



Microstructure and temperature dependent lithium ion transport of ceramic–polymer composite electrolyte for solid-state lithium ion batteries based on garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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ARTICLE INFO

Article history:

Received 29 January 2016

Received in revised form 13 April 2016

Accepted 19 April 2016

Available online 3 May 2016

Keywords:

Composite electrolyte
Lithium solid electrolyte
Garnet-type oxide
PEO
Solid-state battery
Lithium ion conductivity

ABSTRACT

In this paper we present the fabrication of a composite electrolyte for solid state batteries consisting of Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) ceramic particles dispersed in a poly(ethylene oxide) (PEO)₂₀-LiClO₄ matrix. The Al-substituted cubic garnet like LLZO solid-state electrolyte filler is obtained by wet-chemical synthesis followed by a solid state lithiation of the as-prepared amorphous mixed hydroxides. Combining both components LLZO powder can be processed directly into a bifunctional electrolyte-separator membrane eliminating any further ceramic processing steps. Homogeneous composite membranes with different ceramic/polymer composition ratio were obtained by tape casting method with ceramic filling up to 40 vol%. Due to addition of the LLZO ceramic filler the crystallinity of the polymer electrolyte matrix within the composites is greatly reduced, which is proved by differential scanning calorimetry (DSC) measurements. It is further demonstrated that the lithium ion conductivity of the membranes strongly depends on the physical condition of the polymer electrolyte. Composite electrolytes show temperature dependent lithium ion conductivity behaviour similar to polymer electrolyte. Ionic conductivity of the composite ceramic/polymer membranes is analysed by impedance spectroscopy and it falls between $7\text{--}10^{-9}$ S/cm at 20 °C and $5\text{--}10^{-5}$ S/cm at 80 °C for a composite with 40 vol% LLZO.

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1. Introduction

Solid-state lithium ion batteries are a promising type of batteries for future applications. Replacing the liquid electrolyte with a solid alternative offers advantages in safety, efficiency and reliability. Replacing liquid electrolyte with low density ($\rho \sim 0.8\text{--}0.9$ g/cm³) with a solid electrolyte material with higher density (theoretical densities are typically 2.5–6 g/cm³) the gravimetric energy density of a battery cell is vastly reduced. Furthermore, the majority of solid electrolytes possess ionic conductivities lower than organic liquid electrolytes. Therefore, thin and dense electrolyte layers are needed for sufficient cell performance and adequate gravimetric energy density. Recently $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [1] and related compounds have emerged as promising candidates for solid state electrolytes. They offer high lithium ion conductivity even at room temperature and are stable against lithium metal anodes. The material has successfully been synthesised using solid state reaction [1–4] or wet chemistry methods, such as co-precipitation [5–7], citrate method combustion [8,9] and sol–gel synthesis [10]. All these synthesis

methods result in a powder product that has to be pressed and sintered to form a pellet shaped ceramic electrolyte membrane. However, processing LLZO powder into a thin film electrolyte is quite difficult. Physical vapour deposition methods (e.g. pulsed laser deposition [11–14] or magnetron sputtering [15]) can be used to create thin film layers of LLZO. Unfortunately, these methods are limited, since precise control of the stoichiometry during the PVD-process is inevitable for the sufficient functionality of the prepared ceramic thin layers (i.e. ionic conductivity) and especially PLD processes are not suitable for large scale production. Furthermore, the processed thin ceramic electrolyte films are not self-supporting. In this case, application of a suitable support is necessary. However, in a practical system the integration of larger amounts of electrochemically inactive components (e.g. support material) into the cell for sufficient mechanical strength leads to a dramatic reduction of the practical volumetric and gravimetric energy density of the battery cell. Here, a bifunctional self-supporting solid state electrolyte offers advantages in battery cell design. Not only does it act as the lithium ion transport medium, its application also allows the reduction of electrochemically inactive components by eliminating a separator or support within the battery cell. A more appropriate route for creating thin ceramic membranes is tape casting [16].

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Several decades ago Skaarup et al. [17] proposed the concept of mixed phase conductors to simplify production of thin electrolyte membranes. Li_3N powder was mixed with an ionically conductive polymer to avoid additional temperature treatment and simplify production of solid state electrolytes. The ceramic fraction well exceeded 50 wt.% and the polymer was used as a binder only. A similar approach was investigated by Syzdek et al. [18] who used a polymer to add further mechanical stability to their porous ion conductor pellet. Research efforts today focus on designing polymer composite electrolytes, a mixture of polymer electrolyte and usually small amounts (up to 10 wt.%) of ionically conductive [19,20] or inactive ceramic fillers [21–24]. The focus of these works is optimising polymer electrolytes with regard to mechanical stability and ionic conductivity. So far only few studies tried to incorporate LLZO into a polymer ceramic composite system. Micron-sized LLZO has been dispersed in a poly(ethylene oxide) (PEO) matrix as an active filler material to enhance conductivity of the polymer [20]. Computational work focused on the mechanical stability of a sintered LLZO pellet infiltrated with polymer electrolyte [25]. Two further studies used LLZO based composite electrolyte in a full battery cell [26,27]. Indeed, focus of these studies was not the investigation of the electrolyte itself, but the performance of the full electrochemical cell.

The objective of the present study is the feasibility of a self-supporting composite electrolyte membrane consisting of Al-substituted LLZO ceramic particles and a polymer electrolyte. In contrast to previous works, the focus of the work presented here is not an improved polymer electrolyte, but the investigation of a less complex processing of LLZO ceramic electrolyte into a bifunctional electrolyte-separator membrane. Al-substituted LLZO powder is obtained using a facile wet chemistry synthesis route, while calcining at low temperatures. Thin composite electrolyte membranes are obtained using the tape casting method. Ceramic content of the composite electrolyte is varied up to 50 vol% (corresponds to 80 wt.%) in order to investigate the maximum amount of ceramic possible to process using tape casting method. The temperature dependent lithium ion transport of the composites is investigated as a function of ceramic content and is discussed in detail.

2. Experimental

Al-substituted LLZO powder with a theoretical sum formula of $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ was prepared as described previously in Ref. [5]. In short, metal ions were precipitated from an aqueous solution to obtain an amorphous powder of mixed hydroxides. This precursor was mixed with a lithium salt and calcined in air. Calcination time was increased to 24 h in a lid covered ZrO_2 crucible to increase crystal size. After calcination in air, the LLZO powder was transferred into an argon filled glovebox. For comparison of electrochemical properties LLZO pellets were prepared as described in Ref. [5].

LLZO-PEO composite electrolyte membranes were prepared by tape casting method. All steps were carried out in an argon filled glove box with oxygen and water concentration below 0.1 ppm. All chemicals were dried in vacuum at room temperature before use. Appropriate amounts of PEO ($M_w = 10^5$ g/mol, Sigma Aldrich), LiClO_4 (Sigma Aldrich, battery grade, dry, 99.99%) and LLZO powder were mixed with acetonitrile (99%, VWR company) forming a highly viscous slurry. The ratio of ethylene oxide monomer units to lithium ions (EO:Li) was kept constant at 20:1. LLZO content was varied from 30 vol% to 50 vol%. Additionally polymer electrolyte samples without LLZO were prepared for comparison purposes. After homogenisation, the dispersions were casted in poly (tetrafluoro ethylene) (PTFE) dishes and dried slowly at ambient temperature. Thickness of the dried composite membranes was measured with a micrometre screw and is about 110 μm to 150 μm across the whole area (about 65 cm^2) of the casted ceramic polymer membrane. Samples for further characterisation were taken from the dried membranes.

Phase composition and crystal structure of prepared LLZO powders were verified by X-ray diffraction (XRD, D5000, Siemens) in Bragg-Brentano geometry using $\text{Cu K}\alpha$ radiation. The diffractometer was operated in step scan mode (step width $0.02^\circ 2\theta$) with fixed divergence slits (0.5°). Data was collected in a range of $15^\circ 2\theta$ to $90^\circ 2\theta$. Scanning electron microscopy (SEM, Helios NanoLab™ 600 DualBeam™, FEI company) was used to evaluate the particle morphology of the prepared LLZO powder. The dried composite electrolyte membranes proved to be sensitive to the electron beam, so SEM images were taken under N_2 -cryo conditions. Focussed ion beam (FIB) cross sectional analysis was performed under cryo condition, as well. To avoid morphological changes of the composites, the samples were transferred from the glove box into the microscope under inert conditions. Surface area of the powder was determined using nitrogen adsorption technique (Nova 2200E, Quantachrome Instruments). Brunauer-Emmet-Teller (BET) theory was applied to calculate the specific surface area. Differential scanning calorimetry (DSC, DSC 7, Perkin Elmer) was performed in order to investigate thermal behaviour of the composites and determine the influence of LLZO powder on the crystallisation of the polymer. Samples were left to crystallise for one month and were then heated from 25°C to 100°C with a heating rate of 5 K/min. Electrochemical impedance spectroscopy (EIS, Alpha-A measurement system, Novocontrol) was carried out in a frequency range from 10^7 to 1 Hz (10 mV) to examine lithium ion conductivity. Samples were cut out from the dried membranes and melted into 500 μm thick non-conductive ring-shaped spacers. Stainless steel electrodes were pressed onto the samples' surface as blocking electrodes. Measurements were carried out in a temperature range from 80°C to 20°C in a custom made sample holder, which was placed in a climate control chamber (Espec). Prior to measurements, temperatures were held constant for 1 h for equilibration purposes.

3. Results and discussion

The XRD pattern of the calcined LLZO powder is presented in Fig. 1. All major Bragg reflections can be assigned to cubic garnet type LLZO (JCPDS # 80-0457). Further Bragg reflections with lower intensities originate from impurity phases and can be attributed to few amounts of secondary phases La_2O_3 (JCPDS # 71-5408) and $\text{La}_2\text{Zr}_2\text{O}_7$ (JCPDS # 17-0450).

In Fig. 2a a characteristic scanning electron microscope back scattered electron (SEM-BSE) image of the calcined LLZO powder is presented. As it can be seen from the image, the powder has a polydisperse

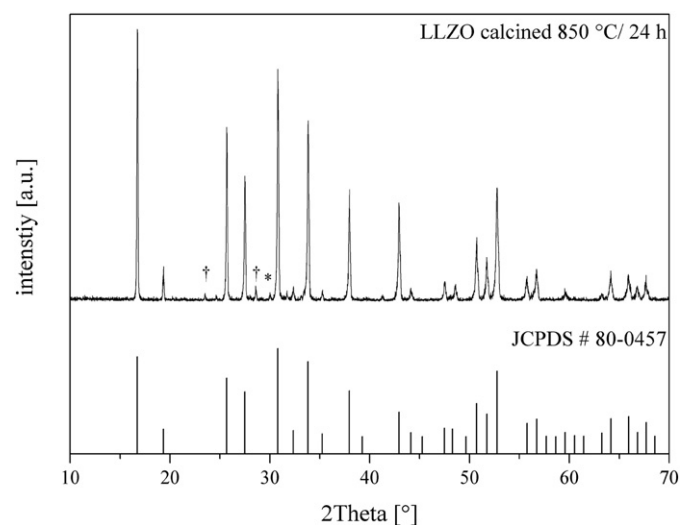


Fig. 1. Diffraction pattern of a) calcined powder and b) simulated pattern of LLZO (JCPDS # 80-0457), † $\text{La}_2\text{Zr}_2\text{O}_7$, * La_2O_3 .

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