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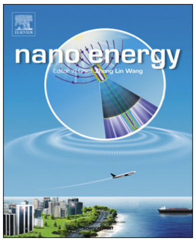

RAPID COMMUNICATION

In-operando optical imaging of temporal and spatial distribution of polysulfides in lithium-sulfur batteries

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Abstract
Understanding the behavior of soluble intermediate lithium polysulfide species is vitally important for improving the electrochemical performances of lithium-sulfur batteries. Herein we explore a simple *in-operando* lithium-sulfur cell design to enable direct visualization of the formation of the soluble polysulfide species and their temporal and spatial distribution over the entire discharge/charge cycle under an optical microscope. Our results reveal detailed evidence of electrochemical degradation in lithium-sulfur batteries and help us to understand the improvements in electrochemical performances using advanced lithium-sulfur cell designs. As examples, we show that a cathode consisting of hollow sulfur nanoparticles with a conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) coating exhibits significantly reduced dissolution of polysulfides into the electrolyte, and thus superior electrochemical performance could be achieved. Moreover, the trapping of soluble polysulfide species in the cathode side was also confirmed in our designed *in-operando* lithium-sulfur cell with a Nafion modified separator.

Introduction

Lithium-sulfur is an attractive battery chemistry to meet the increased demand from portable electronics, electrical transportation and large-scale stationary energy storage

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due to its high specific density (2600 Wh/kg), high natural abundance of sulfur, and low cost potential [1]. However, several issues still remain to make it a viable technology. A critical problem is the quick capacity decay upon cycling due to the dissolution of the intermediates (lithium polysulfides, Li_2S_x, $4 \leq x \leq 8$) into the electrolyte and the "shuttle effect" of these soluble species [2-5]. To overcome these problems, extensive research has been conducted with a focus on engineering the electrode structure and composition [2]. To date, several important strategies, including nanoporous carbon-sulfur composites [6-9], graphene (oxide)-sulfur composites [10-12], conductive polymer-sulfur composites [13,14], as well as oxide coating/composites [15], have been explored to encapsulate polysulfides to suppress their dissolution during cycling. In our group, we also demonstrated rational internal hollow space design such as hollow carbon encapsulated sulfur [16,17], sulfur-TiO_2 yolk-shell nanoparticles [18] and polymer-encapsulated hollow sulfur particles [19,20]. Despite these exciting progress, there still exists appreciable polysulfide dissolution (10-20%) in the electrolyte as measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) [18-20].

Recently there have also been several reports taking the direction of increasing the utilization of soluble polysulfide species, including spatial control deposition of polysulfides on patterned electrodes [21], insertion of a microporous carbon paper between the cathode and separator [22], modification of separators (e.g., separators coated with a Nafion film [23] and a graphene membrane [24]). Moreover, a breakthrough has been achieved in the electrolytes for lithium-sulfur batteries. It is found that the dissolution of lithium polysulphide can be inhibited by using a "solvent-in-salt" electrolyte with ultrahigh salt concentration and high lithium-ion transference number [25]. These works demonstrate improved cycling performance and represent exciting progress as well.

For all the above studies, it is vitally important to understand the behavior of polysulfide species in lithium-sulfur batteries. To this end, a great deal of work has been done to examine sulfur cathodes and polysulfides using *ex-situ* techniques, including Raman, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectra (XPS) and X-ray diffraction (XRD) [26-28]. Very recently, *in-operando* Raman [29] and *in-operando* X-ray diffraction and imaging [30] investigations have been carried out, providing valuable information. Despite all the above achievements, a direct visualization and full understanding of the spatial and temporal distribution of polysulfides in lithium-sulfur batteries is still lacking.

Here we demonstrate a simple *in-operando* lithium-sulfur cell design, which allows us to directly visualize the spatial and temporal distribution of lithium polysulfide species over the entire charge/discharge cycle under an optical microscope. Because of this capability, this *in-operando* technique affords an excellent diagnostic tool to determine quickly the effect of polysulfide encapsulation in sulfur cathodes and trapping with modified separators. As examples, the effect of encapsulation of hollow sulfur nanoparticles with a conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was confirmed by our technique. The localization of polysulfides was also directly shown with a Nafion-modified separator.

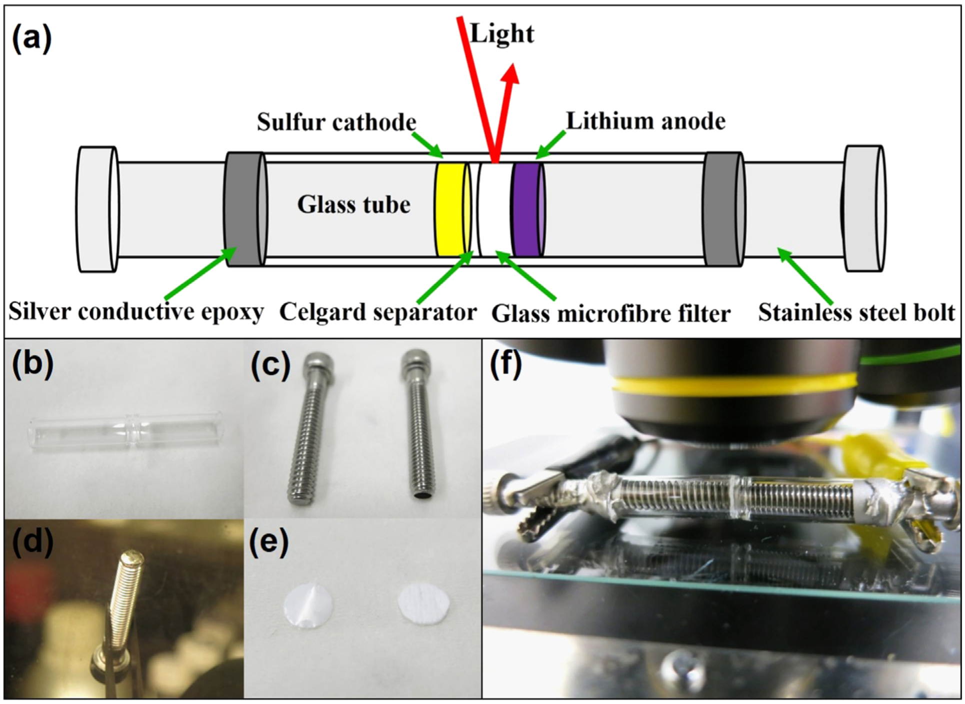

Fig. 1 An *in-operando* lithium-sulfur cell design and its assembly: (a) schematic of an *in-operando* lihium-sulfur cell, (b) a glass tube used for housing the *in-operando* cell, (c) a stainless bolt before (left) and after (right) loading of a sulfur cathode, (d) a lithium metal counter electrode attached on a stainless bolt, (e) a Celgard 2300 separator (left) and a glass microfiber filter (right), (f) an assembled *in-operando* cell working under the optical microscope.