



Full paper

Heteroatoms dual-doped hierarchical porous carbon-selenium composite for durable Li–Se and Na–Se batteries

Xiaosen Zhao^{a,1}, Lichang Yin^{b,1}, Tong Zhang^a, Min Zhang^a, Zhibo Fang^a, Chunzhong Wang^a, Yingjin Wei^a, Gang Chen^{a,c}, Dong Zhang^{a,*}, Zhenhua Sun^{b,*}, Feng Li^{b,*}

^a Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, China

^b Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

^c State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

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ABSTRACT

Selenium (Se) is a prospective candidate of cathode material for high-energy batteries. However, the dissolution of high-order lithium selenides and the shuttle effect in electrolytes lead to low Se utilization, inferior capacity and poor cycling performance. Herein, a heteroatoms (N and O) dual-doped hierarchical porous carbon (HDHPC) with interconnected macro/meso/micropores is used to confine Se composite and developed as a cathode material for advanced Li/Na–Se batteries in low-cost carbonate electrolyte. For Li–Se batteries, Se/HDHPC cathode delivers an initial charge capacity of 613 mAh g⁻¹ and maintains stable reversible capacity of 545 mAh g⁻¹ with a capacity decay as low as 0.0074% per cycle after 1500 cycles at a current density of 0.5 C (1 C = 675 mA g⁻¹). For Na–Se batteries, Se/HDHPC exhibits a high initial charge capacity of 619 mAh g⁻¹ and retains as high as 402 mAh g⁻¹ after 500 cycles at a current rate of 0.5 C. Moreover, Se/HDHPC composite also exhibits an excellent rate performance both in the Li–Se and Na–Se batteries even at a high rate up to 20 C (13.5 A g⁻¹). Such excellent electrochemical properties of Se/HDHPC are mainly contributed from two aspects. One is the hierarchical porous structure of the HDHPC, which benefit the penetration of electrolyte and also act as micro reaction chambers to effectively suppress the volume change of the electrode. The other is the strong interaction between lithium/sodium selenide and carbon host induced by heteroatoms (N and O) dual-doping, which can strongly anchor the Se-contained species, thus preventing the side reaction of Se anions with electrolyte.

1. Introduction

High energy density, long cycle life and high efficiency are major requirements of the new generation batteries in order to meet the needs of the popularization of portable electronic devices, the rapid development of electric vehicles and the large-scale energy storage. In recent years, Se cathode materials have attracted considerable attention owing to their high theoretical volumetric capacity (3253 mAh cm⁻³) based on the high density 4.2 g cm⁻³. Moreover, the high electronic conductivity of Se (1×10^{-3} S m⁻¹) further benefits a high utilization rate of the active materials in batteries. These advantages of Se make it a promising cathode material for high-energy rechargeable batteries. However, Se cathode also suffers from the shuttle effect of high-order polyselenides during redox reaction, thus showing a rapid capacity decrease and low coulombic efficiency [1,2]. Recently, researchers have been searching for methods to incorporate Se with various

conductive materials, such as porous carbon [3], carbon aerogels [4], graphene [5,6], carbon nanotubes/nanofibers [7,8] or conductive polymers as the cathode [9]. Although these carbon–Se hybrids have shown good electrochemical performance during initial cycles, their performance usually decreases rapidly in subsequent long-run cycles because of the weak interaction between the Se and carrier, large volume expansion [10,11] and the side reaction between Se anions and electrolytes [12]. Hence, it is highly desirable to design a Se hybrid composite electrode with effective physical confinement of and strong chemical binding to Se-contained species, simultaneously. It is worth noting that Cheng's [13,14] and Zhang's [15,16] group found that heteroatom doping (N, O, P, etc.) can effectively enhance the interaction between sulfur/polysulfide guests and carbon host, thus improving the electrochemical performance of lithium-sulfur battery.

Here, we design and prepare a Se/Carbon (Se/C) composite by incorporating Se into a heteroatoms (N and O) dual-doped hierarchical

* Corresponding authors.

E-mail addresses: dongzhang@jlu.edu.cn (D. Zhang), zhsun@imr.ac.cn (Z. Sun), fli@imr.ac.cn (F. Li).

¹ These authors contributed equally to this work.

porous carbon (HDHPC) matrix. The obtained HDHPC with large surface area and high pore volume possesses a unique structure with interconnected macro/meso/micropores. Such unique structure not only exhibits large electronic conductivity and offer abundant electrolyte pathways, but also facilitates the interaction between carbon with Se and acts as micro reaction chambers to effectively suppress the volume change of the electrode and trap the polyselenides intermediates during cycling. Additionally, the heteroatom dopants (N and O) help to enhance the interaction between carbon and Se/Li₂Se/Na₂Se. Therefore, the synergic effect of heteroatom (N and O) dual-doping and porous structure can effectively improve the electrochemical properties [11,17,18]. As expected, using Se/HDHPC composite as the cathode material for both lithium-selenium (Li-Se) and sodium-selenium (Na-Se) batteries, a high-rate performance and high cycling stability have been achieved in low-cost carbonate electrolyte. For Li-Se battery, at a current density of 0.5 C (1 C = 675 mA g⁻¹), the Se/HDHPC cathode delivers an initial charge capacity of 613 mAh g⁻¹ and a reversible capacity of 545 mAh g⁻¹ with coulombic efficiency nearly 100% and a capacity decay as low as 0.0074% per cycle after 1500 cycles. For Na-Se battery, the Se/HDHPC composite cathode exhibits a high initial charge capacity of 619 mAh g⁻¹ and retains as high as 402 mAh g⁻¹ after 500 cycles at a current rate of 0.5 C. Moreover, the Se/HDHPC composite presents a durable cycling performance at high rate of 20 C (13.5 A g⁻¹) for both Li/Na-Se batteries.

2. Experimental section

2.1. Materials preparation

2.1.1. Synthesis of poly dopamine (PDA)

All the reagents in the experiments were used as received. Firstly, dopamine hydrochloride (DA·HCl, 98%, Sigma) was dissolved in the Tris-HCl buffer solution (Tris, AR, ≥99.8%, Aladdin, pH = 8.5) to get a 2.0 g L⁻¹ dopamine solution. Then the reaction mixture was stirred vigorously in air at 60 °C for 1 h, and (NH₄)₂S₂O₈ (APS, AR, Aladdin) was added to the solution to give a solution with a pH value around 2.0. A brown precipitate was gradually formed under stirring at 60 °C. After reaction for 24 h, the solution was cooled down to room temperature and filtered with a 0.4 μm membrane. The remaining solid material was then washed with water and absolute ethanol several times. Finally, the solid product was dried at 180 °C for a day to obtain PDA.

2.1.2. Synthesis of heteroatoms-doped hierarchical porous carbon (HDHPC)

HDHPC was prepared by pyrolysis of PDA with KOH. Briefly, PDA and KOH were mixed at a weight ratio of 1:3 in 10 mL deionized water to prepare a solution. After the solution was dried, the mixture was placed in a tube furnace to be heated up to 600 °C at a heating rate of 3 °C min⁻¹ and incubated for 1 h in N₂ protection. After cooling to room temperature, the solid product was washed with 1 M HCl solution and deionized water until the filtrated solution became neutral. Then, the sample was dried overnight at 60 °C in an oven to gain the N, O-doped hierarchical porous carbon (HDHPC).

2.1.3. Synthesis of the Se/HDHPC composites

Se/HDHPC composites were prepared via a simple melt-diffusion method. Firstly, the bulk Se and HDHPC were mixed in an agate mortar at a weight ratio of 5:5, 6:4 and 7:3, respectively. After drying, the mixture was transferred to a polytetrafluoroethylene autoclave and held at 260 °C for 20 h in an Ar atmosphere to obtain the Se/HDHPC composite, denoted as Se₅₀/HDHPC, Se₆₀/HDHPC and Se₇₀/HDHPC.

2.2. Characterizations of the materials

The crystal structure of the materials was studied by X-ray diffraction (XRD) on a Rigaku AXS D8 diffractometer with Cu Kα radiation in

the 2θ range of 10° – 80°. The morphology of the materials was analyzed by means of a Hitachi SU8020 scanning electron microscope (SEM). The microstructure was obtained by a FEI Tecnai G2 electron microscope (TEM) coupled with an X-ray energy dispersive spectroscopy (EDS, BRUKER AXS), which was used to detect the elemental distribution. The thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo thermal gravimetric analyzer in N₂ flow with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Raman spectroscopy was carried out using a LabRAM HR Evolution Raman spectrometer with a 523 nm diode-pumped solid state laser with an Nd-line laser source. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB spectrometer with a Mg-Kα light source. Fourier transform infrared (FT-IR) spectra were recorded on a FTIR spectrometer (Bruker Tensor IFS-66V/S, Germany). Brunauer-Emmett-Teller (BET) analysis was carried out to analyze the specific surface area and the pore size distribution of the composite (Beijing Builder, kubo-x1000, China). The pore size distribution of the material was measured by the Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) methods.

2.3. Electrochemical tests

The electrochemical performances of Se/HDHPC electrodes were tested using 2032-type coin cells which were assembled in an argon-filled glove box. The electrodes were prepared by scraped slurry, which prepared by mixed Se_n/HDHPC, super P carbon, and sodium alginate binder at a weight ratio of 8:1:1, onto the aluminum foil, then, dried at 120 °C for 12 h in vacuum and cut into 8 × 8 mm² small squares with an area active materials mass loading of around 1.5 mg cm⁻². Coin cells for Li-Se batteries were assembled with lithium foil as the counter electrode, 1 M lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, by volume ratio) as the electrolyte, the amount of electrolyte is 60 μL for per cell, and Celgard 2320 as the separator. Coin cells for Na-Se batteries were assembled with sodium foil as the counter electrode, 1 M Sodium perchlorate (NaClO₄) in a mixture of EC and propylene carbonate (PC) (1:1, by volume ratio) as the electrolyte, the amount of electrolyte is 60 μL for per cell, and Celgard 3501 as the separator. Galvanization charge/discharge was investigated by the LAND-2100 (Wuhan, China) instrument at room temperature. Cyclic voltammograms (CV) were recorded on a VSP multichannel potentiostatic-galvanostatic system (Biologic SAS, France). The test condition of CV was a scanning rate of 0.1 mV s⁻¹ in the voltage range from 1.0 to 3.0 V (vs. Li/Li⁺) for Li-Se battery and 0.5–3.0 V for Na-Se battery.

3. Computational methods

The first-principles calculations were performed by using the Vienna Ab-initio Simulation Package [19] with the projector augmented wave method [20]. The Perdew-Burke-Ernzerhof (PBE) functional [21] for the exchange-correlation term was used for all calculations. The projector augmented wave method (PAW) was used at a plane-wave cutoff of 400 eV to describe the electron-ion interaction. Only the Γ point was used to sample the first Brillouin zone for all calculations. A poly-aromatic hydrocarbon (PAH) molecule of C₁₉H₁₁ was constructed to represent the carbon framework of hierarchical porous carbon with a "20 Å × 20 Å × 15 Å" supercell. Spin polarized calculations were performed for systems with an odd number of electrons. N-doped, O-doped, N/O-codoped carbon with different doping configurations were considered by substituting, removing, and/or adding relevant atoms based on the C₁₉H₁₁ molecule. The binding energies between Li₂Se and different carbon materials are calculated by following definition:

$$E_b = E_{C/Li_2Se} - E_C - E_{Li_2Se}$$

where E_C , E_{Li_2Se} , and E_{C/Li_2Se} are, respectively, the total energies of different carbon systems (including pristine carbon, N-doped carbon, O-

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