

Full paper

Designing solid-electrolyte interphases for lithium sulfur electrodes using ionic shields



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ABSTRACT

Lithium metal is among the most sought-after anode chemistries for next-generation electrical energy storage due to its high theoretical capacity (3860 mAh g⁻¹) and low reduction potential (− 3.04 V vs S.H.E.). To realize its promise, reactive Li anodes must be paired with high-energy conversion cathodes, such as sulfur or oxygen. Chemical and physical instability at both electrodes pose formidable challenges to development of practical lithium metal batteries. These instabilities are compounded by problems with active material loss and anode passivation when Li is paired with conversion cathodes, such as elemental sulfur. Here, we report on design principles and a process for creating artificial solid electrolyte interphases composed of ionic shields that are able to stabilize electrochemical processes at both the anode and cathode of Li-S electrochemical cells. We show that ASEI composed of negatively-charged nanoparticles on Li stabilize deposition of Li at the anode by multiple fundamental mechanisms. A similar concept is used to design interphases composed of positively charged conductive nanoparticles at the cathode and shown to be effective at intercepting dissolved polysulfide anions and for enhancing sulfur reutilization. We combine the two ASEI design strategies to create Li-S cells based on high-loading sulfur cathodes and demonstrate their long-term cycling stability.

1. Introduction

As consumer demand for portable electrical devices escalate with the rise of the microelectronics industry, expeditious advancement of commercializable electrical energy storage (EES) systems is regarded as a requirement. An EES system that offered substantial improvements in energy and power densities with high electrochemical reversibility is therefore a highly sought after goal. In order to realize this goal, lithium metal batteries (LiMBs) were first proposed in the 1970s, but deployment of these cells was impeded by their poor Coulombic efficiency and cyclability, as well as by the tendency of lithium to form rough deposits upon battery recharge that led to the proliferation of dendrites and other morphological instabilities (e.g. orphaned Li) that reduce battery lifetime and trigger safety issues. Lithium ion batteries (LiBs) with ion intercalation based electrodes overcome many of these problems and were first commercialized in 1991. Notwithstanding the commercial success of LiBs, new types of rechargeable batteries based on metallic anodes, such as Li-metal [1–4]/sulfur [5–9]/air [10–12], Na-

metal [13–15]/sulfur [16,17]/air [18,19], and Al-metal [20,21]/sulfur [22,23]/air [24–26], continue to garner significant attention by researchers because they offer high energy density and prospective economic benefits [27,28].

Among these cell chemistries, Lithium-sulfur batteries (Li-SBs) are arguably the most promising candidates to supplant conventional LiBs as the rechargeable battery platform of choice, both because of the high theoretical specific capacities of the Li anode (3860 mAh g⁻¹) and sulfur cathode (1675 mAh g⁻¹) and the low cost and high earth abundance of the active cathode materials [29]. Such cells are however not commercially viable today because parasitic physical and electrochemical processes at both electrodes deplete the active species and limit lifetime [28]. An extensive body of work is now available that describes the physico-chemical processes responsible for these modes of cell failure. Three specific problems have been diagnosed that provide the foundation for the current study: i) lithium polysulfide (LiPS) dissolution and shuttling; [30,31] ii) electrode passivation by reaction with and redeposition of dissolved active species, [3,32–41] and iii)

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proliferation breakage and short-circuits induced by lithium dendrites [3,4,33,35,38–40,42–45]. LiNO_3 and LiPS have emerged as powerful electrolyte additives in ether-based solvents for stabilizing lithium anodes [39]. Unfortunately, continuous dissolution of LiPS and consumption of LiNO_3 during repeated cell cycles dissipate the beneficial effects of these additives when cells are subjected to practical performance cycles, including repeated deep discharges and high active material loadings in the cathode to produce the $> 350 \text{ W h kg}^{-1}$ cell-level specific energy promised by Li-SBs [46]. As lithium metal anode improvement is essential for practical application of Li-SBs, [47] several anode protection techniques are reported accordingly. Kozen et al. proposed an atomic layer deposition method to protect Li with $\sim 14 \text{ nm}$ thick Al_2O_3 thin film from side reactions with electrolyte and active materials; however, relatively high interfacial impedance and limited lithium migration reversibility are reported [38]. Ma et al. proposed *in-situ* formation of ionically conducting Li_3N protective layer on lithium anode that helps Li^+ migration for Li-SBs [48]. Although formation of the ion selective protection layer is noteworthy, small cracks formed on the protective layer under volume changes of the anode can quickly proliferate lithium dendrites which destabilizes lithium migration and side reactions as the protective layer is thin (200–300 nm) and non-porous. Furthermore, hybrid anode structure is developed to protect lithium metal anode and alleviate undesired side reactions for Li-S system [49]. Providing lithium host such as graphite on top of lithium metal is beneficial for controlling side reactions and lithium preservation, but the dual configuration anode reduces the energy density for practical Li-SBs. Therefore, advanced lithium protection layer should have high conductivity with ion selectivity, high physico-chemical stability, and semi-hosting features for lithium, which we aim to develop in this study.

Herein, we consider the role of artificial solid electrolyte interphase (ASEI) layers composed of ionic shields deployed on both anode and cathode facing a separator (Fig. 1) in remedying the problems of Li-SBs. We focus in particular on cell designs that do not utilize LiNO_3 electrolyte additives to determine the design rules for ionic shields that are able to address current limitations of Li-SBs. To fabricate the ASEI used in the study, lithium terminated sulfonated titania (LTST) nanoparticles are synthesized *via* one-pot solution method as an ingredient for the Li

protection film. Then, the film is created on a solid substrate *via* Langmuir-Blodgett scooping (LBS) method [8,9] to be directly transferred to Li using a roll-press machine to fabricate LTST coated Li (LTST-Li). These processes are briefly summarized in Fig. 1a. Functionalized metal-oxide nanoparticles on Li are thought to serve two functions: i) to maintain high conductivity at the anode/electrolyte interface when the cell is polarized and ii) to electrostatically shield the Li anode and to prevent interfacial accumulation of soluble anionic polysulfide components at the anode [50]. To ensure good ionic conductivity and preservation of the protection layer over repeated volumetric changes of the Li anode, the nanoporous hybrid electrolyte composed of LTST nanoparticles is directly deposited by *ex-situ* method on Li to form a robust conformal coating. On the Li electrode, the functionalized metal-oxide nanoparticles spontaneously form a porous framework that stabilizes the anode by a combination of mechanical [3] and dimensional effects [4]. The ASEI on the cathode side was created using Air-brush technique with ethanol as suspending medium to deposit, on the cathode facing side of the separator, a thin coating of hybrid nanostructures composed of polyethylenimine attached reduced graphene oxide (PEIrGO). The coating is designed to simultaneously enable localization of solvated polysulfide (PS) anions (*via* electrostatic attraction of PS^- to the multi-amine groups in PEI) and to enable re-utilization of the captured material (*via* facilitated electron transport in rGO). The PEIrGO synthesis and procedure used for creating the PEIrGO ASEI on the separator are summarized in Fig. 1b. The overall, cell design illustrating both ASEIs is summarized in Fig. 1c. We show later that the combination of high sulfur utilization and protection of the Li anode lead to cells with prolonged electrochemical and cycling stability.

2. Material and methods

2.1. Materials synthesis

2.1.1. Lithium terminated sulfonated TiO_2 (LTST) nanoparticle

3 g of TiO_2 nanoparticles (~ 30 to 50 nm , 99% purity, Rutile, Inframat Advanced Materials™) are mixed with 125 ml deionized (DI) water and sonicated for 30 min at room temperature. 3 ml of 3-(tri-hydroxysilyl)-1-propanesulfonic acid (30–35% in water, Gelest) is added

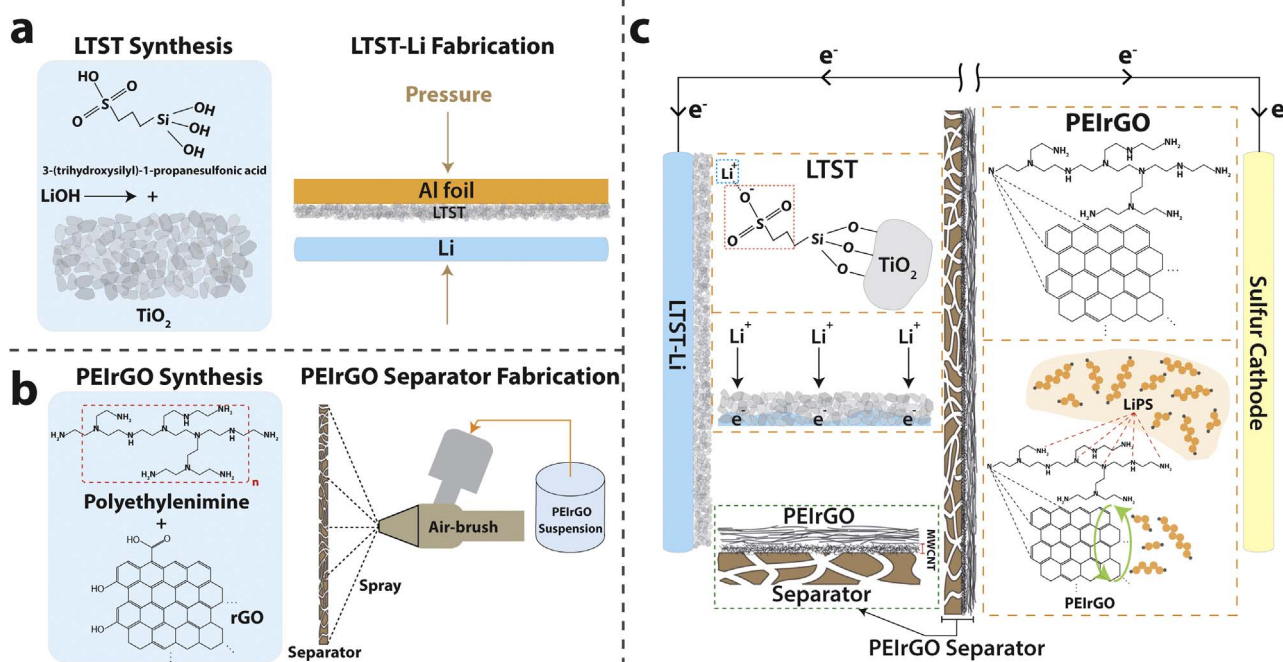


Fig. 1. Schematic illustration showing ASEI designs for Li-SB electrodes, and their respective fabrication processes. a) LTST synthesis (left) and LTST-Li fabrication process (right). b) PEIrGO synthesis (left) and PEIrGO separator fabrication (right) processes. c) Illustration of synergistic effects of LTST and PEIrGO ASEIs for Li-SBs.

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