



Analysis of composite electrolytes with sintered reinforcement structure for energy storage applications[☆]



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HIGHLIGHTS

- We study effective conductivity and mechanical properties of composite electrolytes.
- A novel structure with sintered ceramics reinforcement is considered to block Li dendrites.
- Finite element analyses are performed to compute the properties.
- Minimum size of sintering necks necessary to provide desired properties is determined.

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ABSTRACT

Effective conductivity and mechanical properties of composite polymer electrolytes, in which the reinforcement phase is a sintered packed bed of Li-ion conductive ceramics particles, were estimated using finite element analyses. The computations targeted estimation of the effect of sintering degree, i.e. size of the inter-particle connective necks, on the overall properties of the composite. Methods for micro-structure generation and computational procedures were presented. The mechanical ability of the membrane to block lithium dendrites was assessed based on a stability criterion, which depends on the computed effective stiffness. It was found that the minimum size of the inter-particle connections necessary to provide mechanical stability without losing the enhancement in conductivity was 0.05 times the mean particle radius.

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1. Introduction

Development of solid electrolytes for electrochemical energy storage devices, such as Li-ion batteries (LIBs), is mainly driven by the flammability concerns associated with the liquid electrolyte compositions, which involve flammable solvents. Improved safety

is expected when the thermodynamically unstable and flammable liquid electrolytes are replaced with solid membranes, which in addition to good conductivity would possess adequate mechanical properties to serve as separators between anode and cathode, capable of preventing electrical shorts in a cell caused by formation of lithium dendrites. Finally, stable solid electrolytes are necessary for lithium–air batteries that possess high specific energy density of 11.14 kW h kg⁻¹ [1] – close to that of gasoline fuel.

Three general classes of solid electrolytes for LIB applications have been under extensive research – fast ion conducting ceramics, glasses and polymers. In addition, combinations of the above as composite materials have been studied. Ion-conducting ceramics and glasses appear to be promising candidates for solid electrolytes, since they are stable over a wide temperature range. Significant amount of sulfide, oxide and phosphate compounds has been

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developed, some of which exhibit outstanding ionic conductivity at room temperature. Extensive reviews of available materials can be found in Ref. [2,3]. Sulfide-based conductive glass-ceramics $(1-x)\text{Li}_2\text{S}-x\text{P}_2\text{S}_5$ showed room temperature conductivity of $\sim 0.1\text{ S m}^{-1}$ (when $x = 0.2$) – much greater than that of the conductive glass of the same composition [4,5]. Within the group of Li-ion conducting sulfides termed as thio-LISICON (Lithium Superionic CONductor), crystalline $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ has conductivity as high as that of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass-ceramics [6]. Among the phosphates, compounds of sodium conducting NASICON type received most of attention by the researchers with the $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ glass-ceramics (LATP) developed by Ohara Inc. showing very high conductivity of 0.12 S m^{-1} at room temperature [1,7,8]. Powders of LATP were mixed with polymer matrix consisting of polyethylene oxide (PEO) and polypropylene oxide (PPO) with LiTFSI ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$) to form a composite electrolyte. The latter was used in a full cell containing LiCoO_2 as a positive electrode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a negative electrode, and the cell exhibited good cycling characteristics [7]. In the oxide family, the perovskite Li-ion conductor $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) demonstrated high grain conductivity at $x = 0.125$ [9], the total conductivity however is orders of magnitude lower suggesting the negative influence of grain boundaries [2]. Recently developed oxides with garnet type structure $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) can achieve high room temperature conductivities (1×10^{-2} to $1 \times 10^{-1}\text{ S m}^{-1}$) when the cubic phase is stabilized with Al and/or Ta [10,11].

A lithium-ion conductive glass with typical composition $\text{Li}_{3.3}\text{PO}_3.8\text{N}_{0.22}$ (LiPON) has been developed at Oak Ridge National Laboratory and has a good lithium conductivity of $2.3 \times 10^{-4}\text{ S m}^{-1}$, and is stable with lithium at high cell voltage [12–14]. Hasegawa et al. demonstrated that LiPON coating of NASICON-type $\text{Li}_{1+x+y}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LATP) glass-ceramics electrolyte created the water stable Li/LiPON/LATP system with LiPON serving as a protection from the direct reaction between Li metal and LATP [1].

It should be mentioned that the primary driving force behind the development of solid electrolytes has improvement in ionic conductivity. The importance of mechanical properties, as a part of the overall equation for successful electrolyte, was quantified by Monroe and Newman [15] with the theoretical study of the interplay between shear modulus and compressibility of a material necessary to prevent amplification of non-uniformities on the surface of Li metal anode. Built upon this analysis a mechanical stability criterion was introduced [16]. While Li-ion conductive glasses and ceramics alone are presumed to be stiff enough to prevent lithium dendrite nucleation [17] they are brittle in nature and may not be suitable for applications beyond thin film cells. Polymer electrolytes on the other hand possess very low stiffness but have high degree of incompressibility (resistance to volumetric strain). In addition their conductivity is typically orders of magnitude lower than the conductivity of fast ion conducting ceramics [2]. The combination of the two in form of a composite material should provide adequate mechanical properties and, if formed with the volumetric fraction of ceramics filler being above the percolation threshold, should result in high effective conductivity values. It has been shown, that with the very modest values of Young's modulus of the polymers available for electrolyte applications, the fraction of the ceramics reinforcement should be rather high in order for composite to satisfy the mechanical stability criterion [16]. By introducing polystyrene–polyethylene oxide block copolymers arranged in lamellar structure, polymer electrolytes with excellent conductivity on the order of $3.6 \times 10^{-2}\text{ S m}^{-1}$ were obtained, and with increase in PEO molecular weight the improvement in elastic properties was observed [18–20]. The modulus however remained in the range of fractions of 1 GPa, which is much lower than the value needed to stop Li dendrite growth, thus the necessity of reinforcement with a hard phase is still in place. In

addition, the contact inter-particle resistance may contribute to lower than expected values of the effective conductivity.

In order to overcome the above limitations, a structure consisting of sintered ceramics (“foam”) filled with the polymer is envisioned and is assessed in the current work. With sintered connections between the ceramic particles the additional contact resistance concern is eliminated; the rigid inter-connected ceramic structure would provide appropriate stiffness while mixing with a polymer yields compressibility properties and ductility necessary for mechanical stability. Effective conductivity and mechanical properties were computed based on simulated microstructures with different geometric parameters and different properties of constituents, and the results are discussed in terms of suitability for battery applications. The mechanical stability criterion [16] will be used in current work to estimate the performance of the proposed composite polymer electrolytes (CPEs).

2. Material properties

As a base system a mixture of garnet ceramics [10] and polymer in form of PEO with LiTFSI salt was considered in this paper. The properties of these constituents are listed in Table 1. In the numerical simulations considered, the mechanical properties and conductivity of the ceramics reinforcement phase were kept constant, while the properties of the polymer varied. This was done in order to investigate the influence of polymer properties on overall effective properties of the composite system and screen the possible trade-offs in terms of combination between conductivity and mechanical stability with the lithium metal. It should be mentioned that mechanical properties of PEO available in literature vary by orders of magnitude depending on the measurement technique. Young's modulus of PEO was measured to be 0.2–5 GPa for thin films [21] and 0.29 GPa for highly crystalline bulk material [22]. The Poisson's ratio of PEO was 0.49 [22]. The high value (5 GPa) for the Young's modulus was obtained for thin films using large force indentation experiments [21] and may be relevant to the composites produced by pressing techniques. For PEO nanofibers, Bellan et al. (2005) reported Young's modulus values between 0.5 and 7.0 GPa [23]. The chain Young's modulus of 13 GPa was determined from Raman measurements [24] and can serve as the upper limit of the elastic modulus. Mechanical properties of LLZO ceramics were assumed to be similar to those of Alumina. Conductivity of $\text{PEO}_{10}:\text{LiTFSI}$ was measured by the authors (Fig. 1) and the results are in agreement with the data available in literature [2,25]. The ionic conductivity of $\text{PEO}_{10}:\text{LiTFSI}$ was characterized using AC impedance spectroscopy (Solartron 1260). The polymer electrolyte was sandwiched between two parallel stainless steel plates, and the conductivity was calculated using $\sigma = l/RA$, where l is the thickness of the sample, R is the resistance and A is the electrode area.

3. Computational methodology

The computational methodology involves two major steps: (a) microstructure generation, and (b) finite element analysis (FEA).

Table 1
Properties of the constituents (at room temperature).

	σ , S m^{-1}	E , GPa	ν	Ref.
LLZO	4.0×10^{-2}	375	0.22	[11,26]
$\text{PEO}_{10}:\text{LiTFSI}$	1.37×10^{-4}	0.29	0.49	[2,22,25]

σ – Ionic conductivity.

E – Elastic modulus.

ν – Poisson's ratio.

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