Nanomaterials: Recharging Research in the Lithium Sulfur Battery

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Literature Seminar

November 3, 2016

High energy density batteries are critical for the advancement of electric cars and portable electronics.¹⁻³ Conventional lithium ion batteries are based on intercalation chemistry of Li⁺ ions into host materials. While this technology is the standard for today's portable electronics, lithium ion batteries only have energy densities between 100-250 Wh kg⁻¹ and specific capacities between 100-275 mA h g⁻¹ depending on the cathode material.² Lithium sulfur batteries have a much higher specific theoretical energy and capacity of 2600 Wh kg⁻¹ and 1673 mA h g⁻¹ respectively.² These batteries are promising not only for their high theoretical energy density but also because sulfur is a low cost material and with high abundance in the Earth's crust.¹ Lithium sulfur batteries involve plating and stripping of the lithium metal anode. The electrochemical reaction of the discharge is: S₈+16Li \rightarrow 8Li₂S.³ During discharge, the lithium metal anode (negative electrode) is oxidized to form lithium ions and electrons travel through the external circuit. Both lithium ions and electrons arrive at the sulfur cathode (positive electrode) to reduce sulfur to form lithium sulfide (S₈ +16Li⁺ +16e⁻ \rightarrow 8Li₂S). The opposite reaction occurs during the charge cycle while an external load is applied.³

Lithium sulfur batteries have yet to reach commercialization due to three main challenges. First, sulfur is inherently insulating.^{1–3} As batteries involve the flow of electrons, a conductive additive to the sulfur cathode is required.^{1–3} Secondly, during the lithiation process, sulfur undergoes high volumetric expansion (up to 80%), which can destroy the battery if not accounted for in the battery design. Finally, polysulfide side products in the redox reactions of the charging process cause the polysulfide shuttle effect.⁴ In this shuttling process, higher order polysulfides (Li₂S_n, 2<n< 8) are formed at the sulfur cathode. Due to their solubility in the electrolyte, higher order polysulfides can be transported to the anode, where they are reduced to lower polysulfides. Reduced polysulfides can transport to the cathode and become re-oxidized, allowing return to the anode and repetition of the process. This shuttle hinders the polysulfides from being fully oxidized back to the sulfur active material. The reduction can proceed to form insoluble Li₂S₂ or Li₂S deposits on the lithium anode. Li₂S and Li₂S₂ are electronically and ionically insulating, making deposited films problematic. This internal shuttling pathway is

depicted in Figure 1. The polysulfide shuttle consumes active material in both electrodes, causes selfdischarge, and limits the shelf life of lithium sulfur batteries. The role of nanomaterials to mitigate these three challenges will be the focus of this discussion.



Figure 1. Schematic illustration of the parasitic polysulfide shuttle effect in a lithium sulfur battery. Adapted from Ref. 4.

Research into lithium sulfur batteries can be traced back to the 1960's.⁵ In the past decade, there have been a surge of studies on nanomaterials rationally designed to address the challenges faced by the sulfur cathode.⁶ This discussion will give a brief survey of some of the best performing batteries making use of different nanomaterial morphologies.

In one of the seminal papers for nanomaterial based sulfur cathodes, published in 2009, Nazar and coworkers described the incorporation of CMK-3 mesoporous carbon with a polyethylene glycol (PEG) coating into the cathode.⁷ Carbon is the most common conductive additive for increasing the conductivity of sulfur.² This mesoporous morphology of carbon greatly improves utilization of the sulfur active material and the PEG coating helps hinder the polysulfide shuttle. However, the PEG material is insulating and researchers have since sought conductive coatings to help mitigate the polysulfide shuttle and improve conductivity.

In 2014, Zhen et. al. developed hybrid nanoarchitectures building off the original design from Nazar and coworkers.⁸ Zhen et. al designed sulfur cathodes with highly ordered mesomicroporous core/shell carbon (MMCS). The core consists of mesoporous carbon (pore diameter between 2 and 5 nm) structure loaded with sulfur. The large pore volume allows for good sulfur loading (60.6 wt% sulfur) and utilization of the active sulfur material. The microporous carbon shell (0.5-1 nm pore diameter) loads smaller sulfur molecules (S_{2-4}) and acts as a physical barrier to suppress diffusion of the dissolved polysulfides from the core (Fig 2a). This conductive microporous shell stabilizes cycle capacity of the composite and is the central advancement in design relative to original work from Nazar and coworkers in 2009. After the first two activation and stabilization cycles, the discharge capacity of sulfur loaded MMCs (S/MMCs) battery was 1212 mAh g⁻¹ and 734 mAh g⁻¹ (calculated based on total mass of sulfur and the S/C composite respectively). After 100 cycles the S/MMC battery retains 80% of this capacity at 0.2 C (5 hour discharge rate) as seen in Fig. 2b. The S/MMC battery still retains 80% of its capacity at higher current densities of 0.5 C (2 hour discharge rate).



Figure 2. a) Schematic of the mesoC/S₈microC/S₂₋₄ core/shell structure (MMCS) b) Cycle performance of MMCS at 0.5 C.

The S/MMC battery performed better over more cycles compared to a sulfur loaded microporous carbon battery and a sulfur loaded mesoporous carbon batteries, suggesting the microporous shell is responsible for the S/MMC battery's higher performance and stability. However, compared to the paper from Nazar and coworkers in 2009, the specific capacity is comparable. The main improvement of Zhen et. al. is an increase of length of cycle performance from 35 to 200 cycles. Further cycling measurements would give a more realistic idea of the cycle performance for these materials if they were applied in an industrial setting.

In the next example, Seh et al. designed 'yolk-shell' TiO₂-sulfur nanostructured cathodes.⁹ Instead of the traditional carbon additive, a porous and amorphous TiO₂ shell was grown around the sulfur nanoparticles as a protective layer to prevent polysulfide dissolution. The sulfur in the core was partially dis-solved to create void space, reminiscent of an egg yolk,

and to allow for sulfur expansion. When incorporated into a cathode, the 'yolk-shell' TiO₂-sulfur nanoparticles performed remarkably well over 1,000 cycles with a 67% capacity retention. Next, the sulfur–TiO₂ yolk–shell nanostructure battery was cycled at various discharging current densities to judge their robustness. When the C-rate was changed quickly from 2 to 0.2 C (30 mins to 5 hour discharge rate) the original capacity was recovered, demonstrating the robustness and stability of the cathode material.



Figure 3. a) 'Yolk-shell' TiO₂-sulfur nano-structure synthesis. b) Cycle performance of 'yolk-shell' TiO₂-sulfur nanostructure at 0.5 C.

A small sampling of the highest performing lithium sulfur batteries which have incorporated nanomaterials are given. These materials have been designed in ways to increase conductivity and mitigate damage from sulfur volume expansion during lithiation. However, the main goal of these materials have been to taper the polysulfide shuttle. Currently, there is a large gap in knowledge about the mechanism of this polysulfide shuttle. The field is making gains with implementing operando multimodal studies to understand better these mechanisms. The combination of techniques such as x-ray diffraction¹⁰ and x-ray absorption¹¹, visible¹² and Raman¹³ spectroscopies can aide in providing a more complete picture of lithium sulfur batteries. However operando studies of batteries present their own unique challenges which must be overcome. A fundamental understanding of the complex reactions in these high performing nanostructured sulfur cathodes will allow for more rational design of lithium sulfur batteries.

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