



Hydrogen-enriched porous carbon nanosheets with high sodium storage capacity



Dohyeon Yoon ^a, Dong Hyun Kim ^b, Kyung Yoon Chung ^b, Wonyong Chang ^b,
Seung Min Kim ^c, Jaehoon Kim ^{a, d, *}

^a Department of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^b Center for Energy Convergence, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 02792, Republic of Korea

^c Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Chudong-ro 92, Bongdong-eup, Wanju-gun, Jeonranbuk-do, Republic of Korea

^d Sungkyun Advanced Institute of Nano Technology, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

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ABSTRACT

A simple supercritical alcohol route was developed to fabricate hydrogen-enriched porous carbon nanosheets (H-PCNs). The as-prepared H-PCNs were tested as an anode active material for sodium ion batteries. Due to the unique hydrogen donation and alkoxylation ability associated with supercritical isopropanol, the hydrogen-to-carbon ratio of H-PCNs was as high as 2.3. The H-PCNs electrode exhibit an excellent reversible capacity of 300 mAh g⁻¹ at 50 mA g⁻¹ and remarkable cycling stability up to 2000 cycles at 1–5 A g⁻¹. A high rate-performance of 74 mAh g⁻¹ was also obtained at the high current density of 5 A g⁻¹. The excellent electrochemical performance of H-PCNs for Na ion uptake is attributed to the high hydrogen-terminated groups and large amount of defects on the carbon sheets. In addition, the large interlayer spacing (0.38 nm), high specific surface area (147 m² g⁻¹) and high porosity (58%) would also contribute to the high Na ion uptake.

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1. Introduction

Because of increasing concerns over global warming and the depletion of fossil resources, the use of clean and renewable energy sources, such as wind and photovoltaic power generation, and their grid utilization are currently receiving considerable attention. Large-scale energy storage systems (ESSs), which can integrate the intermittent energy productions of renewable resources into stable electrical grids, are some of the most promising candidates for effectively utilizing and distributing renewable energy. The successful realization of ESSs is highly dependent on the development of low cost, highly durable, safe, and efficient energy storage technologies. Although lithium ion batteries (LIBs) are the current technology of choice for ESSs, the increasing demand for large amounts of lithium, a minor metal species that is unevenly distributed on earth [1], is a major obstacle hindering the low-cost

realization of ESSs. The natural abundance and global availability of sodium have led to considerable interest in sodium ion batteries as low-cost alternatives to lithium ion batteries [2–6]. However, the volume of a Na ion is approximately 80% larger than that of a Li ion and, thus, most of the active materials that are suitable for Li ion insertion/deinsertion are not well suited to hosting Na ions. For example, graphite, a well-established material that is commercially used in LIBs, does not accommodate Na ions to any appreciable extent, likely because the interlayer spacing of graphite is not sufficiently large [7,8]. Therefore, the development of suitable anode active materials is crucial to the successful implantation of sodium ion batteries (NIBs).

Although a wide variety of potential candidates has been identified for use as cathode active materials in NIBs [9–12], very few materials have been shown to be practical for use in anodes. Of the various types of anode materials, such as TiO₂ [13,14], Na₂Ti₃O₇ [15], Na₃Ti₂(PO₄)₃ [16], Fe₃O₄ [17], Sn [18], and amorphous phosphorus [19,20], non-graphitic carbons are considered to be the most promising for practical use in NIBs because they are abundant, cost-effective, have low toxicities, and their Na storage mechanisms are similar to those observed in Li ion anode materials [8,21–33]. The

* Corresponding author. Department of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea.

E-mail address: jaehoonkim@skku.edu (J. Kim).

low Na ion uptakes and the rate capabilities associated with hard carbons [8,34–37] have been overcome using nanostructured and two-dimensional carbons; examples include porous carbon nanostructures [28–30,32,33], carbon nanofibers [21,23,26], carbon microspheres [25], reduced graphene oxides (RGOs) [31], hard carbon/carbon nanotube composites [27], carbon nanobubbles [24], and carbon nanosheets [22]. These works have successfully demonstrated that Na ion uptake and rate-performance can be increased substantially by combining the effects of graphene interlayer spacing dilation, pore structure and porosity adjustments, and the incorporation of heteroatoms (e.g., nitrogen doping). Reversible capacities of 100–290 mAh g⁻¹, at current densities of 25–100 mA g⁻¹, and improved room temperature rate capabilities have been reported for such carbon materials, as listed in Table S1. Overall, new types of carbon-based materials with better room temperature high-rate capacities and long-term cyclabilities are greatly needed.

A survey of the literature published on carbon-based materials for NIBs indicates that interlayer spacing, surface area, pore structure, and heteroatom doping are all important factors that contribute to battery performance [11]. However, although it is known that the presence of hydrogen-terminated groups in carbon-based materials enhance Li ion uptake significantly, by providing additional Li binding sites (Li–H–C interactions), to date, no attention has been paid to the role of hydrogen-terminated carbon in NIB anode materials [38–45]. For example, reversible capacity could be increased from 400 to 900 mAh g⁻¹ by increasing the H/C ratio from 0.05 to 0.4 [44]. If a Na ion storage mechanism that is analogous to the Li ion storage mechanism of non-graphitic carbon is assumed, this suggests that incorporating hydrogen-terminated groups into carbon-based materials could greatly enhance NIB performance [8]. In this context, with the goal of fabricating high-performance NIBs, herein, we develop a new strategy to incorporate sufficient numbers of hydrogen-terminated groups into porous carbon nanosheets to give a hydrogen-to-carbon (H/C) ratio of 2.3. The hydrogen-enriched porous carbon nanosheets (H-PCNs) produced herein demonstrated an excellent reversible capacity, 300 mAh g⁻¹ at 50 mA g⁻¹, remarkable cycling stability over 2000 cycles at high current densities of 1–5 A g⁻¹, and outstanding rate-performance of 74 mAh g⁻¹ at the extremely high current density of 5 A g⁻¹.

2. Experimental section

2.1. Materials

Natural graphite flakes (size < 45 μm, purity 99.99%), phosphorous pentoxide (P₂O₅, purity ≥ 98.5%), potassium persulfate (K₂S₂O₈, purity ≥ 99.0%), potassium permanganate (KMnO₄, purity ≥ 99.0%), and 2-propanol (IPA, purity ≥ 99.8%) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Hydrogen peroxide (H₂O₂, 35% aqueous solution) was purchased from Junsei Chemical Co. (Tokyo, Japan). Concentrated sulphuric acid (H₂SO₄, purity ≥ 98.3%) was supplied by J.T. Baker (Phillipsburg, NJ, USA). Hydrochloric acid (HCl, 35% aqueous solution) was purchased from Daejung Chemicals and Metals Co. (Gyunggido, Korea). De-ionized (DI) water was prepared by a Cascada AN-water purification system from the Pall Corporation (New York, NY, USA). Mixed cellulose ester filters (pore size of 0.45 μm) were supplied by Advantec (Toyo Roshi Kaisha, Ltd., Japan), and FP-Vericef[®] poly(vinylidene fluoride) membrane filters (pore size of 0.45 μm) were supplied by the Pall Corporation.

2.2. Synthesis of graphene oxides and double-oxidized graphene oxides

Graphene oxide (GO) was prepared using the modified Hummers method [46,47]. For the preparation of double-oxidized graphene oxide (DGO), temperature of a jacketed glass reactor (1.8 L) was maintained at 10 °C, and the concentrated H₂SO₄ (550 ml) was introduced into the glass reactor with mechanical stirring. The GO prepared using the modified Hummers method was added to the reactor, and then KMnO₄ (36 g) was introduced into the mixture slowly over 10 min. During the KMnO₄ addition, the reactor temperature was kept at below 10 °C. The temperature of the mixture was raised up to 35 °C, and the oxidation was carried out for 2 h. The temperature of the external circulator was then cooled down to –5 °C. DI water (1.1 L) was then added to the mixture with stirring. The DI water was added very slowly over ca. 2 h to prevent fire. The temperature of the reactor was then increased to 35 °C, and the mixture was stirred for 2 h. The reacted mixture was moved to a glass bottle (5 L), and DI water (3.4 L) was added to the mixture to quench the oxidation. A 30% H₂O₂ aqueous solution was added to ionize the remaining manganese, and the purple color of KMnO₄ disappeared. The mixture was decanted overnight and washed with 10% HCl aqueous solution, followed by washing with DI water (6 L). The obtained DGO was filtered with the mixed cellulose ester filter, dried in a vacuum oven at 50 °C overnight, grinded, and sieved using a mesh size of 75 μm. Starting from 12 g of natural graphite, 8–9 g of DGO can be obtained, and thus the yield of DGO was 65–75 wt%.

2.3. Synthesis of reduced graphene oxides and hydrogen-enriched porous carbon nanosheets

For the synthesis of RGO, GO (1 g) was dispersed in IPA (8 ml) using a vortex mixer. The mixed suspension was sonicated for one hour in a glass vial (20 ml). Then, the mixed suspension (3.5 ml) was introduced into a SUS 316 reactor with an inner volume of 11 ml. After being tightly sealed, the reactor was immersed into a molten salt bath (salt weight ratio of KNO₃:NaNO₃:Ca(NO₃)₂ = 46:24:30) and reacted for one hour at 400 °C. It took less than 2 min to reach 400 °C. After the reaction, the reactor was taken out from the salt bath and quenched in a cold water bath. After the cooling, the produced RGO suspension was rinsed and filtered through a FP Vericef[®] poly(vinylidene fluoride) membrane filter. Wet RGO powder was dried in a vacuum oven at 70 °C overnight, and sieved using a mesh size of 75 μm. The synthesis of H-PCNs using DGO followed the same procedure to the synthesis of RGO.

2.4. Material characterization

The phase structure of the samples was analyzed using a D/Max-2500V/PC Rigaku X-ray diffractometer (XRD, Tokyo, Japan) with Cu Kα radiation at 40 kV and 50 mA. The morphology of the samples was observed using a Hitachi S-4100 field emission scanning electron microscope (FE-SEM, Tokyo, Japan) and a Tecnai-G² high-resolution transmission electron microscope (HR-TEM, FEI Co. Ltd., OR, USA). The Brunauer–Emmett–Teller (BET) surface area was measured using a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). The functional groups on the surface of the samples were characterized using a NICOLET iS10 Fourier-transform infrared (FT-IR) spectrometer (Thermo Electron Co. NJ, USA). The structure of the samples was characterized using a Nicolet Almega XR dispersive Raman spectrometer (Thermo Fisher Scientific Inc. MA, USA) equipped with an Nd:YAG laser. X-ray photoelectron spectroscopy (XPS) was performed on the samples using a PHI 5000 Versa Probe spectrometer (ULVAC-PHI Inc., Kanagawa, Japan). Elemental

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