Carbon 122 (2017) 547–555

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Alkaline lignin derived porous carbon as an efficient scaffold for lithium-selenium battery cathode

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ARTICLE INFO

Article history:
Received 6 March 2017
Received in revised form
2 June 2017
Accepted 2 July 2017
Available online 3 July 2017

ABSTRACT

As one of the most abundant natural aromatic polymers with plentiful oxygen-containing groups in molecular backbones, commercial lignin can be regarded as a sustainable precursor to develop porous carbonaceous frameworks for the encapsulation of elemental selenium. In this paper, an initial combined carbonization/activation of commercial alkaline lignin and subsequent selenium-loading are adopted to fabricate serial composites of lignin-derived porous carbon (LPC) and elemental selenium (i.e., serial Se/LPC composites) for high-performance lithium-selenium (Li-Se) batteries. The high specific surface area, large pore volume and good electron conductivity of each LPC scaffold facilitate the reversible electrochemical reaction of selenium towards metallic Li, and at 0.5 C a Se/LPC composite electrode exhibits a reversible capacity of 596.4 mAh g^{-1} in the 2nd cycle and a capacity retention of 453.1 mAh g^{-1} over 300 cycles with an average decay of 0.08% per cycle. The facilely obtained microporous features of LPC scaffold, as well as the high-rate performance of corresponding Se/LPC composites (e.g., 363.2 mAh g^{-1}, 4 C), indicate that large-scale treatment of the biomass feedstock may find its potential application in renewable green energy sources.

1. Introduction

Lignin is a heterogeneous and amorphous polymer that constitutes a large portion of the cell walls of vascular plants, making it one of the amplest biomass just after cellulose on earth [1,2]. It can be obtained from a variety of low-cost woody plants and even from industrial waste such as paper mill effluents [3]. As we know, the estimated natural production of lignin is in the range of $5–36 \times 10^8$ tons annually [2,4], which has no structural regularity within its polymeric framework and is mainly composed of carbon and oxygen [1,5]. Especially, the low-cost, high carbon content, biodegradability, antioxidant activity and favorable stiffness of lignin have attracted people great interests in developing value-added products such as sorbents of exhaust gas CO_2 and electrode materials of supercapacitors and lithium-ion batteries [1,2,4,6–15].

Lithium-selenium (Li-Se) batteries are appealing for one kind of high-capacity energy storage devices, owing both to the high electronic conductivity (1×10^{-3} S m^{-1}) of elemental selenium and its good electrochemical activity and to the comparable theoretical gravimetric or volumetric capacity density (675 mAh g^{-1} or 3253 mAh cm^{-3}) [16–23]. Analogous to electrochemically cycled lithium-sulfur (Li-S) systems, Li-Se batteries also suffer from fast capacity fading, poor cyclability, and low coulombic efficiency because of the intermediate formation of electrolyte-soluble lithium polyselenide (Li_2Se_n, $3 \le n \le 8$) [17,20,24,25]. In this regard, combining electrical insulator S or semi-conductor Se with micro-/mesoporous carbons has been proved an effective method to improve the specific capacity and rate capability of Li-S or Li-Se batteries, because micro-/mesoporous carbon can encapsulate S or Se, then may prohibit the formation and diffusion of intermediate polysulfide (Li_2S_n, $3 \le n \le 8$) or polyselenide (Li_2Se_n, $3 \le n \le 8$), and then can act as a hierarchical and conductive architecture [20,26–36].

Superior to the preparation of porous carbon spheres after the traditional hard/soft template carbonization methods

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http://dx.doi.org/10.1016/j.carbon.2017.07.004
0008-6223/

[25,29,37–42], naturally abundant lignin with surface-rich oxygen-containing functional groups can be facilely transferred into porous carbonaceous materials such as lignin-derived carbon fibers, activated carbons and so on [1,2,4,7,11–14,43,44]. Taking the porosity manufacturing of synthetic carbon into consideration, traditional methods at least deal with the two steps of carbonization and activation, whereas commercial alkaline lignin can dissolve into water under alkaline circumstance and thus few amount of porogen KOH is further needed for this purpose [25,31,45–48]. Therefore, a facile and large-scale preparation of lignin-derived porous carbon (LPC) scaffolds may be a sustainable protocol, and the subsequently derived Se/LPC composites make a working electrode of Li-Se batteries both inexpensive and environmentally friendly to a great extent.

Herein, at a KOH:lignin mass ratio of 0.5, 1.0, 1.5 or 2.0, as-obtained LPC was tentatively applied as effective scaffold for the impregnation of elemental Se, and then at a fixed Se:LPC mass ratio of 6:4, the resulting Se/LPC composites interestingly presented good electrochemical properties for Li-Se batteries. As usual, the more amount of KOH was used the higher specific surface area or pore volume of resulting LPC was obtained. Herein, the resulting LPC-1.0, denoted according to the KOH:lignin mass ratio of 1.0 and hereafter, could acquire a high specific surface area of 1810.8 $m^2\ g^{-1}$ and a micropore volume of ~ 0.75 $cm^3\ g^{-1}$ (the total pore volume is ~0.92 $cm^3\ g^{-1}$). However, after the encapsulating of elemental Se, the corresponding Se/LPC-0.5, Se/LPC-1.0, Se/LPC-1.5 and Se/LPC-2.0 composites unexpectedly exhibit almost the same electrochemical cycling stability when applied as Li-Se battery cathodes. Aside from experimental design, both the structural properties of serial LPC scaffolds and corresponding Se/LPC composites and the electrochemical performances of these Se/LPC composite cathodes are investigated systematically. Also, a possible structure-function relationship, between as-obtained LPC matrices and their derived Se/LPC composites [18,20,24,26,27,31,34,49–53], indicates the possibly large-scale production of LPC scaffolds and their potential application for the green energy-storage system of Li-Se batteries.

2. Experimental

2.1. Materials and sample preparation

Commercial alkaline lignin was purchased from Geyi Energy (Anhui province, China) and was used as supplied. Solid state KOH, aqueous HCl and powdered selenium (200 mesh) are of analytical grade and were used as purchased. Ultrapure water (18.2 MΩ cm) was used for solution preparation and sample rinse.

Lignin-derived porous carbon (LPC) was prepared using a combined carbonization/activation method, and a typical process was shown as below [45,46,54,55]. Firstly, solid-state KOH (8.0 g) and powdered lignin (8.0 g) were added into a 50-mL beaker containing 28.5 mL H_2O in sequence and then were vigorously stirred by a Teflon-coated magnetic bar for 60 min. The resulting homogeneous polymer solution was dried in 80 °C oven for 24 h, which guarantees the uniform distribution of pore-forming reagent (i.e., solid-state KOH) in solid-state lignin at the KOH:lignin mass ratio of 1:1. Secondly, after a thoroughly grinding in an agate mortar, the 1:1 admixture was transferred into a nickel crucible, put in the N_2-atmosphere tube furnace programming at 5 $^\circ C\ min^{-1}$ and then carbonized at 700 °C for 2 h. Thirdly, the heat-treated sample was washed with aqueous HCl (2 M, 150 mL) for 30 min to remove any inorganic impurities then thoroughly rinsed with ultrapure water until pH~7 and then dried at 80 °C for 12 h, resulting in the porous scaffold of LPC-1.0. Finally, a melt-diffusion method was used to prepare Se/LPC-1.0 composite [25,28,39,56]: (i) at first elemental Se and scaffold LPC-1.0 were ground in an agate mortar at a fixed Se:LPC-1.0 wt ratio of 6:4; (ii) subsequently the ground mixtures were transferred into a porcelain crucible and then heat-treated at 260 °C under N_2 atmosphere (flow rate: 0.10 $L\ min^{-1}$) for 6 h.

2.2. Structural characterization

X-ray diffraction (XRD) data were collected on a Siemens D-500 diffractometer using Cu Kα radiation. Raman spectra were recorded on a LABRAM-HR confocal laser micro-Raman spectrometer employing a 20 mW laser at 632.8 nm. Scanning electron microscopy (SEM) was carried out with Hitachi SU8020, and transmission electron microscopy (TEM) was carried out with JEOL JEM-2200FS field emission electron microscope. Elemental analysis on the surface of sample was identified by energy-dispersive X-ray spectroscopy (EDS). Thermogravimetric analysis (TGA) measurements were carried out on a Mettler Toledo TGA/SDTA851 machine at a heating rate of 10 $^\circ C\ min^{-1}$ under N_2 atmosphere. Brunauer-Emmet-Teller (BET) isotherms and specific surface area (i.e., BET surface area) were performed on a Kubo X1000 instrument at 77 K. Pore size distribution and pore volume were derived using the analysis methods of Barrett-Joyner-Halenda (BJH) and Horvanth-Kawazoe (HK). X-ray photoelectron spectroscopy (XPS) analysis was performed on a ESCALab250Xi X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray source. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

2.3. Electrochemical measurements

Lithium foil was used as the counter electrode, Celgard 2300 polymeric film as the separator, and commercial LBC 305-01 $LiPF_6$ solution (Shenzhen Xinzhoubang) as the electrolyte. After the mixing of Se/LPC composite, acetylene black and sodium alginate binder at a weight ratio of 80:10:10, the resulting slurry was pasted onto an aluminum foil and dried at 80 °C for 12 h. The aluminum foil with a mass loading of 2.4 ± 0.3 $mg\ cm^{-2}$ was cut into discs with a diameter of 12 mm, and then as a working electrode. CR 2032 model cells were assembled in an argon-filled glove box.

Galvanostatic cycling tests were conducted on a Land CT2001A battery system in the voltage range of 1.0–3.0 V (vs. Li^+/Li), performed at 30 °C in a thermostatic desiccator. Cyclic voltammetry (CV) tests were performed on an LK 2005A electrochemical workstation at 0.1 $mV\ s^{-1}$ in the voltage range of 1.0–3.0 V. CHI 660E electrochemical analyzer (Shanghai Chenhua) was used to perform electrochemical impedance spectroscopy (EIS) tests, in the frequency range from 100 kHz to 0.1 Hz with AC voltage amplitude of 5 mV.

3. Results and discussion

Lignin can be directly extracted from its botanical source through a pulping chemical process of kraft, lignosulfonate, soda or organosolv [1,2,5]. The alkaline medium of kraft or soda pulping process could induce the breakdown of protolignin, the dissolution of fragments and the final recondensation, and thus, as alkaline chemicals, commercial alkaline lignin can be easily dissolved into KOH aqueous solution [1,5]. Herein, the combined carbonization/activation utilizes the alkaline-soluble property of the commercial biomass (Fig. 1), which guarantees the completely mixing of solid-state porogen and carbonaceous materials and thus costs a few amount of solid-state KOH to generate porous carbonaceous scaffolds uniformly in structure.

In fact, various biomass-based materials derived from plants and animals have been applied as precursors to obtain porous