

Electrochemical characterization and performance improvement of lithium/sulfur polymer batteries

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Abstract

Electrochemical properties and performance of lithium/polymer electrolyte/composite sulfur cells are presented. The composite sulfur cathode prepared by two ways were characterized and compared by X-ray diffraction (XRD), thermogravimetry (TG), differential thermoanalysis (DTA) and scanning electron microscopy (SEM). The all-solid-state Li/S battery operated at 75 °C with P(EO)₂₀Li(CF₃SO₂)₂N–10 wt.% γ-LiAlO₂ as electrolyte exhibited an average capacity of 290 mAh g⁻¹ for the sulfur melted together with poly(ethylene oxide) (PEO) during 50 cycles. The mechanisms for capacity degradation of the Li/S polymer battery were discussed.
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1. Introduction

The lithium-ion rechargeable batteries have been popularly used in portable electric applications. Based on the purposes to develop lithium batteries for electric vehicles, a battery system with high specific energy, safe operation and low cost would be developed. A lithium/sulfur battery, which use polymer as electrolyte, is expectative due to the theoretical capacity of 1675 mAh g⁻¹, low cost, environment amity of elemental sulfur [1].

Previous reports on Li/S batteries indicated that these problems are incompatibility of lithium and polysulfide with liquid electrolyte, low utilization of sulfur obtained at room temperature, poor cycle performance with aggregation of sulfur after charge–discharge process [1–10]. Shin et al. [7] showed that sulfur of #325mesh particle size was fully utilized for a single discharge at 90 °C and Wang et al. [5,10] reported that the Li/S battery has a high specific capacity value at room temperature when particle size of

sulfur less than 10 nm. Consequently, increase of working temperature and reduction of sulfur particle size enhance its utility. Because it is both ionic and electronic insulator, sulfur should be combined well with conductive agent when prepared to electrode. Moreover, the method to prepare composite sulfur cathode is contributing significantly to the electrochemical performance of the Li/S polymer battery.

Solid polymer electrolytes attracted a great deal of interest for using in the Li/S battery, which presented serious defects while liquid electrolyte was employed [8,9]. The poly(ethylene oxide) (PEO) with lithium salts and ceramic filler has been investigated widely during the past decade and has obtained good mechanical properties and ionic conductivity [11–15]. In this work, the PEO with Li(CF₃SO₂)₂N salt and γ-LiAlO₂ filler was used as polymer electrolyte for the Li/S battery because of its favorable interfacial stability and electrochemical properties [11–13].

In this paper, we aimed to prepare a stable all-solid-state Li/S polymer battery system and improve its electrochemical performance by developing a new method to prepare composite sulfur cathode.

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2. Experimental

2.1. Preparation of composite sulfur cathode and electrolyte

Elemental sulfur (#200mesh) and PEO ($M_w = 9 \times 10^5$) at a weight ratio of 3:7 were blended by two kinds of route to prepare sulfur-based composite materials marked as SPM, which was blended by mechanical milling at room temperature, and SPT, blended by thermal melting at 180 °C in a sealed container. The speed of mechanical milling was 200 rotations per minute for 120 min and a ball-to-powder weight ratio of 20:1 was chosen. To make composite cathode, the mixed slurry of 80 wt.% SPM (or SPT), 10 wt.% acetylene black (AB) and 10 wt.% polyvinylidene fluoride (PVDF) in *N*-methylpyrrolidinone (NMP) was spread uniformly on a thin aluminum foil.

The composite polymer electrolyte of P(EO)₂₀Li(CF₃SO₂)₂N–10 wt.% γ -LiAlO₂ was prepared in an argon-filled glove box. The stoichiometric mixture of PEO ($M_w = 9 \times 10^5$) and Li(CF₃SO₂)₂N was dissolved in acetonitrile into which γ -LiAlO₂ powders were added. The suspension was cast on a Teflon sheet and then heated to evaporate solvent at 50 °C. After evaporation, the electrolyte film was dried under vacuum at 80 °C for 10 h to the remove residual solvent.

2.2. Measurements

All-solid-state Li/S cells were assembled by sandwiching the polymer electrolyte film (360 μ m thick) between a lithium foil (200 μ m thick) and the composite sulfur cathode (1.5 cm² area) in an Ar-filled glove box. The charge and discharge performance of the cells was measured galvanostatically at 0.1 mA cm⁻² between 1.5 and 3.2 V with a CT2001A cell test instrument (LAND Electronic Co.) at 75 °C. A Solartron Model 1287 Electrochemical Interface was used for cyclic voltammogram measurements. X-ray diffraction (XRD) patterns were recorded using D/max 2550 V XRD spectrometer. Thermogravimetry (TG) and differential thermoanalysis (DTA) were carried out with a ZRY-1P thermal analyzer at the heating rate of 5 °C min⁻¹. The morphology of the electrodes was investigated by scanning electron microscopy (SEM) using a JEOL electronic microscope JSM-6700F.

3. Results and discussion

3.1. XRD and TG/DTA analysis of sulfur composite materials

The fulvous flaky sample of SPT is obtained from a sealed container in which mixture of sulfur and PEO with a weight ratio of 3:7 was melted at 180 °C. Fig. 1 shows the XRD patterns of the sulfur, PEO and SPT. It is clear that the XRD pattern of sulfur shows the characteristic pattern of S₈ and

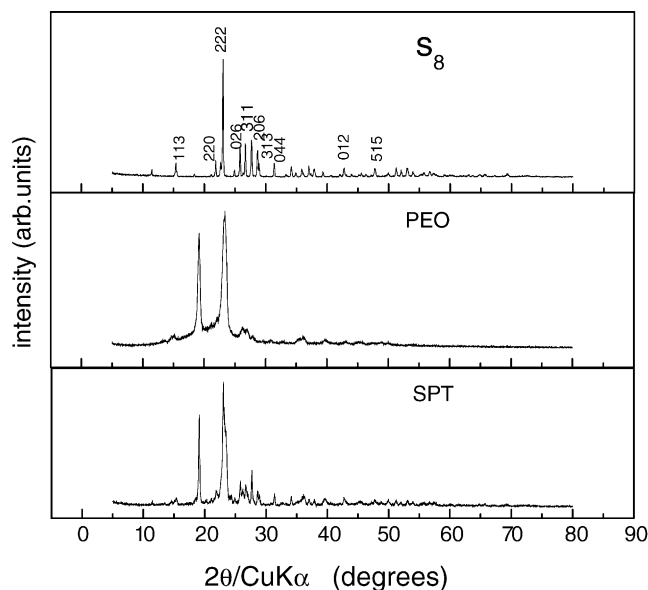


Fig. 1. X-ray diffraction patterns of S₈, PEO and SPT.

conforms to Fddd orthorhombic structure [16,17]. It is therefore suggested on the basis of phase analysis that SPT is only a mixture of sulfur and PEO.

Fig. 2 shows the TG/DTA profiles of SPM and SPT. In the DTA curve, the endothermic peaks around 65 and 120 °C are respectively attributed to the vitrification of PEO and solid–liquid transition of sulfur. In the TG curve, the weight of the sample shows a drop in the range between 180 and 290 °C. This weigh loss around 30% could be attributed to the volatilization of sulfur, and then the gently decline after 290 °C is corresponding to decomposition of PEO with an exothermic peak in the DTA curve. The TG/DTA patterns of both SPM and SPT are very similar, although the peak temperature of SPT shifts to higher temperature compared to that of SPM.

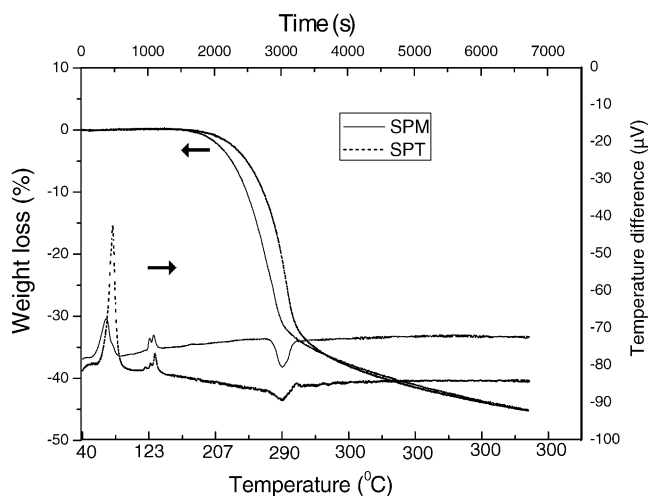


Fig. 2. TG/DTA curves of the SPM and the SPT at a heating rate of 5 °C/min from 40 to 300 °C and then kept at 300 °C under N₂ atmosphere.

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