



High temperature stabilization of lithium–sulfur cells with carbon nanotube current collector

Hyea Kim, Jung Tae Lee, Gleb Yushin*

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

HIGHLIGHTS

- ▶ The effect of high temperature on the Li–S cell performance was investigated.
- ▶ When operating at 70 °C the cells demonstrated the best rate capability and capacities.
- ▶ SEM/EDS studies revealed thicker SEI on the Li anode surface at higher temperatures.
- ▶ Thicker SEI prevented polysulfides diffusion and their irreversible reduction into Li₂S.
- ▶ The increase in inorganic components of the SEI suppressed the Li dendrite growth.

ARTICLE INFO

Article history:

Received 17 August 2012

Received in revised form

3 October 2012

Accepted 11 October 2012

Available online 2 November 2012

Keywords:

Li–S

Li ion battery

Carbon nanotube

Temperature

Nanocomposite

Cathode

ABSTRACT

Lithium–sulfur (Li–S) chemistry has been considered for an alternative future generation of rechargeable lithium batteries because of its higher theoretical capacity, safer operation and lower material cost. Here, we report on the impact of temperature on Li–S cell performance. The Li–S coin-cells were prepared by using S infiltrated vertically aligned carbon nanotube arrays (S-CNT) as cathodes and lithium metal foils as anodes. The cells were operated at 25, 50, 70 and 90 °C. Higher temperature operation resulted in higher specific capacity, better rate capability and more stable performance. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and electrochemical impedance spectroscopy (EIS) studies reveal the major impact of temperature on the solid electrolyte interphase (SEI) on Li foil. Thicker SEI with higher content of inorganic phase formed at elevated temperatures greatly reduced both the dendrite formation and the capacity fading resulted from the irreversible losses of S. At 70 °C specific capacities up to ~700 mAh g⁻¹ were achieved at an ultra-high current density of 3.3 A g⁻¹. At 90 °C and the same current density Li–S cells showed an average capacity of ~400 mAh g⁻¹ and stable performance for over 150 cycles.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Lithium ion batteries (LiBs) have been serving as power sources for various portable devices such as laptops, smart phones and electric vehicles. However, ever-rising power demands for these devices have surpassed the current technology of LiB. The specific energy of the commercialized LiB has become insufficient due to the relatively low capacity of the electrode materials [1] and the growth in the energy density of LiB has reached the stagnation.

In order to increase the energy density of the LiB, new electrode materials with higher gravimetric and volumetric capacities should be developed [2–7]. There have been some improvements in the

developments of high capacity silicon (Si)-based anodes, which offer over several times higher capacity than the traditional graphite anodes and are produced of similarly low cost and abundant materials [8–18]. To maximize the advantages of Si-based anodes, however, one needs to develop cathode materials with comparably high volumetric capacity. Such developments, however, have shown smaller progress.

Sulfur (S)-based materials are considered to be attractive candidates for the next generation cathodes due to the very low cost and abundance of S in nature combined with enhanced safety associated with the use of low-voltage cathode materials [19–36]. Sulfur offers very high theoretical gravimetric capacity of 1672 mAh g⁻¹, which is an order of magnitude higher than state of the art commercial electrodes. The volumetric capacity of S-based electrodes depends on the electrode microstructure and porosity, but even if S occupies 33% of the electrode volume (the rest being

* Corresponding author.

E-mail address: yushin@gatech.edu (G. Yushin).

reserved for the carbon additives and the pre-existing porosity) and the S utilization is 90%, it may easily approach $\sim 1000 \text{ mAh cc}^{-1}$, which is about two times higher than that of commercial cathodes.

Yet there are several challenges preventing commercialization of S cathodes for the next generation lithium batteries. The largest challenge is an extensive capacity degradation occurring during cycling because of the high solubility of some of the polysulfides (such as Li_2S_8 or Li_2S_4 , reaction intermediates during discharge) in electrolytes [23,35,36]. This dissolution also leads to the self-discharge and to the eventual precipitation of electrically insulative and insoluble Li_2S_2 and/or Li_2S onto the surface of both electrodes during the battery operation, which commonly further limits the cell performance. Such deposits may contribute to the permanent losses of the active material (Li and S) and to the increased ionic resistance of the cell, as the deposits partially block the ion transport. The dissolution of polysulfides and their re-deposition on the cathode surface is often referred to as a “shuttle mechanism” [23,37]. While the cathode dissolution is often considered to be highly undesirable, a well-controlled “shuttle mechanism”, involving fully reversible dissolution and re-deposition of polysulfides on the surface of conductive cathodes could be a viable option if a barrier could be built to prevent polysulfides from reaching the anode and forming insoluble precipitates.

Another challenge is highly electronically insulating properties of S, which require the uniform introduction of electrically conductive material, such as carbon and conducting polymers, into the electrode in order to improve the utilization of S [19–21,24,28–35].

Finally, Li-free low-voltage cathodes require the use of Li-containing low-voltage anodes, which may increase the overall cost of LiB production because of the need to use more expensive production facilities. The use of metal Li as an anode does carry some benefits too. Its low potential and very high volumetric and gravimetric capacities can maximize the energy density of

lithium–sulfur (Li–S) cells. In conventional LiBs, Li anodes are never used because they form dendrites during repeated Li plating–dissolution cycles, which eventually result in an internal short circuit. With S cathodes, however, some of such issues can be mitigated. The formation of electrically isolative Li_2S may self-limit the short circuit reaction processes, while some of the polysulfides deposited on Li may suppress the dendrite formations.

Many of the key Li–S processes governing the cell performance, including the polysulfide dissolution rate, the ionic transport and the solid electrolyte interphase (SEI) on the Li foil, shall be thermally activated. Surprisingly, we could not find any systematic studies on the effects of cell operating temperature. Therefore, in this work we were interested to reveal how this temperature may impact the performance of Li foil–S cells, where the dissolution of the polysulfides is not restricted by S incorporation in a porous matrix [24,29,38,39] or by surface coating of S particles with various barriers for solvent and polysulfide molecules. In order to achieve high electrical connectivity within the S electrode, we have utilized vertically aligned carbon nanotubes (VACNTs), which have recently shown great promises for high capacity anodes [40] and cathodes [41] due to their excellent thermal and electrical properties. In addition, high porosity of the VACNTs allow for uniform deposition of the active material. Due to high strength and excellent mechanical properties of CNTs, the compression of the VACNT-based electrodes to achieve higher volumetric capacity does not induce cracks or any other undesirable mechanical defects.

We observed the in-situ formation of a protective coating on a Li foil anode at elevated temperatures of 70–90 °C. At 90 °C, the Li–S cells with $\sim 50 \mu\text{m}$ thick compressed VACNT/S electrodes could be charged and discharged within 6 min, while maintaining average capacity in the range of $\sim 400 \text{ mAh g}^{-1}$ and showing cycle life stability in excess of 150 cycles. The combination of high capacity, high rate performance and moderately high stability of the thick VACNT/S electrodes is unprecedented. While higher cycle stability

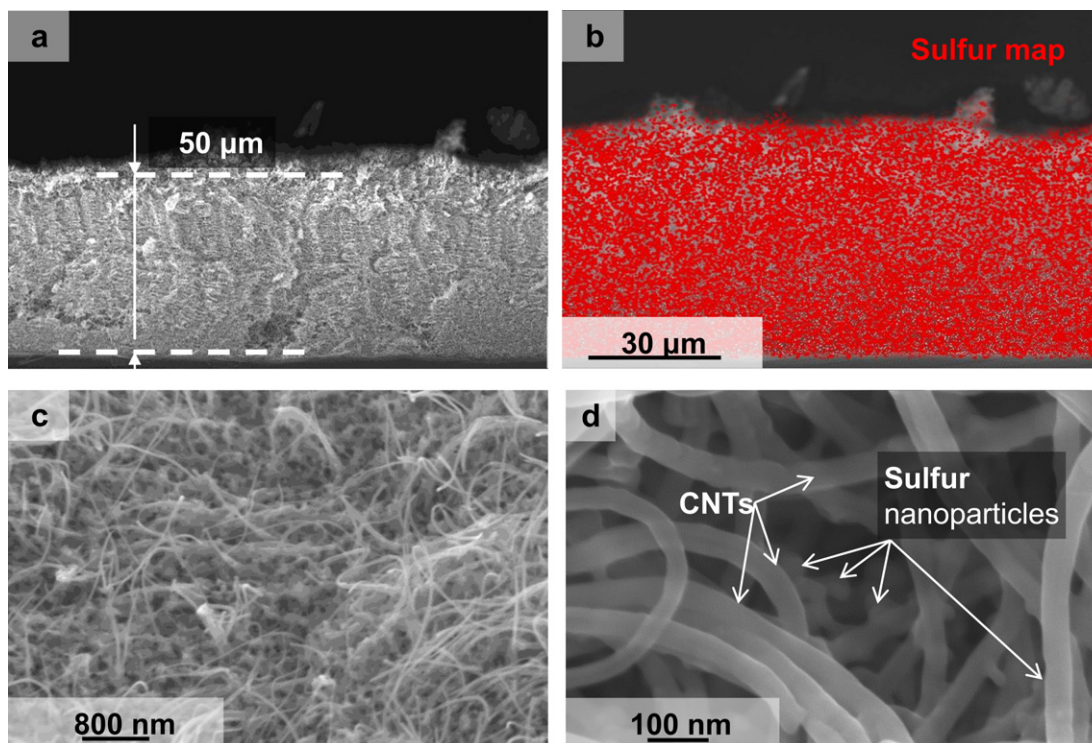


Fig. 1. Electron microscopy of S-CNT cathode. (a) SEM micrograph of the cross-section. (b) EDS mapping of the S distribution within the electrode superimposed on the SEM micrograph. (c, d) SEM micrographs of the top of the electrode recorded at different magnifications.

Download English Version:

<https://daneshyari.com/en/article/7741587>

Download Persian Version:

<https://daneshyari.com/article/7741587>

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