



Present understanding of the stability of Li-stuffed garnets with moisture, carbon dioxide, and metallic lithium



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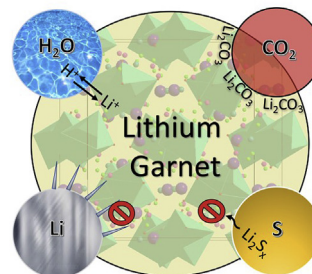
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HIGHLIGHTS

- Lithium garnets undergo reversible spontaneous Li^+/H^+ exchange.
- After protonation, carbonaceous species form on garnet surface.
- Lithium garnets show a wide electrochemical stability window up to 9 V vs. Li.
- Area specific resistance for Li ion transfer range from $> 2000 \Omega \text{ cm}^2$ to $1 \Omega \text{ cm}^2$.

GRAPHICAL ABSTRACT

Current knowledge of chemical, electrochemical and structural stability of lithium stuffed garnets in humid and carbon dioxide rich environments as well as in contact with metallic lithium.



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ABSTRACT

Fast lithium-ion conducting garnet-type metal oxides are promising membranes for next-generation all-solid-state Li batteries and beyond Li-ion batteries, including Li-air and Li-S batteries, due to their high total Li-ion conductivity and excellent chemical stability against reaction with elemental Li. Several studies have been reported on structure-chemical composition-ionic conductivity property in Li-stuffed garnet-type metal oxides. Here, an overview of the chemical and electrochemical stability of lithium-based garnets against moisture/humidity, aqueous solutions, carbon dioxide, sulfur, and metallic lithium are analyzed. Moisture and aqueous stability studies focus on understanding the crystal structure stability, the proton exchange capacity as a function of Li content in Li-stuffed garnets, and how the protonated species affect the crystal structure and mass transport properties. H^+/Li^+ exchange was found to be in the range of 2–100%. Stability concerning Li-ion conductivity and morphology under carbon dioxide are discussed. Interfacial chemical stability with lithium metal characterized by electrochemical stability window, Li dendrite formation and area specific resistance (ASR) for the reaction $\text{Li} \rightleftharpoons \text{Li}^+ + e^-$ are presented. Recent attempts to suppress dendrite formation and to reduce ASR via surface modification are also highlighted. Li and Li-stuffed garnet interface ASR values are shown to be as high as $> 2000 \Omega \text{ cm}^2$ and as low as $1 \Omega \text{ cm}^2$ at room temperature for surface modified Li-stuffed samples. Furthermore, recent studies on Li-S battery utilizing chemically stable Li – garnet electrolyte are also discussed.

1. Introduction

Worldwide, utilization of fossil fuels is continually increasing which leads to rising greenhouse gas emissions. Thus, attempts have been

made to shift towards renewable sources such as wind and solar. However, due to the intermittency of these renewable resources, the energy must be captured while the sun is shining and the wind is blowing so we can utilize it during the downtime. Most efforts are

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focused on secondary batteries and electrochemical electrolysis cells. Li-ion batteries (LIBs) have found application ranging from pacemakers (10 mWh) to grid storage (> 100 MWh). However, the state-of-the-art battery chemistry is still limited due to its safety and moderate volumetric and gravimetric energy densities. Commercially available Li-ion cells make use of organic solvents and Li-salts-based electrolytes that are susceptible to combustion [1–3] and possess energy densities in the range of 100–190 Wh kg⁻¹ and 265 Wh l⁻¹ [4]. Recently, the United States' Department of Energy set targets to increase the specific and volumetric energy density of LIBs to 250 Wh kg⁻¹ and 400 Wh l⁻¹ respectively, by 2022 for electric vehicles [5]. To meet these metrics, we need alternative battery chemistry with improved overall safety and performance. Solid-state (ceramic) electrolytes have been proposed as a replacement for flammable organic electrolytes due to their non-flammable nature and their superior mechanical strength that prevents the penetration of Li dendrites [6–8]. The use of solid-state electrolytes also offers further development of alternative battery chemistries [9] such as lithium-air (Li – O₂) and lithium-sulfur (Li – S) and the possibility of high voltage Li cathodes and lithium metal anode, resulting in higher specific energy density LIBs [8,10].

Both Li – O₂ and Li – S have been of high interest due to their high theoretical energy density (3505 Wh kg⁻¹/2234–3436 Wh l⁻¹ for Li – O₂ and 2567 Wh kg⁻¹/2199 Wh l⁻¹ for Li – S) over conventional Li-ion batteries [11]. It is worth noting that lithium-air chemistry refers to the reaction between lithium and oxygen, rather than all contents in ambient air. Other battery chemistries have been proposed which take into account other species in air such as metal – CO₂ battery [12,13]. Li – O₂ batteries typically fall into one of four proposed architectures: (i) aprotic – use an organic based ion electrolyte with a Li anode; (ii) aqueous – use water and dissolved salt electrolyte, while a Li anode is coated with a protective layer; (iii) all-solid-state – a lithium ion conducting solid electrolyte with a Li anode; and (vi) mixed aprotic/aqueous – elemental Li anode is submerged in an organic electrolyte, which is separated from the air cathode by a lithium ion conducting electrolyte. Li – O₂ batteries make use of high capacity Li as the anode, and the cathode is typically a porous carbon-based support with a catalytically active material for the ORR (oxygen reduction reaction) and OER (oxygen evolution reaction). The conventional Li – S battery [14] consists of a sulfur-carbon composite cathode, an organic liquid electrolyte, and a lithium metal anode.

Due to the higher capacity of elemental Li, it is of great interest to use over conventional carbon based anodes. However, utilization of elemental Li anode in Li – O₂ and Li – S batteries remain a major challenge due to undesired side reactions at the Li anode and electrolyte interface that may be addressed by the integration of solid-state (ceramic) electrolytes. Due to the chemical reaction of metallic Li with aqueous media, a Li-ion conducting but electronically insulating ceramic membrane, which is stable to both metallic Li and the aqueous environment must protect Li in aqueous batteries. In Li – S battery, Li dendrite penetration through a conventional separator presents a significant safety hazard due to internal electronic short circuit. In this case, the use of solid-state electrolyte that is impermeable to polysulfides can effectively suppress the formation of dendrites [14].

Steven Visco and colleagues suggested using Li⁺-conducting Li_{1.3}Al_{0.3}Ti_{1.7}P₃O₁₂ (LATP) as a protective Li layer in Li-O₂ battery [15]. However, LATP is unstable in direct contact with metallic Li due to the reduction of Ti⁴⁺ to Ti³⁺ leading to electronic conductivity [16]. This instability requires an additional protective layer between Li and LATP, increasing the complexity and resistance of the overall cell. For Li – S battery, Hassoun and Scrosati [17] employed a poly(ethylene oxide)-type polymer electrolyte containing finely dispersed nanosized zirconia, while Hayashi et al. [18] used Li₂S-P₂S₅ glass ceramic electrolyte in solid-state Li – S cell configuration. Although no dendrites were formed in their cells, the low ionic conductivities in the solid-state electrolytes limit their cell performance. Therefore, alternative materials that can show high ionic conductivity (~10⁻³ S cm⁻¹) with high

aqueous, sulfur/polysulfides, metallic Li stability are being investigated for application in both Li – O₂ and Li – S batteries. A group of materials that are being studied currently due to their combination of high ionic conductivity and Li metal stability are garnet-type structure materials such as Li₅La₃Ta₂O₁₂ and Li₇La₃Zr₂O₁₂ (LLZO) [19]. Several review articles have already discussed the crystal structure, chemical compositions, Li-ion transport, and processing techniques and synthesis of lithium-rich garnet-type metal oxides [19–21]. Kerman et al. [22] discussed some challenges relating to full cell integration of LLZO in all-solid-state batteries. Duan et al. provided an overview of the stability of LLZO in ambient air, Li metal, and Li-based cathode materials [23]. In this review article, we discuss the chemical and structural stability of wide range of Li-stuffed garnet-type metal oxides, including LLZO, in aqueous/moisture environment, CO₂ and in contact with metallic lithium as well as application of Li-based garnets in Li-S batteries.

2. Stability of Li-stuffed garnets in aqueous/moisture environment

With the intention of applying lithium-based garnet-type metal oxides in next generations batteries such as aqueous Li – O₂ cell, deep understanding of the chemical and electrochemical stability of lithium garnets in aqueous media is a necessity [24]. Initially, lithium-stuffed garnets were believed to be chemically stable and unreactive with humid and aqueous conditions [25]. However, preliminary studies done by Nyman et al. where sintered powders of Li₅La₃M₂O₁₂ (M = Nb or Ta) were stirred in water, noted that an instant increase in pH to 11 [26]. This increase in pH was attributed to the exchange of H⁺ for Li⁺ in the garnet lattice [26–28], i.e.,



Table 1 shows proton-exchange property of various Li-stuffed garnet-type metal oxides [24,26,27,29–42]. Although the increase of pH is observed to occur within the first few seconds [27], the exchange has also been shown to continue at a reduced rate for up to four days [33]. The rate and extent of proton-exchange depend on particle size, samples with high surface area will exchange more quickly and to a greater extent in the same time frame as large particles.

2.1. Structural stability of Li-based garnets in aqueous media

Many lithium garnet compositions have been studied for their structural stability in aqueous solutions [24,29–32,42]. Typically, after treating Li-rich garnets with aqueous solutions, the powder X-ray diffraction patterns have shown no change with respect to un-treated samples, as shown for Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO₁₂ in Fig. 1A [29,30]. It has been noted that although the crystal structure is retained after most aqueous treatments, a subtle increase [31,32] or decrease [24,42] in the cell constant have been observed. An increase has often been associated to the replacement of strong Li – O bonds with weaker O – H···O bonds [31,32], where a decrease is attributed to the smaller ionic radii of protons over lithium ions.

In general, lithium-based garnets typically fall into the space group of *Ia-3d* for cubic symmetry and *I4₁/acd* for tetragonal symmetry [19,43], however, after protonation, a change in space group has been observed. Galven et al. noted from neutron diffraction that when tetragonal (*I4₁/acd*) Li₇La₃Sn₂O₁₂ was subjected to proton exchange, the resulting crystal structure was cubic (*Ia-3d*) phase [32]. Similarly, Larraz et al. [34] have shown that tetragonal Li₇La₃Zr₂O₁₂ (LLZO) phase transforms to cubic phase under moisture. Tetragonal LLZO sample left in ambient condition shows trace amount of proton exchange (Li_{6.86}H_{0.14}La₃Zr₂O₁₂, 2%) [34]. The partially hydrated Li_{6.86}H_{0.14}La₃Zr₂O₁₂ has shown the presence of cubic phase up to 150 °C, where tetragonal LLZO sample left in dry condition does not show cubic structure transition until 650 °C [34], suggesting that protonation of the garnet lowers the temperature in which the cubic phase

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