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Silicon oxycarbide produced from silicone oil for high-performance anode material in sodium ion batteries

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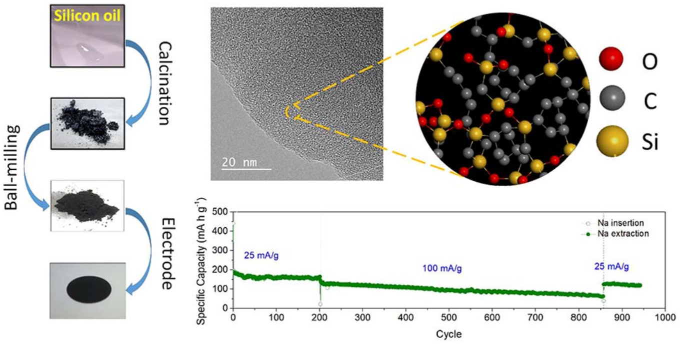
HIGHLIGHTS

- Silicon oxycarbide was synthesized using simple pyrolysis of low-cost silicone oil.
- Stable capacity of 160 mAh g^{-1} for 200 cycles was achieved as an anode in NIBs.
- Excellent cyclability of 0.09 mAh g^{-1} decay/cycle for 650 cycles was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Sodium ion batteries (NIBs) have gained considerable attention for large-scale energy storage applications because of the lower cost and higher abundance of Na than Li. In this study, we demonstrate that silicon oxycarbides (SiOCs), in which free carbon phases are imbedded in amorphous glassy SiO_xC_y phases, can be promising candidates as anodes for NIBs. The SiOC samples were synthesized by the pyrolysis of low-cost silicone oil in a H_2/Ar flow condition. When tested as an anode in NIBs, the SiOC sample calcined at 900 °C exhibited an excellent reversible capacity of 160 mAh g^{-1} at 25 mA g^{-1} after 200 cycles and a high rate performance of 62 mAh g^{-1} at 800 mA g^{-1}. More importantly, the SiOC electrode exhibited an excellent long-term cycling performance of 0.09 mAh g^{-1} decay per cycle for 650 cycles. The electrochemical properties of SiOC in an NIB were compared with those in an LIB to gain an insight into its ion storage mechanism. The effects of calcination temperature, calcination time, and ball milling time on the physicochemical and electrochemical properties of the SiOC electrode are discussed.

1. Introduction

Because of the current global warming crisis and depletion of fossil fuels, the use of clean and renewable energy sources, such as wind and solar power, has received considerable attention. To compensate for the intermittent power production of renewable sources, it is essential to develop large-scale energy storage systems. Even though lithium ion batteries (LIBs) are the current choice for electrical energy storage in portable electric devices and electric vehicles, the high cost, limited resources, and non-uniform terrestrial distribution of lithium is a major

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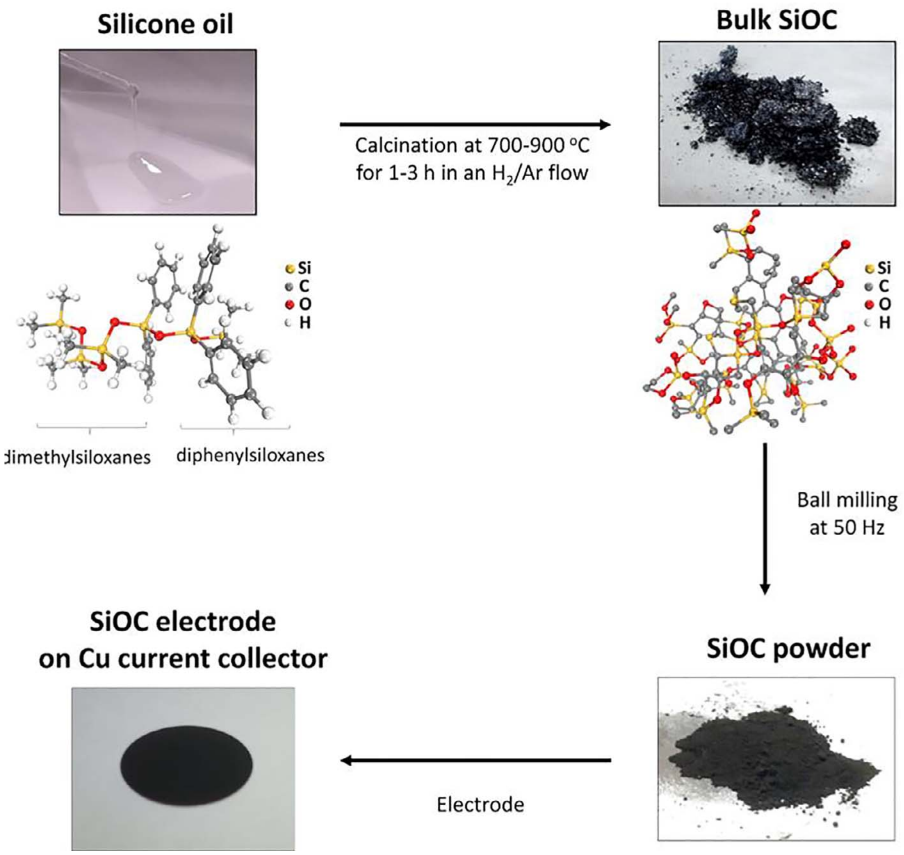

Scheme 1. A schematic of the synthesis procedure of SiOCs from silicone oil.

concern in developing grid-scale electrical energy storage systems. Room-temperature sodium ion batteries (NIBs), which employ sodium ions as the energy carriers, are one of the most promising alternatives to LIBs because of the wide distribution and global availability of low-cost sodium [1–4]. However, the large radius of Na^+ (0.98 Å) as compared to Li^+ (0.69 Å) requires the development of new design concepts for electrode materials [5]; for example, graphite, which is a commercial electrode material for anodes in LIBs with a theoretical capacity of 372 mAh g^{-1}, cannot uptake a large amount of Na in its interlayer spaces because of the large ionic radius of Na [6,7]. Another example is silicon; the preferential alloying reaction between Si and Li can result in an outstanding theoretical capacity of 4200 mAh g^{-1} when Si is used as an anode in LIBs. However, reversible sodium ion capacity in a typical silicon anode has been remained unsatisfactory [8,9] except for amorphous silicon [10] and Si/carbon composite with a yolk-shell structure [11]. Therefore, to meet the growing demands for large-scale energy storage systems, it is critical to develop a low-cost, safe, and high energy density electrode material for NIBs.

Recently, silicon oxycarbides (SiOCs), which comprise of a glassy silicon oxide phase (SiO_xC_y) and a free carbon phase (C_{free}), are being considered as promising alternatives to graphite in LIBs because of their high reversible capacity in the range of 500–1000 mAh g^{-1} upon cycling and low discharge voltage profiles below 0.5 V, which are beneficial for the development of high energy density anode materials [12–22]. However, the lithium storage mechanism in SiOCs is still a subject of ambiguity; the interstitial spaces or edges of graphene layers in the free carbon phase (C_{free}), the glassy SiO_xC_y phase, and the micropores could be responsible for the storage of lithium ions [12–14,21,23]. Various types of SiOC precursors including siloxane [17,20,22], polysiloxane [13,14,19,21], polysilane [12,16], and silicone oil [15] have been used to control the relative content of free carbon phase to glassy SiO_xC_y phase ($x + y = 4$) and the textural and morphological properties of SiOCs to enhance Li ion storage properties.

Although the use of SiOC as an anode in LIBs has been widely investigated, there are only a few studies on its potential as an anode in NIBs [16,24]. Furthermore, some contradictory results have been reported previously. Weinberger et al. produced SiOCs using a sol-gel method using phenyltriethoxysilane and tetraethoxysilane as the precursors [16]; at 25 mA g^{-1}, spherical $SiC_{0.3}O_{1.4} + 2.89C_{free}$ particles with a carbon content of 41 wt% delivered an initial discharge capacity of 188 mAh g^{-1} with an initial coulombic efficiency (CE) of 47% and a reversible discharge capacity of 150 mAh g^{-1} at 40 cycles. On the other hand, bulk $SiC_{0.34}O_{1.31} + 3.49C_{free}$ particles with a higher carbon content of 46 wt% exhibited a very low initial discharge capacity of 83 mAh g^{-1} at 25 mA g^{-1}. Kaspar et al. reported that the presence of SiOC had a detrimental effect on the Na ion insertion/extraction in the hard carbon phase [24]. As the C_{free} content decreased from 100 wt% to 68.7 wt%, the reversible discharge capacity after 50 cycles decreased significantly from 192 mAh g^{-1} to 42 mAh g^{-1} at 37 mA g^{-1}. In addition to these contradictory results regarding the effect of SiOC phase on Na ion uptake, the Na ion storage mechanism in SiOC has not been discussed in detail.

In this study, SiOCs were synthesized using silicone oil—a commercially available low-cost precursor—using a simple pyrolysis technique in H_2/Ar flow conditions and the electrochemical performance of SiOCs as anodes in NIBs was analyzed. The silicone oil used in this study was a copolymer of poly(dimethylsiloxane) and poly(methylphenylsiloxane). Because of its non-toxic and environmentally benign nature as well as high thermal and chemical stability, silicone oil is widely used in various applications, including personal care items and cosmetics. The chemical compositions and morphologies of the synthesized SiOC samples were controlled by adjusting the calcination temperature and ball milling time. The electrochemical properties of the SiOC anodes in NIBs were characterized using galvanotactic charge-discharge tests,