and 1000 mA/g. CV curves of (D) PDD0-15 and (E) PDD10-15 at various scan rates from 0.1 to 1.0 mV/s. (F) Calculated b values at the potentials of 0.05 and 0.5 V for PDD0-15 and PDD10-15. (G) Capacity contributions from diffusion and surface controlled processes for PDD10-15. The Na$^+$ diffusion coefficients of PDD0-15 and PDD10-15 during (H) discharge and (I) charge.

The sloping region is attributed to the adsorption of Na$^+$ ions on the surface and near-surface. After these active sites are occupied, Na$^+$ ions start to diffuse into the graphite nanocrystallites with a slow kinetics. Then, nanopores are filled by Na$^+$ ions diffused from the nanocrystallites, accompanied by an increased diffusion coefficient. In addition, the more obviously elevated diffusion coefficients of PDD10-15 than other samples in the potential range of 0.05–0.01 V, indicate that a more apparent pore filling reaction is happening inside the PDD10-15. In comparison with PDD0-15 and PDD10-15, PDD4-15 and PDD6-15 exhibit lower diffusion coefficients at around 0.05 V. The reason is that more Na$^+$ ions can insert into the carbon layers of PDD4-15 and PDD6-15 than that of PDD0-15, but their interlayer spacing is smaller than PDD10-15, leading to a slow diffusion process. The result is consistent well with GC profiles, confirming the sodium storage model of “adsorption—insertion—pore filling.” During the desodiation process (Figure 6I), the variation of diffusion coefficients shows an opposite trend to the sodiation process, indicating that these processes are highly reversible. In addition, the electrochemical impedance spectroscopy was recorded to give more information on the electron/ion transport properties of the electrodes, of which results are shown in Supporting information Figure S12A. It could be found that all the Nyquist plots are composed of a semicircle in the mid-high frequency and a straight line in the low frequency. Resistance associated with SEI formation ($R_{SEI}$), charge transfer ($R_{ct}$), and solid-state diffusion of Na$^+$ could be attained by fitting these plots to an equivalent electric circuit, and the results are displayed in Supporting information Table S4. The $R_{ct}$ value of these
samples increases gradually from 263.6 Ω for PDD0-15 to 481.5 Ω for PDD10-15. This phenomenon is attributed to the high graphitization degree of PDD0-15, which endows the electrode a low resistance. Moreover, the Warburg factor obtained from the $\omega^{-1/2}$-$Z'$ curve can be used to evaluate the Na$^+$ ions diffusion coefficient ($D_{Na^+(EIS)}$) by using Supporting information Equation S2.54,55 of which results are listed in Supporting information Table S4. \(D_{Na^+(EIS)}\) for PDD0-15, PDD2-15, PDD4-15, PDD6-15, PDD8-15, and PDD10-15 are 4.03×10^{-13}, 3.14×10^{-13}, 2.06×10^{-13}, 1.75×10^{-13}, 2.08×10^{-13}, and 2.30×10^{-13} \text{cm}^2/\text{s}, respectively. High \(D_{Na^+(EIS)}\) of PDD0-15 is attributed to its low resistance, and the increased \(D_{Na^+(EIS)}\) from PDD6-15 to PDD10-15 may be caused by the increased interlayer spacing of the samples, which is beneficial for the transport of Na$^+$ ions.

Furthermore, the ex-situ HRTEM and ex-situ XRD tests were employed to detect the variation of the interlayer spacing and internal nanopores during sodiation or desodiation process (Figure 7). It can be found that the average interlayer spacing of PDD10-15 increases from 0.390 nm for pristine electrode to 0.407 nm for electrode discharged to 0.1 V (Figure 7A), while it increases further and reaches the high value of 0.418 nm when discharging to 0.05 V (Figure 7B), accompanied by the obviously expanding of carbon fringes and the nanopores. Then, a slight change in interlayer spacing is observed after further sodiating to 0.01 V, but the nanopores become blurred, indicating the pore filling reaction occurs (Figure 7C). Further, the average interlayer spacing recovers to 0.409 nm after fully desodiating, and the nanopores are reappeared (Figure 7D), demonstrating that the pore filling process is highly reversible. In addition, the change of the interlayer spacing during sodiation and desodiation can also be observed in the ex-situ XRD patterns (Figure 7E), these consistent results imply that both the insertion and pores filling process are happened in the plateau region, and the model of “adsorption—insertion—pore filling” is well demonstrated.

Overall, our experimental results provide an understanding of the relationship among the molecular structure, pyrolysis mechanism, microstructure of the carbon and its sodium storage behaviors. As illustrated in Figure 8, by regulating the molecular chains of polymers, their crosslink density, thermal stability, and pyrolysis mechanism can be precisely controlled. During pyrolysis, residues from aryl-rich resins exhibit better structural stability, so that replacing the alkyl groups with aryl groups in precursors will inhibit the degradation and rearrangement of carbon skeleton to some extent. It is worth noting that regulating these groups will not affect the open pores and total pore volumes of the products, but their interlayer
spacing and closed pores can be well adjusted. Hard carbons with large interlayer spacing and abundant accessible closed pores can be attained by using aryl-rich resins. Further, the sodium storage mechanism in hard carbons can be reasonably concluded to consist of three parts: (1) capacitive adsorption of Na\(^{\text{+}}\) ions on the surface and defect sites is supposed to occur at a high potential above 0.1 V; (2) after the surface is saturated with Na\(^{\text{+}}\) ions, Na\(^{\text{+}}\) ions will intercalate into the carbon layers (0.1−0.05 V), causing an expanded interlayer spacing; (3) then, more Na\(^{\text{+}}\) ions will diffuse into the closed pores until the cut-off potential (0.05−0.01 V). Therefore, constructing hard carbons with abundant closed pores as well as accessible channels provided by sufficiently wide interlayer spacing is necessary for high performance anode, while adjusting the molecular structure of the precursors is demonstrated to be an effective method to achieve this goal.

To further evaluate the practical application prospect of PDD10-15, the coin-type full cells were fabricated with Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) (NVP) as the cathode materials and precy-
CONCLUSIONS

In summary, a series of carbon materials with carefully tuned microstructure was fabricated by controlling the molecular structure of epoxy resins. It is proved that adjusting the molecular chains of the precursor is an efficient method to control its crosslink density and pyrolysis process. Resins with more alkyl groups are tend to form highly ordered carbon. By replacing these alkyl groups with aryl groups, resins with higher crosslink density and thermal stability are obtained. The two-step degradation process and the obvious structural rearrangement of alkyls-rich resins are inhibited, resulting in carbon materials with large interlayer spacing and more accessible closed pores. Further, a clear relationship among the molecular structure, pyrolysis mechanism, microstructure of the carbon and its sodium storage behavior is well established. Based on the analysis of electrochemical performance, kinetic process, and ex-situ tests, the sodium storage mechanism of “adsorption-insertion-pore filling” is well proved. In briefly, the capacity from sloping region is attributed to the adsorption of Na\(^+\) ions on the surface and defects, while the plateau region capacity is contributed from both the Na\(^+\) ions insertion and the pore filling process. As a result, the optimized PDD10-15 delivers a capacity of 375 mAh/g at a current density of 20 mA/g with a large plateau capacity of 243 mAh/g, and an energy density of 252 Wh/kg is exhibited based on the total mass of active materials on anode and cathode in a full cell. The method of adjusting the molecular chain of the precursor to directionally regulate the microstructure of the carbons provides a rational guide for designing high-performance carbon anodes with tailored interlayer spacing and abundant accessible closed pores, which could be extended to other carbons and afford more possibilities for designing advanced SIBs.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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