



# Selenium encapsulated into 3D interconnected hierarchical porous carbon aerogels for lithium–selenium batteries with high rate performance and cycling stability



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## HIGHLIGHTS

- Selenium was encapsulated into hierarchical porous carbon aerogels for Li–Se batteries.
- The HPCA/Se composite showed outstanding rate capability and cycling stability.
- The LiNO<sub>3</sub> modified electrolyte signally improved cycling performance for Li–Se batteries.
- The ionic liquid PYR<sub>14</sub>TFSI modified electrolyte signally improved coulombic efficiency.
- The HPCA/Se composite would be a promising cathode material for Li–Se batteries.

## ARTICLE INFO

### Article history:

Received 7 April 2014

Received in revised form

9 May 2014

Accepted 22 May 2014

Available online 2 June 2014

### Keywords:

Lithium–selenium batteries  
Hierarchical porous carbon aerogels  
Ionic liquid modified electrolyte  
High rate performance  
Polyselenides

## ABSTRACT

Selenium encapsulated into 3D interconnected hierarchical porous carbon aerogels (HPCA) as a carbon/selenium composite material is prepared for lithium–selenium batteries. Scanning electron microscope (SEM) and transmission electron microscope (TEM) observations show the hierarchical porous structures of the carbon aerogels and the homogeneous distribution of selenium in the composite. The performance of the HPCA/Se cathode is evaluated in lithium–selenium batteries using cyclic voltammetry, galvanostatic charge–discharge, and electrochemical impedance spectroscopy. It is found that the HPCA/Se cathode shows high rate performance, coulombic efficiency and cycling stability. The HPCA/Se cathode has a highest coulombic efficiency which is kept above 98% after 50th cycle in ionic liquid *N*-methyl-(*n*-butyl) pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI) modified electrolyte and retains 309 mAh g<sup>−1</sup> after 100 discharge/charge cycles at a high rate of 0.5 C (337.5 mAh g<sup>−1</sup>) in LiNO<sub>3</sub> modified electrolyte, respectively. Even at the current density of 5 C (3375 mAh g<sup>−1</sup>), it can still maintain at a reversible capacity of 301 mAh g<sup>−1</sup>. The excellent electrochemical properties benefit from the high electron conductivity and 3D interconnected hierarchical porous structures of the carbon aerogels, which contribute to disperse selenium and absorb polyselenides, and suppress the formation of residual Li<sub>2</sub>Se layer.

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## 1. Introduction

Lithium–sulfur (Li–S) batteries have been studied as one of the most promising systems for the next generation high-energy rechargeable lithium batteries due to their high theoretical specific capacity (1675 mAh g<sup>−1</sup>) and energy density (2600 Wh kg<sup>−1</sup>) [1–4]. However, lithium–sulfur (Li–S) batteries suffer from the electronically and ionically insulating nature of sulfur and the

solubility of reductive polysulfides in organic electrolyte during cycling [4–8].

As a congener of sulfur, selenium being electrochemically similar to sulfur can be expected to react with lithium to generate selenides. However, compared with sulfur ( $5 \times 10^{-28} \text{ S m}^{-1}$ ), selenium ( $1 \times 10^{-3} \text{ S m}^{-1}$ ) has higher electrical conductivity than that of sulfur. Although the theoretical gravimetric capacity of the selenium (675 mAh g<sup>−1</sup>) is lower than that of sulfur (1672 mAh g<sup>−1</sup>), the theoretical volumetric capacity of selenium (3253 mAh cm<sup>−3</sup> based on 4.82 g cm<sup>−3</sup>) is comparable to that of sulfur (3467 mAh cm<sup>−3</sup> based on 2.07 g cm<sup>−3</sup>) [9–11]. The advantages of Se make it a prospective candidate for cathode material in high

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energy density lithium batteries for specific applications. However, at present, researches on lithium–selenium (Li–Se) batteries are still at a very early stage. Similar to sulfur, the selenium cathodes also face the dissolution issue of high-order polyselenides, resulting in fast capacity fading, poor cycle performance and low coulombic efficiency [10–13].

Recently, several efforts have been made to improve the electrochemical performance of lithium–selenium batteries, such as synthesized nanoselenium with various morphologies [13,14], used porous carbon interlayer [15], prepared selenium–conductive polymer composite [16], selected suitable electrolyte and binder [10,11]. Lately, Wu et al. [13] synthesized the nanoporous selenium as a cathode material with a reversible capacity of 206 mAh g<sup>-1</sup> at the current density 100 mA g<sup>-1</sup> after 20 cycles. In particular, the selenium/carbon composite has been considered as one of the most promising cathode materials for advanced lithium–selenium batteries, because porous carbon materials are effective to improve the electrical conductivity of selenium and restrain the solubility of lithium polyselenides [11,12]. Abouimrane et al. [9] conducted pioneering work on the use of Se/CNT composite as a cathode material with a reversible capacity of 350 mAh g<sup>-1</sup> at low current density C/12 (50 mA g<sup>-1</sup>) with ether-based electrolyte after 50 cycles. Although Se/CNT composite can improve the electrical conductivity of Se containing cathodes, the porous structure of the carbon electrode materials still needs optimization to obtain higher surface area, higher electrical conductivity, larger pore volume, and more abundant pore size. Recently, a highly ordered mesoporous carbon (CMK-3) [11] with a large surface area of 1386 m<sup>2</sup> g<sup>-1</sup> and a large pore volume 1.276 cm<sup>3</sup> g<sup>-1</sup> were served as the scaffold for carbon/selenium composites with excellent cycling stability. Therefore, we urgently need select versatile properties of carbon electrode materials to improve the utilization of Se and the electrochemical performance of Li–Se batteries.

Carbon aerogels (CA), as a novel and special type of carbon material, have been recognized as promising electrode materials due to their three-dimensional (3D) interconnected structure, high surface area, large pore volume, high electrical conductivity and controllable pore size [17,18]. Importantly, the unique characteristic for CA materials is the abundant micropores and mesopores [19,20]. The micropores as microcontainers for elemental Se will play a significant role in dispersing Se and absorbing the polyselenides and restraining the shuttle phenomenon, the high surface area of the micropores provides sufficient contact to the insulating Se and conveys a high electrical conductivity to the composite material. The mesoporous offer an avenue for the mass transport of Li ions during the electrochemical cycling and accommodate the polyselenides resulting from the electrochemical reactions. However, selenium encapsulated into 3D connected hierarchical porous carbon aerogels as cathode materials has been rarely reported in Li–Se batteries.

Herein, we were motivated to prepare carbon/selenium composite by a melt-diffusion strategy which selenium was encapsulated a three-dimensional interconnected hierarchically porous carbon aerogels (HPCA) with microporous walls (<2 nm) and interconnected mesoporous (10 nm). The obtained HPCA/Se composite cathodes demonstrate high rate cyclability and cycling stability. Electrochemical results exhibit an initial discharge capacity of 587 mAh g<sup>-1</sup> and retains 367 mAh g<sup>-1</sup> after 50 cycles at a high rate of 0.5 C. The stable cyclability and high capacities obtained at high rates of 5 C are attributed to the unique HPCA/Se electrode architecture facilitating charge transport, and the trapping of polyselenides and cycled products within the hierarchically structured meso/microporosity in the HPCA electrode materials. In addition, we have also devoted special attention to the development of new electrolyte formulations incorporating ionic liquid *N*-

methyl-*N*-butyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI) as co-solvent and LiNO<sub>3</sub> as additive for lithium–selenium (Li–Se) batteries, respectively. For the first time, we demonstrated that the use of ionic liquid PYR<sub>14</sub>TFSI modified electrolyte and LiNO<sub>3</sub> modified electrolyte can greatly improve the coulombic efficiency as well as cycling performance. Our results demonstrate that HPCA/Se composite is a promising cathode material for high rate performance and cycling stability lithium–selenium batteries.

## 2. Experimental

### 2.1. Materials preparation

The carbon aerogels were prepared by a sol–gel process, drying technique and carbonization [19], were etched by KOH at 800 °C for 120 min using KOH:C in mass ratio of 4:1 under argon atmosphere to obtain hierarchically porous carbon aerogels (HPCA).

A 6:4 weight ratio mixture of hierarchically porous carbon aerogels (HPCA) and Se (Sigma Aldrich, 99.5%) was mixed through wet ball-milling in acetone at 800 r min<sup>-1</sup> for 2 h. After evaporating acetone in air at room temperature, the HPCA–Se mixture was heated at 260 °C for 12 h with heating rate of 5 °C min<sup>-1</sup> in a tubular furnace under argon atmosphere. After cooling down to room temperature, the HPCA/Se composite was obtained. The HPCA/Se composites collected were dried in an air-oven at 50 °C for 24 h.

### 2.2. Material characterization

The morphologies of the samples were investigated by field emission scanning electron microscopy (FESEM, Nova Nano SEM 230) and transmission electron microscopy (TEM, Tecnai G2 20ST). The elements on the surface of sample were identified by energy-dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM, Tecnai G2 F20)/energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD, Rigaku3014) measurements were made with Cu K $\alpha$  radiation. Thermogravimetric analysis (TGA, SDTQ600) was conducted in determining the selenium content in the composite under N<sub>2</sub> atmosphere at a heating rate of 5 °C min<sup>-1</sup>. N<sub>2</sub> adsorption/desorption measurements were performed by using Quantachrome instrument (Quabrorb SI-3MP) at 77 K. The structure of the samples was tested by Raman spectrometer (Jobin-Yvon LabRAM HR-800, Horiba).

### 2.3. Electrochemical measurements

The composite cathode slurry was made by mixing 80 wt.% HPCA/Se composite material, 10 wt.% carbon black and 10 wt.% sodium alginate (SA) binder in deionized water solvent. Then, the slurry was spread onto aluminum foil (20  $\mu$ m), and dried at 60 °C under vacuum overnight. The pristine selenium cathode containing 45 wt.% selenium, 45 wt.% carbon black, and 10 wt.% sodium alginate (SA) binder was prepared in the same way for comparison. The dried electrodes were punched into round discs with a diameter of 1.0 cm and an active material load of about 1.5–2 mg cm<sup>-2</sup>. Coin-type (CR2025) cells were assembled in an argon-filled glove box (Universal 2440/750) in which oxygen and water contents were less than 1 ppm. The basic electrolyte used was 1 M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI, Sigma Aldrich) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxyethane (1:1, v/v) (Acros Organics). The two kinds of modified electrolytes were prepared by adding 0.1 M LiNO<sub>3</sub> and 50 wt.% ionic liquid *N*-methyl-*N*-butyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR<sub>14</sub>TFSI) into the basic electrolyte, respectively. Lithium metal was used as counter electrode and reference electrode and Celgard

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