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Tire-derived carbon composite anodes for sodium-ion batteries

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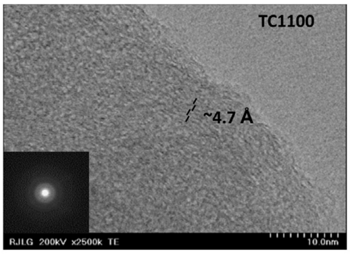
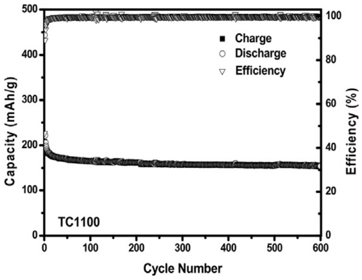
HIGHLIGHTS

- Carbon composites were successfully prepared from waste tires for Na-ion batteries.
- Tire-derived carbon anodes show good capacities and stabilities after long cycling.
- The capacity plateau below 0.2 V increases drastically with pyrolysis temperature.
- Demonstrated a low-cost and environmentally friendly anode for energy storage.

GRAPHICAL ABSTRACT





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ABSTRACT

Hard-carbon materials are considered as one of the most promising anodes for the emerging sodium-ion batteries. Here, we report a low-cost, scalable waste tire-derived carbon as an anode for sodium-ion batteries (SIBs). Tire-derived carbons obtained by pyrolyzing acid-treated tire at 1100 °C, 1400 °C and 1600 °C show capacities of 179, 185 and 203 mAh g^{-1}, respectively, after 100 cycles at a current density of 20 mA g^{-1} in sodium-ion batteries with good electrochemical stability. The portion of the low-voltage plateau region in the charge-discharge curves increases as the heat-treatment temperature increases. The low-voltage plateau is beneficial to enhance the energy density of the full cell. This study provides a new pathway for inexpensive, environmentally benign and value-added waste tire-derived products towards large-scale energy storage applications.

1. Introduction

With the concerns of the limited global availability of lithium resources and high cost, sodium-ion batteries (SIBs) are considered to be an alternative to lithium-ion batteries (LIBs), especially for applications where energy density are of minor importance, such as stationary grid energy storage of electricity produced from renewable sources [1,2]. Due to its high abundance, low cost, and suitable working chemical potential (−2.7 V vs. Standard Hydrogen Electrode), rechargeable sodium-ion batteries are gradually attracting a lot of attention [3]. Sodium shares many similar

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chemical properties with lithium because of its location in the periodic table and the similarities of fundamental principles of SIBs and LIBs. Thus far, several suitable cathode materials have been developed for SIBs [4–7]. However, the absence of good anode material hinders the application of SIBs. The search for suitable electrode materials for sodium-ion batteries, in particular robust anodes for Na^+ storage therefore is of great importance and becomes more urgent. Extensive research has been conducted to develop potential materials, such as alloy anodes [8], conversion anodes [9,10], insertion anodes [11] and carbon anodes. But on the way to commercialize SIBs, carbon based materials have attracted the most attention, respecting to their unique electrochemistry functions and low cost for large-scale application [12]. Compared to carbon anodes, the disadvantages of alloy anodes and conversion anodes for SIBs should be attributed to the large volume changes during sodiation and desodiation, which causes fast capacity fade. In addition, conversion anodes also encounter relative high working potential and the large hysteresis between discharge and charge problems. For intercalation anodes, the low capacity limits their application.

Unlike the successful application of graphite as anodes in LIBs, the electrochemical sodium insertion into graphite to form binary intercalation compound is proven to be not favorable [13,14]. Theoretical calculations suggest that the interlayer distance of graphite is too small to accommodate the large Na^+ ion, and a minimum interlayer distance of 0.37 nm is believed to be good for Na^+ insertion [15]. Very recently, progress has been made by Adelhelm *et al.* through the use of solvent co-intercalation to address the unfavorable graphene layer intercalation [16]. A variety of carbon materials have been investigated as anodes for SIBs, such as hard carbons [17], carbon nanotubes [15], reduced graphene oxides [18], and expanded graphite [19]. Hard carbon is likely to be the most promising anode for commercialization because of its stability, relatively high capacity and easy to scale-up. However, great amounts of the currently studied hard carbons are produced from sucrose [20], banana peels [21] and dopamine [22] *etc*. Most of the precursors are relatively high cost or require complex treatments, which prevent the application in many cost sensitive fields [23]. A low-cost hard carbon anode material is desired for promoting the development of SIBs for large-scale energy storage market.

The widespread use of motor vehicles unavoidably results in large quantities of used tires. Globally, it is estimated that about 1.5 billion waste tires are produced every year [24]. In the past, used tires are mostly disposed in landfills, which is not a sustainable solution. As more and more discoveries find that discarded tires pose serious environmental and health threats to our society, proper recycling of worn-out tires has become a critical issue. By now, the recycling of tires was mainly consumed as fuel, additives to plastics, rubbers, or civil engineering applications. Typically, a tire consists of natural rubber, synthetic polyisoprene, butadiene rubber, styrene-butadiene rubber, carbon black and a fractional amount of additives [25]. The regular direct pyrolysis process results in the production of about 30–40% carbon black, depending on the pyrolysis conditions [24]. A high value-added product produced from used tires will lead more opportunities for the recycling industry and generate more environmental and economic benefits.

Tires are designed to be stable in physical and chemical harsh conditions owing to their cross-linked structure and various additives, which make them hard for recycling. However, such disadvantages are also the desired properties for electrochemical energy storage applications. A method for producing sulfonated and pyrolyzed carbon composite from recycled micronized tire rubber has been reported [26,27]. The sulfonated tire-derived carbon has ~10% higher yield than the controlled carbon that was produced from the direct pyrolysis of powder rubber. Since the vulcanized tire formulation consists of a mixture of diene-rubbers such as polybutadiene, polyisoprene, or styrene-butadiene copolymer, desulfonation of rubbers or aliphatic hydrocarbon during the pyrolysis step will form unsaturated moieties that are relatively better char-forming materials [26]. This process also improves the carbon yields. Relatively low packing density and higher operating voltage are among the main obstacles for hard carbons to be used as an anode in LIBs. However, such problem will not be a big issue for SIB application since sodium-ion batteries are mostly targeted for stationary energy storage and also the Na/Na^+ couple operates 0.34 V higher than Li/Li^+ couple. To validate our hypothesis on potential use of tire-derived carbons in SIB anodes we present here the performance of these carbons, synthesized at different temperatures. Interestingly, a higher temperature of pyrolysis leads to a larger sodium storage capacity, which behaves opposite to that of some hard carbons produced in the same temperature range and used against lithium. In the meanwhile, unlike most hard carbon voltage profile in LIBs, the plateau capacity at low-potential region increases significantly as the pyrolysis temperature increases, which is beneficial to increase the cell voltage and energy density.

2. Experimental details

2.1. Tire-derived carbon synthesis

Pulverized tire rubber powder in the size range of 80–120 μm was obtained from Lehigh Technologies, Inc., Georgia. Typically, 50 g of tire rubber powders were soaked in a 100 mL concentrated sulfuric acid bath (kept at 120 °C for overnight) to yield the sulfonated tire rubber which was then washed and filtered off. The washed sulfonated tire rubber was then pyrolyzed from room temperature to 400 °C at a ramp rate of 1 °C/min and then the temperature was further increased to 1100 °C, 1400 °C, and 1600 °C, respectively at a ramp rate of 2 °C/min, in a tube furnace under flowing nitrogen gas, and they are hereafter designated as TC1100, TC1400, and TC1600. Currently, the reported synthesis method can be scaled up to produce nearly 500 g of materials in a batch and soon will be scale-up to few kg of materials.

2.2. Material characterization

The X-ray diffraction (XRD) data were collected with a PANalytical Empyrean diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å). Nitrogen adsorption desorption isotherms were obtained with a Quantachrome NovaWin1000 surface area & porosity analyzer at 77.4 K. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was obtained by the Barret-Joyner-Halenda (BJH) method. Raman spectra were collected with a Horiba LabRam HR using an excitation wavelength of 473 nm, a 600 gr/mm grating and an 800 mm monochromator. A Zeiss Merlin VP scanning electron microscope (SEM) operated at 3 kV was used to characterize the surface morphologies of the samples. Interlayer distances of the carbons were determined by a Hitachi HD-2300A scanning transmission electron microscope (STEM) with a field emission source operated at 200 kV in bright-field imaging mode at a 2.1 Å resolution. XPS data were collected with a Thermo-Fisher K-alpha XPS with a monochromatic Al-K_{alpha}, a 1486.6 eV source, 400 μm spot, and an argon ion flood gun.

2.3. Electrochemical measurements

Electrochemical properties were characterized with half cells against a sodium-metal electrode. The working electrode was