



Pitch-derived amorphous carbon as high performance anode for sodium-ion batteries

Yunming Li, Linqin Mu, Yong-Sheng Hu*, Hong Li, Liquan Chen, Xuejie Huang

Key Laboratory for Renewable Energy, Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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ABSTRACT

Carbonaceous materials hold the most promising application among all anode materials for sodium-ion batteries (SIBs) because of the high storage capacity and good cycling stability. However, the high cost and the low initial Coulombic efficiency limit their further commercialization. Herein, an amorphous carbon material was fabricated through direct pyrolysis of low-cost pitch and phenolic resin at heat treatment temperatures between 1200 and 1600 °C. The electrochemical performances of the amorphous carbon were systematically investigated in SIBs with inexpensive Al foil as current collector and environmentally benign aqueous sodium alginate as binder. By optimizing the carbonization temperature and precursor, we achieved an initial Coulombic efficiency of 88% – the highest reported so far for carbon-based anodes in SIBs with a high reversible capacity of 284 mA h g⁻¹ and excellent cycling performance. It was found that both the carbonization temperature and the mass ratio of pitch to phenolic resin have significant impact on the local structure of amorphous carbon, which leads to various electrochemical behaviors. When coupled with an air-stable O3-Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O₂ cathode, the full cell shows excellent electrochemical performance with an initial Coulombic efficiency of 80%, a good cycling stability and an energy density of 195 Wh/kg. This contribution provides a new approach for the development of low-cost sodium-ion batteries.

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1. Introduction

Energy storage systems (ESSs) with low-cost and high-performance are an indispensable component for the realization of electric vehicles and the effective utilization of renewable energy resources. Lithium-ion batteries (LIBs), which have been developed as power sources for portable electronic devices, are an alternative storage technology for ESSs, but the high geographic concentration of lithium in nature and lithium's rising cost may severely restrict LIBs' prospects in grid energy storage applications [1–3]. Sodium-ion batteries (SIBs) have recently been considered as an alternative to LIBs for grid energy storage applications due to their potentially low cost and the wide distribution of sodium resources [4–6]. The other important aspect is that new chemistry and new materials could be developed by using the Na⁺ ion charge carrier to further decrease the cost of the SIBs system. For example, sodium cannot form the alloy with aluminum, therefore aluminum foil can be used as the current collector for the anode without the overdischarge problem. However, the absence of

suitable negative electrode materials remains a challenge to overcome in SIBs in order to meet the requirement for a high-performance power source in the future commercial applications.

Graphite, which has been widely used as anode material for LIBs, shows poor electrochemical performance in SIBs, with extremely low capacity of ~30 mA h g⁻¹, because of the thermodynamic issue [7–9]. Recently, unusual Na⁺ ion intercalation in natural graphite was reported by utilizing Na⁺-solvent co-intercalation, when using the appropriate electrolyte system [9,10]. Although the cycling performance of the graphite anode is excellent, the reversible capacity is only 150 mA h g⁻¹ and the average storage voltage is 0.6 V. Expanded graphite was also fabricated as an anode material for SIBs, but its initial Coulombic efficiency is as low as 49% [11]. Alternatives, including alloys [12–14], Ti-based oxides [15–18] and organic compounds [19–21] were proposed as anode materials for SIBs. However, they often show poor structural stability, low reversible capacity, and sometimes, low initial Coulombic efficiency. Among all the anode candidates for SIBs, amorphous carbon materials may be the most promising alternative, considering their electrochemical performance. Hard carbon, also known as non-graphitizable carbon, has been extensively investigated as anode material for SIBs, due to its disordered structure, which benefits Na insertion and extraction [22–25]. The promising performance of hard carbon as anode for both LIBs and SIBs, with low

* Corresponding author.

E-mail address: yshu@aphy.iphy.ac.cn (Y.-S. Hu).

Table 1
Physical parameters and electrochemical properties for different PPAC.

Sample	PPAC111200	PPAC111400	PPAC111600	PPAC731400	PPAC371400
PI/PR	1/1	1/1	1/1	7/3	3/7
HTTs ^a (°C)	1200	1400	1600	1400	1400
d ₀₀₂ (Å)	3.90	3.77	3.65	3.52	3.86
L _c (nm)	1.56	1.64	1.74	3.20	1.52
L _a (nm)	4.31	4.00	3.75	4.11	3.57
S _{BET} (m g ⁻¹)	3.2	2.1	5.1	11.4	3.0
ICC ^b (mA h g ⁻¹)	254	259	210	182	284
SC ^c (mA h g ⁻¹)	100	81	67	67	82
PC ^d (mA h g ⁻¹)	154	178	143	115	202
ICE ^e (%)	86	86	84	79	88

^a The heat treatment temperatures.

^b The initial charge capacity.

^c The sloping capacity in the initial charge.

^d The plateau capacity in the initial charge.

^e The initial Coulombic efficiency.

average potentials and high specific capacities, has been demonstrated by previous studies [8,26]. However, the high cost arising from the low carbon yield and the low initial Coulombic efficiency (lower than 75%), caused by the prominent formation of solid electrolyte interphase (SEI) layer, limit its development and practical application. Improving hard carbon's carbon yield and its initial Coulombic efficiency remain significant challenges for its industrialization. Soft carbon, another amorphous carbon material, which can be graphitized above 2800 °C, delivers larger reversible capacity than graphite in LIBs, but it exhibits low reversible capacity in SIBs – below 100 mA h g⁻¹.

Pitch, which is often used as a paving material, is a low-cost petrochemical byproduct, it is also an important precursor with high carbon yield for the preparation of soft carbon and artificial graphite. Nevertheless, there are very few reports of using pitch to fabricate carbon-based anode materials with the storage capacity below 100 mA h g⁻¹ for SIBs [27]. It is crucial for the application of pitch in SIBs to find an alternative method that is effective in restraining pitch graphitization. Phenolic resin, an important polymeric material, is a typical precursor for producing hard carbon. Previous studies have reported using hard carbon material prepared by direct pyrolysis of phenolic resin in Argon atmosphere as a negative electrode material for LIBs, but there is less research for SIBs [28,29].

Herein, we report an effective strategy to adjust the disorder of pitch-derived carbon by introducing phenolic resin into pitch in order to apply pitch in SIBs. Several novel amorphous carbon materials were obtained by adjusting the mass ratio of pitch to phenolic resin, and the carbonization temperature, and the influence of both on microstructure; and electrochemical performance was systematically investigated. The results show that the structure of the pitch/phenolic resin-derived amorphous carbon (PPAC) is significantly more disordered than that of the pitch-derived carbon, which demonstrates that the introduction of phenolic resin can be used to adjust the microstructure of pitch-derived carbon. When evaluated as an anode for SIBs, the PPAC samples exhibited a high sodium storage capacity and very stable cycling performance, especially in achieving the highest first-cycle Coulombic efficiency value (88%) reported so far for carbon-based anodes in SIBs.

2. Experimental

2.1. Materials synthesis

PPAC was prepared by the pyrolysis of the mixture of pitch and phenolic resin. The precursor materials of pitch and phenolic resin

with different proportions were first mixed in alcoholic solutions by the ball-milling dispersion method, then the slurry was dried at 50 °C for 24 h to remove the alcohol. The obtained black powder was carbonized for 2 h in a tube furnace under Argon flow. The carbonization temperatures were 1200 °C, 1400 °C and 1600 °C, respectively. The fabricated amorphous carbon materials denoted as PPAC111200, PPAC111400, PPAC111600, PPAC731400 and PPAC371400 were prepared as summarized in Table 1.

2.2. Materials characterization

The structure was characterized by an X'Pert Pro MPD X-ray diffractometer (XRD) (Philips, Netherlands) using Cu-K α radiation (1.5405 Å) and Raman spectra (JY-HR 800). The morphologies of the samples were investigated with scanning electron microscope (SEM) (Hitachi S-4800). High-resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) patterns were recorded on a FEI Tecnai F20 transmission electron microscope. TGA data were obtained using a NETZSCH STA 409 PC Luxx simultaneous thermal analyser (Germany) from room temperature to 1000 °C at a heating rate of 5 °C min⁻¹ under a nitrogen gas atmosphere. Nitrogen adsorption and desorption isotherms were determined by nitrogen physisorption on a Micromeritics ASAP 2020 analyzer.

2.3. Electrochemical measurements

All the electrochemical tests were conducted in coin cells (CR2032). The working electrode was prepared by spreading the mixed slurry of active material and sodium alginate binder in water solvent with a weight ratio of 9.5:0.5 onto Al foil, and then dried at 100 °C in vacuum for 10 h. The electrolyte was a solution of 0.6 M NaPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume). A sodium foil was used as the counter electrode and glass fiber was used as the separator. All the operations were performed in the Argon-filled glove box. The discharge and charge tests were carried out on a Land BT2000 battery test system (Wuhan, China) in a voltage range of -0.01 to 2 V at various C-rates under room temperature. A sodium-ion full cell was constructed using PPAC111400 as the negative electrode and O3-Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O₂ as the positive electrode in a CR2032 coin-type cell. Synthesis method of the Na_{0.9}[Cu_{0.22}Fe_{0.30}Mn_{0.48}]O₂ material was a conventional solid state reaction [30]. The weight ratio of the two electrodes (negative/positive) was 1:2.86. The full cells were charged and discharged in a voltage range of 1–4.06 V at 0.2 C current rate.

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