



Low temperature synthesis of polyhedral hollow porous carbon with high rate capability and long-term cycling stability as Li-ion and Na-ion battery anode material



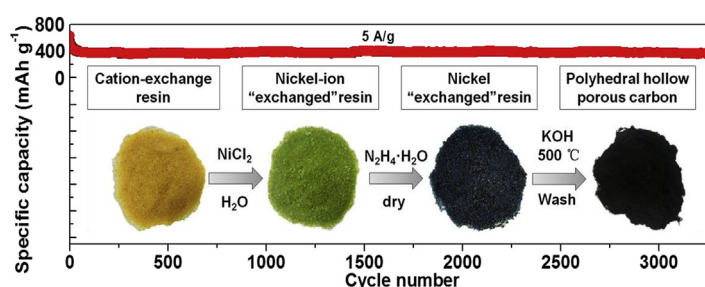
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HIGHLIGHTS

- A novel polyhedral hollow porous carbon (PHPC) is simply prepared.
- Bulk synthesis is achieved at low temperature.
- PHPC has thin, interconnected, hierarchically porous walls.
- As a Li-ion and Na-ion battery anode, PHPC delivers high specific capacity.
- In long-term high rate cycling, PHPC has exceptionally stable high capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

A unique polyhedral-shaped hollow porous carbon with high specific capacity, high rate capability, and excellent cycling stability as both lithium-ion and sodium-ion battery anode material has been prepared from a Ni-ion exchanged resin at significantly low temperature (500 °C). Low temperature synthesis is achieved by room temperature exposure of Ni-ion exchanged resin to hydrazine hydrate, which reduces Ni²⁺ to active Ni metal catalyst prior to calcination. As an anode material for lithium-ion and sodium-ion batteries, the material delivers large reversible capacity and long-term cycle stability even at high current densities. As a lithium-ion battery anode material, it delivers 620 and 225 mAh g⁻¹ at 1 and 20 A g⁻¹, respectively, and 380 mAh g⁻¹ after 3000 cycles at 5 A g⁻¹. As a sodium-ion battery anode material, it delivers 227 and 133 mAh g⁻¹ at 1 and 20 A g⁻¹, respectively, and 144 mAh g⁻¹ after 9000 cycles at 5 A g⁻¹. The high rate capability and cycling stability arises from an appropriate balance of graphitization, nanoporosity, and thin-walled interconnected hollow structure. Overall, the performance of the material is exceptional for porous carbon, especially considering its low temperature bulk synthesis method.

1. Introduction

Cost and energy density are critical factors in determining the application niches for different types of rechargeable batteries. Lithium-

ion batteries (LIBs) offer very high energy density for portable electronics and electric vehicles and also have long cycle life and acceptable safety [1–4]. However, for large-scale stationary storage of renewable energy, the relatively low abundance of lithium on earth makes it an

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expensive option. In contrast, the abundance of sodium (having nearly five orders of magnitude higher concentration than lithium in sea water) makes sodium-ion batteries (SIBs) potentially a far cheaper option for renewable energy storage [5]. In the case of commercial LIBs, graphite is typically used as the anode material due to its low voltage, relatively high specific and volumetric capacity, good stability, and low cost [6]. However, graphite's slow kinetics for electron and Li-ion transfer require long charge/discharge times to access its full capacity [7,8], and the theoretical specific capacity of Li-intercalated graphite (LiC_6) at 372 mAh g^{-1} is relatively low. Furthermore, in the case of SIBs, the larger size of the Na-ion fails to intercalate within the limited interlayer spacing of graphite (0.335 nm). Therefore, much research has focused on developing alternative, higher specific capacity, anode materials for LIBs and SIBs, which includes transition metal oxides [9,10], transition metal phosphides [11,12], and metal alloys [13] etc. However, realization of fast-charge and high-rate capabilities still remain key challenges for LIB and SIB anode material development [14].

Recent reports point towards partially graphitized porous carbon materials as promising LIB and SIB anode materials. In particular, some reported porous hard carbons have extremely high capacity and high rate capability [15–17]. These carbons contain single-layer graphene sheet units that randomly pack in a disordered so called “house of cards” arrangement to provide nano-sized pores for Li^+/Na^+ insertion [18,19]. However, such carbons often have poor stability in both long-term and high-rate cycling. This is due to: (1) micro/nano-structural degradation during fast repetitive Li^+/Na^+ insertion/extraction; (2) swelling induced by Li^+/Na^+ insertion/extraction causing material detachment from the current collector; and (3) kinetic limitations associated with the discontinuous electron-transfer structure of the electrode [14,20,21]. More recently, three-dimensional (3D) porous carbon electrode materials comprising thin-walled, interconnected structural networks with well-developed porous channels were reported [7,22]. This structure facilitates fast charge-transfer in multi-dimensions, which limits structural damage and swelling of the material, thus allowing long-term cycling at high charge-discharge rates [22–25]. However, such structures are difficult to produce and are therefore not suited to large scale production: e.g. requiring techniques such as chemical vapor deposition (CVD) of low production yield and high consumption of energy [24], or electrophoresis with costly templating requirements [26].

In the present study, we introduce a cost effective temperature reducing strategy to obtain a unique polyhedral-shaped hollow porous carbon (PHPC) that delivers strong performance as a LIB and SIB anode material. The method uses Ni-ion exchanged resin for even graphitization [27], room temperature hydrazine hydrate treatment to reduce graphitization temperature, and KOH activation for carbon expansion [22] during calcination. The resultant PHPC (synthesized at only 500°C) has thin hierarchically porous walls forming adjoining cells that have interconnecting macroporous channels. As anode material, the combination of structural features offers high Li^+ and Na^+ specific capacity with fast ion transfer and good electrical conductivity, which together help prevent structural collapse during fast Li^+/Na^+ insertion and extraction [14,20]. Accordingly, PHPC has long-term cycle stability and excellent rate capability as LIB and SIB anode material, as well as outstandingly high Na^+ reversible capacity among porous carbons.

2. Experimental section

2.1. Synthesis of PHPC

Polyhedral hollow porous carbon (PHPC) was synthesized as follows. A macroporous acrylic cation-exchange resin (50 g) was soaked in 0.6 mol L^{-1} nickel chloride hexahydrate solution (70 mL) with stirring for 6 h. The resultant Ni-ion exchanged resin was then washed with deionized water, filtered and dried. Then, 80 mL hydrazine hydrate (40% in water) was added to the Ni-ion exchanged resin and allowed to

react for 12 h at room temperature, followed by thorough washing with deionized water and drying at 90°C for 12 h. Next, 70 mL of a KOH/deionized water solution (containing 50 g of KOH) was added with stirring while heating at 90°C to evaporate the water. Finally, the sample was heated at a rate of 2°C min^{-1} in a N_2 atmosphere and held at 500°C for 2 h. After cooling to room temperature, 100 mL of 3 mol L^{-1} HCl solution was added to the product with stirring at 80°C for more than 6 h to remove nickel nanoparticles and other impurities. Finally, the product was repeatedly washed with deionized water to a resultant wash value of pH 7, and then dried at 90°C in an oven for 12 h.

2.2. Characterization

X-ray diffraction analysis was carried out on samples at a scan rate of 10°min^{-1} with Cu K α radiation ($V = 40 \text{ KV}$, $I = 30 \text{ mA}$) using an X-ray diffractometer (Rigaku Corporation, SmartLab). Raman spectroscopy was carried out on a Horiba Jobin Yvon, LabRam HR Evolution Raman spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 spectrometer with monochromatic Al K α radiation (150 W, 1486.6 eV). The samples were determined by thermal gravimetric analysis (TGA, SDT600) using a heating rate of $10^\circ\text{C min}^{-1}$ in air from 30 to 900°C . Scanning electron microscopy (SEM, Hitachi Corporation, FESEM SU8220) and transmission electron microscope (TEM, FEI Company, Tian ETEM G² 80–300) were used to characterize the morphology of the prepared material. Brunauer–Emmett–Teller analysis (BET, MICROMERITICS INSTRUMENT CORP, ASAP2460) was carried out to calculate the specific surface area, and density functional theory (DFT) was used to describe the pore size distribution in the material. CHN analysis was carried out using a VarioELIII elemental analyzer.

2.3. Electrode preparation and electrochemical measurements

The electrochemical performance of PHPC was evaluated in 2016-size coin cells. For LIB testing, Li metal was used as the counter/reference electrode with Celgard 2325 separator and 1 mol L^{-1} LiPF_6 in dimethyl carbonate (DMC) and ethylene carbonate (EC) (1:1 by volume) as electrolyte. For SIB testing, Na metal was used as the counter/reference electrode with glass fiber (Whatman GF/D) separator and 1 mol L^{-1} NaClO_4 in a mixture of EC and diethyl carbonate (DEC) in a volume ratio of 1:1 as electrolyte. The working electrode slurry comprised 80:10:10 wt% (PHPC, Super P, and polyvinylidene fluoride (PVDF) binder) and *N*-methyl-2-pyrrolidone (NMP) as a liquid carrier. The wet slurry was coated at a $150\text{-}\mu\text{m}$ doctor blade thickness on $10\text{-}\mu\text{m}$ -thick copper foil current collectors, then dried at 85°C for 10 h in a vacuum oven, followed by calendaring at 6.5 MPa. The typical mass loading density of dry slurry was $\sim 0.6 \text{ mg cm}^{-2}$ at $\sim 7\text{-}\mu\text{m}$ thickness after calendaring, which equated to a compressed slurry density of $\sim 0.86 \text{ g cm}^{-3}$, with PHPC at 80% mass at $\sim 0.69 \text{ g cm}^{-3}$. Galvanostatic charge–discharge cycling was carried out between 0.01 V and 3 V on a NEWARE battery tester. Cyclic voltammetry was carried out on an IM6e electrochemistry workstation (Zahner-Elektrik, Germany) between 0 and 3 V vs. Li/Li^+ or Na/Na^+ at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

Scheme 1 outlines the PHPC synthesis scheme. Nickel chloride hexahydrate (metal source) is first combined with the cation-exchange resin (carbon source) to form the green-coloured Ni-ion exchanged resin. The Ni^{2+} ions, when later heated in the presence of forming carbon, will reduce to Ni metal, which serves as a well known graphitization catalyst [28], while the uniform dispersion of Ni^{2+} in the resin facilitates uniform graphitization throughout the sample [22]. However, prior to heating, we introduce hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) at

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