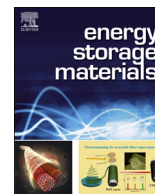




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Unique electrochemical behavior of heterocyclic selenium–sulfur cathode materials in ether-based electrolytes for rechargeable lithium batteries



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ABSTRACT

Mixed chalcogenide systems represent a new class of promising cathode materials for high performance rechargeable lithium batteries. Among them, heterocyclic selenium–sulfur (Se_xS_y) cathodes, coupling the good conductivity of Se and high capacity of S, have attracted great attention in recent years. However, further research is still needed to better understand the lithiation/delithiation process of Se_xS_y cathodes in ether-based electrolytes. Herein, Se_xS_y-based composites with covalent Se–S bonds were prepared by infiltrating various proportions of S and Se powders into the mesoporous carbon microsphere (MCM) host at 500 °C in vacuum. As cathodes for rechargeable lithium batteries, Se_xS_y/MCM composites exhibit unique electrochemical behavior rather than a simple hybrid of Li–S and Li–Se batteries in ether-based electrolytes. The Se–S bonds in Se_xS_y/MCM could anchor S during cycling, and effectively reduce the formation of long-chain polysulfides. As a result, the Se_xS_y/MCM cathodes demonstrate superior overall electrochemical performance than Se/MCM or S/MCM. Moreover, Se/S ratio could also affect the electrochemical behavior of Se_xS_y/MCM composites. The optimal Se₂S₅/MCM cathode delivers the best performance with a high reversible capacity of 796.4 mAh g⁻¹ at 0.5 C over 100 cycles, and good rate capability of 688.8 mAh g⁻¹ at 5 C. Especially, a superior coulombic efficiency of ~100% is achieved without addition of LiNO₃. This work could help us to better understand the inherent synergistic mechanism behind Se_xS_y cathodes for high performance rechargeable lithium batteries in ether-based electrolytes.

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1. Introduction

The energy density of current lithium-ion batteries is mainly limited by the cathode materials as the capacities (120–160 mAh g⁻¹) of commercial lithium transition metal oxides are much lower than the counterpart anodes [1–5]. Discovery and optimization of new cathode materials is, thus, a key to meeting the future demand for higher energy density [6–8]. Chalcogen in Group 16(VIA), such as O₂, S, and Se, are the most promising cathode materials due to their amazing energy density and wide availability [9]. However, Li–O₂ batteries are far from commercialization because their cycling is seriously limited by electrolyte decomposition and large cell polarization [10–12]. Li–S batteries

are considered to be extremely promising due to their high specific capacity (1675 mAh g⁻¹) as well as the natural abundance and environmental benign of S [13–15]. Nevertheless, Li–S batteries suffer from low S utilization and fast capacity decay caused by the insulating nature of S and dissolution of intermediary polysulfides. As a congener of element S, Se rivals S in many aspects, including the much higher electronic conductivity (1 × 10⁻³ S m⁻¹) than S and the comparable volumetric capacity (3254 mAh cm⁻³) to S [16]. However, Li–Se batteries have inferior gravimetric capacity (675 mAh g⁻¹) and cost.

Both Li–S and Li–Se batteries suffer from severe shuttle effect and fast capacity fading. Carbonaceous materials are the most widely used host materials to confine S/Se species in Li–S/Se batteries. Nevertheless, the poor adsorption capabilities of carbon hosts toward polar natured polysulfides/polyselenides have further triggered research interest in finding alternative host materials [17]. Heteroatom (N, O, etc.) doped carbon [18–22] and polar compound additives or hosts [23–26] (such as metal oxides/

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sulfides) are two effective routes to anchor polysulfides/polyselenides via strong chemical interaction. However, most metal oxides/sulfides are not conductive [27] and the additional modifications bring in electrochemically inactive mass, and thus hinder the full demonstration of energy density. In addition, the major stream of these studies has focused on the design of S/Se hosts, but modification on the S/Se-containing guests could be a new way to improve the performance of the Li–S/Se batteries. Recently, Qian et al. [28] reported that introducing a small amount of Se into S molecules could anchor S during cycling, and thus effectively reduce the dissolution of polysulfides and shuttle effect. Subsequently, Yu et al. [29] conducted similar research by employing a flexible $S_{1-x}Se_x$ @porous carbon nanofibers thin film for Li–S batteries and room-temperature Na–S batteries. These S-rich $S_{1-x}Se_x$ composites demonstrated excellent electrochemical performance in carbonate-based electrolytes. Therefore, exploring new cathode materials, beyond the present S or Se, with suppressed formation or dissolution of polysulfides/polyselenides could also be a promising strategy for efficient Li ion storage.

Heterocyclic selenium–sulfur molecules (Se_xS_y) represent a broad class of new cathode materials with higher theoretical capacities than Se alone, and improved conductivity compared S alone [9]. To date, several Se_xS_y -based composite cathodes for rechargeable lithium batteries have been reported with optimal comprehensive performance [30–34]. However, compared with Se_xS_y cathodes in carbonate-based electrolytes, few research has focused on ether-based electrolytes except for the work by Amine's group [32,33] and Zhang et al. [34]. Generally, ether-based electrolytes could guarantee faster redox reaction and higher reversible capacity for S/Se cathodes than that of carbonate-based electrolytes [14]. S and Se have been reported to undergo the similar two-step lithiation process in ether-based electrolytes [32,35], but the reaction process still remains unclear and overlooked for Se_xS_y cathodes. Amine et al. [33] reported amorphous Se_2S_5 confined in micro/mesoporous carbon cathode and evaluated its performance in ether-based electrolyte. Nevertheless, their work mainly focused on the study of (de)lithiation and capacity fading mechanism of the Se component in ether-based electrolytes. What's more, the results indicated that the electrochemical behavior of Se_xS_y cathodes was more of a simple hybrid of the Li–S and Li–Se batteries. Previous work [28,29,31,33] suggested that the as-prepared Se_xS_y is a new compound with Se–S bonds instead of a physical mixture of S and Se. It is therefore rational to anticipate that the Se–S interaction could enable Se_xS_y cathodes to exhibit unique electrochemical behavior. In this sense, further research to better understand the lithiation/delithiation process of Se_xS_y cathodes in ether-based electrolytes is still necessary.

In this work, we are motivated to investigate and correlate the inherent synergistic effect of Se and S with the electrochemical performance of heterocyclic Se_xS_y -based composite cathodes in ether-based electrolytes. Mesoporous carbon microspheres (MCMs), prepared via a high-throughput spray drying-assisted hard template method, were used as carbon matrix to confine active materials. Se_xS_y /MCM composites were then prepared by a melting-impregnation method starting from elemental S and Se powders in various proportions. X-ray photoelectron spectroscopy (XPS) and diffraction (XRD) analysis demonstrate the existence of Se–S bonds in the composites. Cyclic voltammetry (CV) tests also suggest that the Se_xS_y /MCM composites present a unique electrochemical behavior with formation of new intermediate phases in addition to the conventional polyselenides and polysulfides. Furthermore, optimization on Se to S ratio of the Se_xS_y /MCM composites was also carried out and discussed. The optimal Se_2S_5 /MCM cathode delivers higher discharge capacity, better cycling stability and superior rate capability than Se/MCM or S/MCM

cathode alone. This work could help us to better understand the inherent synergistic effect of Se and S behind Se_xS_y -based cathodes for high performance rechargeable lithium batteries.

2. Experimental

2.1. Preparation of MCMs

The Mesoporous Carbon microspheres (MCMs) were prepared via a high-throughput spray drying-assisted hard template method as our previous report [36]. Typically, resorcinol and formaldehyde (RF) with a mole ratio of 1:2 were added to the colloidal silica solution under continuous magnetic stirring. The mass ratio of RF/silica was fixed at 1:1. The mixed solution was then spray-dried using a spray-dryer (Blon-6000y, Shanghai Bilon Instrument Co., Ltd). Specific parameters were fixed as: inlet temperature of 120 °C, inlet pressure of 0.3 MPa, air-blower relative rate of 90, and feed rate of 1000 mL h⁻¹. Fine powder was discharged continuously from the drying chamber and then collected using a cyclone separator. The powder was then carbonized in a nitrogen flow at 800 °C for 3 h with a heating rate of 5 °C min⁻¹. Finally, the MCMs were obtained by the dissolution of silica nanoparticles in 2 M NaOH solution at 80 °C, isolated by filtration, washed with distilled water and ethanol, and dried at 100 °C.

2.2. Preparation of Se_xS_y /MCM composites

The Se_xS_y /MCM composites were prepared following a conventional melt-diffusion strategy. In a typical synthesis, Se powder, S powder, and MCMs were mixed homogeneously and sealed in a glass tube under vacuum. The sealed glass tube was heated up to 500 °C with a heating rate of 5 °C min⁻¹ and then held for 2 h before cooled down to room temperature naturally. In this work, Se_xS_y /MCM composites with molar ratio of Se to S=1:5, 2:5, 4:5 were prepared and the carbon contents in the composites are fixed at 50 wt%. The final collected black powder were denoted as Se_xS_y /MCM, where x and y represented the Se/S mole ratios in the composites. For Se_xS_y without carbon, the preparation procedure is similar, except the adding of MCMs.

2.3. Material characterization

The morphologies of the samples were observed on scanning electron microscopy (SEM, JEOL 7100F) and transmission electron microscopy (TEM, JEOL 2100F). Elemental mapping analysis was carried out using a scanning transmission electronic microscope (STEM, Tecnai G2 F30). The Se_xS_y contents in the Se_xS_y /MCM composites were determined by thermogravimetric analysis (TGA, TA Instrument Q600 Analyser) under argon atmosphere. Nitrogen adsorption-desorption isotherms were performed at 77 K with a Quadrasorb SI analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). The pore size distribution was derived from desorption branch by using the Barrett-Joyner-Halenda (BJH) model. The total pore volumes (V_T) were estimated using a single point at the maximal relative pressure of 0.985. X-ray diffraction (XRD) were performed using Cu ($K\alpha$) radiation ($\lambda=1.5406 \text{ \AA}$) with the 2θ -angle recorded from 10–80° (Rigaku D/Max 2550). The surface chemistry of the samples was analyzed using an Axis Ultra DLD X-ray photoelectron spectroscopy (XPS). The X-ray source operated at 15 kV and 10 mA. The working pressure was lower than 2×10^{-8} Torr (1 Torr=133.3 Pa). The C 1s, Se 3d, S 2p and Se 3p XPS spectra were measured at 0.1 eV step size. The binding energies were calibrated taking C 1s as a standard with a measured typical value of 284.8 eV. The Se 3d, S 2p and Se 3p XPS signals were fitted with

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