



Novel positive electrode architecture for rechargeable lithium/sulfur batteries

Céline Barchasz^{a,b,*}, Frédéric Mesguich^a, Jean Dijon^a, Jean-Claude Leprêtre^{b,**}, Sébastien Patoux^a, Fannie Alloin^b

^a French Atomic Energy and Alternative Energy Agency (CEA), Laboratory of Innovation for New Energy Technologies and Nanomaterials (LITEN), 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

^b Laboratoire d'Electrochimie et Physicochimie des Matériaux et Interfaces (LEPMI), UMR 5250, Grenoble-INP, CNRS, Université de Savoie, Université Joseph Fourier, 1130 rue de la Piscine, BP75, 38402 Saint Martin d'Hères, France

ARTICLE INFO

Article history:

Received 30 November 2011

Received in revised form

6 February 2012

Accepted 18 March 2012

Available online 10 April 2012

Keywords:

Rechargeable batteries

Lithium/sulfur cells

Positive electrode morphology

Porous current collectors

Electrochemical performances

ABSTRACT

The lithium/sulfur battery is a very promising technology for high energy applications. Among other advantages, this electrochemical system has a high theoretical specific capacity of 1675 mAh g^{-1} , but suffers from several drawbacks: poor elemental sulfur conductivity, active material dissolution and use of the highly reactive lithium metal electrode. More particularly, the discharge capacity is known to be dictated by the short lithium polysulfide precipitation. These poorly soluble and highly insulating species are produced at the end of discharge, and are responsible for the positive electrode passivation and the early end of discharge. Nevertheless, the discharge capacity can be improved by working on the positive electrode specific surface area and morphology, as well as on the electrolyte composition. In this paper, we focused on the positive electrode issue. To this purpose, various current collector structures have been tested in order to achieve a high positive electrode surface area and a stable morphology during cycling. We demonstrated that the discharge capacity could be increased up to 1400 mAh g^{-1} thanks to the use of carbon foam. As well, the capacity fading could be dramatically decreased in comparison with the one obtained for conventional sulfur composite electrodes.

© 2012 Elsevier B.V. All rights reserved.

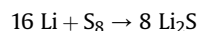
1. Introduction

The development of rechargeable batteries has received an increasing attention due to the growth of portable devices energy consumption. Lithium-ion battery is one of the most popular electrochemical storage systems due to high energy density, high operating voltage and low self-discharge [1]. However, the gravimetric energy density is known to be limited to 250 Wh kg^{-1} at the cell level, which is not enough to meet the electric vehicle requirements for extended range. Moreover, cobalt, which is used in commercial batteries, is toxic and expensive, and layered oxides usually have safety concerns [2].

Elemental sulfur is a promising positive electrode material for lithium batteries due to its high theoretical specific capacity of about 1675 mAh g^{-1} , much greater than the $100\text{--}250 \text{ mAh g}^{-1}$

achievable with the conventional lithium-ion positive electrode materials [3]. The average discharge potential is around 2.1 V, and the complete lithium/sulfur (Li/S) system should allow to reach a gravimetric energy density close to 500 Wh kg^{-1} . In addition, elemental sulfur is readily available and non toxic, advantages that should allow to produce cheap and safe high energy batteries [4]. All these features explain quite well the increasing number of communications on that topic.

The sulfur reduction is a multistep electrochemical process that involves different intermediate species [5,6]. Lithium metal reacts with elemental sulfur (S_8) to produce lithium polysulfides with a general formula Li_2S_n ($2 \leq n \leq 8$). The first polysulfides that are produced have a long chain length, such as Li_2S_8 and Li_2S_6 . Along the discharge, this polysulfide chain length is shortened as the sulfur is being further reduced. At the end of discharge, the final product is lithium sulfide (Li_2S), and the overall reaction equation is [7]



This technology has attracted attention of the electrochemistry community for many years [4,8]. However, several drawbacks still

* Corresponding author. French Atomic Energy and Alternative Energy Agency (CEA), Laboratory of Innovation for New Energy Technologies and Nanomaterials (LITEN), 17 rue des Martyrs, 38054 Grenoble Cedex 9, France. Tel.: +33 438 78 91 62; fax: +33 438 78 51 98.

** Corresponding author. Tel.: +33 476 82 65 62; fax: +33 476 82 67 77.

E-mail addresses: celine.barchasz@cea.fr (C. Barchasz), jean-claude.lepretre@ujf-grenoble.fr (J.-C. Leprêtre).

exist. Indeed, sulfur and lithium sulfide are highly insulating materials [9,10], and the positive electrode must contain enough of electronic conductor material, such as carbon or metallic element. To benefit from the presence of this additive, it has to be well-dispersed in the composite. Sulfur and lithium polysulfides are also soluble in organic electrolytes [11]. They can spontaneously diffuse through the liquid electrolyte, thus leading to lithium metal corrosion and self-discharge, and to an increase in the electrolyte viscosity [12,13]. At the opposite, the reduced compounds, *i.e.* Li_2S_2 and Li_2S , are insulating and insoluble. Thus, they may form a passivation layer on both positive and negative electrodes [14–16]. For these reasons, the sulfur utilization is usually very low, and the cycle life of Li/S cells is poor. Finally, the use of a lithium metal negative electrode is known to be an issue for a large-scale commercialization, as it may lead to dendrite formation, short-circuits and explosions.

Different strategies can be found in the literature to improve the Li/S cell electrochemical performances. Regarding the cathode side, carbon–sulfur composites can be prepared so as to trap the sulfur and lithium polysulfide compounds [17–21]. The use of mesoporous or nanostructured carbon materials enables to decrease the shuttle mechanism as well as the self-discharge, by preventing sulfur compounds from diffusing through the electrolyte. The authors indeed report a high discharge capacity along with an improved cycle life using such carbon materials. However, they finally point out that lithium polysulfides may diffuse progressively, whatever is done on the positive electrode morphology and/or on its composition [17,18]. Moreover, the use of these nanostructured carbon materials requires the vaporization of sulfur into the carbon micro porosities, which leads to strong interactions between sulfur and carbon and results in a decrease of the cell potential [21]. Other papers suggest the coating of active material using polyaniline for example [22,23]. According to authors, this treatment allows to improve both discharge capacity and fading by preventing the contact between elemental sulfur and electrolyte. Another strategy consists in studying the electrolyte composition. Many studies have been carried out on the optimization of liquid electrolyte compositions. The discharge capacity can be increased thanks to the use of ether-based electrolytes [24–26]. Additives can also be added within the electrolyte to improve the battery performances [8,27,28].

Previous works report that the discharge capacity is governed by the precipitation of short lithium polysulfides, which induces the positive electrode passivation [14–16,29,30]. It was demonstrated that the discharge capacity is dictated by the positive electrode morphology and its specific surface area [29]. Thus, this study was focused on the investigation of the positive electrode morphology impact on both cell capacity and cyclability. Two approaches were considered in this paper, either to further understand the Li/S cell functioning and limitations or to improve the electrochemical performances. In the first approach, the nature of carbon black material, which is used as a conductive additive for the sulfur composite electrodes, was investigated. Using carbons with different specific surface areas and particle sizes, we were able to point out the significant impact of the electrode morphology on the electrochemical performances. In the second approach, the starting system was not composed as usual of a composite sulfur electrode. An innovative cell design was considered to improve the Li/S cell electrochemical performances.

In the literature, the lithium battery current collectors are generally metallic foils of aluminum, copper or stainless steel [1]. They can also be made of carbon or metal-coated polymer layers, such as poly(ethylene terephthalate) (PET) or polyamide (PA) [31]. These current collector foils are then coated with the active material, as for example by doctor blade coating technique [29]. On the

contrary, porous metallic current collectors are not commonly used in lithium batteries, even if conventionally used in other battery technologies, as for example nickel/cadmium or nickel/metal hydride batteries [32]. Regarding Li/S cells, there are only a few publications dealing with the use of such porous current collectors [4,33]. In this paper, a non-conventional cell design was considered to improve the Li/S cell electrochemical performances. The active material was introduced in the electrolyte through the dissolution of lithium polysulfides. As using such a catholyte [33], a rigid and porous bare current collector could be used as a positive electrode, without any sulfur source. Various current collector structures were investigated in order to provide the positive electrode with a high surface area and a stable morphology during cycling.

2. Experimental

2.1. Composite positive electrode preparation

Bare sulfur (Refined, – 100 mesh, Aldrich) was mixed with poly(vinylidene fluoride) (PVdF 1015, Solvay) and carbon black in *N*-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5%, Aldrich). The S/C/binder mixing ratio was 80/10/10 wt%. A list of the investigated carbon black materials is presented in Table 1, where some of the important characteristics are summarized. Super P® (SP) carbon material was purchased from Timcal and the corresponding composite sulfur electrode refers as “reference”. Ketjen Black® (KB) carbon and Activated Carbon (AC) materials were purchased from AkzoNobel (EC-300J) and Pica (Picactif® BP10), respectively. After homogenization, the slurry was coated onto a 20 μm thick aluminum current collector by doctor blade technique. The resulting electrodes were dried at 55 °C for 24 h, and then cut into Ø14 mm disks and finally dried 24 h under vacuum at room temperature. The coating thickness was about 100 μm so as to obtain a 20 μm thick electrode after drying. The positive electrode area was 1.539 cm², and the sulfur loading was about 2 mg cm⁻².

2.2. Composite positive electrode-based 2-electrodes cell assembly

The Li/S cell assembly was performed in an argon-filled glove box into CR2032 coin cells. A lithium metal foil was used under as a negative electrode and a Celgard 2400® foil as a separator. A non-woven Viledon® separator (polypropylene-based membrane) foil was also added between the composite positive electrode and the Celgard® separator. The liquid electrolyte was introduced in the cell before sealing, and was composed of LiTFSI 1 mol L⁻¹ and TEGDME/DIOX in a 50/50 vol%.

2.3. Porous current collectors-based 2-electrodes cell assembly

In such cell, the positive electrode was only composed of a bare rigid and porous current collector without sulfur. A list of the investigated current collector samples and their characteristics is given in Table 2. The nickel Incofoam® (Ni foam) was gracefully provided by Inco. The glassy carbon plate was gracefully provided

Table 1

Summary of the investigated carbon black materials involved in the composite sulfur electrodes and some of their important characteristics.

Name	Grade and supplier	Specific surface area (BET)/m ² g ⁻¹	Particles size/nm
SP	Super P®, Timcal	60	40
KB	Ketjen Black®, EC-300J, AkzoNobel	800	30
AC	Picactif®, Pica	1900	8000–15,000

Download English Version:

<https://daneshyari.com/en/article/1284509>

Download Persian Version:

<https://daneshyari.com/article/1284509>

[Daneshyari.com](https://daneshyari.com)