



# Garnet structured solid fast Li<sup>+</sup> conductor as polysulfide shuttle inhibitor in Li-S battery

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## ARTICLE INFO

### Keywords:

Lithium garnet  
Lithium-sulfur battery  
Polysulfide shuttle inhibitor  
Interfacial engineering

## ABSTRACT

Herein, we demonstrate strategies to control polysulfide shuttling phenomenon in Li-S batteries using lithium garnet solid electrolyte Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub> (LLZTO). Thin-walled LLZTO membrane and polypropylene (PP) separator decorated with LLZTO (PP-D (LLZTO)) and infiltrated with small amount of liquid electrolyte (LE) have been used to control the polysulfide diffusion in Li-S batteries. The fabricated Li||PP-LE-LLZTO-LE||S coin cell delivered an initial discharge capacity of 1100 mA h g<sup>-1</sup> at a current density of 0.03 mA cm<sup>-2</sup> (~16.55 mA g<sub>sulfur</sub><sup>-1</sup>) and discharge capacity of 706 mA h g<sup>-1</sup> with nearly 100% coulombic efficiency at the 30th charging/discharging cycle. The Li||LE-PP-D(LLZTO)||S coin cell delivered an initial discharge capacity of 855 mA h g<sup>-1</sup> at a current density of 0.39 mA cm<sup>-2</sup> (~167.3 mA g<sub>sulfur</sub><sup>-1</sup>) and a discharge capacity retention of nearly 560 mA h g<sup>-1</sup> after 40th charging/discharging cycle.

## 1. Introduction

Electrical energy storage is considered as one of the most crucial needs of modern society. Among various electrochemical energy storage devices secondary Li<sup>+</sup> batteries have proven to be successful in the portable electronics market. However the practical achievable capacity of nearly 250 mA h g<sup>-1</sup> [1] is too low and could not meet the energy requirement of EVs to travel to large distances between the charges. Higher gravimetric energy density, higher capacity, environmental benignity and cost effectiveness make the Li-S battery a strong contender to meet rising energy demand of modern society. Elemental sulfur is chemically active material that can accept two electrons per atom at a potential of nearly 2.1 V vs Li/Li<sup>+</sup> [2]. The theoretical specific capacity of elemental sulfur is of the order of magnitude 1672 mA h g<sup>-1</sup> [3] which is much higher than conventional insertion type Li<sup>+</sup> batteries. However there are several critical challenges in commercializing the Li-S battery. The major challenges include the non-conducting nature of elemental sulfur and polysulfide shuttling which are considered as fundamental reasons for the Li-S failure [4–10]. Attempts have been made to design the structurally and morphologically robust conducting host composites to trap the sulfur nanoparticles for enhanced cell efficiency and shelf-life in Li-S batteries [11–19]. In order to prevent the shuttling phenomenon bi-functional interlayers have been introduced as polysulfide-diffusion inhibitors in Li-S batteries [20–24]. The separators modified using different fillers such as metal oxides [25] or polymeric additives [26] can effectively localize the

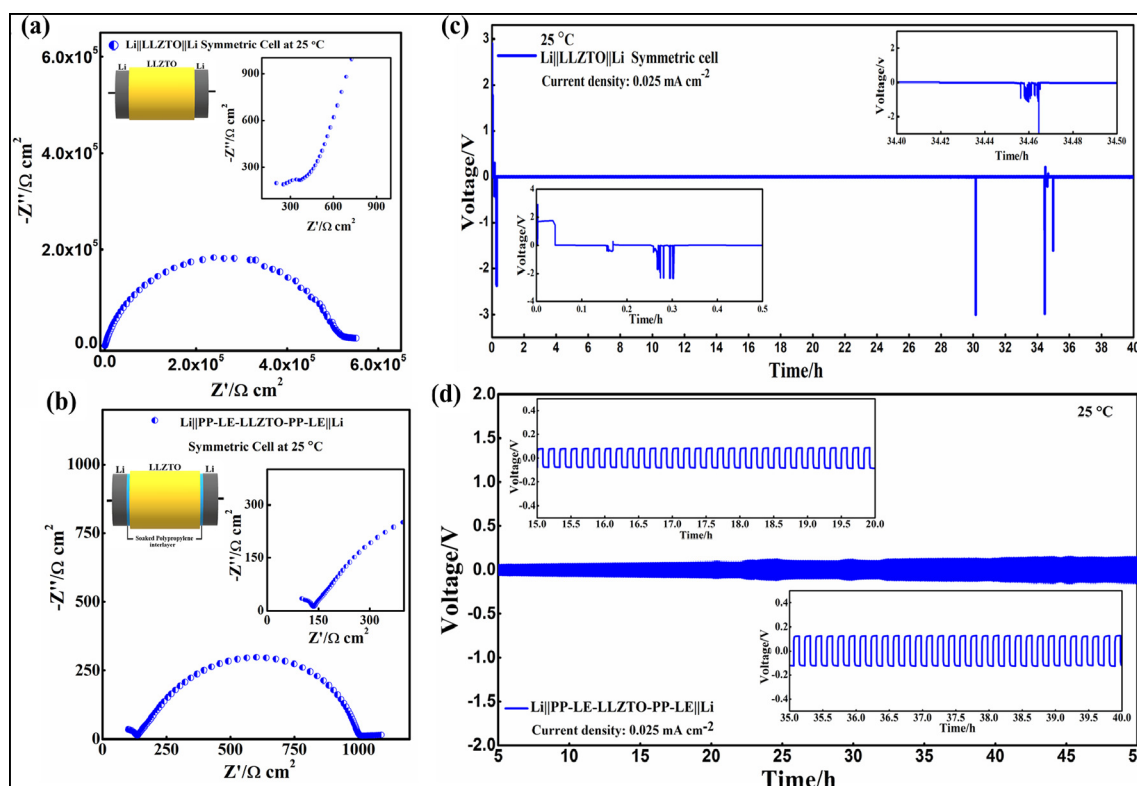
polysulfides within the cathode side of cell, resulting in improved active material utilization and long cycle life of the battery [7]. The other strategies include the integration of high Li<sup>+</sup> conductive solid electrolytes with sulfur cathode to completely inhibit the polysulfide shuttling. Although various solid electrolytes such as LISICON [27], LiN<sub>3</sub> as protective layer for Li anode [28], amorphous glass electrolytes [29, 30] and other ceramic electrolytes [31] have been reported in recent times, the lower Li<sup>+</sup> conductivity and formation of unstable electrolyte/electrode interface limits the application of these solid-state electrolytes in Li-S batteries.

A series of garnet type solid electrolytes are gaining interest in recent times due to their striking properties. Among them garnet-structured solid electrolyte with nominal composition of Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) invented by Murugan et al. [32] has been proved to be the potential candidate for its reasonable Li<sup>+</sup> conductivity [33] and intrinsic chemical stability when in contact with metallic lithium [34]. Despite these advantages garnet structured solid electrolyte suffers from a serious limitation of making poor interface contact with metallic lithium. Introducing thin interlayer of Au [35], Al [36] and oxide like Al<sub>2</sub>O<sub>3</sub> [37] over LLZO have been demonstrated in recent times to reduce the interface resistance and to improve the contact area between lithium metal anode and LLZO solid electrolyte.

Herein we propose a soft polypropylene interlayer infiltrated with 10 μL of liquid electrolyte (PP-LE) to reduce the interfacial resistance and to achieve smooth stripping and plating of lithium across the metallic Li and LLZTO interface. Thin-walled LLZTO and PP separator

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**Fig. 1.** Electrochemical impedance spectra of symmetric cells: (a) Li||LLZTO||Li and (b) Li||PP-LE-LLZTO-PP-LE||Li. Insets show the schematics of symmetric cells Li||LLZTO||Li and Li||PP-LE-LLZTO-PP-LE||Li and impedance data of respective symmetric cells in high frequency regions, respectively. (c) Voltage profile of Li||LLZTO||Li symmetric coin cell showing non-homogeneous stripping and plating of lithium. The insets represent the enlarged voltage profiles for specific cycles. (d) Voltage profile of Li||PP-LE-LLZTO-PP-LE||Li symmetric cell establishing stable stripping and plating of lithium. The insets represent the enlarged voltage profiles for specific cycles.

decorated with LLZTO (PP-D (LLZTO)) particles have been used to control the diffusion of polysulfide species across the membrane and to enhance the cycle performance with improved capacity retention in Li-S battery.

## 2. Experimental details

### 2.1. Synthesis of LLZTO

Ta doped LLZO powder was synthesised according to the procedure described elsewhere [38]. The powder was pressed into pellets of 15 mm diameter and sintered at 1200 °C for 12 h in air atmosphere using alumina crucible. The sintered pellets were polished using 1200 grit sandpaper to remove any insulating layer formed during sample transfer which otherwise would impede the Li<sup>+</sup> transport. The total (grain and grain boundary) Li<sup>+</sup> conductivity of LLZTO was found to be  $2.8 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C.

### 2.2. Preparation of PP-D(LLZTO)

To prepare the LLZTO decorated PP interlayer (PP-D(LLZTO)), dense and high Li<sup>+</sup> conductive LLZTO pellet was crushed into fine powder in agate mortar and then sieved to get particles with uniform size. The grounded LLZTO powder was mixed with poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) in a weight ratio of 90:10 to make uniform slurry. The slurry was cast onto the PP surface using doctor blade. The thickness of LLZTO layer was around 20 μm. After drying in vacuum at 50 °C for 24 h the modified PP was transferred to argon filled glove box for coin cell assembling.

### 2.3. Preparation of composite sulfur cathode

The composition of elemental sulfur and activated charcoal in a weight ratio of 1:1 was ball milled for 3 h and transferred into glass tube. The glass tube was sealed in argon filled glove box and later heat treated at 155 °C for 12 h in vacuum to melt the sulfur and allow it to diffuse into porous activated charcoal. After cooling down to room temperature the sulfur-carbon composite (active material) was collected. Composite sulfur cathode was prepared by mixing the composition consisting of active material, acetylene black and poly(vinylidene fluoride) (PVDF) in *N*-methyl-2-pyrrolidone (NMP) in a weight ratio of 8:1:1 was mixed to make slurry. The slurry was coated onto the aluminium foil using doctor blade and then vacuum dried.

## 3. Results and discussion

Symmetric cells (2032 coin cell) in the stacking configurations; Li||LLZTO||Li and Li||PP-LE-LLZTO-PP-LE||Li were assembled inside the argon filled glove box. The diameters of the metallic lithium foil and PP-LE interlayer were chosen slightly smaller than ceramic LLZTO to prevent any possible crossover of liquid electrolyte around LLZTO. Electrochemical impedance spectroscopy (EIS) measurements were carried out with AC frequencies ranging between 0.1 Hz and 7 MHz and with 10 mV excitation amplitude using Bio-Logic battery tester. All the electrochemical characterizations were performed under room temperature condition (25 °C). Fig. 1a and b show the Nyquist impedance plots of the fabricated LLZTO/Li symmetric cells. The large semicircle at lower frequency corresponds to interfacial resistance. The interfacial resistance of symmetric cells was calculated by dividing the low frequency semicircle diameter by a factor of two, as the total interfacial resistance corresponds to two symmetric interfaces. The Li||LLZTO||Li

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