Research article

Enhanced electrochemical performances of coal liquefaction residue derived hard carbon coated by graphene as anode materials for sodium-ion batteries

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ABSTRACT

A graphene coated coal liquefaction residue (CLR) derived hard carbon (HC@G) composite anode for sodium ion batteries was prepared by thermal annealing the mixture of the chemically modified hard carbon with graphene oxide. The irregular shaped hard carbon particles were coated uniformly by wrinkled graphene sheets. Both HC and HC@G possess large inter-layer spacing and poor porosity, but a richer pore structure that facilitating ion transport was generated after graphene coating. Because poor conductive hard carbon particles are bridged by graphene sheets, a better conductivity of HC@G is detected by voltammetry test and the EIS analysis. Graphene coating contributes little to the sodium storage capacity. However, HC@G exhibits a much better rate performance and a dramatic improvement of cycling capability with the capacity retention 83% after 2000 cycles at a high current density of $2\,A\cdot g^{-1}$. The impressing rate and cycle performances of HC@G anode are attributed to the hierarchical structure with rich ion diffusion channels and extensive electronic conduction path.

1. Introduction

In recent years, China has proposed and promoted clean energy projects, but coal still holds the dominant position in China's energy structure [1,2]. As an important clean coal utilization technology, coal direct liquefaction has strategic significance in the current energy technology in China [3–5], and it is also an important part of the national energy security [1]. On the basis of liquefaction conditions of coal, the coal liquefaction residue (CLR), which contains heavy liquid hydrocarbons and solids (including carbonaceous matters, minerals in coal and remaining catalysts), usually accounts for 30 wt% of raw coal. In the past decades, coal liquefaction industry is booming in China, thereby it is very important to utilize CLRs effectively, in both economic and environmental terms [6]. Solvent extraction is an effective way to separate the useful hydrocarbon components in coal liquefaction residues solid wastes. The residue extract contains about 50 wt% of the heavy organic matters, which are rich in aromatic ring structures, especially condensed aromatic ring and heterocyclic structure components [6–9]. How to take advantage of the composition and structure characteristics of the heavy organic matters extracted from CLR and produce high added-value products, is an important issue of efficient use of heavy carbon resources and improving the overall economic efficiency of coal liquification technology [10,11].

Currently, lithium ion batteries (LIBs) are overwhelming energy storage systems in mobile electronic devices and electric vehicles [12,13], since their commercialization in 1991 by Sony. However, the widespread utilization of LIBs with Li ion as an energy delivery medium has encountered the problem of limited and uneven distribution of lithium sources on Earth [14]. Rich reserves of sodium and similarities in physicochemical properties with lithium as well as the same rocking-chair operation mechanism as LIBs have prompted scientists to investigate sodium-ion batteries (SIBs) since the 1970s. Unfortunately, the commercial graphite anode for LIBs is not a suitable solution for SIBs due to the larger radius of Na ion (0.76 Å for Li^+ and 1.06 Å for Na^+) [15–18].

To date, hard carbon (HC) is one of the most promising anode materials for SIBs owing to its low cost, low average potential and high reversible capacity [19–24]. HCs are generally prepared from biomass [25,26] or synthetic polymers [16], which are seasonal, low in transportation efficiency and costly. And the low conductivity due to its disordered microarchitecture usually leads to a poor electrochemical stability. In this work, the CLR extract was chemically cross-linked to obtain polycondensed fused polynuclear aromatic (COPNA) resin with 3D network structure. Then, the COPNA resin was cured and carbonized to produce HC anode. In order to increase the conductivity of CLR derived HC anode for SIB, graphene coating technology was adopted for the preparation of graphene coated HC (HC@G) composite anode. Moreover, the electrochemical performances of HC and HC@G were

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investigated in detail.

2. Materials and methods

2.1. Materials synthesis

The CLR extract, which is the tetrahydrofuran soluble content of the residue produced by the direct coal liquefaction process, was provided by China Shenhua Coal to Liquid and Chemical Co., Ltd.

Hard carbon precursor COPNA resin was synthesized by cross-link the CLR extract at 140 °C with p-phenylenedimethanol (PXG) as cross-linking agent and 20 wt% sulfuric acid as catalyst under N_2 atmosphere. The obtained COPNA resin was dried in vacuum at 80 °C followed by curing at 300 °C. The cured COPNA resin carbonized at 800 °C for 3 h under N_2 atmosphere, the sample was noted as HC-800.

To prepare the HC@G composite anode materials, the cured resin precursor was first subjected to thermal treatment at 600 °C for 2 h under N_2 atmosphere, and the sample was chemically modified by HNO_3 to improve the hydrophilicity. GO was prepared from natural graphite flakes by a modified Hummers method [27]. Then the modified precursor was mixed with GO in a weight ratio of 100:5 by ultrasonication and was fully dried to obtain the solid mixture. The mixture was grinded and carbonized at 800 °C under N_2 for 3 h to obtain the graphene coated HC composite noted as HC@G-800. For comparison, a graphene sample was prepared by annealing the GO at 800 °C.

2.2. Physical characterization

Powder X-ray diffraction (XRD) data were collected on the Rigaku D/Max 2400 type X-ray spectrometer (CuKα). Raman measurements were performed on Thermo Fisher DXR Microscope Raman microscope. Fourier transform infrared (FT-IR) spectra were collected on Thermo Fisher Nicolet 6700. Scanning electron microscopy (SEM) images were captured on HITACHI UHR FE-SEM SU8200. Specific surface area and pore size distribution were measured and calculated according to the data recorded on Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K. To measure the I–V curve of the materials, a copper cylindrical mould was used to compress the powder with same weight into a tablet under a same pressure and as the current collector. And the I–V curves were tested with CHI 660C electrochemical workstation.

2.3. Electrochemical characterization

The electrochemical performances were tested via assemble the as-obtained materials into CR2016 coin cell. The anode electrode was prepared through applying the slurry made by mixing the active materials, acetylene black and polyvinylidene difluoride (PVDF) in a weight ratio of 7:2:1 on a copper foil and dried at 120 °C in a vacuum drying oven overnight. The SIBs were obtained by filling the CR2016 coin cells up with 14 mm diameter anode slices, glass fiber separator, Na foils, spacer and electrolyte (1 M $NaClO_4$ in ethylene carbonate and diethyl carbonate (volume ratio 1:1)) in an Ar-filled glovebox with concentrations of water and oxygen below 0.1 ppm. The rate and cycle performances of the as-prepared SIBs coin cells were characterized by the galvanostatic charge/discharge tests using a LAND CT2001A electrochemical workstation at different current densities within a cut-off voltage window of 0.01–3.0 V and the cells were rested for 1 min between each cycle. The specific capacity was calculated based on the mass of active material. The cyclic voltammetry test was performed using Bio-logic VSP electrochemical workstation between the voltage range of 0.01–3 V with the scan rate of 0.1 mV·s^{-1}. The EIS test was also conducted using Bio-logic VSP electrochemical workstation from 100 kHz to 10 mHz with the voltage amplitude of 5 mV at open circuit potential.
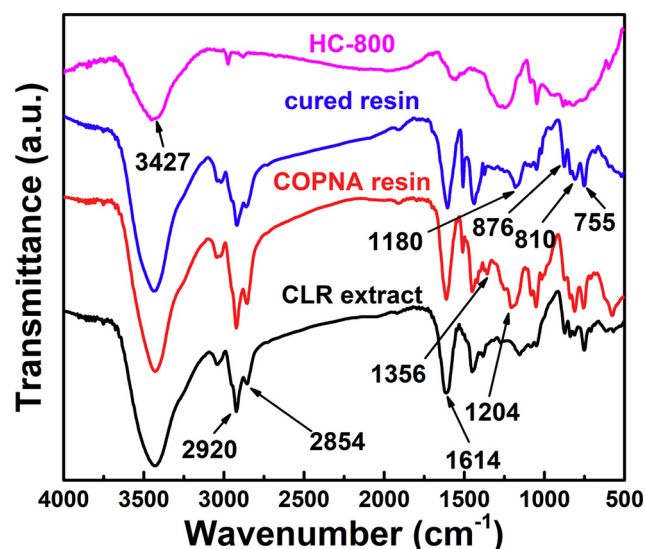

Fig. 1. FT-IR spectra of the CLR extract, COPNA resin, the cured hard carbon precursor and the HC-800.
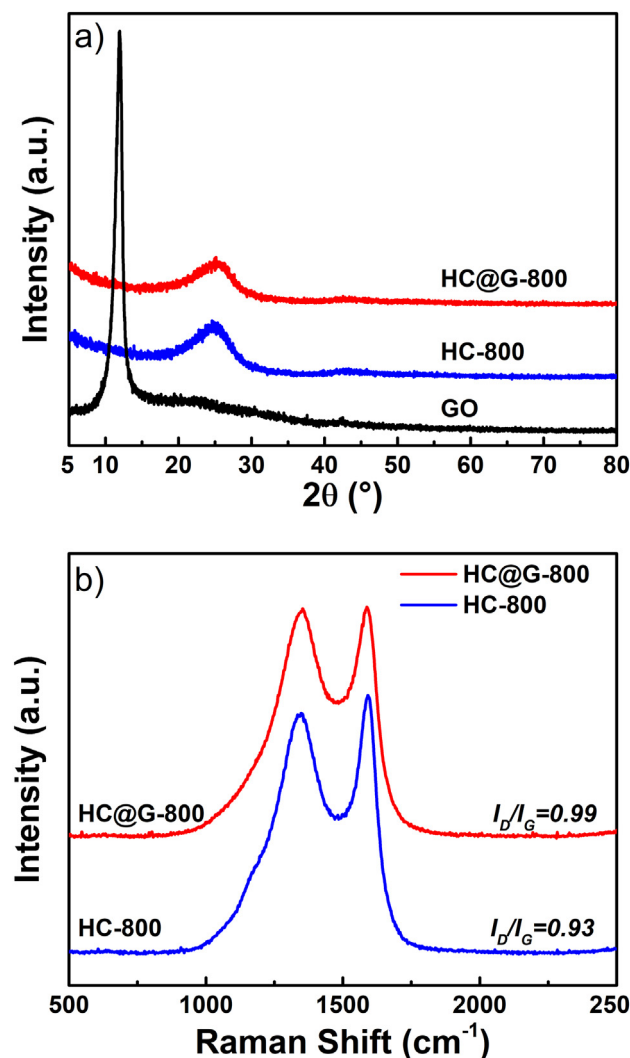

Fig. 2. a) XRD patterns of HC-800 and HC@G-800 and GO; b) Raman spectra of HC-800 and HC@G-800.