



Full paper

A stable lithium–selenium interface via solid/liquid hybrid electrolytes: Blocking polyselenides and suppressing lithium dendrite



Yucun Zhou, Zhejun Li, Yi-Chun Lu*

Electrochemical Energy and Interfaces Laboratory, Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, Shatin, N.T. 999077, Hong Kong Special Administrative Region, China

ARTICLE INFO

Keywords:

Lithium–selenium battery
Hybrid electrolytes
Solid electrolyte
Lithium dendrite

ABSTRACT

Here we report a novel lithium–selenium (Li–Se) battery with hybrid electrolytes that permit fast solution-phase Li–Se redox reactions, eliminate polyselenides-shuttling and suppress the formation of lithium dendrite. The hybrid electrolytes consist of NASICON-type $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) ceramics sandwiched by tetraethylene glycol dimethyl ether (TEGDME) electrolyte, enabling the use of low-cost and highly-scalable carbon, demonstrating full utilization of the Se cathode (e.g., 677 mA h g^{-1} at 0.1 C (100% of theoretical capacity)), superior cycling stability (e.g., 613 mA h g^{-1} over 500 cycles at 0.8 C, fading rate = 0.008% per cycle), and promising rate capabilities (e.g., 540 mA h g^{-1} at 1.5 C). With the hybrid electrolytes, we further demonstrate a high Se loading of 5.9 mg cm^{-2} with a stable discharge capacity of 454 mA h g^{-1} ($2.68 \text{ mA h cm}^{-2}$). Our work demonstrates that combining solid state electrolyte with liquid glyme electrolyte is key to achieve stable and high-performance Li–Se batteries.

1. Introduction

The development of rechargeable lithium–chalcogens (sulfur (S), selenium (Se) and tellurium (Te)) batteries is rapidly increasing to achieve a low-cost and high-energy-density energy-storage system [1–8]. Owing to the high volumetric capacity and high electronic conductivity, Se has gained increasing attention as a promising cathode material for rechargeable lithium batteries recently [5,6,9]. Although the theoretical gravimetric capacity of Se (678 mA h g^{-1}) is lower than that of S (1675 mA h g^{-1}), the high density of Se promises for a theoretical volumetric capacity that is comparable to S (Se: $3270 \text{ mA h cm}^{-3}$ based on 4.82 g cm^{-3} ; S: $3467 \text{ mA h cm}^{-3}$ based on 2.07 g cm^{-3}). In addition, the electric conductivity of Se ($1 \times 10^{-5} \text{ S cm}^{-1}$) is approximately 20 orders of magnitude higher than that of S ($5 \times 10^{-30} \text{ S cm}^{-1}$), which is desirable for efficient utilization of active materials and high power applications [5,10,11]. Furthermore, Li–Se batteries are safer than Li–S batteries due to the higher melting point and autoignition point of Se than those of S [5].

Carbonate-based electrolytes have been widely used for Li–Se batteries owing to its high chemical compatibility with the Se cathode and that the operation is free from polyselenide-dissolution since the Li–Se reactions only involve solid phases in the carbonate-based electrolytes [5]. Due to the sluggish kinetics of the solid-solid reaction and the significant volume change ($\sim 98\%$) between Se and Li_2Se in the

carbonate-based electrolyte, the resulting Li–Se batteries using bulk Se cathodes exhibited a low utilization rate of Se and a fast capacity fading [12–15]. To overcome these issues, one of the most effective strategies is to encapsulate Se into porous conductive matrixes with high surface areas and special pore structures (e.g., microporous/mesoporous carbon) [16–26]. These conductive matrixes could facilitate the charge transfer process and accommodate the volumetric expansion of Se during lithiation, thus improving the rate and cycling performance of the Li–Se batteries. Limited by the single solid-phase Se reactions in the carbonate-based electrolyte, many Li–Se batteries reported to-date were obtained with a relatively low Se content ($< 60 \text{ wt\%}$, Se/total weight of cathode) [18,19] and a low Se loading ($< 1 \text{ mg cm}^{-2}$) [18,20,21,24]. In contrast to the dominant solid-solid reactions in the carbonate-based electrolyte, the solid/liquid reactions along with the formation of soluble polyselenides in the glyme-based electrolyte can facilitate the electrochemical processes and enable a high utilization rate of Se at a high Se loading [9]. However, similar to challenges related to polysulfide dissolution in the Li–S batteries, Se cathodes in glyme-based solvents suffer from the shuttle issue due to the dissolution of polyselenides during electrochemical cycling, resulting in the loss of active materials, low coulombic efficiency and poor cycling stability [27].

Here we report a novel lithium–selenium (Li–Se) battery employing hybrid electrolytes that take advantages of the shuttle-free characteristic of the solid electrolyte and the fast solution-phase Se redox

* Corresponding author.

E-mail address: yichunlu@mae.cuhk.edu.hk (Y.-C. Lu).

reactions in the glyme-based electrolyte. The hybrid electrolytes consist of a solid ion-conductor $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) sandwiched by 1.0 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) in the positive electrode and 1.0 M LiTFSI + 2 wt% LiNO_3 in TEGDME in the lithium negative electrode. The hybrid electrolytes effectively block the shuttling of the polyselenides and suppress the formation of lithium dendrite, leading to high-performance Li–Se batteries with superior performances in current density, discharge capacity, Se loading and cycling stability/efficiency.

2. Experimental section

2.1. Materials

Ketjen Black EC-600JD (KB) was received from AzkoNobel. Sulfur (S, 99.98%), lithium sulfide (Li_2S , 99.98%), alumina oxide (Al_2O_3 , nanopowder, < 50 nm), selenium powder (Se, 99.5%), lithium nitrate (LiNO_3 , 99.99%), lithium bis(trifluoromethane) sulfonamide (LiTFSI, 99.95%), tetrahydrofuran (THF), 1 M lithium triethylborohydride in THF solution, 1,2-dimethoxyethane (DME) and tetraethylene glycol dimethyl ether (TEGDME, 99%) were received from Sigma-Aldrich. Lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, A. R.), germanium oxide (GeO_2 , 5 N) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, A. R.) were received from Sinopharm Chemical Reagent Co., Ltd. LiNO_3 and LiTFSI were dried overnight under dynamic vacuum in a glass oven (Büchi, Switzerland) at 110 °C. Lithium foils (thickness of 0.5 mm) were received from Shenzhen Meisen Electromechanical Co. Ltd.

2.2. Preparation of Se–KB and S–KB cathodes

Both of the Se–KB and S–KB composites were prepared by the melt-diffusion method. As for the Se–KB composite, Se powder and KB were mixed at a weight ratio of 4:1 and heated at 260 °C for 12 h under Ar flow in a tube furnace. While for the S–KB composite, S powder and KB were mixed at a weight ratio of 4:1 and heated at 155 °C for 6 h. The Se–KB/S–KB composite was mixed with Super P, and gelatin binder (dissolved in deionized water with a weight percent of 2 wt%) to form a slurry at the weight ratio of 8:1:1. The Se–KB/S–KB cathode was prepared by casting the slurry onto the aluminum foil and dried in a vacuum oven at 60 °C overnight.

2.3. Preparation of LAGP electrolytes

NASICON-type structured $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) lithium ion conductor was synthesized by a solid-state reaction method. Specifically, stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (10 wt% excess), Al_2O_3 , GeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ were used as the starting materials. The precursors were thoroughly mixed by planetary ball milling at 400 rpm for 12 h in acetone and then heated at 600 °C for 2 h. The mixture was then cooled, ball milled and heated at 800 °C for 6 h. After that, the milling process was repeated and the obtained powder was dried and pressed into pellets and sintered at 850 °C for 6 h.

2.4. Assembly of Li–Se/S batteries with liquid/hybrid electrolytes

Li–Se batteries with the liquid electrolyte were assembled using CR2025 coin cells with Li foil ($\Phi 16$ mm) as the anode, 1 M LiTFSI in TEGDME (50 μL , 2 wt% LiNO_3) as the electrolyte, Celgard 2325 ($\Phi 19$ mm, LLC Corp., USA) as the separator and Se–KB as the cathode ($\Phi 12$ mm, Se loading = 1–1.5 mg cm^{-2}). Li–Se/S batteries with hybrid electrolytes were assembled using the lab-designed cell and details of the cell configuration were shown in our previous work [28]. Briefly, a piece of Li foil ($\Phi 16$ mm) was placed on the stainless steel negative cell case. Then a piece of glass fiber ($\Phi 16$ mm, QMA, Whatman) soaked with 1 M LiTFSI in TEGDME (100 μL , with/without 2 wt% LiNO_3) was added onto the Li foil. A piece of LAGP solid electrolyte ($\Phi 16$ mm,

thickness ~ 0.2 mm, density = 3.2 g cm^{-3}) was placed onto the glass fiber followed by the Se–KB/S–KB cathode ($\Phi 12$ mm, Se loading = 1–1.5 mg cm^{-2} , S loading = 0.8–1 mg cm^{-2}) on the top. To reduce the interfacial resistance between the solid electrolyte and the cathode, a piece of Celgard separator ($\Phi 12$ mm) soaked with 1 M LiTFSI in TEGDME was placed between the Se–KB cathode and the LAGP solid electrolyte. For the cathodes with normal Se/S loadings (0.8–1.5 mg cm^{-2}), 10 μL liquid electrolyte was added in the cathode side, while for the high Se loadings, 15 and 25 μL electrolyte were applied for the cathode containing 3 and 5.9 mg cm^{-2} Se, respectively. The above cells were assembled in an Ar-filled glovebox (H_2O < 1.0 ppm, O_2 < 1.0 ppm, Etelux, China).

2.5. Material characterizations

X-ray diffraction (XRD) characterization was performed by a SmartLab XRD (Rigaku, Japan) using $\text{CuK}\alpha$ radiation. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed using a JSM-7800F field emission scanning electron microscope (JEOL, Japan). Thermogravimetric analysis (TGA) was performed under N_2 atmosphere at a heating rate of 10 °C min^{-1} using a Perkin-Elmer STA 6000 simultaneous thermal analyzer (USA). Lithium ionic conductivities of the solid LAGP electrolytes were measured at 25–80 °C by the traditional AC impedance method with Au thin films sputtered on both sides of the polished pellet as blocking electrodes. The impedance data were collected on a VMP3 electrochemical testing unit (Bio-Logic) with the frequency measured from 1 MHz to 0.1 Hz. The impermeability of the solid electrolyte was demonstrated by sandwiching a piece of LAGP membrane (thickness ~ 0.2 mm) between two plastic tubes with 1 M LiTFSI in TEGDME on one side and 0.3 M Li_2Se_8 /0.5 M Li_2S_8 + 1 M LiTFSI in TEGDME on another side. Li_2Se_8 and Li_2S_8 solutions were prepared with stoichiometric amount of Li_2Se , Se powders ($\text{Li}_2\text{Se} + 7 \text{ Se} \rightarrow \text{Li}_2\text{Se}_8$) and Li_2S , S powders ($\text{Li}_2\text{S} + 7 \text{ S} \rightarrow \text{Li}_2\text{S}_8$), respectively, followed by stirring in TEGDME until no precipitates were left in an Ar-filled glovebox. Li_2Se was synthesized by lithium triethylborohydride reduction of selenium powder in THF as reported [9]. Cycled Li anodes for SEM characterization were prepared by rinsing the Li foils in DME, and followed by drying under vacuum.

2.6. Electrochemical measurements

Cyclic voltammogram (CV) measurements were conducted using a VMP3 electrochemical testing unit (Bio-Logic) at a scan rate of 0.1 mV s^{-1} . Galvanostatic discharge/charge tests were performed on a LAND CT2001A battery test system (Wuhan LAND electronics Co., Ltd, China). For the rate capability test, the cut-off voltage was set to be 1.7–3 V at various current densities for the battery with liquid electrolyte. Due to the high voltage polarizations derived from the solid electrolyte, the cut-off voltages of the battery with hybrid electrolytes were set to be 1.6–3 V at 0.1, 0.2 and 0.5 C, and 1.2–3 V at 1, 1.5 and 2 C. Electrochemical impedance spectroscopy (EIS) measurements were performed by using the Bio-Logic with the frequency range of 1 MHz to 0.1 Hz at an amplitude of 20 mV. The calculation of specific discharge/charge capacities is based on the mass of elemental selenium/sulfur.

3. Results and discussion

3.1. Conductivity/permeability/interfacial resistance of the hybrid electrolytes

The cell configuration is shown in Fig. 1a, in which the LAGP membrane with a NASICON-structure (Fig. S1) is sandwiched between the Li metal foil anode and the Se–KB cathode (Se content in the Se–KB composite is 78 wt%, Fig. S2). Liquid TEGDME electrolyte is added between the solid electrolyte and the electrodes. In this architecture, the solid electrolyte acts as a barrier to prevent the diffusion of soluble

Download English Version:

<https://daneshyari.com/en/article/5452391>

Download Persian Version:

<https://daneshyari.com/article/5452391>

[Daneshyari.com](https://daneshyari.com)