

EFFECT OF PREPARATION METHOD OF SULFUR-MWNT COMPOSITE ELECTRODE ON ELECTROCHEMICAL PROPERTIES OF Li/S BATTERY

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1. Introduction

Lithium-ion battery (LIB) is recognized as a widely used power source for portable electronic devices, in which carbon and lithium metal oxides were used for anode and cathode, respectively. However, the development of electronic devices and ecological transportations like electric vehicle (EV) has triggered extensive studies to replace conventional costly materials with new materials with higher energy densities, but lower price than current LIBs.

One that meets the requirements of new battery materials for cathode is the elemental sulfur. It has high theoretical capacity of 1675 mAh g⁻¹ assuming the complete reaction of sulfur with lithium to form Li₂S and theoretic specific energy of 2600 Wh kg⁻¹ [1,2]. Though its use for cathode is advantageous in terms of energy densities, there are some problems for realization of lithium-sulfur batteries such as the insulating nature of sulfur and sulfur products and the dissolution of polysulfides which are generated during sulfur reduction. These cause long cycling failure and capacity fading, etc. Recently performed research efforts have been oriented to addition of conductive agents, i.e. carbon in sulfur electrodes to increase the conductivity of sulfur electrodes and the utilization of active material as well as to absorb polysulfides. [3-5]. Multi-walled carbon nanotube (MWNT) is attractive because it provides superior electronically conductive network to conventional

carbon black and acetylene black effectively [6,7]. Thus, the elemental sulfur and MWNT composite (S-MWNT) would be a good choice to development of Li/S batteries.

In preparation of S-MWNT electrode for Li/S battery, it is necessary to consider the homogeneous mixing because MWNT is difficult to disperse in the composite. So, it is significant to make a uniform S-MWNT composite for its advantageous features. Moreover, S-MWNT composite should be combined using a binder, which is up to 20wt % of electrodes [3-8]. Even though the binder does not participate in the redox reaction of a cell, homogeneous mixing of the binder, active materials can be a factor to increase the electrochemical properties.

In this work, we investigated the effect of preparation methods for S-MWNT composite electrodes. S-MWNT composites were prepared by mechanical milling of sulfur and MWNT. For mixing of S-MWNT composite and the binder, two methods (stirring and sonication) were adapted to make S-MWNT composite electrodes at different conditions. The effect of the methods on the electrochemical properties was evaluated.

2. Experimentals

S-MWNT composites were prepared by mechanical milling using planetary ball-mill. First, sulfur and MWNT were mixed in the weight ratio of 3:1. The ball-milling was performed in a zirconia jar with

zirconia balls for 1h. The weight ratio of balls and powders was 20:1. The binder, Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP, $M_w=1.54 \times 10^5$, Elf Atochem Co.) was added to S-MWNT composite with NMP. The final weight ratio of components (Sulfur, MWNT and PVdF-co-HFP) was 60:20:20. Slurries prepared in different conditions were then coated on Al foils (current collector). S-MWNT composite cathodes were dried in an oven at 80°C for 12h until the solvent was completely evaporated.

The mixing of slurry for S-MWNT electrodes was carried out in two ways: stirring and sonication. The parameter controlling the mixing condition was stirring and sonication time. The list of samples fabricated along different preparation parameters is tabulated in table 1.

Table. 1. List of samples fabricated along different preparation parameters.

Samples	Stirring (h)	Sonication (h)
S1	48	-
S2	1	0.5
S3	1	1
S4	2	1

As-prepared cathodes were characterized by scanning electron microscopy (SEM, Philips XL30 S FEG, Netherland) and X-ray diffractometry (XRD, D8 Advance, Bruker AXS, Germany) with $\text{CuK}\alpha$ ($\lambda = 1.5418$) in the range of 20–80° at a scan rate of 5°/min.

Cells for measurement of electrochemical properties were assembled in stainless-steel apparatus (Swagelok®) by stacking in sequence of a lithium foil, polypropylene separator (Celgard® 2400) and S-MWNT composite cathode. The liquid electrolyte was prepared by dissolving 1M LiCF_3SO_3 in Tetra (ethylene glycol) dimethyl ether (TEGDME) and dioxolane (DOXL) (v/v, 5/5). Redox profiles of cells were measured by cyclic voltammetry method in 1.5–3.2V (vs. Li^+/Li) at 0.01mVs⁻¹ scan rate. The charge/discharge cycling performances were tested by the galvanostatic method using WBCS3000 battery cycler (WonA Tech. Co). The cut-off voltage and current density were 2.8/1.5V (vs. Li) and 100mA g⁻¹-S, respectively.

3. Results and discussion

Sulfur and MWNT were composited by mechanical milling so the observation of raw materials using scanning electron microscopy (SEM) was carried out to see the morphologies in their initial states. In Fig. 1 (a), commercial sulfur powders (from Aldrich) are over 15μm and connected arbitrary round shapes. In Fig. 1 (b), MWNT of several or several tens of micrometers in length and less than 50nm in diameter are densely entangled together. PVdF-co-HFP is flossy cotton shape of average 5μm in diameter in Fig. 1 (c). The phase examination of each material was also conducted using X-ray diffractometry (XRD). At the lower right corner in Fig. 1, three XRD patterns are presented. The commercial sulfur powders (a) are indexed to alpha sulfur phase (orthorhombic structure). MWNT (b) shows a typical pattern with graphite peaks and PVdF-co-HFP (c) broad amorphous polymer pattern.

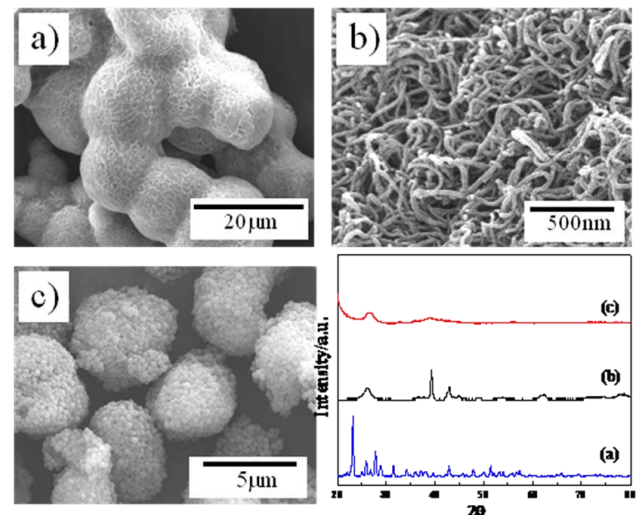


Fig. 1. SEM images and XRD patterns (lower right) of raw materials for S-MWNT composite electrodes: (a) sulfur, (b) MWNT and (c) PVdF-co-HFP.

The morphologies of S-MWNT composite electrodes prepared according to parameters in table 1 are shown in Fig. 2. The composite electrodes were successfully fabricated by ball milling, which unwound the entangled MWNT. The binder covered S-MWNT composite completely. So, not a thread of MWNT is seen throughout the entire material. However, as one can know at a glance, their appearances are very similar, so no distinguished change was seen. XRD Analysis in Fig. 3 indicates

that there are no phase transformations: sulfur structure of alpha phase (orthorhombic structure) predominantly and a trace of MWNT peaks except peaks ($2\theta = 38, 45, 65, 78^\circ$) from Al current collector. Thus, the crystallinity and morphologies were not varied by ball-milling and different mixing parameters.

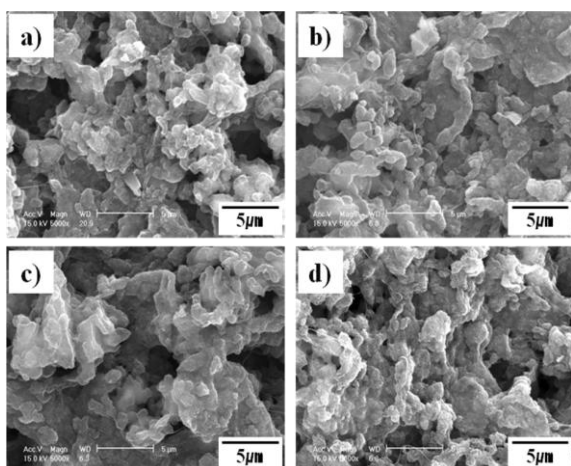


Fig. 2. SEM images of S-MWNT composite electrodes: (a) S1, (b) S2, (c) S3 and (d) S4.

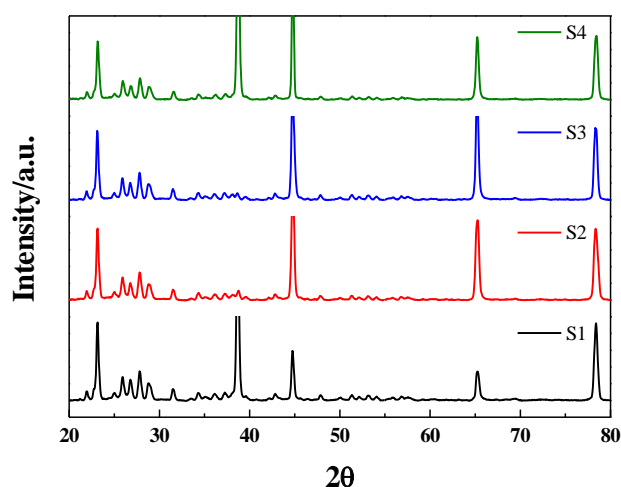


Fig. 3. XRD patterns of S-MWNT composites.

Cyclic voltammograms (CV) profiles of S-MWNT composite electrodes were shown in Fig. 4. All samples have two reduction peaks and two oxidation peaks. Two reduction peaks appeared at ca. 2.4V, and between 1.8 and 1.9V. This result is analogous to previous results [5, 8]. The former peak near 2.4V corresponds to the formation of polysulfides (S_6^{2-} and S_4^{2-}) by reduction of cyclooctasulfur (S_8). The

latter peak near 1.9V corresponds to the formation of sulfides (S_2^{2-} and S^{2-}) by reduction of polysulfides (S_6^{2-} and S_4^{2-}) [9,10].

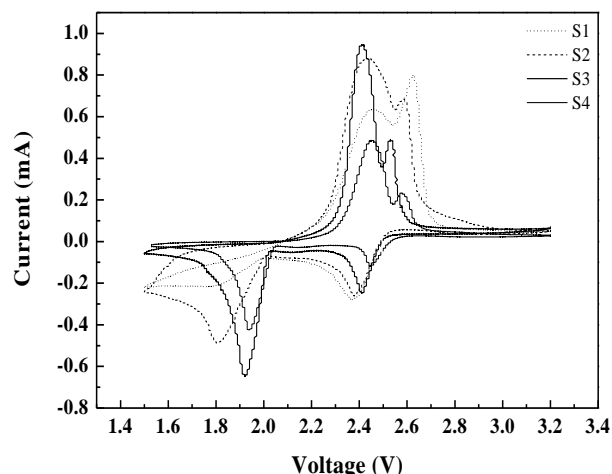


Fig. 4. Cyclic voltammogram (CV) of S-MWNT composites.

From CV observation, we could notice obvious changes in the redox peaks and peak areas. S1 has two reduction peaks appeared near 2.4V and 1.8V. While, the peaks of S2, S3 and S4 shifted to higher potential. The peak shift toward higher potential in reduction profile means the decrease of inner resistance in cells. S1 has two oxidation peaks occurred near 2.5V and 2.6V. Compared with S1, the peaks of S2, S3 and S4 shifted to lower potential slightly. These peak shifts can be reasoned that if the inner resistance in cells decreases, the potential in oxidation peaks shift towards lower. Also, overall potential gap between reduction and oxidation becomes wide with increasing inner resistance. In this CV result the least IR loss (inner resistance) was seen in CV curve of sample S3. In addition, reduction peak area is related with discharge capacity of a cell. In our four samples, the discharge capacity of S3 could be higher than others because of its wider reduction peak area. In this condition much more electron conduction paths (MWNT) might be provided to the insulating materials (sulfur and its reduced materials) through homogeneous mixing induced by sonication. As a result, we could improve the electrochemical properties by controlling preparation parameters of S-MWNT composite electrodes through stirring and sonication time.

Figure 5 shows first discharge profiles of four samples. The discharge capacities at cut-off, 1.5V were 966 mAh g⁻¹ (S1), 1074 mAh g⁻¹ (S2), 1255 mAh g⁻¹ (S3) and 1122 mAh g⁻¹ (S4) based on sulfur content. S3 sample achieved 30% more capacity than S1. The sample S1 stirred for 48h was lowest among four samples and S3 treated by stirring (1h) and sonication (1h) was better than other samples. This result is consistent with CV result. Also, there are two plateaus at 2.4V (upper) and 2.0V (lower) of which potentials are related with the formation of polysulfides at upper plateau potential and lithium sulfides at lower plateau potential as described previously. In the marked area with an oval, lower plateau potential of S2~4 were slightly higher than S1. This means sonication treated samples were decreased in inner resistance. In other words, IR loss of cells is inhibited through homogeneous mixing driven by the better preparation condition, (i.e. S3).

From the electrochemical results, we could know (1) sonication would improve the utilization of the active material and prevent IR drop and (2) long stirring is not a good way to improve the electrochemical properties.

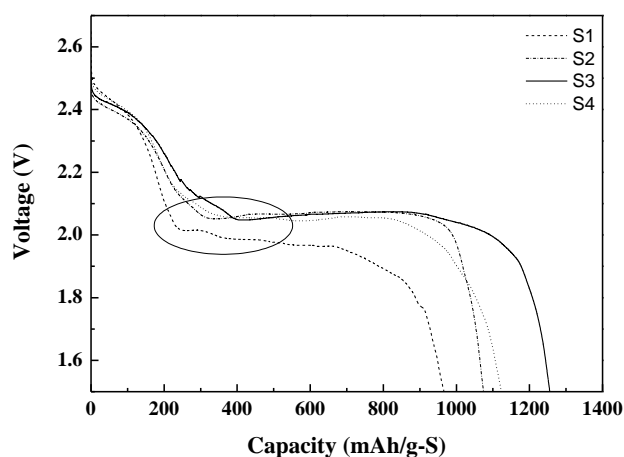


Fig. 5. First discharge profiles of S-MWNT composites.

From electrochemical results of CV and first discharge test, sample S3 is unarguably better than the others. Cycling test of sample S3 was continued and the result was presented in Fig. 6. A specific capacity of 1255 mAh g⁻¹ was delivered in the first discharge. However, reversible discharge capacity was sharply decreased and 841mAh g⁻¹ was

remained in the second cycle, corresponding to 67.0% sulfur utilization (the ratio of 2nd over 1st discharge capacity). Also discharge capacity after 40th cycle remains 420 mAh g⁻¹ which is 33.5% of initial discharge capacity. The voltage gaps are 0.2V (lower plateau voltage) and 0.01V (higher plateau voltage) in the charge/discharge curves. The voltage gap was not changed with cycling.

Changes of discharge capacity of sample S3 is shown in Fig. 7. The cell had high discharge capacity of 1255 mAh g⁻¹ which is similar to previous work [8,10]. Discharge capacity was sharply decreased until 5th cycle and then was gradually decreased until 40th cycle.

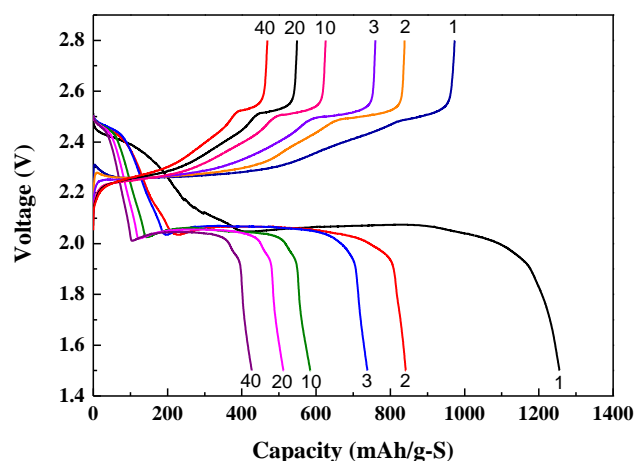


Fig. 6. Discharge/charge curves of S3 (current density: 100 mAh g⁻¹, cut- off voltages: 1.5V and 2.8V).

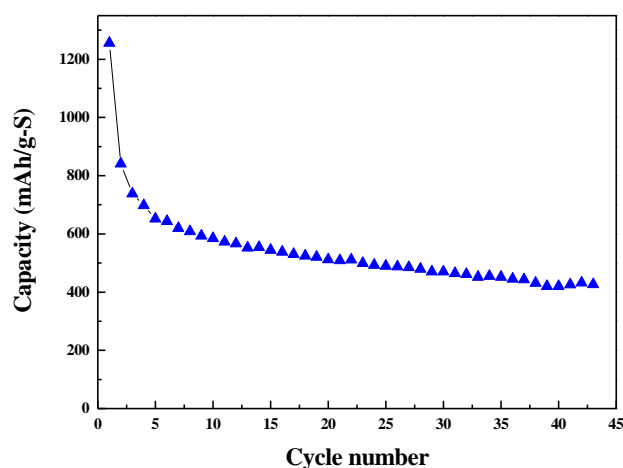


Fig. 7. Cycle life property of S3 (current density : 100mAh g⁻¹, cut- off voltages : 1.5V and 2.8V).

4. Conclusions

S-MWNT composites were prepared by mechanical milling and the electrodes with the composites were fabricated using stirring and sonication. Even though there were no significant changes in morphologies and the phases of sulfur electrodes prepared at different conditions, the electrochemical properties of samples were changed in inner resistances and discharge capacities. Application of sonication to fabrication of slurry was a effective way to improve electrochemical performances of S-MWNT composites. In our case, S-MWNT composite treated by 1h stirring and 1h sonication yielded best results of 1255 mAh g⁻¹ initial capacity and cycle performance. It would be caused by the increase of homogeneity through a proper treatment of sonication and stirring.

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