CYCLING INDUCED SULFUR DIFFUSION IN LITHIUM-SULFUR BATTERIES REVEALED BY LAB-BASED X-RAY TOMOGRAPHY

Shaogang Wang[1*], Guangmin Zhou[1], GuangjianHu[1], Ruopian Fang[1], Feng Li[1], Sucheng Wang[1], Lei Zhang[1]

[1]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, PR China

Keywords: X-ray tomography, in-situ, multi-scale, Li-S battery, diffusion, evolution

Summary: In situ x-ray tomography allows researchers to visualize and trace the internal structure evolution of various materials with the changes of environmental conditions. Li-S batteries with different microstructure and setup for XRT were designed. 3D characteristics and evolution of sulfur within the electrode during electrochemical process were successfully visualized and tracked by multi-scale in situ and ex-situ XRT.

1. INTRODUCTION

Li-S batteries are considered to be a promising next generation high energy electrochemical energy storage system with the potential applications on portable electronic devices and green electric vehicles. Specific capacity and energy density are two basic factors that decide the application prospect of the Li-S batteries. It is well known that the specific capacity and energy density of Li-S batteries is strongly related to its sulfur loading (mg cm^{-2}) and sulfur content (wt. %). Unfortunately, the highly soluble polysulfides in the electrolyte which can shuttle between the anode and cathode affect the utilization of the active sulfur material. A deposition of discharge solid product Li_2S on the cathode and anode can cause an irreversible loss of sulfur. Besides, large volume change (80%) between sulfur and Li_2S during charge/discharge induces stress in the electrode and destroys its structural stability, which leads to rapid capacity decay and potential safety problem. State of the art design of cathode, anode and separator microstructure can maximize the performance of Li-S batteries.

The complex behaviour of sulfur migration during cycling in high performance Li-S batteries with new electrode microstructure is still a puzzle. The microstructure units of the cathode are often composed of several layers, but the overall thickness is quite thin. Precise measurement of the thickness of separate layer is very important to understand the volume expansion during the cycling process of Li-S batteries. Traditional 2D techniques such as SEM are not easy to measure the thickness because the edge of the layer often curls naturally. When the Li-S batteries are assembled in the form of button cell, the assemble technology is key for the cell to be safe or flammable. Such an invisible danger of sealed button cell also needs a non-invasive and non-destructive 3D technique. Moreover, the sulfur evolution characteristics such as the 3D distribution and the size change of the sulfur during charge and discharge, which are key factors for understanding the role of new structure in controlling the shuttle effect, are hard to acquire from 2D techniques and rare to be found in the literatures.

X-ray tomography (XRT), as a non-destructive 3D technique, provides not only the spatial information of the microstructure, but also process evolvement with time resolution. Recently, the application of ultra-high resolution lab-based XRT system facilitates the researchers to reveal the details of materials in 3D and 4D. Now, we try to use in-situ and ex-situ lab-based XRT to solve the observation problem of sulfur migration in the Li-S batteries.

In this work, the morphology, size and distribution of the sulfur in several Li-S batteries with different delicate microstructure design of the electrode were measured and analysed via 3D XRT technique. To improve the sulfur loading and sulfur content, the advantages of different microstructures were discussed. Combined with electrochemical tests and the 3D XRT technique, in-situ and ex-situ experiment was designed to investigate the correlation between sulfur diffusion and specified microstructure. Multi-scale 3D XRT techniques with the pixel size from 65 nm to 20 μm were also explored to discuss the sulfur characteristics in 3D with different perspectives.

2. EXPERIMENTAL METHOD

XRT with pixel size between 0.3 μm and 20 μm was performed using a Zeiss Versa XRM-500 desktop

*e-mail: wangshaogang@imr.ac.cn

system. The sample was placed on a rotating stage between the X-ray source and a 2048 × 2048 pixel array CCD detector equipped with a lens with a magnification of 40×. The exposure time was approximately 15-25 s for each of 2000 projections while the sample was rotated 360° along its vertical axis. The projection data were reconstructed by a filtered back-projection algorithm, and then processed and visualized using Avizo Fire 7.1. XRT with pixel size of 64 nm was achieved on an Xradia 800 Ultra system to act as a complement of the sub-micro system.

3. RESULTS

Different strategies were successfully adopted to fabricate high performance Li-S batteries **[1-5]**. These new Li-S batteries own unique electrode microstructure such as a current collector that composed of a 3D hybrid graphene hierarchical network macrostructure **[2]** and a sulfur electrode that consists of a graphene–pure-sulfur sandwich structure **[3]**.

In-situ and ex-situ 3D XRT technique were very effective in revealing 3D and 4D characteristics of sulfur in the electrode. The reconstructed slice could be used to not only measure the thickness of both the graphene layer and the separator but also check the adherence of the adjacent layers. 3D volume renderings of the electrode clearly showed the morphology, size and distribution of the sulfur. Some typical features of sulfur were also found. For example, 3D XRT image of the electrode before and after cycling (Fig.1) shows sulfur particle refinement and redistribution in the active material layer and graphene membrane **[4]**. A number of evidences acquired during the charge and discharge process clearly gave the fact that the ingenious design of electrode can effectively accommodate the large volumetric expansion of sulfur during lithiation, mitigate the shuttle effect of dissolved polysulfides and improving the cycling stability.

Multi-scale 3D XRT technique was quite necessary to draw a complete map of the electrode. New techniques are still needed to be developed to capture the real-time 3D electrochemical characteristics of the same electrode.

Our results would lay insight on the design and development of high specific capacity, high specific energy density and long life Li-S batteries and the final cell diagnostics.

References

[1] R.P. Fang, S.Y. Zhao, P.X. Hou, M. Cheng, S.G. Wang, H.M. Cheng, C. Liu, F. Li, Advanced Materials, 28 (2016) 3374-3382.

[2] G. Hu, C. Xu, Z. Sun, S. Wang, H.M. Cheng, F. Li, W. Ren, Advanced Materials, 28 (2016) 1603-1609.

[3] G. Zhou, S. Pei, L. Li, D.W. Wang, S. Wang, K. Huang, L.C. Yin, F. Li, H.M. Cheng, Advanced Materials, 26 (2014) 625-631.

[4] G. Zhou, L. Li, D.W. Wang, X. Shan, S. Pei, F. Li, H.M. Cheng, Advanced Materials, 27 (2015) 641-647.

[5] G. Zhou, L. Li, C. Ma, S. Wang, Y. Shi, N. Koratkar, W. Ren, F. Li, H.M. Cheng, Nano Energy, 11 (2015) 356-365

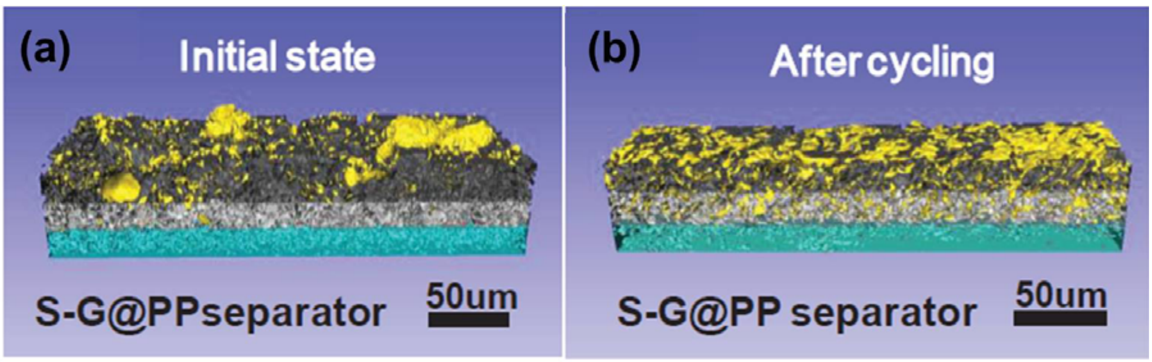

Figure 1: X ray tomography images of a S-G@PP separator electrode a) before cycling, and (b) after 100 cycles **[4]**