

Elucidating electrochemical intercalation mechanisms of biomass-derived hard carbon in sodium-/potassium-ion batteries

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Abstract

Hard carbon materials are characterized by having rich resources, simple processing technology, and low cost, and they are promising as one of the anode electrodes for commercial applications of sodium-/potassium-ion batteries. Simultaneously, exploring the alkali metal ion storage mechanism is particularly important for designing high-performance electrode materials. However, the structure of hard carbon is more complex, and the description of energy storage behavior is quite controversial. In this study, the *Magnolia grandiflora* Lima leaf is used as a precursor, combined with simple pyrolysis and impurity removal processes, to obtain biomass-derived hard carbon material (carbonized *Magnolia grandiflora* Lima leaf [CMGL]). When it is used as an anode for sodium-ion batteries, it exhibits a high specific capacity of 315 mAh/g, and the capacity retention rate is 90.0% after 100 cycles. For potassium-ion batteries, the charge specific capacity is 263.5 mAh/g, with a capacity retention rate of 85.5% at the same cycling. Furthermore, different electrochemical analysis methods and microstructure characterization techniques were used to further elucidate the sodium/potassium storage mechanism of the material. All the results indicate that the high potential slope region represents the adsorption/desorption characteristics on the surface active sites, whereas the low-potential quasiplateau region belongs to the ion insertion/extraction in the graphitic microcrystallites interlayer. It is noteworthy that potassium ion is randomly

intercalated between the graphitic microcrystallite layer without forming a segmented intercalation compound structure.

KEYWORDS

biomass, energy storage mechanisms, hard carbon, potassium-ion batteries, sodium-ion batteries

1 | INTRODUCTION

In recent years, the use of energy sources on a global scale is still dominated by fossil fuels, and the resulting environmental pollution and resource shortage problems have not been solved by the development of new energy sources (wind, solar, tidal energy, etc.). To alleviate the above problems, new high-efficiency energy storage systems represented by lithium-ion batteries have been developed rapidly, and their commercial applications are gradually changing the energy consumption structure.¹ Na and K are abundant and widely distributed elements, which can also ensure a sustainable, low cost, and stable growth of large-scale energy storage system market. However, the radius of sodium and potassium ion is larger than that of lithium ion, which makes it more difficult for them to insert/extract the electrode materials. Compared with lithium ion, sodium and potassium ions can result in a larger volume change of the materials greatly, which thus rapidly reduces the capacity.²⁻⁴ Through the unremitting efforts of the researchers, the development technology of sodium-/potassium-ion batteries (SIBs/PIBs) has made great progress.

At present, when used as an anode material for SIBs and PIBs, hard carbon material composed of disordered graphitic microcrystallites exhibits excellent electrochemical performance. For instance, its higher specific capacity, lower operating potential, and excellent cycle performance have received great attention from researchers.⁵⁻⁷ Besides, biomass in nature has a wide range of sources and can supply a wide variety of precursor materials. According to the view of industrial economics, biomass-derived hard carbon materials have a great potential for development. At present, the biomass used for energy storage included banana peel, cherry petal, oatmeal, pomelo peel, and hard carbon microspheres, all of which show excellent performance.⁸⁻¹² Hong et al.¹¹ obtained derivatized hard carbon material by pyrolysis of phosphate-treated pomelo peel, which exhibited a reversible capacity of 314.5 mAh/g at a current density of 50 mA/g and still maintained as 181 mAh/g after 220 cycles of 200 mA/g. Jian et al.¹² comparatively researched the electrochemical performance of hard carbon microspheres (HCSs) as both PIBs and SIBs anode. In PIBs, the capacity of HCS is 262 mAh/g and the retention rate in 100 cycles is 83%. Also, due to the higher diffusion coefficient of potassium ion in

HCS than that of sodium ion, and the larger gap between the potassium-ion insertion potential and potassium-metal plating potential than the narrow gap for sodium, the rate performance of PIBs is better than that of SIBs.

The energy storage mechanism of hard carbon materials in SIBs and PIBs is controversial. In this respect, there are relatively few related research studies, which brings a large amount of uncertainty to the material modification research. In addition, to achieve higher specific capacity, researchers often use more complicated preparation processes to improve, which will increase the difficulty and cost of industrial production.

Magnolia grandiflora Lima is a kind of widely cultivated green ornamental tree species all over the world. Its leaves contain a high content of cellulose, hemicellulose, and lignin, which can be carbonized by pyrolysis at high temperatures. In this study, *Magnolia grandiflora* Lima leaf was used as a precursor, and after a simple carbonization and pickling process, the pure electrode materials were obtained. In SIBs, the electrochemical performance test results show that carbonized *Magnolia grandiflora* Lima leaf (CMGL) can exhibit a high initial reversible capacity of 315 mAh/g and a capacity retention rate of 90.0% after 100 cycles. As the PIBs anode, the reversible capacity of CMGL is 263.5 mAh/g, and the capacity retention rate is 85.5% after the same cycle. Impressively, at higher current density, the application of CMGL in PIBs may be more advantageous than that in SIBs. Simultaneously, galvanostatic intermittent titration technique (GITT), cyclic voltammetry (CV) at various scan rates, in situ X-ray diffractometer (XRD), in situ Raman and X-ray photoelectron spectroscopy (XPS) were used to verify the sodium and potassium storage behaviors of the CMGL electrodes in different voltage ranges, which will provide a reference for the development of high-performance electrode materials.

2 | EXPERIMENTAL SECTION

2.1 | Materials synthesis

The collected *Magnolia grandiflora* Lima leaves were washed with deionized water and dried. It was then

transferred to a tube furnace and given a heat treatment at 1200°C for 2 h in an N₂ atmosphere (heating rate was 5°C/min). After cooling to room temperature, the leaves were taken out and immersed in dilute hydrochloric acid at a concentration of 20% for 6 h (60°C) to remove the generated impurities. Finally, they were rinsed and dried.

2.2 | Characterization of the materials

STA 449F3-type thermogravimetric analyzer (NETZSCH) was used for the analysis of precursor pyrolysis information. Bruker TENSOR27-type Fourier-transform infrared spectroscopy (Bruker) was used to detect the changes of the functional groups of the material on the surface before and after carbonization. Hitachi SU8010-type field emission scanning electron microscope (Hitachi) and Tecnai G2 TF30 S-Twin-type high-resolution transmission electron microscope (FEI) were used to observe the morphology of CMGL. D8 Advance-type X-ray diffractometer (Bruker) and LabRAM HR Evolution-type Raman spectroscopy analyzer (HORIBA) were used to characterize the microstructure of the sample. Nitrogen adsorption and desorption isotherms were analyzed on a Micromeritics ASAP 2020 HD88-type analyzer (Micromeritics). The specific surface area and pore size distribution information of the material were obtained by Brunauer–Emmett–Teller (BET) model and density functional theory (DFT) model. The chemical state of the surface of the sample was obtained using a K-Alpha-type X-ray photoelectron spectroscopy analyzer (Thermo Fisher Scientific). For the XPS tests during charging/discharging, the CMGL–Na electrodes were cleaned, transferred through a vacuum chamber, and then tested after etching.

2.3 | Electrochemical measurements

The electrochemical tests in this study were performed by using the half-cell CR2032. The active material, Super P, and carboxymethyl cellulose were fully mixed according to the mass ratio of 8:1:1, and ultrapure water was added to prepare a slurry. Then, the configured slurry was coated on the Cu foil by a mechanical coating process to make a working electrode. Finally, the electrode was placed at 120°C for vacuum drying, pressed with an electric roller press, and cut according to specifications. The cell was assembled in an argon-filled glove box with a metal sodium/potassium plate as the counter electrode and glass fiber as the separator, and the electrolytes were 1 M NaClO₄–propylene carbonate with 5 wt% fluoroethylene carbonate and 0.8 M KPF₆–ethylene

carbonate:diethyl carbonate with volume ratio 1:1, denoted as CMGL–Na electrode and CMGL–K electrode, respectively. The specific capacity, cycle performance, and GITT were tested on the CT2001A-type LAND battery test system (LAHNE); the GITT profiles were obtained in the fourth discharge/charge cycle at a pulse current of 30 mA/g for 0.5 h with rest intervals of 2 h. The CV tests were performed with the Autolab PGSTAT302N-type electrochemical workstation (Metrohm); the scan rates were 0.1–1 mV/s. For the above electrochemical tests, the voltage range was set from 3.0 to 0.01 V (vs. Na⁺/Na, and vs. K⁺/K). In situ XRD and in situ Raman spectroscopy were performed using specific devices, and the charge and discharge parameters remained unchanged.

3 | RESULTS AND DISCUSSION

The carbonization temperature of the precursor material is one of the key factors affecting the electrochemical performance of CMGL. To research the appropriate heat treatment temperature, the mass–temperature relationship of the precursor material during pyrolysis was investigated by thermogravimetric analyzer (TGA). It is well known that the pyrolysis process of biomass can be generally divided into three stages^{13,14}: evaporation of water, fracture and recombination of branch chains, and condensation of aromatic rings into carbon. The precursor materials can be used for the SIBs/PIBs anode after the last carbonization stage. As shown in Figure 1A for the TGA curve, the precursor material begins the carbonization process at a pyrolysis temperature of 650°C. Now, many researchers have found that lower carbonization temperature can lead to a lower degree of graphitization of the material, affecting the electrochemical performance of the sodium/potassium storage process. However, the higher pyrolysis temperature not only reduces the specific surface area of the material and the reactive sites, but also reduces the interlayer spacing, which is not conducive to the fast insertion/extraction of sodium/potassium ion.^{8,15–17} On the basis of the previous research experience, the carbonization temperature of the precursor material is set to 1200°C. The TGA results show that the carbon yield rate of the CMGL is about 30%, and from an ecological and economic point of view, it has broad application prospects.

The surface functional group changes of CMGL and precursor were compared and analyzed by Fourier-transform infrared spectroscopy (FTIR), as shown in Figure 1B. The absorption peaks of the two comparative samples in the wavenumber range 3750–3050 cm^{−1} are the absorption peaks of hydroxyl groups. Among them,

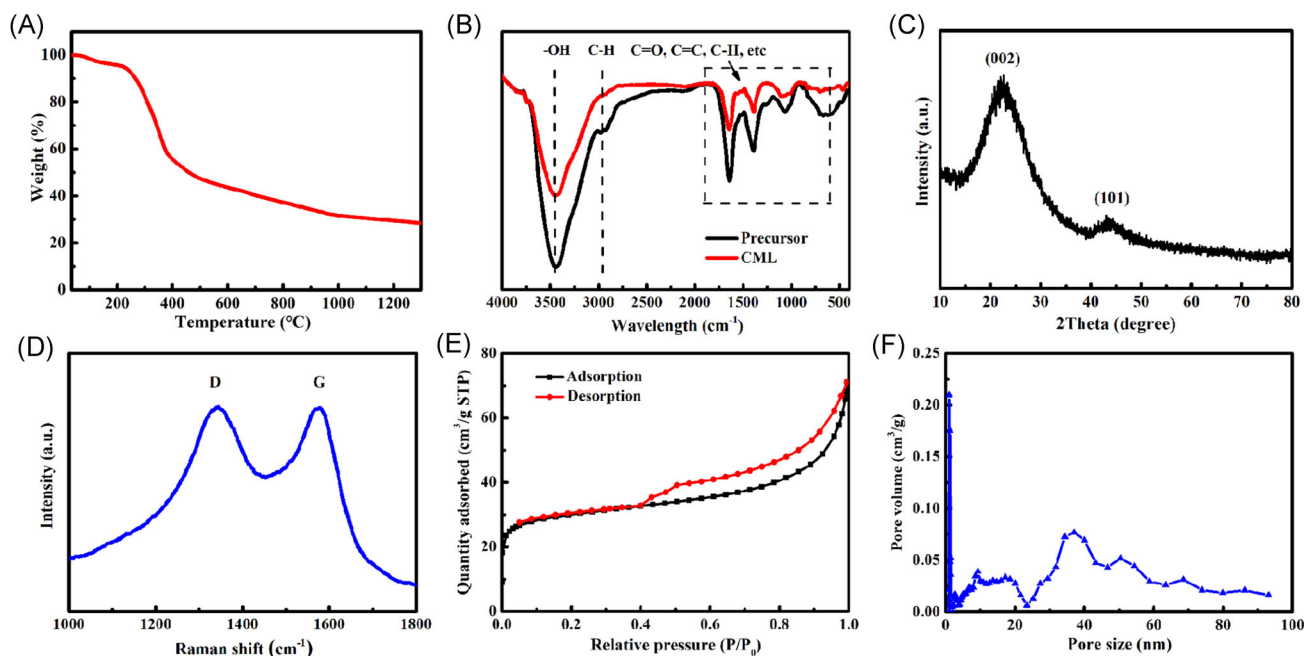


FIGURE 1 (A) Thermogravimetric analysis, (B) Fourier-transform infrared spectroscopy analysis, (C) X-ray diffraction pattern, (D) Raman spectrum, (E) N_2 adsorption/desorption isotherms, and (F) density functional theory pore size distribution of CMGL

there is a strong absorption peak near 3447 cm^{-1} , indicating the $-\text{OH}$ stretching vibration of phenol, carboxylic acid, and alcohol. A weaker absorption peak in the range of $3000\text{--}2800\text{ cm}^{-1}$ corresponds to the C-H of the aliphatic group. The absorption peak around $1900\text{--}600\text{ cm}^{-1}$ represents stretching vibration of the C=O of aliphatic and aromatic groups, the C=C of methoxy group, the C-H of aromatic hydrocarbon, and the carbon-carbon single bond of the aliphatic group.^{9,18} Compared with the precursor material, the functional group strength of CMGL is reduced, which means that a large number of chemical reactions occur within and between molecules during pyrolysis, accompanied by the production of C_2H_6 , CH_4 , C_2H_4 , and CO_2 , CO . In TGA test, this process represents a significant reduction in weight.

XRD and Raman spectroscopy were used to characterize the microstructure of CMGL. As shown in Figure 1C, the XRD peak around 22° corresponds to the diffraction of the (002) plane, and the diffraction peak of the (101) plane appears at around 43° . Compared with the traditional graphite material with high crystallinity, CMGL has a wider diffraction peak, indicating that it has a highly disordered structure.¹⁹ The thickness (L_c) of the graphitic microcrystallites along the c axis direction is calculated to be 1.24 nm using the Scherrer formula, indicating that there is a small amount of stacking of the graphitic microcrystallites inside the structure. The information of molecular vibration and rotation obtained

by Raman analysis is shown in Figure 1D. The G-band produced by the stretching motion of the sp^2 hybridization is located at around 1577 cm^{-1} , and the D-band caused by the defect and disorder induction is at around 1344 cm^{-1} , both of which are typical characteristic peaks of the carbon materials.²⁰ The intensity ratio (I_D/I_G) of the D-band to the G-band of CMGL is 1.09 , which is smaller than that of conventional graphite, and the smaller value indicates that the sample is less graphitized. In addition, the graphitic microcrystallite width (L_a) along the a axis direction can be obtained by I_G/I_D as 4.23 nm , and the smaller graphitic microcrystallite size is favorable for the rapid migration of sodium/potassium ion.

The specific surface area and pore size distribution characteristics of CMGL were obtained by N_2 adsorption/desorption test. As can be seen from Figure 1E, there is a typical IV-type isotherm, reflecting the multistage physical adsorption process of the porous materials. The hysteresis loop belongs to the H4 type, and the reflected pores include micropores and mesopores. The specific surface area calculated by the BET model is $95.7\text{ m}^2/\text{g}$, and the lower surface area can limit the formation of the solid-electrolyte interphase (SEI) film, thereby improving the initial Coulombic efficiency of the materials.²¹ The pore structure of CMGL is calculated by the DFT model, as shown in Figure 1F. It can be known that CMGL belongs to micro-mesoporous carbon material. This hierarchical pore structure not only is conducive to

the storage of sodium/potassium ion, but also can improve their migration rate.^{22,23}

Figure 2A,B show the different magnification field emission scanning electron microscopy (FE-SEM) images of CMGL. CMGL presents a sheet-like structure with evenly distributed small pores on the surface. It is well known that the “open” sheet structure can reduce the diffusion time of ion, and the appropriate pores are conducive to the full contact between the electrolyte and the electrode material. To understand the arrangement of the graphitic microcrystallites inside CMGL, the microstructure was further studied in detail using high-resolution transmission electron microscopy (HRTEM). As shown in Figure 2C, the alternately bright and dark stripes clearly show the morphology of the graphitic microcrystallites is disordered and irregular, with only a small number of stacked regions, which is a typical feature of hard carbon materials. The selected area electron diffraction of the inner image does not show crystal diffraction spots, which also indicates that CMGL has a highly disordered structure of hard carbon materials. According to the calculation analysis of the HRTEM image, as shown in Figure 2D, the interlayer spacing of CMGL is about 0.39 nm, which is much larger than the sodium-/potassium-ion radius.²⁴ The larger interlayer spacing not only facilitates the rapid insertion and extraction of the alkali metal ion and improves the sodium/potassium storage capacity of the material, but also maintains the stability of its internal structure during the charge/discharge process and finally improves the cycle performance.⁹

The composition and chemical bond information of CMGL surface were analyzed by XPS. As shown in Figure 3A, except for the obvious C 1s and O 1s peaks,

there is no peak of other elements, indicating that the impurities on the biomass have been substantially removed after washing with hydrochloric acid. Figure 3B contains the fitting information of peaks; there are three peaks in C 1s spectrum. The C–C bond representing the defect-free graphite lattice is located at 284.6 eV, and the C–O bond and C=O bond corresponding to the defect graphite lattice are located at peaks of 285.8 and 286.6 eV, respectively. Besides, there is no π – π conjugation peak in the C 1s spectrum, verifying that there is only a small graphitic microcrystallite stack structure in CMGL. The analysis of the O 1s spectrum can complement the information displayed by the C 1s spectrum, as shown in Figure 3C. The O 1s spectrum has two peaks, the spectral peak at 530.9 eV can be assigned to the C=O bond and the spectral peak at 532.8 eV belongs to the C–OH bond.^{25–27} The previous research studies have shown that the oxygen-containing functional groups on the surface of the materials can participate in the redox reaction of sodium/potassium ion and enhance their energy storage properties.^{28,29} Therefore, CMGL will likely have a higher sodium/potassium storage capacity.

To analyze the electrochemical performances of the as-obtained CMGL anode for SIBs and PIBs, the galvanostatic charge/discharge measurements were performed at a current density of 30 mA/g, as shown in Figure 4A,D. Both the charge and discharge curves have a slope region in the high-potential range and a quasiplateau region in the low potential range, which indicates that the energy storage behavior can be divided into two different processes. According to the reports, these two regions show that the alkali metal ion is inserted into different substructures or structural sites inside the material, that is, edges or defective sites of graphitic microcrystallites,

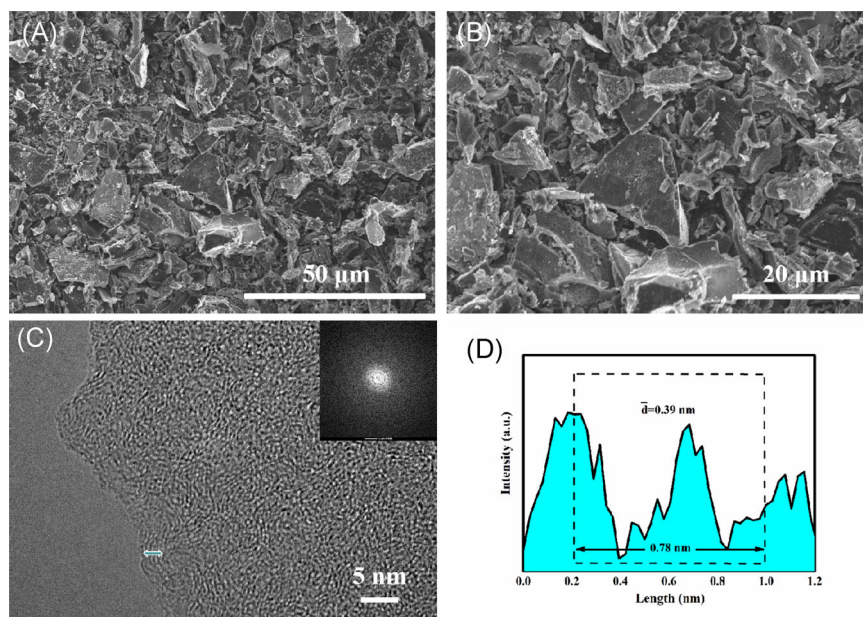


FIGURE 2 Different magnification field emission scanning electron microscopy images of CMGL: (A) $\times 1.0$ k and (B) $\times 2.0$ k. (C) High-resolution transmission electron microscopy and selected area electron diffraction images and (D) contrast profiles along the arrows indicating the interlayer distance of CMGL

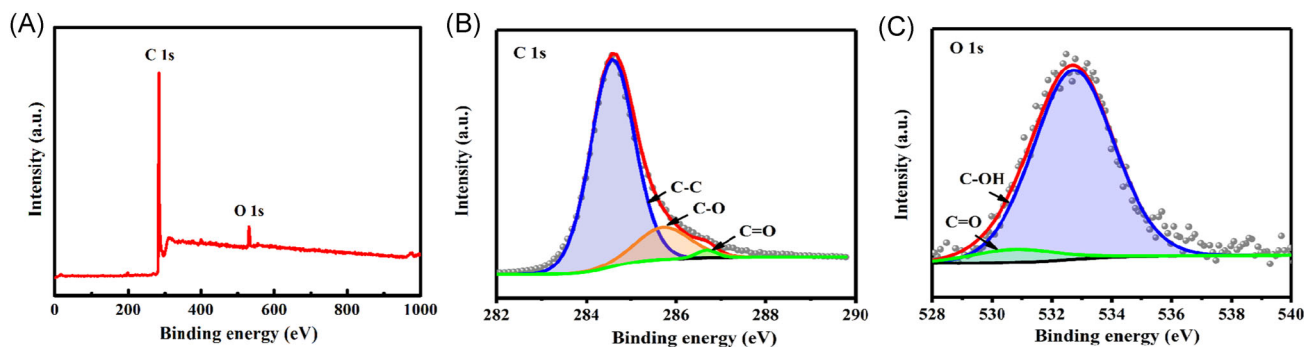


FIGURE 3 (A) X-ray photoelectron spectroscopy (XPS) spectrum, (B) C 1s XPS spectrum, and (C) O 1s XPS spectrum of CMGL

interlayer space inside graphitic microcrystallites.^{12,21,24} Meanwhile, the CMGL-Na electrode exhibits a charge specific capacity of 315 mAh/g with a high initial Coulombic efficiency of 69.4%, and the charge specific capacity of the CMGL-K electrode is 263.5 mAh/g and the initial Coulombic efficiency is 50.3%, which are higher than most electrodes prepared using other carbon materials. Figure 4B,E also show the cycle performance test results, and it can be observed that the specific capacity gradually decreases in the first few cycles. This is because the SEI film consumes sodium/potassium ion during the formation process, which reduces the number of active ions involved in the reaction. As the number of cycling increases, the specific capacity and Coulombic efficiency of the CMGL electrode tend to be stable, indicating that the generated SEI has high stability. The charge specific capacity after 100 cycles is 283.7 mAh/g (CMGL-Na) and 225.4 mAh/g (CMGL-K) respectively, which are 90.0% and 85.5% of the initial charge specific capacity, showing excellent cycle stability.

The differential curves of capacity were used to understand the electrochemical reaction inside the CMGL electrode, as shown in Figure 4C,F. During the initial cycle, a significant current peak occurs at the potential of 1.1 and 0.6 V (vs. Na⁺/Na) for the CMGL-Na electrode (0.6 and 0.2 V for the CMGL-K electrode vs. K⁺/K), which corresponds to the decomposition of the electrolyte at the electrode/electrolyte interface and the formation of an SEI film on the electrode surface.³⁰ The two current peaks disappear in the subsequent cycle, meaning that the formed SEI film is relatively stable and there is no widespread breakage. Simultaneously, the two materials show a pair of sharp current peaks near the relative potential of 0 V, which respectively corresponds to the insertion/extraction characteristics of alkali metal ion between the graphitic microcrystallites, and this will be discussed later. It is worth noting that the relative potential of potassium ion for insertion and

extraction is higher than that of sodium ion, and when alkali metal ion insertion occurs at potentials very close to the plating of the corresponding metal, dendrite formation can be a serious concern, especially at high current rates.¹² Therefore, considering the above reason, PIBs may be more advantageous than SIBs when using CMGL as the anode. Moreover, the capacity differential curves coincide well, indicating that the electrochemical reversibility of both is excellent.

As depicted in Figure 4G, the performance test with different current densities further verify that the CMGL electrode not only has excellent cycle stability but also has good rate performance. It can be observed that at a low current density (30–200 mA/g), the specific ion extraction capacity of the CMGL-K electrode is smaller than that of the CMGL-Na electrode. However, at a current density higher than 500 mA/g, the capacity of the CMGL-K electrode exceeds that of the CMGL-Na electrode. The capacities of the CMGL-K electrode at 500, 1000, and 2000 mA/g are 185.4, 157.4, and 126.8 mAh/g, respectively, whereas the CMGL-Na electrode only shows 142.2, 107.4, and 77.6 mAh/g at the same rates. Moreover, at the above high current density, the CMGL-K electrode retains 70%, 59.4%, and 47.9% of the capacity at 30 mA/g, respectively, such retention is only 45.3%, 34.2%, and 24.7% for the CMGL-Na electrode (Figure 4H). In addition, when the current density returns to the initial value (30 mA/g), their reversible capacity can also rise to 240.6 mAh/g (CMGL-K) and 286.4 mAh/g (CMGL-Na), which are maintained at 90.9% and 91.2% of the initial specific capacity, respectively, indicating that the CMGL electrode has a high reversible capacity and structural stability. The excellent electrochemical performance may be due to the large interlayer spacing of the graphitic microcrystallites, which facilitates the rapid insertion/extraction of alkali metal ion. It should be noted that

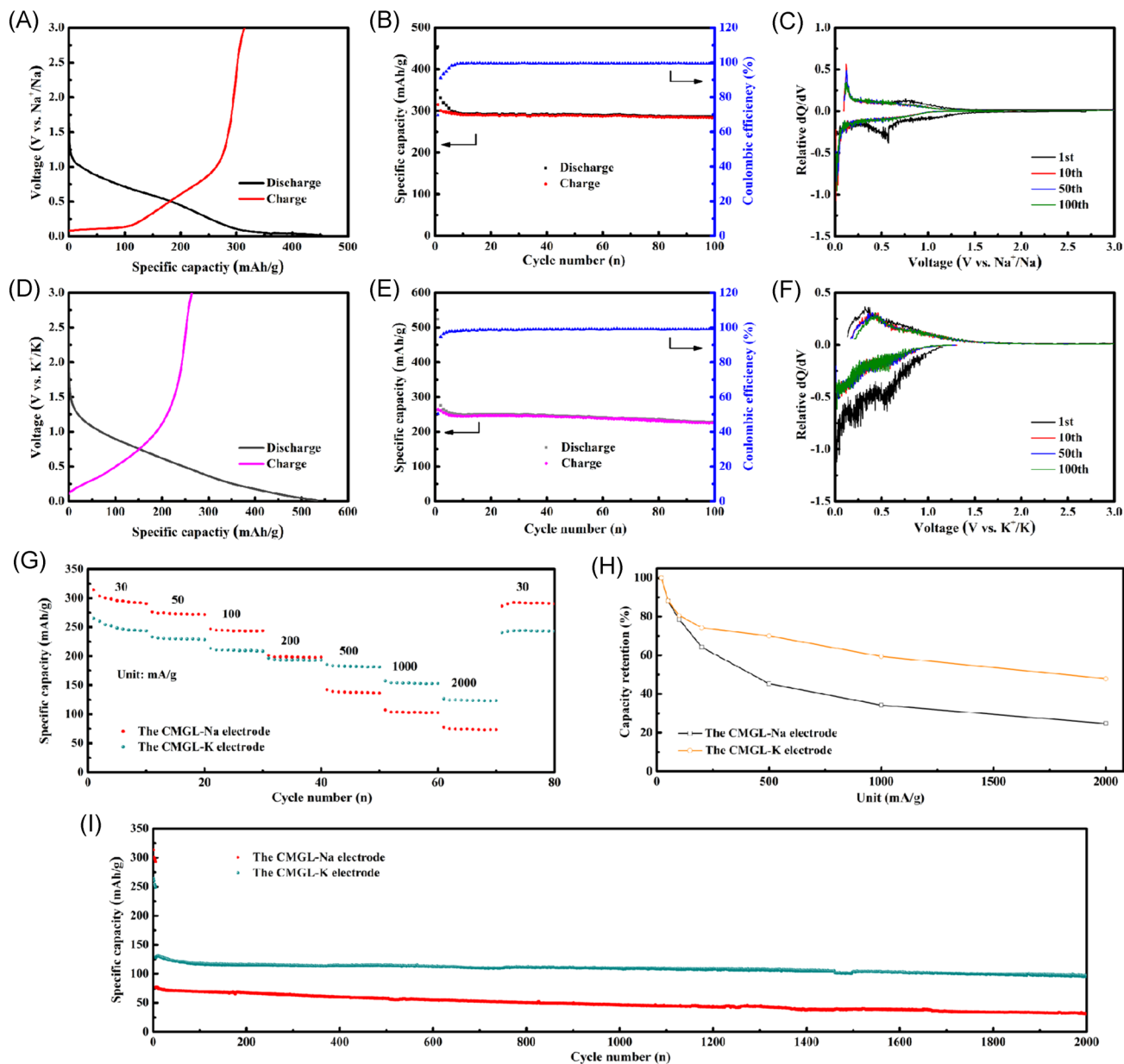


FIGURE 4 (A) Galvanostatic charge/discharge cycling profiles, (B) cycling performance, and (C) differential capacity curves of the CMGL-Na electrodes, (D) galvanostatic charge/discharge cycling profiles, (E) cycling performance, and (F) differential capacity curves of the CMGL-K electrodes. (G) Comparison of rate performance, (H) comparison of capacity retention at increasing current density, and (I) long-term cycle performance

one of the reasons for the higher capacity of the CMGL-K electrode at high current density may be related to the difference in redox potentials. As we all know, the absolute value in cut-off potential of the CMGL-K electrode is higher than that of the CMGL-Na electrode. For the high rates, the overpotential could quickly pull the potential of the CMGL-Na electrode to the lower cut-off potential of 0.01 V (vs. Na⁺/Na), the voltage plateau will disappear, and the capacity decrease significantly. In the CMGL-K electrode with the same level of

overpotential, the electrode potential may be still well above the cut-off voltage (vs. K⁺/K), the voltage plateau can still remain, and the capacity attenuation is small.¹² In addition, to better understand the high rate capability and long-term cycle performance of the material, 2000 cycles were performed at a current density of 2000 mA/g (Figure 4I). The CMGL-K electrode still maintains a reversible specific capacity of 96.6 mAh/g and the capacity decay is as low as 0.01% per cycle, which is better than the CMGL-Na electrode.

To deeply analyze the energy storage behavior of CMGL in SIBs and PIBs, the variation trend of ion diffusion rate during the charge/discharge process was researched by the GITT tests. Figure 5A,D show the GITT curves of the CMGL-Na electrode and the CMGL-K electrode, respectively. When the voltage E_s is linearly related to the pulse duration $\tau^{1/2}$ (Figure 5B,E), according to Fick's second law of

diffusion, the diffusion rate of sodium ion (D_{Na}) and potassium ion (D_{K}) can be calculated as follows⁹:

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2 \left(\tau < \frac{L^2}{D} \right), \quad (1)$$

where m_B is the mass of the active material, V_m is the molar volume of the material, M_B is the molar mass of

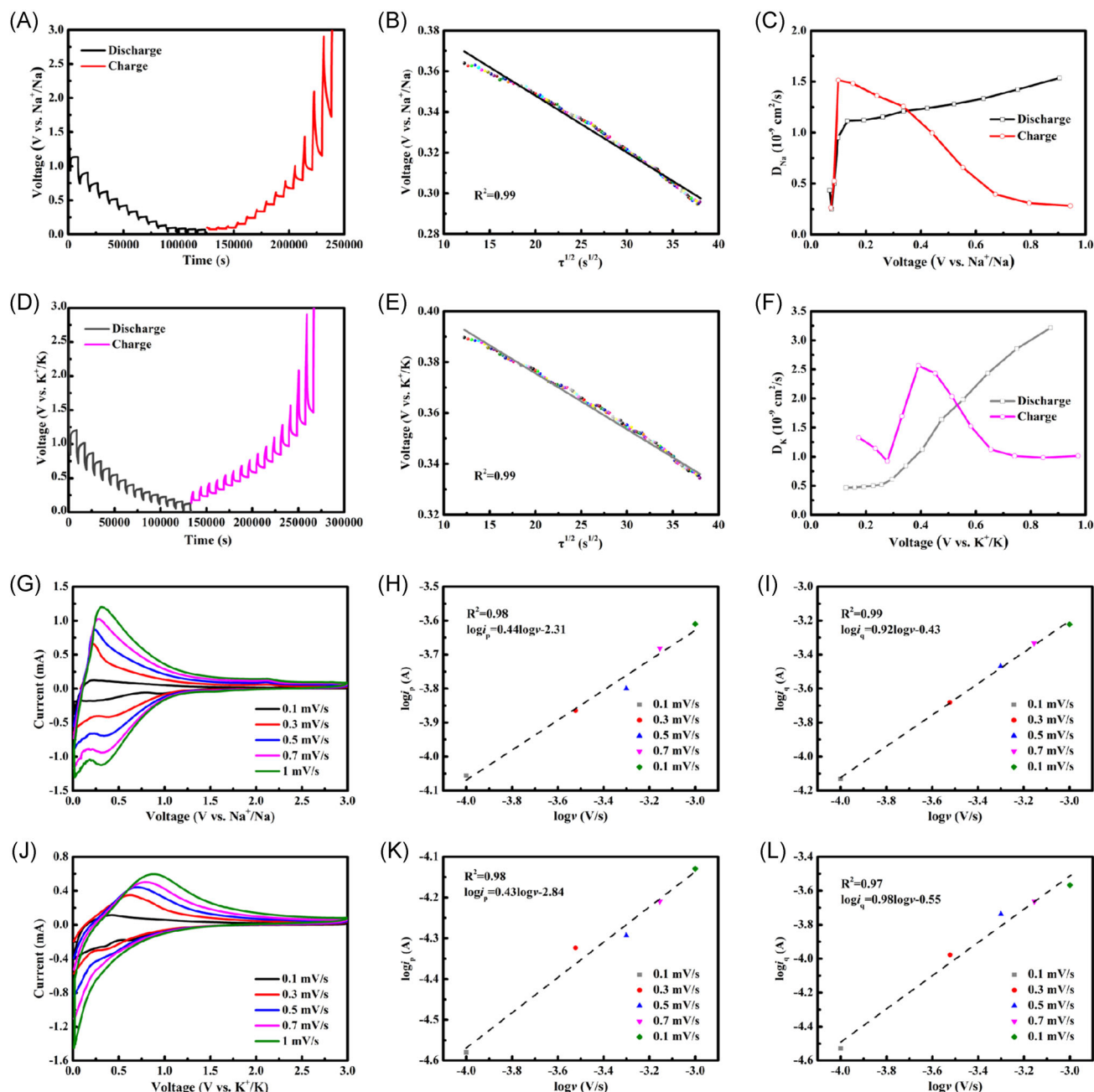


FIGURE 5 Galvanostatic intermittent titration technique potential profiles, potential versus $\tau^{1/2}$ plot with a linear regression line and the apparent alkali metal ion diffusion coefficients: (A–C) the CMGL-Na electrode and (D–F) the CMGL-K electrode. Cyclic voltammetry curves at different scan rates, $\log(i_p)$ versus $\log(v)$ and $\log(i_q)$ versus $\log(v)$: (G–I) the CMGL-Na electrode and (J–L) the CMGL-K electrode

the material, S is the geometric area of the electrode, τ is the pulse duration, ΔE_s is the steady-state voltage change value, ΔE_τ is the voltage change value during the pulse current application (ΔE_s and ΔE_τ can be determined from each current step of the GITT curves), and L is the average thickness of the electrode.

The curves of D_{Na} and D_K with voltage are shown in Figure 5C,F. Their shapes are quite different, indicating the presence of multiple sodium-/potassium-ion storage sites with different sodium-/potassium-ion-carbon binding energies in CMGL. For SIBs, D_{Na} gradually decreases as the voltage decreases. When the discharge depth increases, it decreases rapidly, and when the voltage reaches the cut-off value, D_{Na} increases slightly. During the charging process, the change of D_{Na} showed an increasing trend first and then decreased slowly. As it is known, insertion of an ion into the interlayer space inside graphitic microcrystallites is much more difficult than the adsorption on the surface active sites. Therefore, in the initial high-voltage range (slope region), sodium ion will preferentially occupy the surface active sites, and then it will be inserted into the graphitic microcrystallite layer at a lower voltage range, which corresponds to the quasiplateau region. However, during the insertion process of sodium ion, it is necessary to overcome the repulsive charge gradient from the previously bound sodium ion on the surface site, which will affect the migration rate of sodium ion. This also explains the rapid decrease of D_{Na} in the low potential range.³¹ According to the report, the inserted sodium ion will combine with graphitic carbon to form Na-GICs, which is a reversible structural phase transition process.³²⁻³⁴ At the same time, for PIBs, D_K gradually decreases with the decrease of voltage during the de-potassiation process, until it reaches 0.3 V, which corresponds to the inclined region. It is manifested by the adsorption characteristics of potassium ion on the surface active sites. When the voltage further decreases to the cut-off value, D_K is almost unchanged. According to the research of Alvin et al.,² in the voltage range of 0.3–0.0 V, the change of D_K in graphite is similar to that in hard carbon. As the smooth insertion of potassium ion in graphite has been confirmed, this indicates that it may be inserted into hard carbon. The stable D_K value in the process below 0.3 V may be caused by the low bond energy of potassium ion in the graphitic microcrystallite layer, which does not hinder its diffusion into the microcrystallite area. During the charging process, the repulsive insertion between potassium ion decreases as the number of adjacent potassium ion decreases, making D_K gradually increase. However, in the traditional view, potassium ion with a larger radius in the charge/discharge process diffuses much more slowly than sodium ion inside the material, but, in fact, D_K is

slightly higher than D_{Na} . One view is that due to the lower charge density of potassium ion, the diffusion rate is faster and the activation energy is lower. Another view is that the degree of ionization of potassium ion and sodium ion is different, and the degree of covalent bonding between them and the carbon structure site is also different.

As a kind of dynamic analysis technology, the CV curve test with different scan rates is also an effective method to characterize the storage behavior of sodium/potassium ion in the CMGL electrodes, as shown in Figure 5G,J. The relationship between the peak current (i) and the scan rate (v) in the curve can be expressed as follows⁹:

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

where a and b are the adjustable parameters related to the redox reaction mechanism. The b value can be determined by drawing a $\log(i)$ – $\log(v)$ curve. When the b value is close to 0.5, it means that the electrochemical reaction is a complete diffusion control process, that is, ion diffuses into the graphitic microcrystallite layer, and when the b value is close to 1, it means that the pseudocapacitance controlled by the surface is dominant, that is, the ion adsorption occurs on the surface active sites.³⁵

In the CV curves of SIBs, two current peaks were shown at ~0.15 and ~0.75 V, corresponding to the storage behavior characteristics of sodium ion in the quasiplateau region and the slope region, respectively. By increasing the scan rate, the calculated b values are 0.44 and 0.92 (Figures 5H and 5I), respectively. The CV curves of PIBs have two current peaks when the slope area is ~0.7 V and the quasiplateau area is ~0.3 V, and the calculated b values are 0.98 and 0.43 (Figures 5K and 5L), respectively. This once again indicates that for SIBs and PIBs, the capacity of the slope region is related to the ion adsorption on the surface active sites, whereas the capacity of the quasiplateau region is related to the ion insertion into the interlayer space inside graphitic microcrystallites.

As it is known, if a potassium ion with a larger radius is inserted in the graphitic microcrystallites, the microstructure of the material will expand. In situ XRD measurement of the interlayer spacing changes during discharging, which is the most direct evidence to prove the potassium storage mechanism. However, the crystallinity of CMGL is low and it is difficult to perform broad Bragg reflections. Therefore, this study used high-resolution in situ XRD technology to examine the structural changes during the potassiation/de-potassiation process to provide clearer evidence to support the “adsorption–insertion” model. Figure 6A shows the structure change in situ of the CMGL-K electrode during the discharge process. The

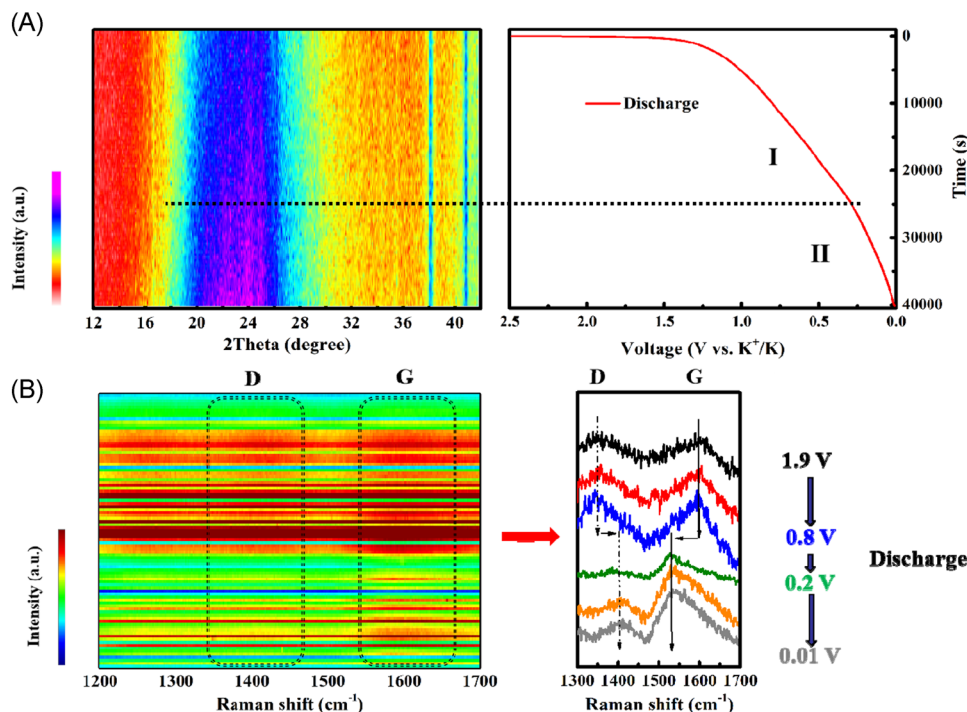


FIGURE 6 (A) In situ X-ray diffraction and (B) in situ Raman tests of the CMGL-K electrode during discharging

XRD mode is divided into two parts according to the galvanostatic discharge curve. Line segment I is the high-potential slope region and line segment II represents the low-potential platform region. It can be observed that there is no obvious peak movement and intensity fluctuation of line segment I. With the discharge depth continuing, the diffraction peak of line segment II appears to be slightly split, a part of the diffraction moves to a low angle, and a new diffraction peak is formed. The splitting and partial shifting of the diffraction peaks are due to the wide distribution of interlayer spacing in the material. The graphitic microcrystallites with a relatively wide interval can allow potassium ion to be inserted, resulting in a negative shift in Bragg reflection and a narrower interval. Some graphitic microcrystallites do not allow potassium ion to be inserted and their reflection peak remains at the initial position.^{21,24} Therefore, it can be concluded that the high-potential slope region represents the adsorption/desorption characteristics on the surface of the material, whereas the low-potential platform region belongs to the potassium-ion insertion/extraction in the graphitic microcrystallites interlayer. The CMGL-Na electrode has also been researched, but the effect is not obvious. It may be that the radius of sodium ion is smaller than that of potassium ion, and the structural change caused by the insertion of the graphitic microcrystallite layer is small.

In situ Raman spectroscopy has been proven to be an effective method in the research of ion insertion into the

carbon materials, which can provide information about the vibrations of atoms in crystals and molecules, and it is often used as a supplementary tool for XRD.³⁶⁻³⁸ From Figure 6B and Video S1, it can be found that the peak position of the G-band remains unchanged at the initial stage of the discharge, whereas the obvious shift occurs after 0.2 V. This is due to the fact that the inserted potassium ion increases the electron density on the graphitic microcrystallite layer and the electrons occupy the antibond π band, weakening the intralayer C-C bonds and resulting in the elongation of the C-C bond length, followed by a red shift of the G-band, which is consistent with the research results of lithium-ion intercalation between the graphitic microcrystallite layer of the mesocarbon microbeads.³⁹⁻⁴¹ Meanwhile, the shift of the G-band is continuous and there is no double peak formation, which means that there is no staged intercalation compound formation. However, the position of the D-band has a blue shift. Hardwick et al.⁴⁰ assumed that the D-band is composed of two components: ring breathing from edge plains of crystalline domains and ring breathing along the rigid cross-linkers.⁴⁰ The wavenumber peaks of these two components appear at different positions, which, as a result of some geometric constraints in the structure, may be caused by changes in the strength of weak intermolecular forces acting on the edge plains or differences in bond strength. When potassium ion is inserted between the graphitic

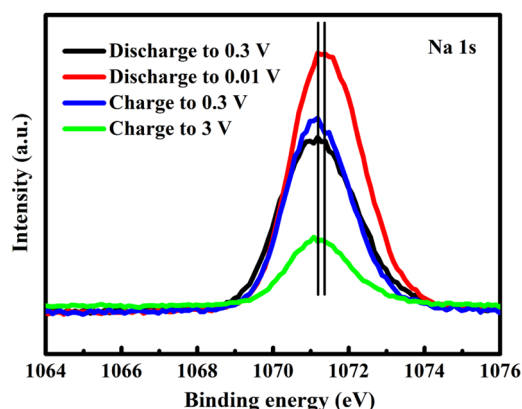


FIGURE 7 Na 1s X-ray photoelectron spectroscopy spectra for the CMGL-Na electrodes test at different cut-off voltages

microcrystallite layer of CMGL, the low wavenumber component of the D-band will disappear, which will shift the peak position. Moreover, previous research studies have shown that if an ion is inserted into various graphite materials, as the D-band contribution of the graphitic regions becomes forbidden, the I_D/I_G value should decrease during the potential extreme. In fact, for the potassium-ion insertion, the I_D/I_G value of CMGL is also significantly reduced. Therefore, it can be concluded that potassium ion is randomly intercalated between the graphitic microcrystallite layer of CMGL in the low-potential platform region without forming a segmented intercalation compound structure, which belongs to a single-phase intercalation mechanism.⁴²

Moreover, the different sodium storage processes will directly affect the chemical state of sodium elements. Therefore, XPS testing at different cut-off voltages can also be used to distinguish the storage form of sodium ion. Combined with the analysis of the galvanostatic charge/discharge curves, the research of Na 1s spectrum was selected for 0.3, 0.01, and 3 V during charging and discharging, as shown in Figure 7. When the CMGL-Na electrode is discharged to 0.3 V, a distinct spectral peak appears at the binding energy of 1071.2 eV, indicating that the sodium ion has successfully entered inside the electrode. With a sustained discharge to 0.01 V, the Na 1s peak shifts to 1071.4 eV, indicating a significant valence change in sodium. As the metal bond formed by the intercalation of sodium ion has a stronger binding energy than the surface adsorption of sodium ion, it further explains that the sodium storage in the low-potential platform region of the CMGL electrode belongs to the sodium-ion insertion into the interlayer of the graphitic microcrystallites.^{43,44} When the electrode is charged from 0.01 to 0.3 V, the binding energy of the Na 1s spectral peak is again transferred to around 1071.2 eV, indicating that this process has high reversibility. However, even if the electrode is charged to

3 V, there is no significant shift in the binding energy of the Na 1s spectrum, indicating that sodium does not produce a high valence state in the high-potential slope region and is more inclined to adsorption on the surface active sites. In addition, charging to 3 V still has a Na 1s peak, which proves that there is also a sodium-containing material on the surface sites, which can be explained as the SEI film formed by electrolyte decomposition; it is also the main reason for the generation of initial irreversible capacity.⁸

4 | CONCLUSIONS

In summary, a simple carbonization and pickling process was used to prepare CMGL in this study, which showed excellent electrochemical performance. For SIBs and PIBs, it exhibits a high specific capacity of 315 and 263.5 mAh/g at a current rate of 30 mA/g, respectively, and the capacity retention rates after 100 cycles are high. Surprisingly, the performance of PIBs is better than that of SIBs at a high rate. In addition, the electrochemical sodium/potassium storage mechanism was analyzed by GITT, CV, in situ XRD, in situ Raman spectroscopy, and XPS, and results show that the high-potential slope region represents the adsorption/desorption characteristics of sodium/potassium on the surface active sites, whereas the low-potential quasiplateau region is related to the ion insertion into the interlayer space inside graphitic microcrystallites. It can be believed that the facile preparation process and the outstanding electrochemical performance of the hard carbon anode can improve the rapid development of SIBs and PIBs, and the analysis of the energy storage mechanism also provides new research ideas for the development of more electrode materials.

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CONFLICT OF INTERESTS

The authors declare no conflict of interests.

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SUPPORTING INFORMATION

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