

Liquid-Phase Mixing of Sulfur-Carbon Replica-Li₁₀GeP₂S₁₂ Composite Electrode for All-Solid-State Lithium-Sulfur Batteries

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All-solid-state Li-sulfur battery attracts much attention because of its high energy density, safety, and reliability [1]. However, poor ion/electron conductivities and a large volume change of sulfur are the problems to be solved. We have focused on carbon replica (CR) structure as electron conducting framework, which was constructed with a three-dimensional pore arrangement within the matrix [2]. Sulfur-carbon replica composites (S-CRs) show high electrochemical activities while deficient ion conduction pathway in the mesopore suppresses the cycle and rate performance of the battery. In the present study, a liquid-phase mixing method was examined to introduce the solid electrolyte into the pore of S-CRs to enhance the battery performance.

Sulfur was mixed with CRs (pore size of approx. 14 nm) by a gas phase mixing [2]. A lithium superionic conductor of Li₁₀GeP₂S₁₂ (LGPS) was used as a solid electrolyte. The S-CR-LGPS composites (S:CR:LGPS=9:21:70wt.%) were fabricated using three methods: (i) mechanical mixing, (ii) liquid-phase mixing, and (iii) combination mixing using both (i) and (ii). Planetary ball milling was used for mechanical mixing. Liquid phase mixing was carried out using THF as a solvent. The obtained composites were characterized by SEM, BET, TG/DTA, and XRD measurements. Electrochemical properties of the composite electrodes were evaluated by the constant current charge-discharge measurements.

The macro-scale analysis confirmed that the methods (i, iii) including mechanical mixing provided dispersed uniform particles with several μm scales, indicating that the mechanical mixing is necessary for pulverizing and uniform distribution of the particles. Also, a mesoscale analysis revealed that the relatively large amount of the LGPS was introduced into the pore through the liquid-phase mixing process; the mesopore volume decreased approx. 23%. All-solid-state battery using the composite prepared by the method (iii) maintained the largest capacity of 1170 mAh g⁻¹ after 50 cycles at 0.1C-rate; relatively high rate capability of the battery is also confirmed. These results indicate that the combination mixing provided the appropriate structural characteristics both in macro- and meso-scales, which enhance the electrochemical performance of the composite. However, the capacity fading continued during the cycles. To improve the battery performance, charge-discharge tests were conducted with external pressure applied [3]. The discharge capacity was maintained approx. 1500 mAh g⁻¹ over 50 cycles with nearly 100% coulombic efficiency. Reduction of ion/electron conduction path due to a volume change of S may contribute to the deterioration of the battery performance in case of without the external pressure. By introducing more S and LGPS to fill up the mesopores, pressure effect by the CR framework could be obtained; consequently, further improvement in the battery performance can be expected.

References:

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