Journal of Power Sources 222 (2013) 237–242

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

All-solid-state Li–sulfur batteries with mesoporous electrode and thio-LISICON solid electrolyte

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HIGHLIGHTS

- ► All-solid-state battery with a composite cathode, sulfur/CMK-3, and solid electrolyte, thio-LISICON was studied.
- ► CMK-3 is a high ordered two-dimensional meso-porous carbon and provides a framework structure for the cathode composite.
- ► The sulfur/CMK-3 cathode exhibited high capacity and excellent cycling characteristics.

ARTICLE INFO

Article history:
Received 23 May 2012
Received in revised form
4 August 2012
Accepted 14 August 2012
Available online 3 September 2012

Keywords:
Lithium secondary battery
Sulfur
All-solid-state battery
Carbon
CMK-3
Mesoporous carbon

ABSTRACT

All-solid-state lithium–sulfur batteries were developed using elemental sulfur as a positive electrode, Li–Al alloy as a negative electrode, thio-LISICON as a solid electrolyte, and mesoporous carbon (CMK-3) as the framework for the positive electrode. The mesoporous framework provided high electrical conduction and improved electrode utilization. The sulfur provided a high reversible capacity and high current charge discharge characteristics. Sulfur introduced into the pore structure of the mesoporous carbon interacts with edges of the graphene sheet and both the sulfur and graphene layers participate in a highly reversible reaction.

1. Introduction

High-capacity rechargeable batteries are promising power storage devices for future portable electronic devices and electric vehicles. Batteries with lithium-based systems have high energy densities, are lightweight, and have low electrochemical potentials. Sulfur positive electrodes in lithium-based systems have a theoretical capacity of 1672 mAh g^{-1}, which is 10 times higher than that of conventional $LiCoO_2$ positive electrodes. This theoretical capacity is based on the charge–discharge reaction, $S + 2Li^+ + 2e^- \leftrightarrow Li_2S$. Due to the abundance of elemental sulfur, batteries based on the lithium/sulfur redox couple have the potential to be inexpensive in addition to being safe and having high energy densities. However, the low electrical conductivity of sulfur (5×10^{-30} S cm^{-1} at room temperature [1]) results in relatively low utilization of the active materials in sulfur electrodes [2,3]. During charging and discharging, sulfur is converted into polysulfides, which are soluble in liquid organic electrolytes; this loss of the active material in liquid electrolytes leads to poor rechargeability. This problem needs to be overcome in future lithium–sulfur batteries [4,5].

Mesoporous carbon consists of a carbon matrix with mesopores [6–9]. These pores have two-dimensional (e.g., CMK-3) or three-dimensional (e.g., carbon replica) arrangements. CMK-3 synthesized from a template of SiO_2 (SBA-15) powder [6,10] has a two-dimensional ordered structure consisting of a hexagonal arrangement of cylindrical rods. As CMK-3 exhibits a high electrical conductivity [7], ordered mesopores may provide a new electrode structure for lithium–sulfur batteries that has the potential to realize close contact between the electrode and the electrolyte and a high electrical conduction in the electrode matrix [11,12].

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http://dx.doi.org/10.1016/j.jpowsour.2012.08.041

Since all-solid-state batteries are more stable and safer than batteries that employ liquid electrolytes, they have the potential to be used as ultra-high energy density systems. Furthermore, an all-solid-state configuration can realize close solid–solid contact, which prevents the dissolution of polysulfides formed by the electrode reaction in lithium–sulfur systems. The non-inflammability of solid electrolytes permits an extremely high capacity to be realized. The solid electrolyte thio-LISICON ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$) exhibits a high ionic conductivity of $(2–4) \times 10^{-3}$ S cm^{-1} at room temperature, which is comparable to those of liquid electrolytes [13,14]. However, all-solid-state batteries suffer from a high interfacial resistance at the SE/electrode interface. We previously reported that a sulfur/acetylene black (AB) composite can enhance the reversibility of the charge–discharge characteristics. This composite structure was formed by mixing elemental sulfur vapor and AB [15]. AB has a random network of macropores between its constituent particles and it has a low Brunauer–Emmett–Teller (BET) surface area. Using an electrode structure with a framework of CMK-3 greatly enhanced the electrode/electrolyte contact and improved the electrical conduction and hence the charge–discharge characteristics [16].

The present study investigates a new electrode structure with the aim of improving the characteristics of all-solid-state lithium–sulfur batteries. The reaction mechanism of a composite electrode consisting of sulfur and the mesoporous carbon, CMK-3, was examined. The composite electrode structure improved sulfur utilization for the charge–discharge capacities and it can thus be used to produce all-solid-state Li–sulfur batteries with high energy densities.

2. Experimental

CMK-3 was synthesized from a template of mesoporous silica SBA-15 [6,10]. The CMK-3/SiO_2 composite was also used as a reference for the composite electrode. The sulfur–carbon composite was prepared by gas-phase mixing, as reported previously [15]. The mixing processes are as follows. Sulfur (Kojundo Chemical Laboratory; >99.99% purity) and CMK-3 or CMK-3 + SiO_2 were weighed in a ratio of 30:70 (weight % (wt.%)), mixed in an argon-filled glove box, sealed in a quartz tube in a vacuum, and then heated at 300 °C. After heating, the tube was slowly cooled to room temperature. The composite was heated for 5 h at 170–230 °C to remove any sulfur outside of the particles. Thio-LISICON ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$) was synthesized by a solid-state reaction and was used as a solid electrolyte [13]. Positive electrodes were fabricated by mixing the sulfur–carbon composite and thio-LISICON with a weight ratio of 50:50 in a planetary ball mill (Fritsch, P-7) for 0.5 h at 380 rpm. The test cell was a polyethylene terephthalate (PET) cylinder with an inner diameter of 10 mm. About 70 mg of the solid electrolyte (thio-LISICON) was pressed into a pellet and 5 mg of the positive electrode was then pressed into one side of the electrolyte pellet at 500 MPa. Lithium–aluminum composites were used for negative electrodes because of their good electrode characteristics for all-solid-state batteries consisting of LiAl and thio-LISICON [17]. The negative electrode was a combination of aluminum foil (thickness: 0.1 mm) and lithium foil (thickness: 0.1 mm; diameter: 10 mm). The Li/Al ratio was about 38/68 mol.%, which provides a potential of 0.38 V vs. Li/Li^+. The aluminum foil was attached to the solid electrolyte by applying a pressure of 500 MPa [17] and the lithium sheet was then attached to the aluminum foil. The preparation and fabrication of the cells were performed in a dry (less than 0.1 ppm H_2O) argon-filled glove box (Miwa Mfg. Co. Ltd.). The electrochemical properties were characterized using a multichannel galvanostat (TOSCAT-3100). The charge–discharge current was in the range 0.013–1.3 mA cm^{-2} at 25 °C.

The charge–discharge capacity of the cell was calculated based on the sulfur content of the electrode matrix, which was determined by thermogravimetric analysis (TGA; Rigaku Thermo plus TG8120). The weight ratio of sulfur to carbon in the composite electrode was measured by TGA measurements. TGA measurements were conducted in a helium atmosphere from room temperature to 600 °C at a heating rate of 10 °C min^{-1}. The weight of sulfur in the composite material was determined from the weight loss of the S/C composite material determined by TGA measurements. The ratio of the composite material to the solid electrolyte in the cathode is 50:50 wt.%; the weight of sulfur in the cathode mixture was calculated from this ratio.

The resistivity of the cells was examined by the ac impedance method for frequencies in the range 10 mHz–1 MHz and an applied ac voltage of 10 mV using a Solartron 1260 frequency response analyzer. The electrodes were characterized by X-ray diffraction measurements using a Rigaku Ultima-IV with Cu Kα radiation. Morphologies of the composite electrodes fabricated by gas phase mixing were investigated by field-emission scanning electron microscopy (FE-SEM; Hitachi S-5200). The porosity of the cathode composite was measured by BET measurements with nitrogen gas (BEL JAPAN BELSORP-mini). The pore distribution of carbon was refined by the BJH method [18].

3. Results and discussion

Fig. 1 shows FE-SEM images of CMK-3 and the sulfur/CMK-3 composite after mixing at 300 °C. Mesoscale carbon rods were clearly observed for both samples and no significant changes in the mesoporous structure of the carbon were observed after mixing sulfur and carbon.

The thermal behavior of the sulfur/carbon composite was examined to determine the composite structure of sulfur and the

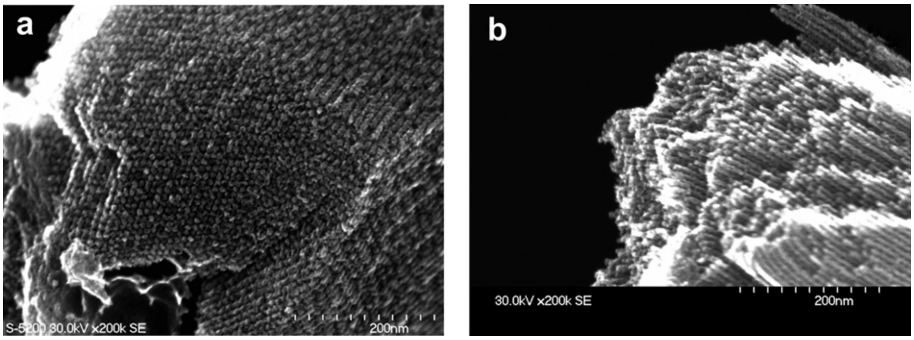

Fig. 1. FE-SEM images of (a) CMK-3 and (b) sulfur/CMK-3 composite.