The structure and electrochemical properties of carbonized polyacrylonitrile microspheres

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ABSTRACT

A hard carbon microsphere (HCS) material with a uniform walnut kernel structure was prepared using polyacrylonitrile (PAN) asa a carbon precursor by a stabilization–carbonization method. The PAN–HCS preserves the original ellipsoidal shapes of natural polyacrylonitrile granules. Structural analysis shows that PAN–HCS is a kind of disordered carbon containing micropores and graphite-like micro-crystallites. The effects of heat-treatment temperature varying from 800 to 1500 °C on electrochemical performance were systemically studied. PAN–HCS–1250 obtained at 1250 °C as a negative material for lithium-ion batteries exhibits a reversible capacity of about 350 mAh g^{-1} at 20 mA g^{-1} with an excellent rate capability and cycling stability.

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1. Introduction

The performance of lithium-ion battery (LIB) is closely related with anode materials which favor lithium ion reversible intercalation/deintercalation. Among all the materials investigated, carbonaceous materials have received widespread attention for their high thermal and chemical stability, environmental friendliness, abundant source and low cost [1–10]. Nowadays the most common carbonaceous material as an anode material in industry is graphite owing to its high initial coulombic efficiency and low electrode potential relative to lithium metal [6,7]. However, low theoretical capacity (372 mAh g^{-1}) and bad rate performance restrict its applications in high-power devices [8]. Hard carbons have been reconsidered as prominent anode active materials of LIB with an expectation of application to power electric vehicles and energy storage components due to their properties of high energy and power density, long life and high safety [2–4], which can be ascribed to their highly irregular disordered structure and associated microporosity [10,11].

Generally, hard carbons contain resin carbons (such as phenolic resin, epoxy resin and poly (furfuryl alcohol PFA-C, etc.), organic polymer pyrolytic carbons (e.g., PFA, PVC, PAN, etc.) and carbon black (acetylene black), etc. Many disordered organic polymer pyrolytic

carbons have been accounted as promising anode materials because their preparation is less harsh than that of graphitized carbon, which only requires low-temperature treatment, and their reversible capacity is much higher than graphite(higher than 372 mAh g^{-1}) [12,13].

Among kinds of organic polymer pyrolytic carbons, PAN is an important precursor of carbon materials for its high carbon residue rate, good thermal stability, low cost, and fast pyrolysis, etc. Pyrolysis polyacrylonitrile has good electrical and ionic conductivity; hence it can effectively charge and discharge, and has a high cycle life. In theory, it should be an ideal electrode material of lithium-ion battery [14–20].

Carbon fibers based on polyacrylonitrile (PAN) have been studied as negative electrodes for lithium-ion batteries [14–18]. However, there have been only few reports about the electrochemical behavior of PAN-based hard carbon microspheres [19,20]. Its spherical morphologies are always prerogative owing to their high tap density, low surface-to-volume ratio and maximal structural stability [21–23].

In this paper, we prepared novel hard carbon microspheres from PAN (PAN-HCS) by a simple stabilization–carbonization method, which retained the original ellipsoidal shapes of PAN. We investigated the influence of pyrolysis temperature (TP) on structural characterization and electrochemical performance of PAN-HCS.

2. Experimental

2.1. Preparation of PAN-HCS

Hard carbon microspheres (HCS) were prepared by a two-step heat treatment consisting of stabilization and carbonization. The dried polyacrylonitrile particles were stabilized by heating polyacrylonitrile

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at around 280 °C for 2 h under controlled air circulation, aiming to improve the carbon yield and initial coulombic efficiency. Then they were carbonized by increasing TP to 800 °C under a nitrogen atmosphere for 0.5 h in a programmable tube furnace, named as PAN-HCS-800. The PAN-based disordered carbons were prepared from PAN by the same pyrolysis condition at 1000 °C, 1250 °C, and 1500 °C, denoted as PAN-HCS-1000, PAN-HCS-1250, and PAN-HCS-1500, respectively. The hard carbon microspheres had a relatively high carbon yield (61.29, 48.48, 47.22, 38.08 wt.%), which can be calculated through the following formula: $CY = Mc/Mn \times 100\%$, in which CY means carbon yield, Mc means mass of carbonized-PAN, and Mn means mass of natural PAN granules.

2.2. Materials characterization

The morphologies of the samples were observed using a field emission scanning electron microscope (FESEM, Nano430). The tap densities were determined by tapping a graduated cylinder containing a certain quality of powders until the volume of the powders did not change any more on a ZS-201 vibrating densimeter. The ratio of the quality and the volume was the tap-density of the powders [24]. Surface area was measured by N_2 adsorption using the Brunauer–Emmett–Teller (BET) method on a Micrometrics ASAP2020 analyzer. Crystallographic structure was characterized by X-ray diffraction (XRD) on a Rigaku D/Max 2500 X-ray diffractometer with Cu K radiation (40 KV, 150 mA, $\lambda = 1.54056$ Å) and Raman spectrum on a Renishaw in Via reflex Raman microscope using 514 nm line of Ar-ion laser as excitation source. The structure parameters calculated from the XRD spectra included the interlayer distance d_{002} and crystallite size:height Lc. Lc value was calculated from width at the half maximum of 002 bands using Scherrer equation. The number of layer-stacked-graphene sheets was calculated by the following equation: $N = Lc/d_{002}$.

2.3. Electrochemical measurements

Electrochemical tests were conducted on coin cells CR2430. PAN-HCS negative electrodes were prepared from slurry containing 86 wt.% hard carbon, 6 wt.% conductive carbon black (Super-P-Li, Timcal), 4 wt.% thickening agent carboxymethylellulose sodium (CMC), and 4 wt.% of binder styrene butadienerubber (SBR). The slurry was uniformly spread on a copper foil and then dried at 120 ºC for 12 h in a vacuum oven, followed by rolling. The electrode area was 1.69 cm^2 and an active material loading was 1.4–1.6 mg cm^{-2}. The cells were assembled in an argon-filled glove box using lithium sheets as the counter electrodes and 1.2 M LiPF$_6$ dissolved in EC/DEC (1:1 by volume) as the electrolyte.

The assembled cells were galvanostatically charged and discharged in the voltage range of 0.002–2.500 V at different current densities of 20, 50, 100, 200, 400, and 800 mA g^{-1} using a multichannel Land Battery Test System. Cyclic voltammetry (CV) measurements were performed on a Parstat 2273 potentiostat/galvanostat analyzer (Princeton Applied Research & AMTECT Company) at a scanning rate of 0.05 mV s^{-1}.

3. Results and discussion

3.1. Characterizations of morphology and structure

Fig. 1 shows the field emission scanning electron microscopy (FESEM) images for the natural PAN granules (Fig. 1a, d), stabilized-PAN (Fig. 1b, e) and carbonized-PAN (Fig. 1c, f–l). As shown in Fig. 1a, the natural PAN granules consist of single ellipsoidal particles with widely dispersed diameters varying from 5 to 50 μm. The surface of the PAN microspheres is very rough, with many bumps and fractures (Fig. 1d). After treatment with the stabilization and carbonization, the material still maintains the morphology characteristics of the original particles without any adhesion (Fig. 1b and c). This may be explained

that the conjugated ladder structure is formed accompanied by several reactions i.e., cyclization, dehydrogenation, aromatization, oxidation, crosslinking, which is thermally stable and might be able to withstand high temperature in the carbonization process [25]. However, the surface becomes smoother after oxidation (Fig. 1e), while the surfaces of hard carbon microspheres exhibit a uniform walnut kernel structure with defects, the single and multiple holes (Fig. 1f, j–l), which are caused by gas evolution (i.e., CO, CO_2, H_2O, etc.). This special morphology increases the contact area between active material and electrolyte, which is favorable for Li-ion diffusion from various orientations. The samples of PAN-HCS-800, PAN-HCS-1000, PAN-HCS-1250 and PAN-HCS-1500 change slightly on the sphere diameter and surface morphology, which is typical for non-graphitizable carbon material. Their tap densities vary from 0.89, 0.90, 0.91 to 0.88 g cm^{-3} and also do not change much. The high tap densities are ascribed to their ellipsoidal morphology, which may increase the batteries' energy densities. All the samples possess very low and almost equal BET surface areas of 0.5 m^2 g^{-1}. Unfortunately, it is difficult to exactly analyze the pore size distribution and pore volume in PAN-HCS through N_2 adsorption–desorption isotherm measurement because of their very low surface area [26]. In other words, the sub-nanopores in PAN-HCS are not accessible to N_2 but can serve as reservoirs for lithium ions.

The crystal structural variation of PAN-HCS treated at different temperatures is studied by XRD (Fig. 2a) and Raman spectroscopy (Fig. 2b). Two weak broad (002) and (100) diffraction peaks indicate that the PAN-HCS is an amorphous carbon containing a highly graphite disordered microcrystalline structure. According to the "Bragg equation", the calculated interlayer spacing (d_{002}) of PAN-HCS is 3.6 Å, significantly larger than the interlayer spacing of Li inserted graphite, which is favorable for insertion and extraction of Li-ion throughout PAN-HCS. As can be seen from the data in Table 1, the interlayer spacing of d_{002} decreases when the TP is above 1000 °C; meanwhile the size of the ordered domains in the c-axis direction (Lc) increases with the temperature, that is, the average size of the graphite crystallite becomes larger with TP increasing. In addition, the XRD results suggest that the carbonized product is composed of disordered graphite crystallites with 1–2 layer-stacked-graphene sheets. The diffraction intensity in low angle region is very strong, thus forms a tail, exhibiting a porous feature of PAN-HCS [27]. The "tail" is not obvious at low temperature; as TP increases, the PAN-HCS-1000 and PAN-HCS-1250 samples display graphite crystallite structures, making pore connectivity and trailing phenomenon gradually enhanced. When temperature further rises, the trailing character of PAN-HCS-1500 becomes weak again, because fullerenes shaped ring structure forms with microcrystalline becoming larger and being crosslinked. It is known that the pore structure in hard carbon acts as "reservoir" for Li-ion storage effectively [28,29]. So the different pore structure of PAN-HCS obtained by heat treatment at different temperatures produces different charge–discharge characteristics, discussed in the following.

The Raman spectra (Fig. 2b) show an increased intensity and a slightly decreased half width at half maximum (HWHM) of the G-band (the sp^2 graphitic configuration) at 1580 cm^{-1} and the D-band (the sp^3 configuration) at 1355 cm^{-1} with increasing TP, which could be caused by increasing intraplanar (La) and interplanar (Lc) microcrystallite dimensions [30]. Generally, the intensity ratio of the D-band over the G-band (I_D/I_G) represents the degree of disorder in the graphite structure [31]. The I_D/I_G numerical value decreases from 1.07 to 0.96 as the heating temperature increases from 800 °C to 1500 °C, indicating improvement of graphitization. A relatively low degree of graphitization of the PAN-HCS is consistent with the XRD results.

3.2. Electrochemical characterization

The lithium insertion/extraction properties of PAN-HCS are revealed by cyclic voltammetry (CV) curves and the galvanostatic charge/discharge profiles.