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High-rate operation of sulfur/mesoporous activated carbon composite electrode for all-solid-state lithium-sulfur batteries

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All-solid-state lithium-sulfur batteries are promising from the perspective of high safety, low cost, and high capability. Herein, composites of sulfur and microporous carbon (MSP20, MSC30) are prepared by a melt diffusion process, and their performance as electrode materials are compared with that of composites based on nanocarbons. In addition to the type of carbon, the degree of mixing with solid electrolytes is an important factor in the formation of ionic/electronic conduction pathways. The all-solid-state cell using S-MSC30-Li₃PS₄ shows a high initial discharge capacity of 1488 mAh per gram of sulfur at 25 °C at a current density of 1.3 mA cm⁻² and operates reversibly at a high current density of 12.7 mA cm⁻² (3C) at 100 °C. The amorphization of sulfur is effective for obtaining high capacity and sulfur impregnated into the meso- and micropores of carbon is more active than sulfur that forms nanocomposites with nanocarbon.

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1. Introduction

Lithium-sulfur batteries are promising as high energy storage devices due to the use of sulfur with a high theoretical capacity of 1672 mAh g⁻¹.^{1)–3)} These batteries suffer from a decline in the volumetric energy density because they require large amounts of conductive carbon and electrolyte solution.^{3)–5)} Furthermore, lithium polysulfides dissolved in the electrolyte may cause side reactions.^{6)–10)}

The dissolution of lithium polysulfides is expected to be suppressed and the battery performance is expected to be enhanced by replacing the organic liquid electrolytes with sulfide solid electrolytes. On the other hand, it is difficult to form good electronic and ionic conduction pathways in the composite electrode layer for achieving a fast charge–discharge reaction. Thus, the selection of an appropriate carbon material and effective composite electrode design are recognized as important for improving the battery performance.^{3)–5), 11), 12)} Kanno et al. reported that high capacity all-solid-state lithium-sulfur battery was obtained by using mesoporous carbon CMK-3 having pore size in the range 1–2 nm.¹³⁾ We previously achieved improved electrode performance by mixing S, acetylene black (AB), and a sulfide solid electrolyte in an appropriate compositional ratio by ball-milling.^{14), 15)} Although the all-solid-state cell showed a high reversible capacity of 1050 mAh g⁻¹ at a current den-

sity of 0.064 mA cm⁻², the capacity decreased by half when the current density was increased to 0.64 mA cm⁻². All-solid-state lithium-sulfur batteries employing a P₂S₅-based composite electrode without solid electrolytes were reported by Nagata and coworkers.¹⁶⁾ The cells operated successfully when P₂S₅ was replaced with an ionic conductor during the first charge–discharge cycle. The composite contained 60 wt % sulfur and the cell employing this composite exhibited a high capacity of 1042 mAh per gram of sulfur at the high current density of 6.4 mA cm⁻² at 25 °C. Recently, we reported all-solid-state lithium-sulfur batteries using mesoporous carbon with 3–5 nm of interconnected pores.¹⁷⁾ The cell showed a high capacity of 1100 mAh g⁻¹ after 400 cycles at 1.3 mA cm⁻² at 25 °C.

In this study, we prepare composite electrodes using mesoporous activated carbon that also contains micropores less than 1 nm, and investigate the effect of micropores on the electrode performance, especially on the rate performance. The electrode performance under a high current density was examined at 25 and 100 °C. The characteristics of the activated carbons are discussed by comparison with AB (Denka) nanocarbon.

2. Experimental

2.1 Preparation of composite electrode

Sulfur (Sigma-Aldrich, 99.98%) and the respective carbon samples were mixed in an agate mortar in a weight ratio of 2:1. In this study, AB (Denka), ketjen black (KB, Lion Corp.), and two active carbons MSP20 and MSC30

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(Kansai Coke and Chemicals Company) were used. The mixture was placed in a porcelain crucible and the sulfur-carbon composites were obtained via melt-diffusion by heating at 155 °C for 24 h in a muffle furnace (KDF S70). 75Li₂S·25P₂S₅ (mol %) (Li₃PS₄ glass) was used as the solid electrolyte. The Li₃PS₄ glass was mechanochemically prepared by ball-milling Li₂S (Mitsuwa Chemical, 99.9%) and P₂S₅ (Sigma-Aldrich, 99%) in a molar ratio of 3:1 using a ZrO₂ pot (45 mL in volume) and 90 g of ZrO₂ balls (4 mm in diameter) with a planetary ball-mill apparatus (Pulverisette 7, Fritsch) at 510 rpm for 45 h. The mixture of the sulfur-carbon composite and Li₃PS₄ was ball-milled using a ZrO₂ pot (45 mL in volume) and 65 g of ZrO₂ balls (5 mm in diameter) with a planetary ball-mill apparatus at 300 rpm for 15 min in a weight ratio of 3:2. The overall S:C:Li₃PS₄ ratio in the composite electrode was 2:1:2 (weight ratio). The ball-mill mixing was performed in the atmosphere and the prepared samples were stored in an Ar-filled glovebox.

2.2 Material characterization

N₂ adsorption and desorption tests were performed using a physical adsorption measurement instrument (TristarII3020, Micromeritics). The carbon samples were degassed at 150 °C on a vacuum line before the measurement. The Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda method were used to measure the surface area, average pore diameter, and total pore volume. X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (SmartLab, Rigaku) equipped with a one-dimensional X-ray detector using Cu-K α radiation ($\lambda = 1.54056 \times 10^{-10}$ m). Thermogravimetric analysis (TGA) was conducted with a Thermo Plus EVO2 Rigaku apparatus under dry N₂ at a heating rate of 10 °C min⁻¹ up to 500 °C.

2.3 Fabrication of all-solid-state cells

All-solid-state cells were fabricated by employing the S–C–Li₃PS₄ composite electrodes. Li₃PS₄ glass was also used as a solid electrolyte separator layer. Bilayer pellets (10 mm in diameter) consisting of a S–C–Li₃PS₄ electrode layer (5 mg) and a Li₃PS₄ separator layer (80 mg) were prepared by uniaxial pressing at 360 MPa for 5 min with stainless-steel rods as the current collector. Lithium (99.99%, Furuuchi Chem.) and indium foils (99.999%, Furuuchi Chem.) were used to form a lithium-indium alloy negative electrode and were attached to the bilayer pellet. The pellet was then pressed at 120 MPa for 2 min. Charge–discharge tests were performed at 25 and 100 °C using a measurement device (BTS-2004, Nagano) with constant current densities of 1.3 mA cm⁻² (0.3C) to 12.7 mA cm⁻² (3C) in an airtight container, outside the glovebox. The capacity was calculated from the weight of sulfur.

3. Results and discussion

3.1 Material characterization of any S–C composite

Figure 1 shows the XRD patterns of the prepared sulfur-

Fig. 1. XRD patterns of S–C composites using AB, activated carbon MSP20, and activated carbon MSC30.

carbon composites. The diffraction pattern attributable to elemental sulfur (S₈) was observed in the XRD patterns of S-AB and S-MSP20 composites. On the other hand, halo pattern was observed in the XRD pattern of S-MSC30, indicating that sulfur was impregnated into the pores of the carbons and adopted an amorphous morphology. The average pore diameter, the BET surface area, and the total pore volume of the carbons were calculated from N₂ adsorption–desorption tests. The average pore diameter of MSP20 and MSC30 was 0.54 and 0.84, respectively. High BET surface areas of 2100 and 2800 m² g⁻¹ were observed for the activated carbon MSP20 and MSC30, respectively. MSC30 had a large pore volume of 1.5 cm³ g⁻¹. In comparison, the pore volume of MSP20 was smaller (0.94 cm³ g⁻¹) and that of AB was close to 0 cm³ g⁻¹. The amount of sulfur in the composite of S-MSP20 (2:1 in weight ratio) is excessive with respect to the pore volume of MSP20. Therefore, excess sulfur that was not contained in the carbon pore was observed in the XRD pattern of S-MSP20 and S-AB.

The sulfur content was determined from the TGA curves presented in Fig. 2. All sulfur-carbon composites showed a weight loss of 66.7%, corresponding to the amount of sulfur added. On the other hand, the shape of the curves and the temperature at which the weight loss occurred differed. Sulfur is expected to be desorbed and this was estimated from the weight loss versus temperature curve. The composite S-AB showed a one-step weight loss in a narrow temperature range around 250 °C. The shape of the curve was very similar to the TGA curve of S₈, indicating that the sulfur in S-AB interacted weakly with the carbon.¹³⁾ In contrast, S-MSP20 showed a two-step weight loss. The first weight loss overlapped with the curve of S-AB, and the second weight loss occurred at a high temperature of over 300 °C, which is similar to the one-step TGA curve of S-MSC30. The high sulfur removal temperature of over 300 °C indicates that a portion of the sulfur was impregnated into the micropores of MSP20 and MSC30. The micropores trapped sulfur more tightly than the mesopores.

Fig. 2. TGA curves of sulfur-carbon composites S-AB, S-MSP20, and S-MSC30 up to 500 °C.

3.2 Electrode performance of S-C-Li₃PS₄ composites

The initial charge-discharge curves and cycle performance of the all-solid-state batteries employing the S-C-Li₃PS₄ composite electrodes are shown in Fig. 3. The composite electrodes were prepared by ball-milling for the mixture of S-C and Li₃PS₄. All cells operated reversibly at a high current density of 1.3 mA cm⁻² at 25 °C. In contrast with the low discharge capacity of the cell with S-AB at 500 mAh g⁻¹, the cells with S-MSP20 and S-MSC30 showed higher initial discharge capacities of 1304 and 1488 mAh g⁻¹, respectively. This is consistent with previous reports that confinement in pores and amorphization are important for obtaining high capacity.^{13),16),17)} The XRD patterns of the S-MSC30 electrodes in the initial state, after the 1st discharge, and after the 1st charge are presented in Fig. S1. Even after charging and discharging, no diffraction peaks of Li₂S and S₈ were observed, indicating that sulfur was still amorphous after lithiation and delithiation. The difference in the initial capacity of MSP20 and MSC30 is due to the excess sulfur that was not entrained in the carbon pores, which lacks an electron conducting pathway and also inhibits electron conduction

between the activated carbon particles. The charge-discharge curves of the all-solid-state cell employing the S-MSC30-Li₃PS₄ composite prepared by hand mixing are shown in Fig. S2. The cell showed a lower initial discharge capacity of 600 mAh g⁻¹ than the cell with the ball-milled composite. Therefore, not only the type of carbon, but also the method of mixing with the solid electrolytes, is important for formation of the ionic/electronic conduction pathway.

3.3 Rate performance of S-MSC30-Li₃PS₄ composite

The charge-discharge curves and rate performance of the all-solid-state batteries employing S-MSC30-Li₃PS₄ at two operating temperatures (25 and 100 °C) are shown in Fig. 4. The ionic conductivity of the Li₃PS₄ solid electrolyte at 25 and 100 °C is 4×10^{-4} and 8×10^{-3} S cm⁻¹, respectively. The cell operated reversibly, even at a current density of 12.7 mA cm⁻² (3C) at 100 °C. Furthermore, the cell exhibited good capacity retention after high current density operation. The cycle performance of the all-solid-state batteries with MSC30 evaluated herein was slightly lower than that in previous reports using mesoporous

Fig. 3. (a) Initial charge-discharge curves and (b) cycle performance of all-solid-state cells using the composite electrode with S:C:Li₃PS₄ = 2:1:2 (wt. ratio).

Fig. 4. Charge-discharge curves and rate performance of all-solid-state cells using the S-MSC30-Li₃PS₄ composite electrode at (a) 25 °C and (b) 100 °C.

carbon with interconnected pores, suggesting the advantage of the interconnected pores and the existence of an optimal pore size.¹⁷⁾ The use of porous carbon and the amorphization of sulfur are apparently effective. However, it is important to elucidate the ionic conduction mechanism inside the S-C composite particles to further improve the electrode performance.

4. Conclusions

A sulfur-carbon composite with sulfur impregnated into the carbon pores was synthesized by a melt-diffusion process. Sulfur adopted an amorphous morphology in the sulfur-carbon composite with microporous MSC30 activated carbon. Compared with AB and MSP20, the highest initial discharge capacity of 1488 mAh g⁻¹ was achieved with the all-solid-state lithium-sulfur battery employing S-MSC30. The results of this study show that sulfur impregnated into the meso- and micropores of carbon is more active than sulfur that forms nanocomposites with nanocarbon. Elucidation of the mechanism of reaction and operation of sulfur in activated carbon under high current density in all-solid-state batteries will be an important undertaking for future development.

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