Toward High-Performance Capacitive Potassium-Ion Storage: A Superior Anode Material from Silicon Carbide-Derived Carbon with a Well-Developed Pore Structure

Jing Wu, Xiaxiang Zhang, Zheng Li, Chenfan Yang, Wenda Zhong, Wenlong Li, Chengzhi Zhang, Nianjun Yang, Qin Zhang,* and Xuanke Li*  

Potassium-ion battery (PIB) using a carbon-based anode is an ideal device for electrochemical energy storage. However, the large atomic size of potassium ions inevitably leads to huge volume expansion and the collapse of anodes, resulting in the severe capacity fading during the long-term cycling. Herein, silicon carbide-derived carbon (SiC-CDC) with a controllable pore structure is synthesized with a concise etching approach. It exhibits a maximum capacity of 284.8 mA h g⁻¹ at a current density of 0.1 A g⁻¹ after 200 cycles as well as a highly reversible capacity of 197.3 mA h g⁻¹ at a current density of 1.0 A g⁻¹ even after 1000 cycles. A mixed mechanism of the potassium storage is proposed for this prominent performance. The interconnected pore structure with a high proportion of mesopore volume provides abundant active sites for the adsorption of potassium ions, a shortened electrolyte penetration path, and enlarged accumulation space for potassium ions, eventually leading to facilitated capacitive potassium storage inside this SiC-CDC electrode. This work provides fundamental theories of designing pore structures for boosting capacitive potassium storage and unveils CDC-based materials as the prospective anodes for high-performance PIBs.

1. Introduction

With the rapid consumption of fossil fuels and aggravated environmental pollutions, the development of novel and efficient energy storage devices has been attracting tremendous interest, such as lithium-ion batteries (LIBs).[1–4] However, LIBs suffer from the future shortages of lithium resources. Alternative batteries based on earth-abundant metals like sodium (2.36 wt%) or potassium (2.09 wt%) thus become crucial and urgent.[5–6] It is known that the redox potential of the K⁺/K couple (~2.93 V vs standard hydrogen electrode (SHE)) is lower than that (~2.71 V vs SHE) of the Na⁺/Na couple. A potassium-ion battery (PIB) is then expected to have a wider voltage window and more importantly provide a higher energy density than a sodium-ion battery.[7,8] To construct a high-performance PIB, a suitable anode is highly demanded. Various carbon-based materials have been frequently utilized as the anode of the PIBs, including expanded graphite,[9] hard carbon,[10] soft carbon,[11] and short-range mesoporous carbon.[12] More recently, a steady potassium intercalated graphite (KC₈) came into the spotlight for the fabrication of PIBs,[13] since it exhibits a theoretical capacity of 279 mA h g⁻¹ and its potassiation/depotassiation in graphite is reversible. However, the large atomic size of K⁺ inevitably leads to huge volume expansion (~61%) and the collapse of graphite in the repeated charge–discharge processes, eventually leading to severe capacity fading during long-term cycling.[14,15] To construct a high-performance PIB with aid of KC₈, the design and synthesis of novel carbon anodes, especially with controllable pore structures are thus highly demanded.

Up to date, carbon anodes with expanded interlayer space between graphite (002) planes[16] and rich defects (e.g., heteroatom) have been utilized for the construction of PIBs. However, those with controllable pore structures appear more effective for the fabrication of high-performance PIBs.[17–20] This is because a carbon anode with an optimal pore structure reduces the diffusion distance of K⁺ ions, eventually boosting the potassium storage inside carbon anodes. Meanwhile, the introduction of a porous structure into a carbon anode leads to a surface-induced capacitance. Such a particular trait that
belongs to a supercapacitor further optimizes the rate capability of a PIB with high reaction dynamics.\cite{21,22} Among various kinds of porous carbon materials, carbide-derived carbon (CDC) that appears as a new category in recent decades is expected to be a very promising anode for the construction of high-performance PIBs. This is because CDC exhibits a high specific surface area (SSA) and a well-controlled pore structure (e.g., size, uniformity/distribution of these pores). Moreover, it can be facilely synthesized by means of selective removal of noncarbon species from a carbide precursor with a halogen molecule.\cite{23} Although CDC has been widely applied as the electrode material for the formation of electrochemical double-layer capacitors,\cite{24} lithium–sulfur batteries,\cite{25} and for oxygen reduction reaction,\cite{26} the application of CDC as the anode for the construction of high-performance PIBs is still missing in the literature. The storage mechanism of potassium ions in a CDC-based anode has not been clarified up to now.

Therefore, the design and synthesis of a CDC-based anode and its further application for the PIB construction have been conducted. In this work, silicon carbide-derived carbon (denoted as SiC-CDC) is synthesized though thermal removal of Si from the precursor of silicon carbide. To tune the pore structure of a SiC-CDC anode, the precursor is etched at disparate temperatures (e.g., 800, 900, and 1000 °C). These as-synthesized SiC-CDC anodes are named as SiC-CDC-800, SiC-CDC-900, SiC-CDC-1000 throughout the whole text. They own well-controlled pore structures and large SSAs. With their mesopore-induced structures, capacitive storage of potassium ions is then realized on these SiC-CDC anodes at high reaction dynamics.\cite{27,28} Meanwhile, more accumulation space and active sites exist on these SiC-CDC anodes for the reversible adsorption and desorption of potassium ions. The storage capacity of K+ ions is thus synergistically enhanced in these SiC-CDC anodes. Among them, the SiC-CDC-900 anode owns a higher proportion of mesoporous volume and a more appropriate SSA, eventually delivering an outstanding capacity and optimized reaction kinetics for the storage of potassium ions. For example, it features a capacity of 284.8 mAh g−1 at a current density of 0.1 A g−1 even after 200 cycles. When the current density increases to 1.0 A g−1, its capacity is still highly reversible and maintained at 197.3 mA h g−1 even after 1000 cycles. Consequently, this work explores successfully novel applications of CDC in the fields of electrochemical energy storage, namely the construction of high-performance PIBs.

2. Result and Discussion

Figure 1a shows the scanning electron microscopy (SEM) image of a SiC-CDC-900 anode. The spherical particles are interlinked with each other and constitute a characteristic aerogel-like framework. Many aperto vesicular textures are observed explicitly. However, the imperceptible nanopores derived during the etching process are not visible. The SiC-CDC-800 and SiC-CDC-1000 anodes feature analogical porous structures (Figure S1, Supporting Information).

X-ray diffraction (XRD) and Raman spectroscopy were then utilized to characterize three SiC-CDC anodes. The XRD
patterns of the SiC precursor reveal its cubic structure (Figure S2, Supporting Information). The XRD patterns of three SiC-CDC anodes (Figure 1b) have two broad diffraction peaks located at 25° and 43°, which belong to (002) and (101) planes of hexagonal graphite (JCPDS card no.41-1487), respectively. An increase of the etching temperature leads to narrowing the width of (002) peak, an indication of more graphite layers at a higher etching temperature. On the other hand, the width of (101) peak appears to be distinctly necking, suggesting the formation of larger-sized graphite sheets at a higher etching temperature.

The Raman spectra of three SiC-CDC anodes are shown in Figure 1c. Two broad peaks are centered at 1353 cm⁻¹ (D-band) and 1567 cm⁻¹ (G-band), corresponding to highly disordered CDC and other amorphous carbons, respectively. It is known that the intensity ratio of these peaks (so-called as ID/IG) represents the disorder degree of these carbons.[29] Clearly, the rise of the etching temperature decreases the amount of defective structures inside the SiC-CDC anodes, since ID/IG is reduced from 0.86 to 0.68 (Figure 1d) when an etching temperature of 800 and 1000 °C is applied, respectively. Such defectless SiC-CDC anodes are more favorable for potassium storage.[30]

The geometric properties of these SiC-CDC anodes were analyzed using N₂ adsorption (Figure 1e). Their N₂ adsorption–desorption isotherms exhibit a combination of type I (a unique trait of micropores) and type IV (typical peculiarity of mesopores).[31] The enlarged N₂ adsorption–desorption isotherms for three anodes (Figure S3, Supporting Information) have analogical hysteresis loops and crescent shapes. Since they are fully consistent with the ideal H3 type curve of mesopores, slit holes/pores are expected to be formed in three SiC-CDC anodes.[32,33] Consequently, the etching temperature has a very minor impact on the shape and sizes of the as-formed pores inside the SiC-CDC anode. In other words, all three anodes feature a similar porosity. Using the Brunauer–Emmett–Teller (BET) model, the SSAs of three anodes were calculated (Table 1). A SiC-CDC-900 anode features the bigger SSA, mesopore volume (Vmeso), total volume (Vtotal), and contribution of a mesopore volume to the total volume (Cmeso). By contrast, SiC-CDC-800 anode possesses the smallest SSA and the minimum Vmeso. It is known that the SSA and Vtotal of the CDCs dramatically increase with an increase of the etching temperature since a higher etching temperature leads to a faster and more efficient etching reaction. When the etching temperature is higher than a critical point, the destruction of graphite layers (or partial collapse of the graphite apertures) occurs, originated from a thermal stress effect under these conditions.[34] This is exactly the situation of the SSA for the as-fabricated SiC-CDC-900 anode. According to their pore sizes and Vmeso, the SiC-CDC-800, SiC-CDC-900, and SiC-CDC-1000 anodes can be categorized into the mesopore–micropore mixed, mesopore-dominated, and micropore-dominated materials, respectively. Note that, mesopores inside a CDC anode are potentially the real active sites for potassium adsorption–desorption.[35] Moreover, they facilitate the diffusion of electrolyte ions,[36] resulting in a broadened transmission depth of K⁺ ions (or additionally introduced capacitance from K⁺ ions during the process of potassium storage).

The pore structures (e.g., size distribution) inside three anodes were further examined (Figure 1f). With aid of the density functional theory method, the calculated pore sizes for three anodes are ranged from 0.52 to 2.71 nm, clarifying the coexistence of hierarchical mesopores and micropores inside three SiC-CDC anodes. The sizes of these pores are much larger than the radius (0.331 nm) of a hydrated K⁺ ion.[37] Therefore, the dynamically transmitted speed and depth of K⁺ ions are expected to be enhanced inside these SiC-CDC anodes. Among them, a SiC-CDC-900 anode with a higher SSA (2205 m² g⁻¹), a larger Cmeso (about 73.3%), a bigger Vmeso or amounts of active sites (1.46 cm³ g⁻¹) will be the best anode for the PIB construction.

High-resolution transmission electron microscopy (HRTEM) was then employed to check the crystal structures of these SiC-CDC anodes. The SiC-CDC-800 anode is presented as sphere-like particles (Figure 2a), similar to the SiC-CDC-900 and SiC-CDC-1000 anodes (Figure S4, Supporting Information). The SiC-CDC-800 anode is composed of homogeneous amorphous carbon (Figure 2b). Such an interconnected network which features like a shape of crooked worms results from the formation of micropores upon etching,[33] enabling this SiC-CDC for accumulating efficiently K⁺ ions.[38] The porous region (amorphous carbon) on the surface of SiC-CDC-900 anode is less homogeneous (Figure 2c,d). Within the porous domains, graphitic layers are stacked into a short range. The SiC-CDC-1000 anode consists of distinct graphitic fringes and amorphous carbon (Figure 2e,f). In other words, noticeable graphitization occurs on the SiC-CDC-1000 anode. Estimated from the TEM image of the SiC-CDC-1000 anode, the lattice fringe on the SiC-CDC-1000 anode is 0.335 nm (Figure S5, Supporting Information), in accordance with the (002) plane of graphite. It has to be pointed out here that the graphite with such narrow interlayer distances is not suitable for the storage of potassium ions since there is no adequate space to be afforded for rapid potassiation/depotassiation processes.[16,39]

| Anode       | SSA_{bet} [m² g⁻¹] | Vmeso [cm³ g⁻¹] | Vtotal [cm³ g⁻¹] | Cmeso [%] |
|-------------|---------------------|-----------------|------------------|-----------|
| SiC-CDC-800 | 1453                | 0.59            | 0.95             | 62.1      |
| SiC-CDC-900 | 2205                | 1.07            | 1.46             | 73.3      |
| SiC-CDC-1000| 1837                | 0.67            | 1.18             | 56.8      |

*Mesopore volume (2 nm < d < 50 nm), estimated by Barrett–Joyner–Halenda method; ¹Total volume calculated at P/P₀ = 0.98; ²Contribution of a mesopore volume to the total volume, calculated from Vmeso/Vtotal.
Figure 2. TEM images of a,b) SiC-CDC-800, c,d) SiC-CDC-900, and e,f) SiC-CDC-1000 anodes.

Figure 3. Performances of SiC-CDC anodes in the half cells of PIBs: a) cycling performance at a current density of 0.1 A g\(^{-1}\) and b) rate performances of three anodes, c) charge–discharge profiles at a current density of 0.1 A g\(^{-1}\), d) CVs, e) long cycling performance at a current density of 1 A g\(^{-1}\) (the first twenty cycles at a current density of 0.1 A g\(^{-1}\)), and f) rate performances of the SiC-CDC-900 anode in comparison with those reported carbon-based anodes for PIBs\([16,43–46]\). The inset in (c) is a magnifying region of the discharge process.
consume a large amount of electrolyte, leading to the formation of a solid–electrolyte interface (SEI) layer.

The rate performances of three anodes were then investigated (Figure 3b). The discharge capacity of the SiC-CDC-900 anode is maintained at 289.9 mA h g$^{-1}$ at a current density of 0.1 A g$^{-1}$, or at 197.3 mA h g$^{-1}$ at a current density of 1.0 A g$^{-1}$. When the current density is set back from 1.0 to 0.1 A g$^{-1}$, the capacity still reaches 285.3 mA h g$^{-1}$, an indication of the superior reversibility (98.4%) of a SiC-CDC-900 anode for the storage of potassium ions. By contrast, the SiC-CDC-800 and SiC-CDC-1000 anodes show relatively inferior rate performances. At a current density of 1.0 A g$^{-1}$, they are only 112.4 and 78.4 mA h g$^{-1}$, respectively. Such outstanding rate performance of the SiC-CDC-900 anode originates from its unique mesopore-dominated pore structure, its more appropriate SSA, and its larger $V_{meso}$, when compared with other two SiC-CDC anodes. In more details, these features of the SiC-CDC-900 anode provide more possible reactivity sites or channels to ensure electrolytes, ions, electrons to be accumulated during the charge–discharge processes.

Superior reaction dynamics ensure electrolytes, ions, electrons to be accumulated during the charge–discharge processes. Under these conditions, the current (i) is assumed to submit a relation (power law) with the scan rate ($\nu$). The $b$ value which is used to describe various reaction kinetics during ion-storage process, can be determined from the slope of log(i) against log($\nu$). For example, the SiC-CDC-900 anode (Figure 4b) and for the SiC-CDC-800 and SiC-CDC-1000 anodes (Figure S6c, Supporting Information) are 0.86, 0.87, and 0.84, respectively. It is known when the $b$-value falls in the range of 0.5–1.0, the emergence of complex mechanism occurs on the anode during the K$^+$-storage process. Therefore, the superior K$^+$-storage behavior inside the SiC-CDC anode is determined by a complex mechanism, namely the combination of a diffusion-controlled process with a capacitive process.

To further differentiate such combined behavior, the separation of the related current response is possible to be conducted under a stationary potential (V) by use of the equation of $i = (V) = k_1V + k_2V^{3/2}$. Here, $k_1$ and $k_2$ denote the contribution ratios of a diffusion-controlled process and a capacitive process to the total current response.

Take the SiC-CDC-900 anode as an example (Figure 4c), it gives a capacitive contribution proportion of 47% at the scan rate of 0.2 mA s$^{-1}$, which gradually approaches 83% when the scan rate is increased to 10 mA s$^{-1}$; while the contribution proportion from the diffusion-controlled process reduces from 53% to 17%. For example, at a scan rate of 2 mA s$^{-1}$ (Figure 4d), a capacitive contribution proportion is 62% and the contribution proportion from the diffusion-controlled process is 38%. A high contribution ratio of the surface-driven behavior at different scan rates is attributed to a well-developed pore structure and an appropriate SSA of a SiC-CDC. Therefore, a capacitive process takes charge of this mixed mechanism during the K$^+$-storage process inside these SiC-CDC anodes. On the SiC-CDC-900 anode, K$^+$ adsorption and vibrat kinetics are much enhanced, leading to the PIB formation with the highest performance.

To interpret the mechanism of K$^+$ storage on the SiC-CDC anodes, two specific K$^+$-storage mechanisms are proposed (Figure 5a): potassiation and adsorption. With respect to
potassiation, it is an electrochemical process that is executed inside the graphitic layers. During such a process, a stage-1 $K^+$ intercalation compound ($KC_8$) is gained.\cite{43} For example, the potassiation is clearly seen on the SiC-CDC-900 anode. A pronounced XRD pattern of $KC_8$ is noticed after the potassiation state of the SiC-CDC-900 anode at 0.01 V (Figure S7, Supporting Information). This pattern totally disappears when a depotassiation state is applied at 3.0 V. The reaction equation of potassiation on the SiC-CDC anode then follows the equation of $8C + K^+ + e^- \rightleftharpoons KC_8$. In other words, potassium ions are speculated to intercalate and deintercalate into/out of the SiC-CDC anode. As for adsorption, it refers to the reversible adsorption of $K^+$ ions on the SiC-CDC anode. For such a process, the anode with an appropriate SSA and an interconnected pore structure are conducive. For example, the coexistence of micropores and mesopores improves the wettability of the SiC-CDC anode, which is in turn in favor of the adequate utilization of its high accessible surface.

To explain the best performance of the SiC-CDC-900 anode for the PIB construction, the diffusion and adsorption processes of $K^+$ ions inside three SiC-CDC anodes are illustrated in Figure 5b. As discussed in Table 1, the SiC-CDC-1000, SiC-CDC-900, and SiC-CDC-800 anodes belong to the mesopore–micropore mixed, mesopore-dominated, and micropore-dominated materials, respectively. The micropores inside the SiC-CDC-1000 anode, which are derived from the continuous etching procedure, assure the spaces for the accumulation of abundant $K^+$ ions and electrons. Although the micropore-dominated SiC-CDC-1000 anode is equipped with a high SSA, it lacks active sites. An obstacle of $K^+$ transportation thus occurs via a fashion of separately squeezing into confined porous channel. Differently, the mesopores inside the SiC-CDC-900 anode can not only serve more active sites for reversible adsorption of potassium ions, but also introduce a higher contribution proportion, which is offered by capacitance behavior of potassium ions on this anode. Moreover, these mesopores shorten the effective transmission distance/path and speed up the diffusion of $K^+$ ions. With an appropriate SSA and a highest $V_{meso}$ among the three SiC-CDC anodes, a larger amount of electrolyte ions is thus accumulated on the surface of the SiC-CDC-900 anode. Meanwhile, an efficient transfer of $K^+$ ions inside the porous channel is possible to be realized and a vibrant capacitance-dominated reaction dynamic is assured.\cite{51} For example, the SiC-CDC-900 anode owns the smallest charge transfer resistance among the three anodes (Figure S8, Supporting Information). Under the situation of sufficient accessible surfaces and adequate active sites for the adsorption of $K^+$ ions, the capacitance-dominated potassium storage is thus boosted.\cite{52,53} Hence, the mesopore-dominated SiC-CDC-900 anode is the best for PIB construction. On other hand, a SiC-CDC-800 anode does possess simultaneously micropore and mesopore. However, its smaller $V_{meso}$ than that of a SiC-CDC-900 anode make it exhibit worse performance than a SiC-CDC-900 anode for the PIB construction.
3. Conclusions

Three SiC-CDC materials with different pore structures have been synthesized by means of etching SiC precursors at different temperatures. A mesopore-dominated SiC-CDC anode synthesized at an etching temperature of 900 °C is the best for the construction of high-performance PIBs, including a high and stable capacity, a fast charge/discharge rate, and a nearly 100% coulometric efficiency. Such an outstanding performance originated from an appropriate SSA of this SiC-CDC anode, its high mesoporous volume, its large number of active sites for the adsorption of K⁺ ions. A surface-controlled capacitive potassium-storage mechanism is proved. More importantly, the performance of these CDC-based PIB anodes is much superior to that of other reported carbon-based anodes. Future utilization of these CDCs as the anodes for the storage of other metal ions is worth to be conducted. In summary, the design and synthesis of such well-developed pore structures is useful to explore the applications of CDCs such as for potassium storage with high performance, as well as to reveal energy storage mechanisms of these CDCs. Therefore, the strategies proposed in this work pave new ways to construct high-performance PIBs as well as to utilize these novel CDC materials as the anodes for the formation of other alkaline-metal-ion batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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