

A Novel Sulphur Cathode Materials for Rechargeable Lithium Batteries

Bo Jin^a

*College of Materials Science and Engineering, Jilin University,
142 Renmin Street, Changchun 130024, P.R. China*

*Department of Electrical Engineering, Chonnam National University,
300 Yongbong-dong, Buk-gu, Gwangju 500-757, Korea*

Kyung-Hee Park and Hal-Bon Gu

*Department of Electrical Engineering, Chonnam National University,
300 Yongbong-dong, Buk-gu, Gwangju 500-757, Korea*

^aE-mail: jinbo@jlu.edu.cn

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Lithium-sulphur batteries were fabricated in a dry room, and their electrochemical properties were analyzed by scanning electron microscopy (SEM), cyclic voltammetry (CV), and charge-discharge tests. SEM results showed that sulphur and nanocarbon powders were mixed homogeneously, and sulphur powders were wrapped by a large amount of carbon powders. The charge-discharge test results demonstrated that the lithium-sulphur battery displayed excellent reversibility and cycling performance, which supplied a discharge capacity of 788.1 mAh g⁻¹ at the first cycle and 796.4 mAh g⁻¹ after 71 cycles at room temperature, respectively.

Keywords : Lithium-sulphur batteries, Reversibility, Elemental sulphur, Cathode materials

1. INTRODUCTION

Rechargeable lithium batteries with high energy density and long cycle life are now attracting the extensive attention due to the wide application including portable electronic devices such as cellular phones, laptop computers and cameras, even including electric vehicles (EV) or hybrid electric vehicles (HEV). The research on the use of LiMn₂O₄, LiCoO₂, LiNiO₂ and LiFePO₄ cathode materials for the positive electrode in lithium batteries is in progress[1-9]. The discharge capacity of LiMn₂O₄, LiCoO₂, LiNiO₂ and LiFePO₄ is 126, 149, 180 and 170 mAh g⁻¹, respectively. However, all these cathode materials possess relatively low specific capacity. Therefore, the development of cathode materials with a specific capacity higher than that of the above cathode materials would be more efficient for increasing the battery's energy density to satisfy the various demands.

Elemental sulphur is also an attractive active material for cathode material due to its low cost, low equivalent weight, nontoxic nature, high theoretical capacity of 1675 mAh g⁻¹-sulphur, and high theoretical specific energy of 2600 Wh kg⁻¹[10,11], assuming the complete reaction of lithium with sulphur to Li₂S. In lithium-

sulphur batteries, lithium metal is oxidized and sulphur reacts with lithium ions during discharging[12-15]. The reverse process occurs during charging. Previous studies on lithium-sulphur batteries mainly focused on using organic sulfides as cathode materials, such as 2,5-dimercapto-1,3,4-thiadiazole (DMcT), which resulted in a significantly lower theoretical capacity, low active material utilization and poor rechargeability[16].

In this paper, lithium-sulphur batteries with sulphur cathode materials were fabricated and their electrochemical properties were analyzed by means of SEM, CV, and charge-discharge experiments.

2. EXPERIMENTAL

Cathodes were made from mixtures of 51.6 wt.% elemental sulphur powders, 26.7 wt.% nanocarbon black powders, 18 wt.% carboxymethyl cellulose (CMC), 2 wt.% polytetrafluoroethylene (PTFE) and 1.7 wt.% poly(ethyleneglycol) dodecyl ether (Brij35P). CMC and PTFE were used as binders, and Brij35P was used as a dispersant. A mixture of distilled water and alcohol (9:1, vol.%) was used as a solvent. The elemental sulphur and nanocarbon black powders were mixed in a blender for

30 s at high-speed. This procedure was carried out for 10 times. The slurry was ball-milled for 10 h, and then coated on to Al foil. The resulting electrode film was pressed with a twin roller, cut into a rectangle plate (area = 84.42 cm²) and dried at 60 °C for 12 h under vacuum. Lithium-sulphur battery was constructed with a separator made from Celgard2500 membrane, the cathode with an area of 84.42 cm², and an anode of lithium metal. The lithium-sulphur battery was laminated and sealed in a pouch under vacuum, and filled with 0.5 g of electrolyte. The electrolyte was 1M LiN(SO₂CF₃)₂ tetraglyme/1,3-dioxolane (1:1, vol.%). The lithium-sulphur batteries were cycled galvanostatically in a potential range of 1.5-2.5 V using a WBCS3000 (WonATech) Battery Tester System.

An EG&G PAR Potentiostat/Galvanostat Model 273A controlled by a personal computer was used for the measurements of CV at a scan rate of 0.1 mV/s. SEM was carried out to observe the morphologies of sulphur powders, nanocarbon black powders, and mixture consisting of sulphur and nanocarbon powders with a Hitachi S-4200 SEM with an accelerating voltage of 5 kV. Cyclic voltammetry of the lithium-sulphur batteries were examined by fabricating Jig batteries. The cathode with an area of 4 cm² was used as the working electrode, and the counter and reference electrodes were lithium metal.

3. RESULTS AND DISCUSSION

3.1 SEM analysis of mixed powders

SEM images of sulphur powders, nanocarbon powders, and mixture of sulphur and nanocarbon powders after being blended at high-speed for 10 times are shown in Fig. 1. As can be seen from Fig. 1, the average particle size of sulphur and nanocarbon powders is around 20 μm and 100 nm, respectively. The sulphur and nanocarbon powders are mixed homogeneously, and sulphur powders are wrapped by a large amount of carbon powders, and proved useful to increase the reaction area between two types of powder particles and electrical conductivity of sulphur. This, in turn, enhances the cycling performance and sulphur utilization.

3.2 Cyclic voltammetry

In order to investigate the practical performance of sulphur as cathode materials for rechargeable lithium batteries, the sulphur cathode material/electrolyte/lithium battery is charged and discharged between 1.5 and 2.5 V at room temperature. A typical cyclic voltammogram is shown in Fig. 2. When the battery is discharged from 2.5 to 1.5 V, a reduction current peak appears at about 2.1 V. After 2 cycles, reduction and oxidation peaks develop at 2.2 and 2.7 V, respectively. The reduction current peak is attributed to the reaction of elemental sulphur with lithium to produce a polysulfide. The oxidation current

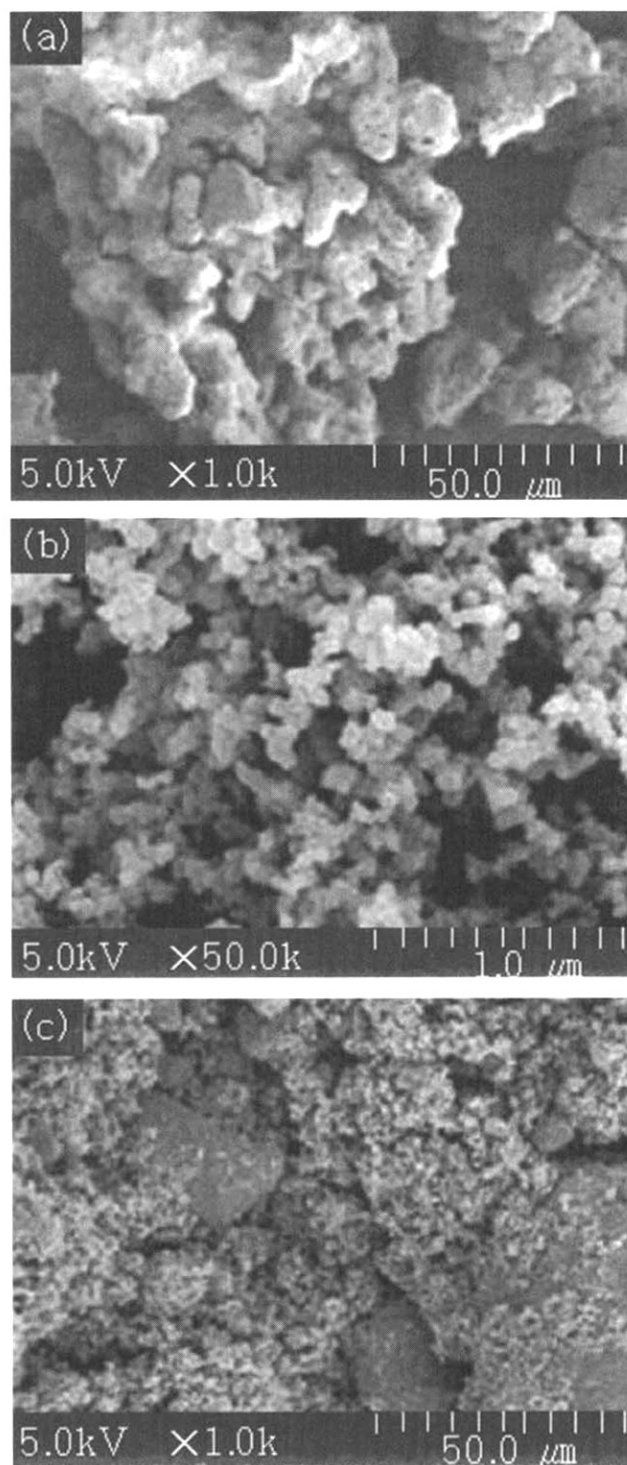


Fig. 1. SEM images of sulphur powders, nanocarbon powders, and mixture of sulphur and nanocarbon powders after being blended at high-speed for 10 times.

peak is attributed to the conversion of polysulfide into sulphur and lithium. It is obvious that reaction of lithium with sulphur is reversible.

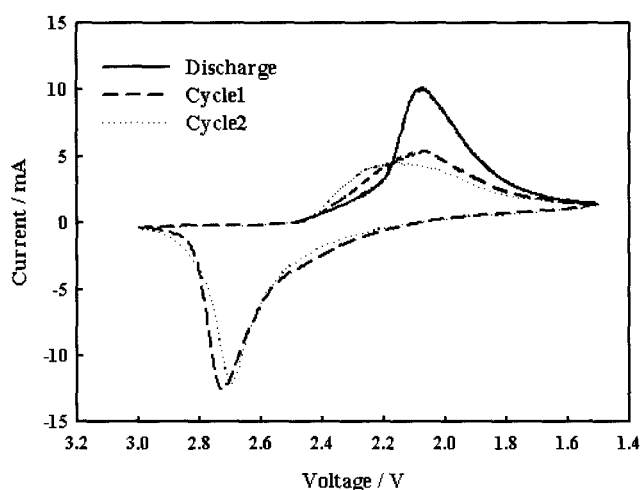


Fig. 2. Cyclic voltammogram of lithium-sulphur battery at a scan rate of 0.1 mV/s.

3.3 Charge-discharge properties

Figure 3 presents the discharge rate characteristics comparison at room temperature. As can be seen from Fig. 3, the discharge capacity of lithium-sulphur battery is 788.1 mAh g⁻¹ at 0.1 C, 710 mAh g⁻¹ at 0.2 C, 602 mAh g⁻¹ at 0.5 C, 500 mAh g⁻¹ at 1 C and 302 mAh g⁻¹ at 2 C, respectively. It indicates that the lithium-sulphur battery may operate at relatively high rates confirming the improved kinetics of sulphur cathode material. It is shown that both discharge capacity and voltage are decreased with an increase of the discharge current density. This phenomenon can be explained in terms of the electric polarization due to an increase in IR drop, where I is a current passing the battery and R is a battery impedance. As shown in Fig. 3, there is a long voltage plateau at about 1.9 to 2.1 V, and this is consistent with the foregoing cyclic voltammetric data that show a reduction current peak at approximately 2.1 V. The convex shape of the plateau may reflect a change in overpotential as the equilibrium between the different polysulfides shifts. The observed small dip may indicate the nucleation of crystalline lithium sulfide phases[17].

Figure 4 shows cycling performance of lithium-sulphur battery at room temperature. The initial discharge capacity of lithium-sulphur battery is 788.1 mAh g⁻¹. On the second cycle, the corresponding discharge capacity is 828.8 mAh g⁻¹. Its discharge capacity after 71 cycles is 796.4 mAh g⁻¹, which is almost the same as the initial discharge capacity. The cycling retention rate of lithium-sulphur battery after 71 cycles is about 96 % of its maximum capacity. It indicates that lithium-sulphur battery maintains stable capacity retention with increase in the cycle number.

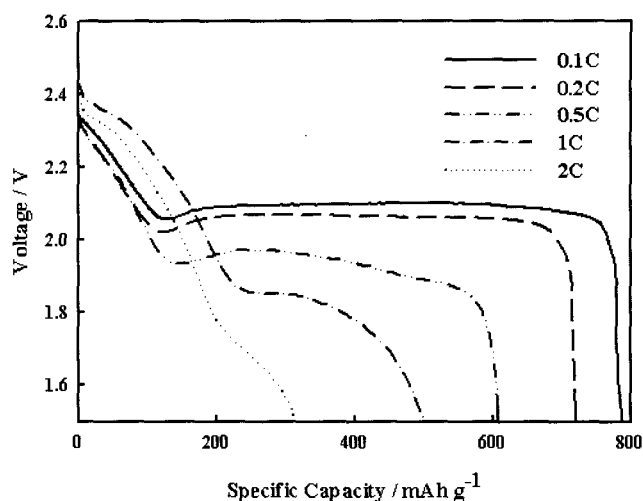


Fig. 3. Discharge rate characteristics comparison at room temperature.

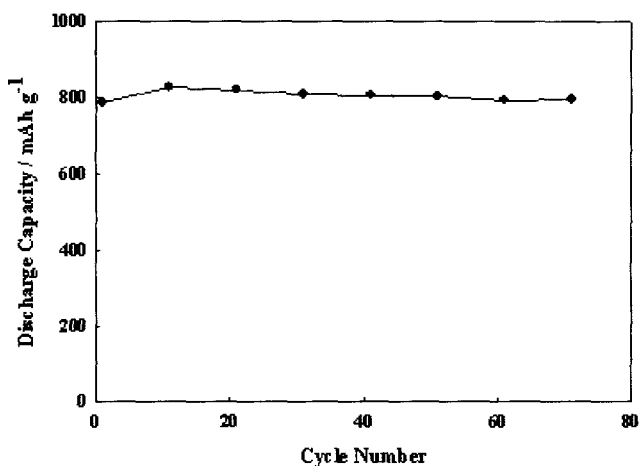


Fig. 4. Cycling performance of lithium-sulphur battery.

4. CONCLUSION

Lithium-sulphur batteries were successfully fabricated in a dry room. The elemental sulphur reported here is a promising candidate as a cathode material for the next generation of rechargeable lithium batteries due to its outstanding electrochemical properties. The sulphur and nanocarbon powders are mixed homogeneously, and sulphur powders are wrapped by a large amount of carbon powders. Lithium-sulphur battery containing 51.6 wt.% sulphur can supply a discharge capacity of 788.1 mAh g⁻¹ at the first cycle and 796.4 mAh g⁻¹ after 71 cycles at room temperature, respectively. It is demonstrated that cycling performance of lithium-sulphur battery is fairly excellent.

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