

Supplementary Information

What differentiates dielectric oxides and solid electrolytes on the pathway toward more efficient energy storage?

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S1. Introduction

1.1 Silicon dioxide (SiO₂)

Silicon dioxide (known as silica with the chemical formula SiO₂) has been the most commonly used insulator material in the semiconductor device industry for more than three decades [1]. SiO₂ is a white or colorless solid-state material with three main structures: α -quartz, tridymite, and cristobalite [2]. This material is highly abundant (it makes up 90% of the Earth's crust), stable, non-toxic, and non-hygroscopic [3], [4]. Its α -quartz structure, Figure 1a, has a relative dielectric constant of $\epsilon_r \approx 3.9$ [5] and a large band gap of 8.9 eV [6]. In general, silicon dioxide has wide applications in different industries, including computer, energy, and aerospace, but also in pharmacy, agriculture, food, construction, etc. Typically, it is used in semiconductors [7,8], transistors [9], MEMS [10], insulators [11], optical devices [12], micro-electro mechanics [13], micromachining processes [14], capacitors [15], solar cells [16], fuel cells [17], and lithium-ion batteries [18–21].

1.2 Magnesium Oxide (MgO)

Magnesium oxide (MgO), or magnesia, is a white, brown, or black material (depending on the presence of other foreign elements) that has a cubic crystal structure and the space group Fm-3m (sg# 225) [22,23]. It is shown in Figure 1b.

MgO has a wide bandgap of approximately 7.3–7.8 eV, high thermal stability, a thermal conductivity of 36 W.m⁻¹.K⁻¹ at 100 °C, a significant dielectric constant of $\epsilon_r \approx 10$, and excellent hole-blocking features [24–27]. It has a density of approximately 3.579 g.cm⁻³ and a high melting point of about 2800 °C [28,29]. The work function of MgO has been reported to be between 4.22 eV and 5.07 eV depending on its different crystal orientations [30]; however, in our study it was found to be considerably smaller while remaining in general agreement with our experimental

results. MgO as a metal oxide has a broad set of applications, including in gate insulators [31] of transistors [32], magnetic tunnel junctions [22], Josephson effect mesoscopic superconducting devices [33], solar cells [34], surface coatings [35], and even fertilizers [36].

1.3 Lithium Oxide (Li₂O)

Lithium oxide (Li₂O), also known as lithia, is one of the simplest oxides and has a white color. This material has a cubic antiferroite structure and the space group Fm-3m [37] (Figure 1c). Li₂O is an inexpensive, safe, and highly hygroscopic material [38,39]. It has a low vapor pressure at elevated temperatures, a high tritium breeding capability, low tritium solubility, high thermal conductivity, and low electrical conductivity [40,41]. This material presents a band gap of 4.99 eV [37], a density of 1.96 g.cm⁻³ [37], and a high theoretical specific capacity of ~571 mAh.g⁻¹ for the Li₂O/Li₂O₂ conversion reaction [42,43] or 1035 mAh.g⁻¹ when used to pre-lithiate Si anodes [38] in batteries.

Lithium oxide is a semiconductor with wide electrochemical, optical, and nuclear features with many applications in fields ranging from ceramics to glass [44–46]. Li₂O has wide applications, including in heterojunctions [47], optical and lasers [48], solar systems [49], energy storage systems [50], microspheres [51], magnetic instruments [52], the nuclear industry [41], and cooling systems [41]. Li₂O may also be used as a sintering additive in electrolyte membrane fabrication to reduce the densification temperature [53]. Li₂O is employed as a thermal stabilizer for glasses. When adding only 3% of this material, the melting temperature is decreased by several degrees and the surface tension is improved [41]. It is one of the main constituents of the solid electrolyte interphase (SEI) layer, which forms spontaneously in Li⁺-ion batteries [44,54–57], behaving as a solid electrolyte; hence, comparing Li₂O with LAGP and Li⁺-glass constitutes an added interest in the present study.

1.4 Na₃Zr₂Si₂PO₁₂ (NASICON) and Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP)

In recent years, there has been a tremendous surge in the hunt for novel, stable, and highly ionic conducting solid electrolytes. Sodium superionic conductor (NASICON) structures, e.g., Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ and Li_{1+x}Al_xGe_{2-x}(PO₄)₃, have been the focus of considerable interest due to their particular characteristics and electrochemical stability [58–61]. The name sodium superionic conductors (NASICONs) was initially applied to the solid solution phase corresponding to Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (0 ≤ x ≤ 3), as first suggested by Goodenough and Hong in 1976 [58,62]. The structure of Na₃Zr₂Si₂PO₁₂ (x = 2; Fig. 1d) is disordered and monoclinic C2/c (sg# 15) at room temperature, but at 150 °C the structure is the characteristic NASICON structure (the hexagonal R-3c). Lithium analogues based on a Li_{1+x}Al_xM_{2-x}(PO₄)₃ NASICON-structure (where M is a

tetravalent cation with high ionic conductivity, $M^{IV} = \text{Ti, Zr, Ge, Hf, Sr, Sn, ...}$, and $x = 0.3\text{--}0.7$) represent one of the most important NASICON-type candidates because of their unique structure, high Li^+ -ion conductivity, wide electrochemical window of up to 6 V [63,64,73–76,65–72,77], low thermal expansion coefficient $< 10^{-6} \text{ K}^{-1}$ [78], absence of crack development during heating and cooling [79], and excellent resistance to water [80]. Among these NASICON-structured ion conductors, lithium aluminum germanium phosphate, $\text{Li}_{1+x}\text{Al}_x\text{M}_{2-x}(\text{PO}_4)_3$ ($M^{IV} = \text{Ge}$), which is usually referred to using the acronyms LAGP or LAGPO solid electrolytes, is a white bulk crystal or powder that is an inorganic ceramic solid substance. LAGP in the compositional range of $x = 0.3\text{--}0.7$ shows an activation energy for Li^+ -ion mobility of $\sim 0.37\text{--}0.31 \text{ eV}$ [81] and an ionic conductivity of $\sim 10^{-4}\text{--}10^{-3} \text{ S}\cdot\text{cm}^{-1}$ [82] at room temperature [81,83–85]. Moreover, above 200°C , it shows an upsurge in conductivity to $\sim 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ [81].

As is displayed in Figure 1e, LAGP shows a rhombohedral structure with the space group $R\text{-}3c$ (sg# 167) [86]. It consists of corner-sharing MO_6 -octahedra (with $M = \text{Ge, Al}$) coupled with PO_4 -tetrahedra to produce 3D interconnected channels and two types of interstitial sites (M' and M'') where mobile cations are dispersed. Mobile cations migrate from one site to another via bottlenecks, the size of which is determined by the nature of the skeleton ions as well as the carrier concentration in both types of sites (M' and M'') [87]. Furthermore, LAGP solid electrolytes have been found to have a high electrochemical oxidative voltage of roughly 6V (vs. Li/Li^+) [88]. A glass–ceramic LAGP was recently highlighted due to its stability in the presence of Li [88–90] and ionic conductivity as high as $4.6 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 27°C [73,80,91]. The partial replacement of Ge^{4+} with Al^{3+} increased the porous density of the LAGP and the Li^+ ion conductivity. As a result of its ionic conductivity, potential window, and chemical stability, glass–ceramic LAGPs with NASICON structures have been deemed some of the most promising solid-state electrolytes [92–94].

Phosphate-based materials with a NASICON crystal structure, particularly LAGP, are promising candidates for solid-state electrolytes in lithium and Li-ion batteries [79], high-voltage cathodes [95], high-energy lasers, precision optics, giant telescope mirrors [90], catalysis supports [96], membranes for heavy metal removal from industrial waste streams [97–99], and greenhouse gas (SO_2 and CO_2) sensors [84].

Finally, LAPG possesses less hazardous materials than sulfide-based solid electrolytes [79], is reasonably cost efficient, and is simple to prepare [79].

1.5 $\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$ (Li^+ -glass)

Glass–ceramics are widely known due to their outstanding thermal, mechanical, and chemical stability properties, as well as their notorious mechanical strength [100–102]. Additionally, these materials show a high dielectric constant and low dielectric loss [103].

The crystal structure of Li^+ -glass at 300 K is shown in Figure 1f when simulated by ab initio molecular dynamics from the optimized cubic structure, Pm-3m. In its crystalline form, Li^+ -glass is an antiperovskite.

$\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$ and its family $\text{A}_{2.9}\text{Ba}_{0.005}\text{ClO}$ ($\text{A} = \text{Li}, \text{Na}, \text{and K}$) are safe, low-cost, ferroelectric amorphous-oxide electrolytes with a dielectric constant in the range of $\epsilon_r \approx 10^7\text{--}10^9$ and an ionic conductivity of $10^{-2} \text{ S.cm}^{-1}$ at 25°C [104–106]. $\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$ has been shown to conduct plasmons (currents of electrons) through the surface owing to its self-charge characteristics and positive feedback that have been demonstrated in previously studied devices such as pouch and structural coaxial batteries [104,107]. Compared to other lithium-based electrolytes, $\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$ shows a lower activation energy of 0.06 eV [108]. In terms of its electronic band structure, it demonstrates a large band gap of 4.74 eV, showing a broad range of electrochemical stability. Braga et al. [104] demonstrated negative resistance and negative capacitance in the same working device for the first time [109]. $\text{Li}_{2.99}\text{Ba}_{0.005}\text{ClO}$ electrolytes have great potential for application in positive-feedback, all-solid-state architectures.

S2. References

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