



# All-solid-state lithium–sulfur batteries with three-dimensional mesoporous electrode structures



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## HIGHLIGHTS

- All-solid-state lithium–sulfur batteries are constructed.
- Composite sulfur/carbon electrodes and the thio-LISICON solid electrolyte are used.
- Three-dimensional highly ordered mesoporous carbon is used as a framework.
- This electrode structure provides a highly reversible reaction.
- Higher battery capacity is achieved by decreasing the pore size of the framework.

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## ABSTRACT

Although the characteristics of lithium–sulfur batteries are advantageous for various applications, batteries with liquid electrolytes show capacity fading due to the dissolution of polysulfides. All-solid-state lithium–sulfur batteries with highly reversible characteristics are developed using a three-dimensional carbon matrix framework structure for the sulfur cathode. Sulfur is introduced into a carbon replica framework with a pore size of 8–100 nm. The composite electrode structure provides high electronic conduction and allows high cathode utilization during the battery reaction. The capacity of cells using a LiAl alloy as the negative electrode and the thio-LISICON (lithium superionic conductor) electrolyte increases when the pore size of the carbon replica is decreased from 100 nm to less than 15 nm. The highest capacity is obtained for the carbon replica with a pore size of 8.6 nm and a wall thickness of 4.7 nm. An examination of the relationship between the charge–discharge capacity and the structure of carbon replicas with different pore sizes and wall thicknesses indicates that three-dimensional highly ordered mesoporous carbon with a small pore size is a promising electrode structure for lithium–sulfur all-solid-state batteries.

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## 1. Introduction

The lithium–sulfur battery as a power storage device is a promising candidate for both small- and large-size applications, such as portable devices, electric vehicles, and stationary

applications. Lithium-based systems have the advantage of a high energy density because they are lightweight with a low electrochemical potential. For lithium systems, the sulfur cathode has a high theoretical capacity of 1672 mAh g<sup>-1</sup>, which is ten times higher than that of the conventional electrode material, LiCoO<sub>2</sub>. The electrochemical reaction of sulfur with lithium is described by the following formula:  $S + 2Li^+ + 2e^- \rightleftharpoons Li_2S$ . Owing to the abundant sources of elemental sulfur and lithium, the lithium/sulfur redox couple might be a promising candidate for safe, inexpensive, and high-capacity batteries. However, lithium–sulfur batteries with a

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liquid electrolyte show significant fading of the charge–discharge capacity owing to the dissolution of polysulfides formed during the battery reaction [1,2]. All-solid-state batteries using sulfide solid electrolytes are more advantageous than batteries with liquid electrolytes because solid–solid contact eliminates the polysulfide dissolution problem. Moreover, the non-flammable characteristic of the solid electrolyte is also an advantage, resulting in extremely high reliability and safety. Furthermore, the all-solid-state configuration has the potential to provide batteries with high power densities [3]. However, the low electronic conductivity of sulfur ( $5 \times 10^{-30} \text{ S cm}^{-1}$  at room temperature) [4] causes rather low utilization of the sulfur electrode in the battery reaction [5,6]. In the present study, we examined a three-dimensional framework electrode structure to improve electronic conduction in composite sulfur cathodes.

Mesoporous carbon has meso-size pores in a carbon matrix [7–10] with ordered arrangements, either in two-dimensions (e.g., CMK-3) or three-dimensions (carbon replica). The carbon replica is synthesized from a template of silica spheres [11] with micro-to nanometer sizes, a uniform size distribution [11–13], and a cubic close packing structure [11,12,14]. The size of the silica spheres can be finely tuned by varying the amount of amino acid in the template [14,15], and thus the size of the pores in the carbon replica (well-ordered mesoporous carbon) can be easily controlled [14,16]. Such ordered mesoporous structures might provide a new electrode framework and allow high electronic conduction in the electrode matrix for all-solid-state batteries.

Previously, we reported that the electrode structure of a sulfur/mesoporous carbon (CMK-3) composite provides highly reversible characteristics to all-solid-state lithium–sulfur batteries. However, the two-dimensional carbon rod structure of CMK-3 provides a fixed pore size in the electrode framework, and the resulting electrode matrix has a large carbon ratio, which reduces the total capacity for practical cells [17]. A new electrode structure that allows for much closer electrode/electrolyte contact might improve electronic conduction and thus the charge–discharge characteristics. Thus, we have optimized the pore size of the electrode framework structure of mesoporous carbon using a carbon replica.

In the present study, the electrode structure was examined to improve the characteristics of lithium–sulfur batteries with thio-LISICON (lithium superionic conductor) [18,19] as a solid electrolyte. Composite electrodes of sulfur and carbon replicas with various pore sizes were fabricated using a gas-phase mixing method. The composite electrode structure improved the utilization of sulfur in the charge–discharge reaction and thus provided a high energy density for all-solid-state lithium–sulfur batteries.

## 2. Experimental

### 2.1. Synthesis of carbon replicas and carbon–sulfur composites

Silica nanospheres with uniform sizes of 8–100 nm were synthesized from tetraethyl orthosilicate and L-arginine [11,16]. Varying the size of the silica nanospheres allowed the pore size in the carbon replicas to be controlled [11,14]. Spheres of 8, 12, 14, 20, 40, and 100 nm were used as templates, and the corresponding carbon replicas were indexed as CR8, CR12, CR14, CR20, CR40, and CR100, respectively. The synthesis methods for the carbon replica have been described elsewhere [16]. Silica nanospheres, furfuryl alcohol ( $\text{C}_5\text{H}_6\text{O}_2$ ), and oxalic acid were used as the template, carbon source, and acid catalyst, respectively. Polymerization of the nanosphere samples in the presence of furfuryl alcohol and oxalic acid was promoted at 100 °C for 48 h. The sample was then crushed and carbonized at 120 °C for 0.5 h and 800 °C for 1 h under Ar. The above treatment produced a black powder, which was treated with

5% HF aqueous solution to remove the silica template.

Sulfur–carbon composites were prepared using a previously reported gas-phase mixing method [20]. Sulfur (Kojundo Chemical Laboratory, >99.99% purity) and the carbon replica in a ratio of 30:70 (wt%) were mixed in an argon-filled glove box, sealed in a quartz tube under a vacuum atmosphere, and then heated at 300 °C for 2 h. After heating, the tube was slowly cooled to 20–30 °C.

### 2.2. Cell fabrication

The test cell was composed of a polyethylene terephthalate cylinder with an inner diameter of 10 mm. A material in the thio-LISICON family,  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ , was synthesized using a solid-state reaction for use as the solid electrolyte [18]. The positive electrode was constructed from the sulfur–carbon replica composite and the solid electrolyte, which were mixed in a ball mill (Fritsch P-7 planetary ball milling apparatus) at a ratio of 50:50 (wt%). The solid electrolyte (~70 mg) was pressed into a pellet. The positive electrode powder (5 mg) was dispersed on one side of the electrolyte pellet, and then aluminum mesh with a diameter of 9 mm and a thickness of 0.1 mm as current collector was placed on the cathode powder. The cathode powder and current collector were pressed together at a pressure of 500 MPa using a uniaxial press machine (Riken Kiki Co., Ltd., P-6). A lithium–aluminum composite, consisting of aluminum foil (0.1 mm thickness) and lithium foil (0.1 mm thickness) with a diameter of 10 mm, was used as the negative electrode [21]. The Li/Al ratio is about 38:68 (mol%), which provides a redox potential of 0.38 V (vs.  $\text{Li}/\text{Li}^+$ ). The aluminum foil was attached to the solid electrolyte at a pressure of 500 MPa [21], and the lithium sheet was then attached to the aluminum foil. Copper mesh with a diameter of 9 mm and a thickness of 0.1 mm was placed on the lithium sheet as a current collector, followed by pressing at 8 MPa. The preparation and fabrication of the cells was carried out in a dry argon-filled glove box ( $\text{H}_2\text{O} < 0.1 \text{ ppm}$ , Miwa MFG Co., Ltd.).

### 2.3. Characterization methods

The electrochemical properties of the cells were characterized using a multi-channel galvanostat (TOSCAT-3100). Constant currents in the range of 0.013–1.3  $\text{mA cm}^{-2}$  were applied to the cells at 25 °C and the cut off voltages for discharging and charging were 0.5 and 3.0 V, respectively. The electrodes were characterized by small angle X-ray scattering measurements using a Rigaku Ultima-IV diffractometer with  $\text{Cu K}\alpha$  radiation. The weight ratio of sulfur and carbon in the composite electrode was measured using thermogravimetry (TG). The TG measurements were conducted from 20–30 °C–600 °C at a heating rate of 10 °C  $\text{min}^{-1}$  under a helium atmosphere. The morphologies of the composite electrodes were investigated using a field emission scanning electron microscope (FE-SEM, Hitachi S-5200) with an acceleration energy of 30.0 kV. The porosity of the cathode composite with open pores was measured using the Brunauer–Emmett–Teller (BET) method with nitrogen gas (Bellsorp-mini). The pore distribution of carbon was calculated using the Barrett–Joyner–Halenda (BJH) method [22].

## 3. Results and discussion

### 3.1. Synthesis of carbon replicas and sulfur composites

The advantage of a carbon replica for application as an electrode matrix is its three-dimensional nanopore structure that can accept sulfur and provide electronic conduction to the sulfur cathode complex. The pore size of the carbon replica is easily controlled by

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