



Nanoporous hard carbon anodes for improved electrochemical performance in sodium ion batteries



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ABSTRACT

The porosity and morphology of sucrose-based hard carbon (SHC) was regulated by varying the amount of bicarbonate salts added during a simple two-stage sintering process. During the first-stage thermal treatment of sugar at 200 °C, CO₂ liberated from bicarbonate contributed to the pulverization of particles and to the formation of submicron-sized pores. Na₂CO₃ entrapped in a precursor matrix also released CO₂ during the second-stage sintering at 850 °C, producing nanometric pores (ca. 10 nm in diameter). The excessively high content of bicarbonates, however, resulted in paper-thin graphitic layers with no submicron-sized pores. These dual roles of bicarbonates produced nanoporous SHC (NSHC) with the submicron-to-nano-sized pores and the largest surface area that was possible for a specific bicarbonate concentration. The optimal nanoporosity of NSHC lent itself to a sharp increase in reversible capacity. Reversible capacity of 324 and 289 mA h g⁻¹ were obtained for the first and 100th cycles at 20 mA g⁻¹, in contrast to 251 and 213 mA h g⁻¹, respectively, for SHC. The rate capability of NSHC also was enhanced due to a substantial decrease in the charge transfer resistance and a 5-fold increase in the Na⁺ diffusion coefficient.

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1. Introduction

Rechargeable Li ion batteries (LIBs) are an efficient energy storage system that is an industry standard due to high energy density and extended cyclic life [1–3]. Despite these advantages, the extensive use of Li ion batteries in large-scale systems is unrealistic because of the limited amount of lithium as a natural resource [4]. In this regard, ambient temperature sodium ion batteries (SIBs) have come to the fore as an attractive alternative for energy storage in the past few years [5–8]. Sodium is naturally abundant and environmentally benign. SIBs and LIBs share many fundamental aspects of chemistry and technology. The size differences between the two ions (0.076 nm for Li⁺ and 0.102 nm for Na⁺), however, limits the material compatibility. This problem becomes more pronounced when carbonaceous materials such as graphite are used as anodes in SIBs. Recently, Wen et al. attempted to solve this issue by using expanded graphite, which had an enlarged interlayer distance of 0.43 nm with a retained long-range order [9]. The expanded graphite delivered a relatively high reversible capacity of 284 mA h g⁻¹ at a current density of 20 mA g⁻¹ when used as an anode in SIBs. In general, however,

the intercalation of Na⁺ into graphitic domains is known to be energetically unfavorable [10,11].

In this regard, much effort has been devoted to the development of porous carbonaceous materials for high-capacity anodes in SIBs [12–16]. The regulation of nanoparticle morphology and the introduction of nanoporosity are common strategies to accomplish highly reversible Na⁺-storage via artificially tailored nanopores [10,11]. Various types of carbonaceous materials such as hollow nanospheres [13], hollow nanowires [14], and hierarchically porous nanoparticles [16] have been reported. These materials exhibited the improvement of rate capabilities, but showed only similar, or inferior, reversible capacities compared with pristine hard carbon. The as-prepared hard carbon normally delivers capacities of ca. 200–250 mA h g⁻¹ [17,18], although there is at least one report of a capacity of ca. 300 mA h g⁻¹ with post-treated hard carbon [19]. The effect of increasing the nanoporosity in hard carbon was systematically studied by Bommier et al., wherein they addressed the inverse relationship of pore volume and surface area to the reversible capacity for Na⁺ ion storage [20]. The porosity of hard carbon was increased through activation in a CO₂ flow at various sintering temperatures. This process consumes a part of the solid carbon thus creating pores in the structure, which is similar to an etching process.

The lack of remarkable improvements in Na⁺-storage capability via nano-structuring and the inverse relationship between pore

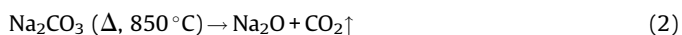
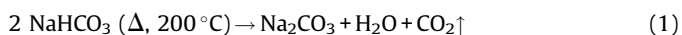
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volume and reversible capacity, suggests that the optimization of a nanoporous architecture is crucial in order to obtain highly efficient nanoporous hard carbon. In the present work, we apply bicarbonates to modify the nanoporosity of hard carbon and gain significant improvement in the electrochemical properties of hard carbon. The complicated role of bicarbonates in nanopore formation during sintering results in the highest electrochemical performance using a medium level of bicarbonates.

2. Experimental

2.1. Synthesis of SHC and NSHC

All chemicals were of high purity and were obtained from Aldrich, USA, unless otherwise noted. For the synthesis of NSHC, 6.0 g of table sugar (commercial grade) was dissolved in 25 mL of DI water in a 600 mL glass beaker. Various amounts of sodium bicarbonate (0.25, 0.5, 1.0, and 2.0 g) were added to the sugar solution and stirred for 10 min. Hereafter, the samples will be referred to as NSHC-2.5, NSHC-5, NSHC-10, and NSHC-20, respectively. The glass beaker was placed over a silica support in a muffle furnace preheated to 180 °C (The beakers must not be placed directly in contact with the floor/wall of a muffle furnace, which would otherwise lead to the ignition of molten sugar during heating). The temperature was raised stepwise from 180 to 300 °C (20 °C per 30 min) and finally to 400 °C. The temperature was maintained at 400 °C for an additional 2 h. The stepwise increment in the temperature was crucial for an even distribution of heat within the reaction mixture. A rapid increase of the furnace temperature led to inhomogeneous heating that resulted in irregular swelling and an eventual ignition of the samples. The precursor was pulverized and subjected to a quick wash in a 10 wt% HCl solution. The precursor was centrifuged and washed with DI water until the pH of the supernatant reached ca. 6.5. The precursor was dried and sintered at 1200 °C in a tube furnace for 6 h (heating and cooling rate of 2 °C min⁻¹). The final product was washed again with 10 wt% HCl and DI water to remove the Na₂O. The synthetic procedure is summarized in [Scheme 1](#). The thermal decomposition of NaHCO₃ proceeded via a two-step process as shown below.



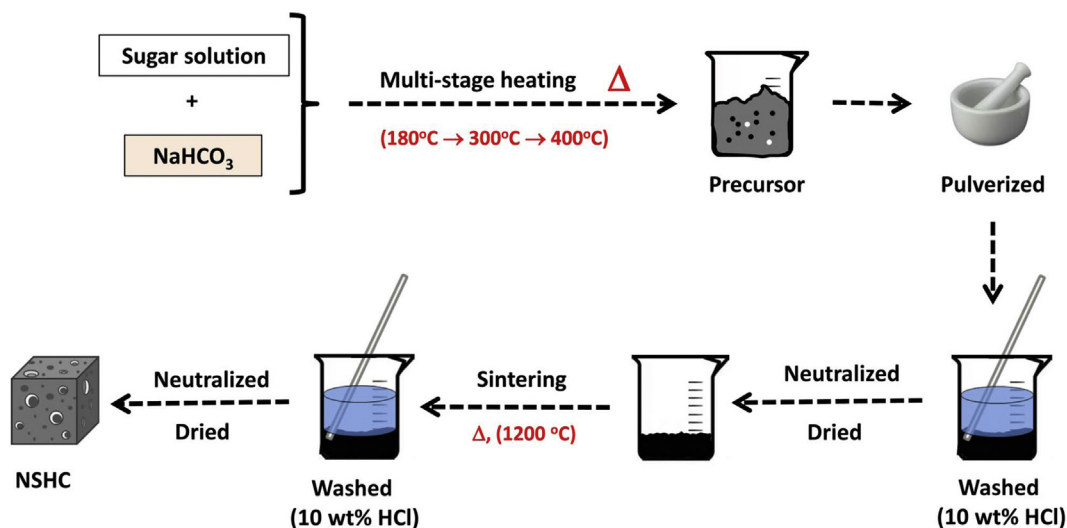
The liberation of CO₂ during the reaction (1) was believed to affect the macroscopic characteristics of NSHC such as particle size and shape. The reaction (2), on the other hand, seemed to control the formation of nanometric voids, which were crucial for a high degree of Na⁺-storage. SHC was synthesized under similar conditions without the addition of bicarbonate salts.

2.2. Characterizations of SHC and NSHC

XRD patterns were recorded using a Rigaku ULTIMA 4 equipped with Cu K α radiation at a scan rate of 5° min⁻¹. XPS was carried out using a Thermo Fisher (K-Alpha) electron spectrometer with an Al K α X-ray source (excitation energy = 1486.6 eV). Field emission scanning electron microscope (FESEM) investigations were carried out using a FESEM, Hitachi S4800. Tap density experiments were performed by equally tapping the samples of the same mass in PVC tubes of the same dimension. The volume was measured using high-precision equipment.

2.3. Cell fabrication and electrochemical tests

The coin cells (CR 2032) were of a Na/electrolyte/NSHC (or SHC) configuration, wherein the separator was sandwiched between two electrodes, and were assembled in an Ar-filled glove box (O₂, H₂O < 1 ppm). The anode electrode was a mixture of 80 wt% NSHC (or SHC), 10 wt% poly(vinylidene fluoride), and 10 wt% acetylene black (MTI, USA). The slurry was coated on a Cu foil and punched into the required size after drying and roll pressing (film thickness = ca. 10 ~ 12 μm , active mass = ca. 0.0025 g). The electrolyte was 1.0 mol dm⁻³ NaClO₄ dissolved in a mixed solvent of equal volumes of ethylene carbonate (EC) and dimethyl carbonate (DEC). Galvanostatic C/D cycle tests were performed using an automatic WBCS 3000 battery cyler (WonATech) in a potential range of 0.01–2.0 V vs. Na/Na⁺. The EIS spectra were obtained by applying a sine wave with an amplitude of 10.0 mV for frequencies ranging from 100 KHz to 0.01 Hz. The extraction of electrochemical parameters was performed using Zview software. For capacitance measurements, the three electrode cell configuration was used using 0.1 mol dm⁻³ aqueous Na₂SO₄ as the background electrolyte. The working electrode was fabricated by coating the slurry onto a stainless steel mesh electrode. A standard calomel electrode was used as the reference.



Scheme 1. Synthetic procedure of NSHC.

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