



High performance all-solid-state lithium-sulfur battery using a Li₂S-VGCF nanocomposite



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ABSTRACT

In lithium-sulfur batteries, cyclability is often strongly limited by a high interfacial resistance caused by poor contact between the active material and electron and lithium ion transporting materials. Here, we develop a Li₂S-VGCF (Vapor Grown Carbon Fiber) nanocomposite positive electrode for an all-solid-state lithium-sulfur battery that significantly improves cyclability. The Li₂S-VGCF nanocomposite is prepared by a solution-based technique with subsequent heat-treatment in order to control the formation of Li₂S nanocrystals within the VGCF electron conducting matrix. The small, well-dispersed Li₂S nanocrystals offer a large contact area with the solid electrolyte and electron conducting carbon in the composite cathode. To further improve conductivity, the composite cathode employs a multi-dimensional approach with long 1-D VGCF fibers supporting long distance electron transport and 0-D carbon powder enhancing the contact area with the Li₂S active material at lower total carbon content. In the all-solid-state batteries, the highest initial capacity of 469 mAh·g⁻¹ is obtained at conditions of 500 °C during heat-treatment. Activation of Li₂S is observed during the first 10 cycles. Subsequently, the capacity gradually increased up to 600 mAh·g⁻¹ (g of Li₂S). The optimized cell exhibits excellent cyclic performance through 20 cycles and a Coulombic efficiency of ~100%.

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1. Introduction

Rechargeable lithium-ion batteries are widely used as power sources for mobile electronic devices such as cell phones and laptops. However, current commercial lithium ion battery material systems are insufficient for large-scale applications such as electric vehicles and renewable energy storage systems due to their limited specific capacity [1]. For example, transition metal oxide or phosphate cathode materials currently used in mobile applications have theoretical capacities limited to about ~300 mAh·g⁻¹ [2,3]. Therefore, finding new cathode materials with a much higher specific capacity is an important direction for research.

Sulfur containing cathode materials are promising because of their high theoretical energy densities. There are two primary approaches: elemental sulfur with a theoretical capacity of 1672 mAh·g⁻¹ and Li₂S with a theoretical capacity of 1166 mAh·g⁻¹

[4–7]. The elemental sulfur has an issue to apply cathode material due to non-lithium-containing material of S. Hence the lithium containing anode materials must be used elemental lithium for cell operation, where the elemental lithium has a significant problem of internal short from dendrite growth [1]. On the other hands, Li₂S based active materials have a distinct advantage over elemental sulfur in that they allow non-lithium containing anodes to be utilized. Additionally, in other point of view, the capacity of elemental sulfur is completely utilized by application of fully lithiated-state of Li₂S.

However, a major challenge for Li₂S cathodes is their low electrical conductivity, which requires supplementing the electron conduction pathways. Many researchers report a fabrication of functional sulfur-carbon composites to improve electronic conductivity in composite cathode for lithium-sulfur batteries [7–10]. Wu et al. reported the preparation of a nanostructured Li₂S-MWCNT composite cathode via a solution-based process [11]. The network of Li₂S on the electrically conductive carbon matrix allows electron transport at the active material interface. A battery built from their nanocomposite and a liquid electrolyte showed excellent capacity (above 500 mAh·g⁻¹ of Li₂S) and good

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cyclability. However, even with Li_2S cathodes, polysulfide dissolution is still a major concern because it limits the maximum capacity and cycle retention. A solid electrolyte would not only eliminate the problem of polysulfide dissolution [12], but also exhibit better safety and reliability than liquid electrolytes due to their inherent inflammability and better electrochemical stabilities.

Furthermore, the combination of Li_2S - P_2S_5 solid electrolyte and the Li_2S cathode would lower the interfacial resistance to ion transport and avoid irreversible capacity commonly observed in oxide based cathodes. Nagao et al. reported an all-solid-state lithium-sulfur cell using Li_2S cathode and Li_2S - P_2S_5 electrolyte [13]. To improve the electrical conductivity, the composite cathode was made of a mixture of active material and conductive carbon at a 1:1 ratio, resulting in a relatively high carbon content. Furthermore the capacity was found to decrease during charge/discharge cycling due to its large volume change during cycling (180% compared to sulfur), which destroys electron conduction pathways. In our previous study, the cyclability of all-solid-state batteries was improved by utilizing multi-dimensional electrical conductors [14]. Intimate contact with the active material is accommodated with 0-D carbon particles, and long range electron conduction is accomplished with 1-D carbon fibers. This combination was found to effectively retain cell capacity during cycling as well as reduce the total carbon level in the composite cathode, resulting in improved energy density.

In this study the Li_2S and Vapor Grown Carbon Fiber (VGCF) nanocomposites are integrated into an all-solid-state lithium-sulfur battery. The Li_2S -VGCF nanocomposite is optimized to improve the charge/discharge cyclability by enhancing the interfacial contact of the Li_2S active materials with the conductive materials and improving long distance transport at a lower carbon content. Crystallization of the Li_2S was optimized to produce nanocrystallites on VGCF, allowing good interfaces with both the carbon fibers and the solid-state electrolyte. The results show a high capacity of around $600 \text{ mAh}\cdot\text{g}^{-1}$ (g of Li_2S), 100% Coulomb efficiency and excellent cyclic performance through 20 cycles.

2. Experimental procedure

Synthesis of the Li_2S -VGCF nanocomposite was adapted from the solution technique of Wu et al. [11]. Reagent-grade Li_2S (Alfa Aesar, 99.9%, USA), VGCF (Showa Denko, Japan) and anhydrous ethanol (Daejung, 99.9%, Korea) were used as starting materials. Li_2S was dissolved in 20 mL ethanol to obtain a 0.2 M Li_2S solution, then 20 wt% VGCF was mixed into the solution. The obtained suspension was sealed in a glass vial to prevent air exposure. Ultrasonic treatment was carried out for 2 h to disperse the VGCF uniformly into the suspension. The ethanol was evaporated from the suspension in a vacuum chamber for 24 h. The resultant product was crystallized at various temperatures in the range of 100–700 °C for 3 h at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ in a quartz tube with Ar flow. The crystallinity of the Li_2S -VGCF nanocomposite was measured via X-ray diffraction (Ultima IV, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$). To avoid air exposure, the samples were sealed in an airtight container covered with polyimide thin film and mounted on an X-ray diffractometer. Primary particle size was calculated by Scherrer's method. Thermal properties were measured by TG-DTA (DTG-60H, Shimadzu, Japan). The sample was sealed in an Al pan to avoid air exposure and then transferred to the TG-DTA chamber under Ar flow. Samples were heated to 500 °C at a rate of $5^\circ\text{C}\cdot\text{min}^{-1}$. Quantitative elemental analysis was performed by ICP-AES (OPTIMA 4300DV, Perkin-Elmer, USA). Nanocomposite microstructures were observed by FE-SEM (S-4300SE, Hitachi, Japan). In addition, energy dispersive X-ray spectroscopy (EDX, Hitachi, Japan) was also investigated to confirm element distribution of Li_2S -VGCF composite.

The $78\text{Li}_2\text{S}\cdot 22\text{P}_2\text{S}_5$ (mol %) solid electrolyte was synthesized based on our previous report [15]. Reagent-grade Li_2S (Alfa Aesar, 99.9%, USA) and P_2S_5 (Aldrich, 99%, USA) powders were weighed and mixed in appropriate molar ratios and put into an alumina pot (volume of 100 mL) with twelve (10 mm in diameter) zirconia balls. Mechanical milling was conducted for 25 h using a planetary ball mill (Pulverisette 7, Fritsch, Germany). To prepare the glass-ceramic electrolyte, the obtained powder was crystallized with a two-step heat-treatment [16]. First, the powders were nucleated at 170 °C for 30 min, then crystal growth proceeded at 230 °C for 3 h. All processing was conducted in an Ar-filled glove box.

The composite cathode powder was prepared by mixing the Li_2S -VGCF composite active material with the $78\text{Li}_2\text{S}\cdot 22\text{P}_2\text{S}_5$ solid electrolyte and Ketchen black conductive carbon (EC-600JD, Akzo Nobel, Netherland) at a weight ratio of 1.2: 2: 0.2 using a rotational mixer (NBK-1, Hohsen, Japan) with small zirconia balls (2 mm in diameter). The final weight ratio of active material, solid electrolyte and electron conductive carbon was 1: 2: 0.4.

A 2032 type coin cell was prepared to measure the electrochemical properties of the Li_2S -VGCF nanocomposite. The composite cathode powder (15 mg) and $78\text{Li}_2\text{S}\cdot 22\text{P}_2\text{S}_5$ solid electrolyte (150 mg) were pelletized using a uniaxial press at 200 MPa (16 mm diameter) for 10 min. Next a Li-In alloy foil negative electrode (0.1 mm thickness) was attached on the opposite side of the composite cathode at 100 MPa pressure for 10 min. The obtained three-layered pellet was inserted into the coin cell for electrochemical measurements. Charge-discharge performance was investigated at 25 °C in a constant-temperature chamber under a current of $0.05 \text{ mA}\cdot\text{cm}^{-2}$ (TOSCAT-3100, Toyo System, Japan). Electrochemical Impedance Spectroscopy (EIS) of obtained cell was measured by using an impedance analyzer (1260, Solatron, UK).

3. Results and discussion

The microstructures of the Li_2S -VGCF nanocomposite versus heat-treatment temperature are shown in Fig. 1. To avoid air exposure, the samples were attached on the sample holder using carbon tape and then gold-coated in an Ar-filled glove box using sputter coater (Cressington, 108auto, UK). The holder was sealed using an airtight container and transferred to FE-SEM measurement. The microstructure of VGCF is also shown in Fig. 1(d) for comparison, where the microstructure was observed using SEM measurement (JEOL, JCM5700, Japan). After ethanol evaporation and prior to heat-treatment, the nanocomposite consists of VGCF fibers buried deep within a porously formed matrix of precipitated Li_2S as seen in Fig. 1(a). Heating the nanocomposite to 500 °C results in the removal of solvent residue and the growth of small Li_2S nanocrystallites dispersed on a network of VGCF fibers, as shown in Fig. 1(b). Heating at 700 °C produces a VGCF network with more significant agglomeration of the Li_2S nanocrystals as seen in Fig. 1(c). The excessive heat-treatment and resulting increased agglomeration will lead to a lower contact area of the active material with both the electron conducting VGCF and the solid state electrolyte in the composite cathode.

Fig. 2(a) shows X-ray diffraction patterns (XRD) of the obtained Li_2S -VGCF nanocomposite samples as a function of heating temperature. The Li_2S and VGCF starting materials are also shown for comparison, and all scans are scaled to unity to compare peak positions among the samples. The non-heated Li_2S -VGCF sample contains small, broad peaks for the VGCF (26°) and Li_2S (27°), demonstrating the nanocomposite is disordered in its as-synthesized state. An impurity peak (unknown) at 23.4° , 25.5° and 28.4° are also observed. As the nanocomposite is heated, both the impurity peaks are eliminated and the crystallinity of the Li_2S

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