Journal of Power Sources 399 (2018) 287–293

Contents lists available at ScienceDirect

Journal of Power Sources

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

Potentiostatic way to fabricate Li_2S_x cathode with suppressed polysulfide formation

Yunwen Wu[a], Takuya Jin[a], Toshiyuki Momma[a,b,*], Tokihiko Yokoshima[b], Hiroki Nara[b], Tetsuya Osaka[a,b]

[a] *Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo, 169-8555, Japan*
[b] *Research Organization for Nano and Life Innovation, Waseda University, 513, Wasedatsurumakicho, Shinjuku-ku, Tokyo, 162-0041, Japan*

HIGHLIGHTS

- Potentiostatic lithiation method is developed to make Li_2S_x cathode.
- Suppressed dissolution of polysulfide is observed by potentiostatic lithaition.
- The applied overpotential plays a key role in lithiation depth.
- The lithiated Li_2S_x cathode is able to pair with graphite anode to make full cell.

ARTICLE INFO

Keywords:
Potentiostatic lithiation
Polysulfide dissolution suppression
Li-S battery
Li metal free full cell

ABSTRACT

The usage of Li metal in lithium sulfur (Li-S) battery has largely hampered the application of Li-S battery due to the formation of Li dendrite during cycling. Here, a novel potentiostatic (p-stat) lithiation method was developed to fabricate Li_2S_x cathode. The pre-lithiated Li_2S_x cathode can be used to pair with the Li metal free anode to make a full cell with better safety. The dissolution of the polysulfide in electrolyte is the main problem in S cathode, which leads to severe active material loss during lithiation process. Normally, the way to alleviate the dissolution of polysulfide is by trapping the polysulfide from diffusing into the electrolyte. In this work, it is innovatively raised the p-stat lithiation method which can suppress the formation of polysulfides. As a result, dissolution of polysulfide species could be kinetically suppressed. The p-stat lithiated Li_2S_x cathode exhibits higher capacity performance (around 400 mAh g^{-1}) than the galvanostatic (g-stat) lithiated Li_2S_x cathode. The Li metal free full cell assembled by pairing p-stat lithiated Li_2S_x cathode with graphite anode shows stable cyclability.

1. Introduction

As it is known that high energy density, high safety, and cost effectiveness are the three essential factors that are considered when selecting energy storage devices to meet the increasing demand for developing electric vehicles and portable electronic devices. Sulfur (S), with its high theoretical energy density of 2600 W h kg^{-1}, and a low price of around \$40 t^{-1}, is considered as a promising cathode material for the Li ion battery [1–7]. Although the theoretical specific capacity (1672 mAh g^{-1} when be fully reduced to S^{2-}) of S is attractive [3], the rapid decrease of capacity after cycles has greatly hindered the application of the S battery [8,9]. Furthermore, the lack of Li ion in S cathode inevitably calls for Li ion rich anode (normally Li metal) [10–13]. However, the growth of Li dendrites on the Li anode could penetrate through the separator and cause internal short. This serious safety hazard in lithium sulfur (Li-S) battery has become the main obstacle hindering the application of Li-S battery. In order to avoid this safety hazard, employing the metallic Li free anodes as substitute for Li anode is a promising approach, as reported [9–14].

Galvanostatic (g-stat) discharge is the normal way to realize the lithiation process in the Li-S battery. It is widely accepted that during the g-stat lithiation, the solid S is first reduced to high order lithium polysulfides (Li_2S_8), and subsequently reduced to lower order polysulfides (Li_2S_4) at a lower voltage. Finally, the Li_2S_4 is reduced to solid state Li_2S_2 and Li_2S. The high solubility of the polysulfide species (from Li_2S_8 to Li_2S_4) in the electrolyte leads to the loss of active material in cathode [3,8,15]. In the meantime, the high order polysulfide species tend to travel to the Li anode and are reduced to low order polysulfide

---

[*] Corresponding author. Graduate School of Advanced Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo, 169, Japan.
E-mail address: momma@waseda.jp (T. Momma).

https://doi.org/10.1016/j.jpowsour.2018.07.107
Received 8 May 2018; Received in revised form 3 July 2018; Accepted 27 July 2018
0378-7753/

species. The low order polysulfides may travel back to the cathode, leading to the notorious shuttle effect. The poor cyclability and inactivation of the Li anode are the main issues that arise from the shuttle effect. Till now, various efforts have been made to confine the dissolution of polysulfides, such as designing different host materials for S cathode [5,6,18,20], optimization of the electrolyte [4,16–18] and chemical modification of the cathode material [19–23]. Although these methods have made a difference in improving the cycling performance due to the confined dissolution of polysulfides, the usage of Li metal remains a major issue in the application of S battery.

With an aim to overcome the safety issue in Li-S battery, this study proposed a potentiostatic (p-stat) lithiation method to pre-lithiate the S cathode into Li_2S_x cathode. In order to promote the industrial-scale fabrication of Li_2S_x cathode, the beaker cell, which contains a large amount of electrolyte (5 mL glyme-based electrolyte), was used to analysis the pre-lithiation process. However, as is well known, the increased amount of electrolyte could cause more serious dissolution of polysulfides. By using the g-stat lithiation process, tremendous dissolution of polysulfides was carried out. Under this circumstance, the p-stat lithiation method which could kinetically suppress the dissolution of polysulfides was applied. After applying a constant potential, less polysulfide was detected in the lithiation bath. Different from the step by step transformation from S to Li_2S during the g-stat lithiation process, p-stat lithiation process showed instant nucleation of solid state Li_2S or Li_2S_2. Furthermore, the pre-lithiated Li_2S_x cathode was successfully paired with graphite anode to make the metallic Li free full cell with stable cyclability and high safety.

2. Experimental

2.1. Preparation

2.1.1. Preparation of S cathode

The S Ketjenblack (KB, LION SPECIALTY CHMICALS) composite was prepared by mixing S powder (Sigma-Aldrich) with KB in a 1:1 weight ratio using a granulator (Balance Gran, AKIRAKIKO). The mixture was then heated in an Ar atmosphere at a temperature of 155 °C for 12 h to form a composite of S and KB. The S/KB composite slurry was prepared in the granulator. The S/KB slurry was made by mixing the S/KB composite with polyvinylpyrrolidone (PVP) binder (Sigma-Aldrich Chemistry) and KB with a weight ratio of 9:0.5:0.5 in N-methylpyrrolidone (NMP, KANTO CHEMICAl), which acted as the solvent. In order to prepare the S/KB composite cathode, the slurry was applied to an Al foil using the doctor blade method and dried for 24 h in a dry atmosphere (at the dew point of below −40 °C, RT). The S/KB cathode used to make the Li metal free full cell was prepared by mixing S, KB and polyvinylidene difluoride (PVDF, Sigma-Aldrich Chemistry) with a weight ratio of 7:2:1. The graphite anode was prepared by mixing graphite, acetylene black (AB, DENKA BLACK) and PVdF with a weight ratio of 90:5:5 in NMP using the granulator. Then the slurry was coated on the copper foil and dried in a dry atmosphere (at the dew point of below −40 °C, RT).

2.1.2. Lithiation process

The lithiation equipment is illustrated in the Supporting Information Scheme S1. In the three-electrode system, the Li metal was used as the counter electrode, the Li metal in an isolate glass tube filled with the glyme-based electrolyte was used as the reference electrode. The S/KB cathode is used as the working electrode. The electrolyte is composed of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Kishida Chemical) in triglyme (Wako Chemicals) with a molar ratio of 1:1. The p-stat lithiation is conducted by applying an outer potential of 1.5 V, 1.0 V and 0.8 V respectively. The cutoff capacity is 1700 mAh g^{-1}. The g-stat lithiation is conducted by applying the constant current with a density of 0.03 C (1C = 1675 mAh g^{-1}).

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained by field emission SEM (SEM, S-4500 S, Hitachi). The crystalline structure of the cathode was obtained by X-ray diffraction (XRD, Rigaku, RINT-Ultima III) with the protection of a Kapton tape. The composite of the cathode was characterized by means of field emission scanning electron microscopy with an energy dispersive X-ray analyzer (SEM-EDX, Hitachi, S-4800) and X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010TR). The Ultraviolet–visible spectroscopy (UV–vis) analysis was taken by Jasco V-660.

2.3. Electrochemical measurement

The electrochemical measurements were conducted by coin type 2032 cells assembled in an argon filled glove box. The electrolyte used for half cell is made by dissolving 1.0 M LITFSI in dioxolane (DOL, Wako Chemicals)/Dimethoxyethane (DME, Wako Chemicals) (1:1 vol ratio) with 1% addition of lithium nitrate ($LiNO_3$, Wako Chemicals). 25 μm thick polypropylene porous film was used as the separator. The electrolyte used for making the Li metal full cell was fabricated by mixing LiTFSI and triglyme with a molar ratio of 1:1 [24]. The galvanostatic charge discharge tests were conducted at different C-rates (0.1 C, 0.2 C, 0.5 C, 1.0 C, 1C = 1675 mAh g^{-1}) using a charge discharge system (TOSCAT-3100, Toyo system) between 1.0 V and 3.3 V after an activation cycle at 0.02 C-rate. Toyo system Cyclic voltammetry (CV) with a scan rate of 0.2 mV s^{-1} was conducted using electrochemical measurement equipment (HZ-5000, Hokuto Denko).

3. Results and discussion

In order to confirm the reduction potential of the S/KB cathode in the glyme based electrolyte, the cyclic voltammogram (CV) analysis was carried out. As shown in Figure S1, a weak reduction peak appeared at 2.1 V, which indicated the transformation from S_8 to S_8^{2-}. The strong reduction peaks appear from 1.5 V to 0.8 V. In comparison, pure KB electrode in the glyme-based electrolyte delivers no reduction reaction peak in Figure S1. The capacity originated from KB in the S/KB cathode was negligible. According to the CV curve of the S/KB cathode in the glyme-based electrolyte, it can be learned that the main reduction reaction of the S species takes place in the range from 0.8 V to 1.5 V. Three typical reduction potentials at 1.5 V, 1.0 V and 0.8 V were chosen for applying the p-stat lithiation without applying any g-stat lithiation process.

Fig. 1a shows the lithiation curve of the normal galvanostatic lithiation process carried out in a beaker cell and coin cell. The step by step potential transformation can be observed clearly in the lithiation curve in a coin cell. The high order polysulfide (Li_2S_8) was formed at around 2.1 V. In the coin cell, the flat plateau at 2.0 V was due to the reduction from Li_2S_8 to lower order polysulfide (Li_2S_4). It is noteworthy that a voltage drop can be observed following a lithiation plateau at 1.8 V, which was caused by the transformation from Li_2S_4 to Li_2S_2. According to the classical electrochemical nucleation theory, it is well known that a certain value of free energy barrier has to be overcome to form a nucleation [25,26]. In electrochemical nucleation, the overpotential is the main driving force for the nucleation of solid products. In the enlarged curve shown in Fig. 1a, the overpotential drop can be assigned to the nucleation overpotential, which indicates the generation of nuclei embryos. The following potential plateau offers a driving force for the nucleation growth [27,28]. However, the lithiation curve obtained in the beaker cell, the flat plateau at 2.0 V disappeared. No overpotential drop can be observed and the plateau at 1.8 V keeps gradually decreasing. It can be deduced that nucleation embryo of Li_2S can barely formed in the beaker cell. The increasing overpotential indicates the reduction of high order polysulfides to low order polysulfides without the constant growth of nucleation. From the time