



Selenium and selenium-sulfur cathode materials for high-energy rechargeable magnesium batteries



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HIGHLIGHTS

- Selenium based composites are studied as cathode materials for magnesium batteries.
- The selenium composites show high volumetric capacity and rate capability.
- The electrochemical mechanism of Mg–Se battery is investigated.

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ABSTRACT

Magnesium (Mg) is an attractive metallic anode material for next-generation batteries owing to its inherent dendrite-free electrodeposition, high capacity and low cost. Here we report a new class of Mg batteries based on both elemental selenium (Se) and selenium-sulfur solid solution (SeS₂) cathode materials. Elemental Se confined into a mesoporous carbon was used as a cathode material. Coupling the Se cathode with a metallic Mg anode in a non-nucleophilic electrolyte, the Se cathode delivered a high initial volumetric discharge capacity of 1689 mA h cm⁻³ and a reversible capacity of 480 mA h cm⁻³ was retained after 50 cycles at a high current density of 2 C. The mechanistic insights into the electrochemical conversion in Mg–Se batteries were investigated by microscopic and spectroscopic methods. The structural transformation of cyclic Se₈ into chainlike Se_n upon battery cycling was revealed by *ex-situ* Raman spectroscopy. In addition, the promising battery performance with a SeS₂ cathode envisages the perspective of a series of SeS_n cathode materials combining the benefits of both selenium and sulfur for high energy Mg batteries.

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1. Introduction

New battery systems with high energy density are being extensively explored in order to meet the demand of rapidly developing market for longer-lasting portable electronics and electric vehicles (EVs). It is recognized that the conventional lithium ion batteries (LIBs) are approaching their theoretical energy density limits and the issues of safety and high cost remain unresolved [1–3]. Rechargeable Mg batteries have been recognized as an attractive alternative for energy storage owing to the inherent merits of Mg metal as anode in terms of high volumetric capacity

(3837 mA h cm⁻³), dendrite-free deposition and low cost [4–6]. However, Mg batteries are hampered by several technical obstacles, such as the lack of electrolyte which is stable in contact with the electrode materials and the quest for practical cathodes offering high accessible capacity and rate capability. In fact, there are a few types of conventional intercalation materials capable of storing Mg²⁺ ions reversibly due to the intrinsically sluggish Mg²⁺ ion diffusion kinetics in the cathode hosts [7]. Thus, the challenges to realize the rechargeable Mg battery technology are not only the improvement of the electrolyte towards high oxidative stability, but also the discovery of practically cathode materials enabling high performance of Mg batteries.

Recent achievements of non-nucleophilic electrolytes with good electrochemical performance have paved the way to employ

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conversion cathode materials for advanced high-energy magnesium batteries [8–10]. Beyond intercalation chemistry, sulfur is an attractive cathode material with a high theoretical capacity, low cost and non-toxicity. The volumetric energy density of the couple of a sulfur cathode and a Mg anode can theoretically reach up to 3200 Wh l⁻¹. The non-nucleophilic electrolytes developed in our laboratory through the reaction between magnesium-bis(hexamethyldisilazide) [(HMDS)₂Mg] and aluminum chloride (AlCl₃) in different ethers have been successfully applied to the magnesium-sulfur (Mg–S) batteries [11,12]. Despite the considerable achievements, the Mg–S batteries still suffer from capacity fading upon cycling mainly due to the dissolution of long-chain magnesium polysulfide (MgS_n, n ≥ 4). While making an effort to address these issues by the fabrication of new S cathode materials [13], we are also attempting to explore new electrode materials for advanced Mg battery systems.

Selenium (Se), a *d*-electron-containing element in Group 16, is proposed as a prospective electrode material, which is chemically similar to S and possesses some merits beyond S. In spite of its lower gravimetric capacity (about 678 mA h g⁻¹) compared to S (1675 mA h g⁻¹), the theoretical volumetric capacity of Se (3268 mA h cm⁻³) is comparable to that of S (3467 mA h cm⁻³). More importantly, Se has an electronic conductivity of 1 × 10⁻³ S m⁻¹, approximately 20 orders of magnitude higher than S (5 × 10⁻²⁸ S m⁻¹) [14]. It is expected that Se based electrodes could bring about higher electrochemical reactivity, better rate capability and greater accessible capacity compared with S in a battery system. In addition, the miscibility of Se and S gives rise to numerous solid solutions in forms of cyclic Se_nS_{8-n} and Se_nS_{12-n} molecules [15,16], which can be potential cathode materials in a battery system. The gravimetric capacity and energy density of the SeS_n cathodes will be accordingly increased with the contribution of S while enhanced electrical conductivity will be offered by Se. Recently, Se based materials have been intensively investigated as potential cathode candidates for high performance rechargeable Li and Na batteries [17–23]. Particularly, it has been reported that the addition of a small amount of selenium to the sulfur cathode material could effectively diminish the problem with the polysulfide shuttle in Li–S batteries [21]. The couple of Se as cathode and Mg as anode has been supposed to be an ideal combination for electrochemical energy storage [23], however, the electrochemistry of Mg–Se battery remains unexplored. Herein, we investigate for the first time the potential of Se and SeS₂ as cathode materials for rechargeable magnesium batteries. Besides the development of high performance Mg batteries, this study is also aimed at enhancing the fundamental understanding of the electrochemistry between Mg and chalcogens.

2. Experimental

The chemi%, magnesium chloride (99%) and sodium alginate were purchased from Sigma Aldrich. Mesoporous carbon material CMK-3 cal operations were either carried out on the bench under Ar (99.9999%) using standard Schlenk techniques, or in an argon-filled glove MBraun glove box with recirculation system and water and oxygen concentrations below 0.1 ppm. The chemicals including anhydrous solvents, magnesium bis(hexamethyldisilazide) [(HMDS)₂Mg, 97%], magnesium chloride (99%) and sodium alginate were purchased from Sigma-Aldrich. Mesoporous carbon material CMK-3 was provided by Nanjing XFNANO Materials. Selenium (Se), selenium disulfide (SeS₂) and Mg powder (99.6%) were purchased from Alfa Aesar.

2.1. Material synthesis and characterization

2.1.1. Electrolyte preparation

The non-nucleophilic electrolyte (denoted as Mg-HMDS) was synthesized according to the previous procedures [11], but using a mixture of tetraglyme and diglyme in a volumetric ratio of 1:1 as solvents in order to lower the viscosity of the electrolyte.

2.1.2. Preparation of SeCMK-3 composite

CMK-3 (0.5 g) and selenium (1.2 g) were ball-milled in a silicon nitride jar filled with silicon nitride balls, with a ball to powder ratio of 20:1 at 200 rpm for 10 h. The mixture was subsequently heated in a closed quartz tube with a rotating furnace at 260 °C under argon for 16 h.

2.1.3. Preparation of SeS₂CMK-3 composite

CMK-3 (0.5 g) and SeS₂ (1.2 g) were ball-milled in a silicon nitride jar with a ball-to-powder weight ratio of 20:1 at 200 rpm for 10 h. The mixture was subsequently heated in an autoclave at 160 °C for 20 h.

2.1.4. Solid-state synthesis of MgSe

MgSe was prepared by ball-milling a mixture of Se (0.02 mol, 1.58 g) and Mg (0.02 mol, 0.48 g) in a silicon nitride jar with a ball-to-powder weight ratio of 20:1 at 400 rpm for 20 h.

2.2. Material characterization

Powder X-ray Diffraction (XRD) patterns were recorded in the 2θ range of 10–75° using a Philips X'pert diffractometer equipped with Cu Kα source. Transition electron microscopy (TEM) was performed on a FEI Titan 80–300 Transmission Electron Microscope operated at an accelerating voltage of 300 kV. Scanning transmission electron microscopy (STEM) images were acquired with a high-angle annular dark field (HAADF) detector (Fischione Instruments). The energy-dispersive X-ray (EDX) spectra were acquired by an EDAX SUTW EDX detector. Scanning electron microscopy (SEM) images were acquired with a Zeiss ultra plus electron scanning microscope.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a PHI 5800 MultiTechnique ESCA system (Physical Electronic). To avoid surface contamination, the samples were transferred under an inert gas atmosphere to the sample load lock of the XPS system. The samples were neutralized with electrons from a flood gun (current 3 μA) to compensate for charging effects at the surface. The spectra were acquired using monochromatized Al Kα (1486.6 eV) radiation. The measurements were performed at a detection angle of 45°, with pass energies at the analyzer of 93.9 eV and 29.35 eV for survey and detail scans, respectively. The main C 1s peak was used as binding energy (BE) reference. For the electrode materials, which contain CMK-3, the BE of the main C1s peak was set to 284.5 eV. In the case of the reference compounds (pristine Se and MgSe without CMK-3), the peak of adventitious C (at 284.8 eV) was used.

Raman measurements were carried out with a confocal Raman microscope (InVia Renishaw) in the spectral range of 200–2000 cm⁻¹ using a 633 nm laser excitation source.

Thermogravimetric analysis (TGA) of the samples was carried out simultaneously with differential scanning calorimetry (DSC) using a Setaram thermal analyzer SENSYS evo instrument. The measurements were conducted from room temperature to 600 °C under helium flow (20 ml min⁻¹) at a heating rate of 10 °C min⁻¹.

The surface area and porosity of the materials were analyzed with the Brunauer-Emmett-Teller (BET) methods and the physorption isotherms were collected on a Micromeritics ASAP 2020

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