



## Hybrid electrolytes for lithium metal batteries

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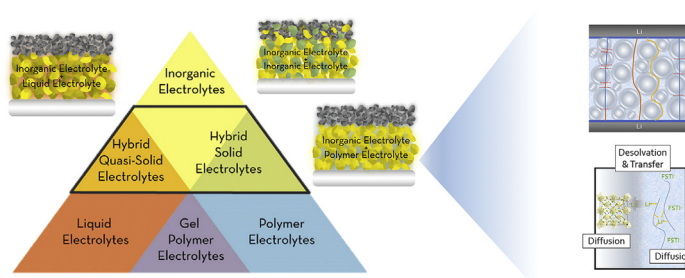
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### HIGHLIGHTS

- Polymer/inorganic hybrid electrolytes for lithium metal batteries.
- Preparation and characterization methods of hybrid electrolytes.
- Ionic conduction mechanism in hybrid electrolytes.
- Impact of hybrid electrolytes Li metal cells energy performance.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

This perspective article discusses the most recent developments in the field of hybrid electrolytes, here referred to electrolytes composed of two, well-defined ion-conducting phases, for high energy density lithium metal batteries. The two phases can be both solid, as e.g., two inorganic conductors or one inorganic and one polymer conductor, or, differently, one liquid and one inorganic conductor. In this latter case, they are referred as quasi-solid hybrid electrolytes. Techniques for the appropriate characterization of hybrid electrolytes are discussed emphasizing the importance of ionic conduction and interfacial properties. On this view, multilayer systems are also discussed in more detail. Investigations on Lewis acid-base interactions, activation energies for lithium-ion transfer between the phases, and the formation of an interphase between the components are reviewed and analyzed. The application of different hybrid electrolytes in lithium metal cells with various cathode compositions is also discussed. Fabrication methods for the feasibility of large-scale applications are briefly analyzed and different cell designs and configurations, which are most suitable for the integration of hybrid electrolytes, are determined. Finally, the specific energy of cells containing different hybrid electrolytes is estimated to predict possible enhancement in energy with respect to the current lithium-ion battery technology.

### 1. Introduction

The early development of lithium metal batteries in the 1970's has strikingly evidenced the incompatibility of the highly reactive lithium metal anode with liquid electrolytes based on flammable organic solvents. Indeed, upon repeated cycling, the formation of lithium dendrites led to internal short circuit of the cells with risk of thermal runaway and, ultimately, explosion. In the 1990s, lithium metal was successfully

replaced by the lithium-ion battery (LIB) technology, whose rocking-chair mechanism avoids the plating of metallic lithium thus effectively eliminating the uncontrolled Li dendrite growth at the negative carbonaceous electrode in normal operation conditions. Since then, graphite is the state-of-the-art anode material, offering reversible intercalation at relatively low potentials ( $< 0.2$  V vs.  $\text{Li}/\text{Li}^+$ ). Although, a substantial reduction of energy density is the price to pay for the improved safety due to the one order of magnitude lower capacity of

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graphite compared to Li metal (theoretically, 372 mAh g<sup>-1</sup> vs. 3860 mAh g<sup>-1</sup>). In spite of this, LIBs offer by far the best performance among all rechargeable battery chemistries operating at room temperature.

Nowadays, however, the increasing demand of powerful consumer electronics, stationary storage and electric vehicles drives the development of evermore high-energy density batteries. Among the next generation battery technologies, safe lithium metal batteries based on a solid-state approach appear to be the most appealing systems. Although inorganic solid electrolytes (ISEs) notoriously suffer from poor ionic conductivity compared to liquids, recent research efforts have yielded to a variety of inorganic conductors with extremely high conductivity at room temperature [1–5]. NASICON-like materials [6–8] (e.g., Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub>), perovskites [9,10] (e.g., La<sub>0.57</sub>Li<sub>0.29</sub>TiO<sub>3</sub>), garnets [11–17] (e.g., Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>) and sulfidic electrolytes [2,18–23] (e.g., Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>) have been intensively explored. NASICON-like materials are stable in atmosphere, show high oxidation voltages and high ionic conductivities but are brittle and unstable with lithium metal [6,24–26]. Perovskites reveal high mechanical strength and high oxidation potential, but high grain boundary resistances [27] and, furthermore, they are unstable in contact with lithium [3,28–30]. Garnets are stable in contact with lithium metal, but react with moisture to form decomposition products depositing at their interface [31–33]. Sulfidic electrolytes reveal the highest ionic conductivities but, at the same time, also the most severe sensitivity towards air and moisture [2,18,20]. Issues such as high resistances at the electrode/electrolyte interface and engineering challenges like the large scale manufacturing of such batteries still hinder their imminent application. Differently, the easily processable solid polymer electrolytes are already applied with success in lithium metal batteries [34], but must operate at elevated temperatures (above 60 °C) due to ionic conductivity limitations. Hence, the necessary continuous heat supply limits their efficiency. Even more detrimental, the most promising polymer, polyethylene oxide (PEO), is electrochemically unstable at high potentials, limiting the operative voltage and thus the energy density of such systems.

The development of hybrid electrolytes comprising inorganic and organic ionic conductors might be the ultimate solution to benefit from each component's virtues. The combination of inorganic conductors with ionic liquids, organic liquids or solid polymer electrolytes (SPEs) may provide many advantages such as, for example, improved charge transfer at the electrode/electrolyte interface [35–37]. Additionally, the flexibility of polymers would ensure easy manufacturing and buffer volume changes occurring during cell operation, while maintaining intimate contacts between the cell components.

## 2. Classification of hybrid electrolytes

The term “hybrid electrolyte” covers a very broad class of composites. These could be divided into two main categories. *Hybrid all-solid-state electrolytes* (HSEs) include combinations of (at least) two, well-defined, lithium-ion conductive solid phases. These can be both inorganic [38], or a combination of inorganic and polymeric phases [39]. Differently, *hybrid quasi-solid electrolytes* (QSEs) integrate an inorganic conductor with an ionic liquid [35,40] or organic liquid [41] phase. An overview of the possible hybrid electrolyte combinations is given in Fig. 1.

It should be mentioned that gel electrolytes, which are constituted by a liquid electrolyte (salt + solvent) embedded in a polymeric matrix could also be considered as “hybrid”. However, in these systems the ion conduction occurs only in the liquid phase, whereas the polymer simply ensures the mechanical stability [42]. As they are already extensively discussed in several previous reviews [42,43], these will not be covered herein. Soaked hybrid membranes comprising an inorganic conductor, an inert polymer and a liquid electrolyte will also be omitted [44–46]. In fact, although these hybrid electrolytes have been applied in lithium-ion batteries, showing superior safety performance compared to

standard separators [45], they do not allow the use of lithium metal as they cannot suppress the reaction between the liquid electrolyte and Li, leading to dendrite formation. Therefore, they are out of the topic of this perspective article.

The aim of this review is to describe the different classes of hybrid electrolytes suitable for lithium metal batteries, and to highlight the characterization techniques most suited to study such hybrid systems. Special focus is put on the ion conduction mechanism, which is still under discussion, and on interfacial properties that severely influence the overall battery performance. Also, the application of hybrid electrolytes in cells with a cathode and a lithium anode is reviewed and discussed. The fabrication methods for large scale application of hybrid electrolytes are discussed, too. Finally, energy density calculations are performed to show that, compared to state-of-the-art LIBs, higher energy densities are achievable by the use of hybrid electrolytes in combination with lithium metal anodes.

## 3. Hybrid electrolytes and their synthesis

### 3.1. Hybrid all-solid-state electrolytes

#### 3.1.1. Inorganic/inorganic

Inorganic/inorganic hybrid electrolytes such as those composed of, e.g., soft sulfide glasses and stiff oxides, can be made to take advantages of their different characteristics, e.g., avoid sintering at high temperature [38,47]. They are prepared by ball milling of compliant nanoporous β-Li<sub>3</sub>PS<sub>4</sub> (β-LPS) and hard oxide garnets [38,47] in spite of their different nature, e.g., the oxides are hard acids and β-LPS is a soft base [47]. Indeed, their chemical stability was experimentally confirmed by X-ray diffraction (XRD) [47]. However, the eventual presence of a sub-micrometric amorphous interphase due to reactions between the different electrolytes cannot be excluded and would need further investigation, e.g., by means of X-ray photoelectron spectroscopy. The combination of hard oxides and compliant β-LPS enables cold pressing of dense pellets even when using only 10 wt% of the softer component (i.e., β-LPS). The highly energetic sintering step to densify pure Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) pellets is therefore avoided since β-LPS can effectively fill the porosity [47]. Interestingly, the ionic conductivity of this hybrid electrolyte can exceed the conductivity of the individual parental materials. Such phenomenon is attributed to the space-charge layer at the β-LPS/LLZO interface, leading to a redistribution of interstitials and vacancies across the interface [38]. The choice of highly conductive parental materials [38], as well as their volume ratio [47], can significantly influence the overall ionic conductivity of the hybrid. The fraction of the oxide should not largely exceed 30 wt% (unfortunately, volume ratios are rarely reported) to avoid the less conductive oxide blocking the motion of lithium ions thus decreasing the overall ionic conductivity of the hybrid electrolyte [47]. In fact, two opposite effects are present: (i) the space-charge effect effectively enhancing the ion mobility and (ii) the blocking effect of the less conductive inorganic electrolyte.

The combination of sulfides and oxides into a hybrid electrolyte appears very promising for enhanced ionic conductivities, improved interfacial stability with lithium [38,47] and ease of processing. However, to the best of our knowledge, only two reports are available on this topic so far. The integration of the high-density oxide (5.1 g cm<sup>-3</sup>) into the low-density sulfide (2.1 g cm<sup>-3</sup>) brings the disadvantage of an increased weight with to the sulfidic electrolyte alone, which impacts the energy density of the whole battery (see section 9, Specific Energy Calculations). Indeed, the solid electrolyte membrane should be as thin as possible to limit the weight of inactive materials in the cell. Additionally, it is still to be proved if a large scale processing of such thin solid membranes is feasible, since so far only pellets were investigated at laboratory scale. A possible approach to tackle this issue is to use a slurry coating process analogous to the manufacturing of sheet-type cells, however, this was reported to be successful with sulfidic

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