



Short communication

Effects of carbon coating on the electrochemical properties of sulfur cathode for lithium/sulfur cell

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ABSTRACT

Carbon-coated sulfur cathodes were prepared by sputtering method and electrochemical properties of lithium/sulfur cells were investigated. As a result of charge/discharge test, sulfur cathode having carbon layer of 180 Å showed the highest capacity of 1178 mA hg⁻¹ at first discharge. Moreover, discharge capacity showed about 500 mA hg⁻¹ until 50th cycle, which is two times larger than that of no-coated sulfur cathode. This capacity increase could be considered due to the decrease of polysulfides dissolution and the enhancement of electrical contact by surface carbon layer. The changes of sulfur cathode during discharge process were investigated by SEM observation, XRD and DSC measurements. From these results, a discharge reaction mechanism of lithium/carbon-coated sulfur cell was suggested.

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1. Introduction

The rapid advancement of electronic technology and the widespread use of mobile devices have been continuously demanding a next generation battery. Lithium/sulfur battery is very attractive because of its high theoretical specific capacity of 1675 mA hg⁻¹-sulfur, assuming a complete reaction to Li₂S. Besides, elemental sulfur is very cheap, abundant and nontoxic material [1,2]. Despite of those advantages, lithium/sulfur battery is difficult to commercialize due to low sulfur utilization and poor cycle life property. Those problems are caused by soluble polysulfides (S_n²⁻, n ≥ 4), which generate during charge/discharge process. Because polysulfides dissolution into the liquid electrolytes cause the active material loss and the viscosity increase of liquid electrolyte as well as the morphology change of sulfur cathode [2–5]. Additionally, 100% sulfur cathode cannot be made due to very low electrical conductivity of sulfur (5 × 10⁻³⁰ S cm⁻¹ at 25 °C) [6,7]. It must contain electronically conductive materials such as carbon and metallic powders [4,8,9].

To solve the problems, Gorkovenko [10] added micro-sized vanadium oxide, silicates and transition chalcogenides into sulfur

cathode in order to prevent the polysulfides dissolution. Although metal oxides are effective for polysulfides adsorption due to their large specific area, those materials are not desirable as additive for lithium/sulfur cells due to their insulating property. Also, the sulfur utilization [11] was increased by addition of multi-walled carbon nanotubes (MWNTs) and cycle life property [12] was improved by addition of carbon nanofibers into sulfur cathode. Because those linear carbon materials give an effective electron conduction path and their network-like structure forms a structural stability of sulfur cathode during charge/discharge process. However, carbon nanotubes and nanofibers are very expensive and the manufacturing process is complex. Recently, many interesting cathode materials, such as LiMPO₄ (M = Fe, Mn, Ni, Co), LiFeBO₃ or Li₂MSiO₄ (M = Fe, Mn, Ni), have been treated by carbon coating to enhance electrical conductivity [13]. A surface modification has been used in anode materials for lithium ion batteries to reduce the large irreversible capacity [14,15].

In this study, in order to enhance electrical conductivity, carbon was coated on a surface of sulfur cathode by using carbon coater and effects of carbon coating on the electrochemical properties were investigated.

2. Experimental

Raw materials for fabrication of sulfur cathode were kept in a vacuum oven (80–120 °C) to remove residual water. To decrease

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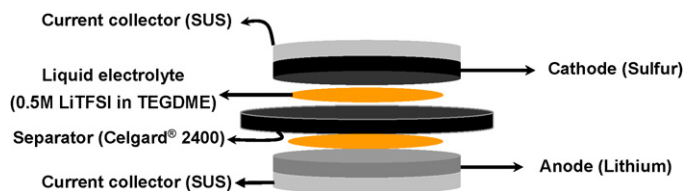


Fig. 1. Schematic diagram of cell components including electrodes.

size of sulfur powder, commercially produced sulfur powder (-325 mesh, Aldrich) was sieved to get size of below $25\ \mu\text{m}$. After sieving, it was mechanically milled by planetary milling machine. Then, sulfur having particle size of below $10\ \mu\text{m}$ was obtained.

Fabrication procedure of sulfur cathode is as follows. Pre-treated sulfur powder, acetylene black ($<1\ \mu\text{m}$, Alfa) and PVDF (Mw = 534,000, Aldrich) were added into zirconia container with NMP (99%, Aldrich) solvent at the weight ratio of 60:20:20. The suspension was mechanically mixed with zirconia ball by planetary ball milling for 3 h. After homogeneous mixing, the slurry was coated on an aluminium current collector. Finally, it was dried at 80°C for 12 h until the solvent was completely evaporated.

To investigate effects of carbon coating, carbon was coated on a surface of sulfur cathode by using carbon coater (CARBON COATER 208, CRESSINGTON) in a vacuum of 10^{-3} Torr for 4 and 12 s, respectively. The thickness of carbon coating layer was measured by using Tencor P-11 surface profiler (KLA-Tencor Corp.).

Liquid electrolyte to evaluate electrochemical properties of lithium/sulfur cells was prepared by dissolving 0.5M LiTFSI ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$, Aldrich) salt into TEGDME (99%, Aldrich) organic solvent. Fabrication of liquid electrolyte was carried out in an argon-filled glove box and water content was kept below 20 ppm by adding $4\ \text{\AA}$ molecular sieve.

The morphology change of sulfur cathode before and after charge/discharge test was observed with scanning electron microscope (JSM-5600, JEOL Co.). Test cell was assembled in a stainless-steel case (Swagelok®) by stacking a lithium foil, polypropylene separator (Celgard® 2400) containing liquid electrolyte and sulfur cathode in turn. Schematic diagram of cell components including electrodes is presented in Fig. 1. All processes of assembling were carried out in an argon-filled glove box. Redox profiles of lithium/sulfur cells were investigated by using cyclic voltammetry method in the voltage range of 1.5–3.2 V (vs. Li^+/Li) at $0.01\ \text{mV s}^{-1}$ scan rate. The interfacial resistance of cell was evaluated by using electrochemical impedance spectroscopy (CMS100, Gamry Instruments Inc.) in the frequency range of 0.1 to 10^5 Hz with 0.1 mV amplitude. The cut-off voltage and current density for charge/discharge tests were 3.2/1.5 V (vs. Li) and $100\ \text{mA g}^{-1}$, respectively. Cell tests were carried out with galvanostatic method by using WBCS3000 battery cyler. To analyze change of reaction product during discharge, X-ray diffraction (RINT2500V, Rigaku Co.) and differential scanning calorimeter (TA2040, TA Instruments) measurements were performed.

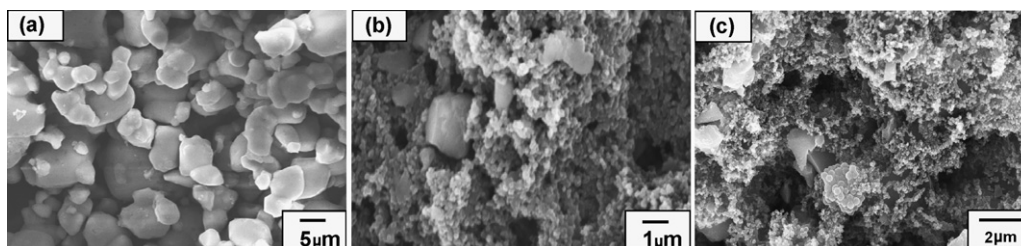


Fig. 2. SEM morphologies of sulfur powder (a), no-coated (b) and carbon-coated sulfur cathode (c).

Table 1
The thickness of carbon coating layer

	The thickness at the number of carbon coating times (\AA)			
	1st	2nd	3rd	Average
4 s	180	175	185	180
12 s	220	250	230	231

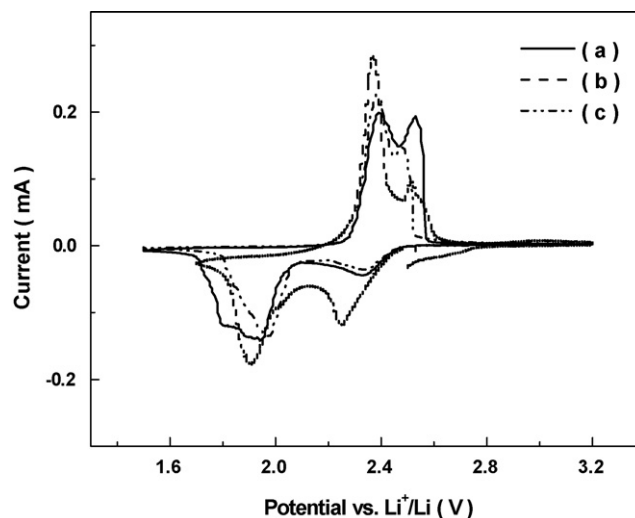


Fig. 3. Cyclic voltammograms of lithium/sulfur cells with $0.01\ \text{mV s}^{-1}$ scan rate: (a) no-coated, (b) coated for 4 s and (c) coated for 12 s.

3. Results and discussion

Fig. 2 shows SEM morphologies of sulfur powder and sulfur cathodes. In a present study, commercial sulfur powder having size of below $45\ \mu\text{m}$ was pre-treated by sieving and mechanical milling to decrease particle size of sulfur. After size decreasing, sulfur particles showed size of below $10\ \mu\text{m}$ as shown in Fig. 2(a). With decreasing sulfur particle size, sulfur utilization would be increased due to the decrease of cathode resistance and the increase of specific surface area [16], because sulfur is an insulator. As shown in Fig. 2(b and c), carbon particles are well dispersed in the sulfur cathodes. In case of the carbon-coated sulfur cathode, surface roughness was increased and sulfur particles were well covered with carbon particles compared to the no-coated sulfur cathode. These differences of surface morphologies could be considered due to carbon coating layer. Table 1 shows the thickness of carbon coating layer at the number of coating times.

Fig. 3 shows cyclic voltammograms of lithium/sulfur cells tested with $0.01\ \text{mV s}^{-1}$ scan rate. Sulfur cathode without carbon coating shows three cathodic peaks at 1.8, 1.9 and 2.3 V as well as two anodic peaks at 2.4 and 2.5 V, respectively. The detailed mechanisms for oxidation and reduction of sulfur, polysulfides and lithium sulfide during charge/discharge were already reported. [17,18]. First

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