



Surface oxo-functionalized hard carbon spheres enabled superior high-rate capability and long-cycle stability for Li-ion storage

Rusheng Fu^{a, b}, Zhenzhen Chang^a, Chengxu Shen^a, Haocheng Guo^{a, b}, Heran Huang^a, Yonggao Xia^{a, **}, Zhaoping Liu^{a, *}

^a Advanced Li-ion Battery Engineering Laboratory and Key Laboratory of Graphene Technologies and Applications of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China

^b University of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 15 November 2017

Received in revised form

5 December 2017

Accepted 6 December 2017

Available online 15 December 2017

Keywords:

Oxo-functionalization

Hard carbon

Lithium ion battery

Lithium ion capacitor

ABSTRACT

Hard carbon is emerging as a highly promising material for power-demanded energy storage devices. Recently, introducing heteroatom such as oxygen is confirmed to be available to improve the capacity. However, it remains a significant challenge to achieve simultaneously superior high-rate capability and long-term cycling stability. Here we demonstrate that the surface oxo-functionalized hard carbon spheres (o-HCS, $4.2 \text{ m}^2 \text{ g}^{-1}$) derived from mild oxidative approach enhance pseudocapacitance lithium-ion storage with improved Li-ion diffusivity and thus exhibit high-rate capacity and long cycle life in both Li-ion batteries and Li-ion capacitors. The o-HCS electrode delivers specific capacity of around 275 mAh g^{-1} at 744 mA g^{-1} (2C) and capacity retention of above 92.0% and about 86.5% after 1100 and 1700 cycles, respectively. Impressively, it delivers above 110 mAh g^{-1} at extreme high current density of 14.88 A g^{-1} (40C). As well, o-HCS electrode in Li-ion capacitor shows a capacitance of 34.8 F g^{-1} (corresponding to 48.5 Wh kg^{-1} and 3.6 kW kg^{-1}) at the current density of 3720 mA g^{-1} , and after 7000 cycles the capacity retention is 96% ($\sim 0.057\%$ decay per cycle).

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1. Introduction

Over the past few decades, lithium ion batteries (LIBs) have been successfully applied to portable electric devices and electric vehicles because of high energy density [1,2]. Nowadays, one of the urgent challenges within lithium ion batteries is to improve power density (namely, fast charge/discharge capability). Decreasing electrons and ions migration barrier enable ultra-fast charge/discharge capability and subsequently receives excellent high-rate capability. Since first commercialized by Sony, carbon-based anodes have gained great success in LIBs [3]. Among numerous carbon materials, state-of-the-art hard carbon and mesophase carbon microbeads (MCMC) access to commercial employment as power-type lithium ion batteries because of isotropous lithium ion diffusion pathway and nice electronic conductivity [4–7]. However, the rate capability decrease upon increasing charge/discharge rate due to the attribution of increasing Ohmic resistance and diffusion

constrains, which are below the levels required for many applications. As we known, enlarging the surface area, for example hollow hard carbon is confirmed to be a typical strategy to improve the dynamics of carriers and then enhance the electrochemical performance [8–10]. Whereas, large surface area accelerates the side-reactions as well.

Another energy storage device, supercapacitors, store charge by adsorption of ions on the surface of electrode materials. Supercapacitors display exceptional power density and prominent cycle stability via this pure physical process, but low energy density [11,12]. Batteries and supercapacitors with separate electrochemical mechanisms determine their relative energy and power density, respectively. Recently, intercalation pseudocapacitive charge storage that is not a diffusion-controlled process demonstrates superior high-rate performance and cycling reversibility. Dunn and co-workers have confirmed great promise towards high-rate electrodes in LIBs driven by an intercalation pseudocapacitive mechanism [13–15]. Lithium ions inserted into mesoporous and nanocrystal orthorhombic Nb_2O_5 (T- Nb_2O_5) does not result in a phase change termed intercalation pseudocapacitive [13]. The key structural feature in T- Nb_2O_5 leads to exceptionally fast kinetics of

* Corresponding author.

** Corresponding author.

E-mail addresses: liuzp@nimte.ac.cn (Y. Xia), xiayg@nimte.ac.cn (Z. Liu).

lithium ions transport [16]. Similar observations were also reported on analogical sodium ion storage. Huang and co-workers have shown that graphene-coupled TiO₂ enables ultrafast sodium ion storage and long-term cycling by Na⁺ intercalation pseudocapacitance, owing to more feasible channel for Na⁺ insertion/extraction in graphene-TiO₂ interface [17]. Accordingly, pseudocapacitive materials hold the promise of achieving battery-level energy density combined with power density and long-term cycle-stability of supercapacitors.

Inspired by these, it is highly expected to achieve prominent rate capability and long cycle life of carbon electrode by introducing intercalation pseudocapacitive charge storage mechanism. One feasible approach is to introduce heteroatoms into carbon [18,19]. As we know, nitrogen and fluorine doping have been demonstrated to induce pseudocapacitance by improving the electrical mobility on carbon surface in aqueous electrolyte [20]. Boron and nitrogen dual-doped carbon is applied in high energy and high power lithium ion capacitors [21]. In addition, surface functional groups containing nitrogen, boron, fluorine and phosphorus can considerably enhance the capacitance of carbon electrodes as supercapacitors applying in aqueous or organic electrolyte [18,22–24]. Moreover, oxygen functionalities, such as C=O, C–O, –COOH, –OH and H₂O are often present on the carbon surface, especially when carbon is prepared below 980 °C and subsequently exposed in air or other oxidant atmosphere [23,25,26]. Surface oxygen-containing functional groups are considered as taking part in the Faradic interactions and thus significantly increase the energy storage in supercapacitors and secondary alkali ion cells [27–29]. Especially carbonyl group (C=O) and carboxyl group (–COOH) have been applied for rechargeable alkali ion batteries showing excellent rate capability [29–32]. Fujimoto and co-workers initially prepared oxygen-doped hard carbon and discovered that high oxygen concentration would yield a high reversible capacity in organic electrolyte [33]. Previously, strong oxidants H₂SO₄, HNO₃ and KMnO₄ were reported to introduce oxygen-containing surface functional groups into carbon matrix [34–36]. However, the present of oxygen-containing groups support extraordinary electrochemical capacity, but cause the capacitance deterioration with poor cycling performance [26].

Here we demonstrate non-porous hard carbon spheres with surface oxygen-containing groups bonded with carbon (o-HCS) display superb rate capability and cycling stability for LIBs anode and superior energy density for lithium ion capacitors (LICs). Hard carbon spheres are synthesized via modified CVD method, in which ethylene is pyrolyzed at high temperature but deposited at relative low temperature. Oxygen-containing functional groups introduced by mild oxidant facilitate the carrier mobility and boost lithium ion intercalation pseudocapacitance. We believe that the ion intercalation pseudocapacitance enabled by oxygen modification using a facile approach, which is a universal strategy, could be extended to other similar carbon-based materials to improve the power density and energy density.

2. Experimental section

2.1. Materials preparation

Hard carbon spheres were prepared by chemical vapour deposition under flowing ethylene (200 sccm) and Ar (200 sccm). Ethylene was pyrolyzed at 900 °C with a ramp rate 10 °C min^{–1}, but the sample was collected at low temperature region (200–500 °C) along gas-flowing direction. Oxo-functionalized hard carbon spheres (o-HCS) were received when the collected sample exposed to flowing H₂O vapour atmosphere (200 sccm for 12–24 h) and followed by drying at 120 °C for 4 h.

2.2. Materials characterizations

The crystal structures were determined by X-ray diffraction (XRD, Bruker D8 Advance) with a Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) operated at 40 kV and 40 mA. Nitrogen absorption and desorption isotherms were collected at 77 K using a Micromeritics ASPA 2020M analyzer. The morphologies and microstructures were examined using field emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, Tecnai F20), respectively. Focus ion beam assembled with Ga ion source was used to obtain cross section (FIB, Zeiss Auriga). Raman spectra (Raman, Renishaw inVia Reflex) were collected from 500 to 3600 cm^{–1} with a He-Ne laser at the wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD) measurements with a monochromatized Al K α X-ray source (1486.6 eV) was used to analyse the surface chemistry of functionalized hard carbon powders.

2.3. Electrochemical measurements

The electrodes were prepared by casting slurries on Cu current collector with active materials, conducting agent (Super-P), styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC) at a mass ratio 80:10:7:3. After casting, the electrodes were dried at 80 °C for 8 h in air followed by 5 h in vacuum at 120 °C (Büchi glass oven B-585), then pressed at 5 MPa. The coin cells CR2032 were assembled using Li foil or active carbon (AC, Power Carbon Technology Co., Ltd. CEP14) as a counter electrode within Ar-filled glove box (Mbraun, H₂O level <0.1 ppm and O₂ level <0.1 ppm). Celgard 2400 was used as separator, 1 M LiPF₆ dissolved in EC/DEC = 1:1 by volume with 5 wt% FEC (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd.) was used as electrolyte. The galvanostatic cycling was performed using Land CT 2100A battery-test system. The LIBs and LICs were charged (Li⁺ insertion) and discharged (Li⁺ extraction) in the potential range of 0.005–1.5 V and 2.2–3.8 V, respectively. Pre-lithiated o-HCS (~250 mAh g^{–1}) was used as anode and AC was used as the cathode with optimized cathode/anode mass ratio 2:1. The capacity (mAh g^{–1}) and capacitance (F g^{–1}) were calculated on the basis of o-HCS and o-HCS + AC, respectively. Cyclic voltammetry (CV) at various scanning rate from 0.005 to 2.0 V and electrochemical impedance spectroscopy (EIS) in the frequency of 10^{–1}–10⁵ Hz with an ac voltage 10 mV were recorded by electrochemical workstation (Solartron 1470E) using CR2032-type coin cells.

3. Results and discussion

3.1. Preparation strategy of oxo-functionalized hard carbon spheres

Recently, for the existing organic electrode materials, a reversible redox reaction usually occurs on an organic group with lone pair electrons such as O [37–40]. Subsequently, surface oxidation on carbon was introduced to improve the lithium ion storage [28]. In this regard, to obtain the oxygen-containing hard carbon, for example air, P₂O₅, (NH₄)₂S₂O₈ and H₂SO₄ were selected as the oxidation agents [33,41]. Oxygen functionalities coupled with carbon often take part in the Faradic interaction and thus significantly increase the electrochemical performance. Dahn and co-workers have shown that pyrolytic temperature makes impressive effect on the sensitivity of carbon when exposing to air [26]. In order to achieve surface oxidation, here we investigate the sensitivity of hard carbon collected at different temperature, as shown in Fig. 1a. Remarkably, more oxo-functionalized groups (C–O, C=O and O–C=O) revealed on the surface, when hard carbon prepared at lower deposited temperature (Fig. 1b). Thus we choose 3-position as the optimal condition to collect hard carbon for further study.

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