



Energy storage capabilities of nitrogen-enriched pyropolymer nanoparticles fabricated through rapid pyrolysis



Young Soo Yun ^{a, b, 1}, Yu Hyun Kim ^{c, 1}, Min Yeong Song ^c, Na Rae Kim ^c, Kyojin Ku ^a, Ji Su An ^c, Kisuk Kang ^a, Hyoung Jin Choi ^{c, *, 1}, Hyoung-Joon Jin ^{c, *, 1}

^a Department of Materials Science and Engineering, Seoul National University, Seoul, 151-742, South Korea

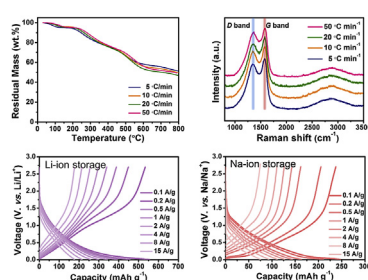
^b Department of Chemical Engineering, Kangwon National University, Samcheok, 245-711, South Korea

^c Department of Polymer Science and Engineering, Inha University, Incheon, 402-751, South Korea

HIGHLIGHTS

- Nanostructured pyropolymers (N-PNs-50) were fabricated by rapid pyrolysis.
- N-PNs-50 exhibited a nitrogen content of 9.8 wt% and amorphous carbon structure.
- N-PNs-50 exhibited a high specific surface area of $875.8 \text{ m}^2 \text{ g}^{-1}$.
- 660 and 255 mAh g^{-1} were achieved for Li-ion and Na-ion storage, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured pyropolymers contain significant amounts of redox-active heteroatoms, have high specific surface areas, and a defective carbon microstructure, indicating good potential for pseudocapacitive charge storage. In this study, nitrogen-enriched pyropolymer nanoparticles (N-PNs-50) are fabricated from polyaniline nanotubes through rapid pyrolysis at $50 \text{ }^\circ\text{C min}^{-1}$. N-PNs-50 exhibit a nitrogen content of 9.8 wt%, a high specific surface area of $875.8 \text{ m}^2 \text{ g}^{-1}$, and an amorphous carbon structure with an I_D/I_G intensity ratio of 0.95. These unique characteristics lead to good electrochemical performances, in which reversible capacities of 660 and 255 mAh g^{-1} are achieved for Li-ion and Na-ion storage, respectively, with favorable voltage characteristics ($<1.5 \text{ V}$ for Li-ions and $<1.2 \text{ V}$ for Na-ions). This study provides a more feasible production method for nitrogen-doped pyropolymers and their practicable electrochemical performances for use as an anode in energy storage devices.

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1. Introduction

Nanostructured carbon-based materials (NCMs) have attracted

much attention as faradic electrode materials for energy storage fields [1–9] because their good electronic transport properties and nanometer-scale effects enable fast ion/electron transfer. Pseudocapacitive charge storage in NCMs primarily originates from the chemisorption of charged ions in the surface redox host, for example at topological defect sites, redox-active heteroatoms, edge defect sites, and imperfect hexagonal carbon structures [4,8–12]. Therefore, more defective NCMs containing numerous redox-active

* Corresponding authors.

E-mail address: hjjin@inha.ac.kr (H.-J. Jin).

¹ These authors contributed equally to this work.

heteroatoms can be highly conductive and deliver much larger charges very quickly. Recently, reduced graphene oxide (RGO) showed high reversible capacities of 650 and 174 mAh g⁻¹ for Li-ion [13] and Na-ion storage [14], respectively, with fast rate capabilities due to its many topological defects, oxygen functional groups, and well-developed conduction pathways [15–17]. Additionally, nitrogen doping of RGO further improves its capacity and rate performance with stable cycles [18–21]. However, RGO has limited scope for large-scale applications due to its complex synthesis and the harsh process required for oxidation of graphene oxide.

Pyropolymers, which are fabricated using pyrolysis of polymer precursors below 1000 °C, have amorphous carbon structures composed of nanometer-sized pseudographitic carbon layers [22]. A diverse range of topological defects, heteroatoms, and edge defect sites are present in pyropolymers, indicating that there are numerous active sites for pseudocapacitive charge storage. Qie et al. [23] reported nitrogen-doped porous carbon nanofibers as an anode for Li-ion storage that showed a high specific capacity of 1280 mAh g⁻¹. For Na-ion storage, similar nitrogen-doped porous carbon fibers exhibited a capacity of 296 mAh g⁻¹, higher than that of RGO anodes [24]. Other types of pyropolymers have also shown high reversible capacities of 400–1000 and 130–250 mAh g⁻¹ for Li-ion storage [25–30] and Na-ion storage [31–34], respectively, with the exact value being dependent on the polymer precursor, heating rate, and temperature. However, in previous studies, real anodic capacities (<1.5 V) were below 350 mAh g⁻¹ after several cycles for Li-ion storage [23,25–30], and slow kinetics [26,29,33,34] (<50% at 2C-rate) and insufficient cyclic stabilities [30] were also observed in both Li-ion and Na-ion storage. However, these studies applied relatively slow heating rates of less than 3 °C min⁻¹ and/or holding times over 6 h for carbonization [23,24,28,30,33,34], which requires a lot of energy and time.

Polyaniline is one of the most widely studied conducting polymers of the past five decades, and it is composed of a polymer backbone with aromatic carbon rings and nitrogen atoms. Through simple heating at 800 °C, the molecular structure of polyaniline can be changed to nitrogen-containing pyropolymers in yields greater than 60% [35]. Additionally, the thermal decomposition of polyaniline occurs via random degradation of polymer chains [36], with three-dimensional Jander's diffusion being the rate-controlling process of thermal decomposition [37]. These results suggest that nanostructured polyaniline can exhibit maximized pyrolytic kinetics and a high carbon yield containing numerous nitrogen atoms.

In this study, nitrogen-enriched pyropolymer nanoparticles (N-PNs) were fabricated through rapid pyrolysis of polyaniline nanotubes (PNTs) caused by simple heating. The rapid heating rate of 50 °C min⁻¹ led to a more defective carbon structure, larger redox-active heteroatoms, and greater specific surface area than N-PNs fabricated at heating rates of 5, 10, or 20 °C min⁻¹, and they showed superior Li- and Na-ion storage performance as anodes.

2. Experimental

2.1. Preparation of N-PNs

PNTs were prepared via a previously reported procedure [35]. In the synthetic process, 2 mmol of aniline monomer (DC Chemical, Korea) and 0.5 mmol of oxalic acid (Sigma-Aldrich) were dissolved in distilled water using sonication for 30 min. Next, 2 mmol of ammonium persulfate (APS, Daejung Co. Ltd., Korea), which was prepared and pre-cooled to 4 °C, was added to the reactor with vigorous stirring. The resulting solution was left for 20 h at 4 °C without stirring. The product was washed several times with distilled water, methanol, and diethyl ether, then vacuum-dried at

80 °C for 24 h. The resulting PNTs were heated from room temperature to 800 °C under a N₂ flow of 200 ml min⁻¹ at four different heating rates (5, 10, 20, and 50 °C min⁻¹) and held at 800 °C for 1 h. The samples were named N-PNs-5, -10, -20 and -50, based on their respective heating rates.

2.2. Characterization

The thermal properties of the samples were examined using differential scanning calorimetry (DSC; DSC404F1, NETZSCH, Germany) and thermal gravimetric analysis (TGA; TG209F3, NETZSCH, Germany). The morphologies of the samples were examined using field-emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Tokyo, Japan) and field-emission transmission electron microscopy (FE-TEM, JEM2100F, JEOL, Tokyo, Japan). Raman spectra were recorded using a continuous-wave linearly polarized laser (wavelength: 514.5 nm; 2.41 eV; power: 16 mW). The laser beam was focused by a 100 × objective lens, resulting in a spot diameter of approximately 1 μm. The acquisition time was 10 s and 3 circulations were used to collect each spectrum. X-ray diffraction (XRD, Rigaku DMAX 2500) was performed using Cu-Kα radiation (wavelength λ = 0.154 nm) operated at 40 kV and 100 mA. The chemical compositions of the samples were examined using X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA, Chanhassen, MN, USA) with monochromatic Al-Kα radiation (hν = 1486.6 eV) and elemental analysis (EA) was performed with an EA1112 instrument (CE Instrument, Italy). The porosities of the samples were analyzed using nitrogen adsorption and desorption isotherms that were obtained using surface area and a porosimetry analyzer (ASAP 2020, Micromeritics, USA) at -196 °C.

2.3. Electrochemical characterization

The electrochemical properties of N-PNs-50 were characterized using a Wonatec automatic battery cycler and CR2032-type coin cells. The coin cells were assembled in a glove box filled with argon using N-PNs-50 as the working electrode and metallic Li or Na foil for both the reference and counter electrodes. LiPF₆ (1 M; Aldrich, purity: 99.99%) was dissolved in a solution of ethylene carbonate and dimethyl carbonate (1:1 v/v) and used as the electrolyte for Li-ion storage. Alternatively, NaClO₄ (1 M; Aldrich, purity: 99.99%) was dissolved in a solution of ethylene carbonate and propylene carbonate (1:1 v/v) and used as the electrolyte for Na-ion storage. A glass microfiber filter separator (GF/F, Whatman) was used as a separator. The working electrodes were prepared by mixing the active material (80 wt%) with conductive carbon (10 wt%) and polyvinylidene fluoride (10 wt%) in N-methyl-2-pyrrolidone. The resulting slurries were uniformly applied to the Cu foil. The electrodes were dried at 120 °C for 2 h and roll pressed. The mass loadings of the active materials were approximately 1 mg cm⁻², and the total electrode weights were 2–3 mg. Electrochemical impedance spectroscopy (EIS) measurements were performed on the cells using an impedance analyzer (ZIVE SP2; Wonatec) at room temperature in the frequency range of 1 MHz–1 mHz.

3. Results and discussion

The PNTs, which had diameters of approximately 150 nm and lengths of several micrometers (Fig. S1), were heated at 5, 10, 20 and 50 °C min⁻¹ using TGA. As shown in Fig. 1(a), the profiles have three abrupt weight loss occurrences at ~200, 200–350 and 450–650 °C [38]. The first weight loss is attributed to the release of residual water trapped in the polyaniline structure. The second weight loss is induced primarily by inter- and intra-macromolecular crosslinking processes [39,40]. The last

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