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Field assisted sintering of fine-grained $Li_{7-3x}La_3Zr_2Al_xO_{12}$ solid electrolyte and the influence of the microstructure on the electrochemical performance

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HIGHLIGHTS

- Combining NSP and FAST methods for LLZO preparation for the first time.
- Dense fine-grained ceramics are obtained with a high Li-ion conductivity.
- A discussion of the influence of the microstructure and microstrain is provided.
- Cell assembly with Li-metal electrodes and testing of the cycling performance.
- Determination of the area specific resistance at the Li|LLZO interface

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ABSTRACT

The synthesis and processing of fine-grained $Li_{7-3x}La_3Zr_2Al_xO_{12}$ (x = 0.15, 0.17, 0.20) solid electrolyte (LLZO) is performed for the first time using a combination of nebulized spray pyrolysis (NSP) and field assisted sintering technique (FAST). Using FAST, the grain growth is suppressed and highly dense ceramics with 93% of the theoretical density are obtained. A tetragonal lattice distortion is observed after the sintering process. Although this structural modification has been reported to have lower Li-ion mobility compared to the cubic modification, the total conductivity of the sample at room temperature is found to be 0.33 mS cm^{-1}, i.e. comparable to phase-pure cubic LLZO. The activation energy of 0.38 eV is also comparable to the literature values. Galvanostatic cycling of a symmetrical cell Li|LLZO|Li shows a good cycling stability over 100 h. The interfacial resistance in contact with Li-metal is determined using alternating current impedance spectroscopy to be 76 Ω cm^2 and 69 Ω cm^2 before and after cycling at different current densities, respectively.

1. Introduction

The Li-ion conducting $Li_7La_3Zr_2O_{12}$ solid electrolyte (LLZO) gained a lot of attention over the past years for its potential application in all-solid-state Li-ion batteries. Besides the increased operational safety of such cells, the elimination of the separator and the possibility to use Li-metal as anode material will result in increased energy densities. The LLZO is a promising candidate since it is considered to be stable against Li-metal [1,2]. It crystallizes in two different garnet structures: a cubic (*Ia*-3*d*) and a tetragonal ($I4_1/acd$) [3] modification. Aliovalent doping by Al^{3+} and Ga^{3+} of the Li-sites as well as Ta^{5+} and Nb^{5+} on the Zr-sites stabilizes the cubic phase by creating Li-vacancies, which enhances the Li-ion conductivity [4,5]. A variety of synthesis methods have been used, such as sol-gel [6] and citrate-nitrate methods [7], solid state reactions [8–10] as well as nebulized spray pyrolysis (NSP) [12]. While field assisted sintering technology (FAST) is usually used as a ceramic

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processing technique to achieve high-density ceramics, recently it has also been successfully utilized as a synthesis method for direct preparation of LLZO starting from oxide powders [11]. It has been found that the synthesis temperature and the details of the procedure highly influence the final microstructure (i.e. crystallite size, grain size and density) with strong impact on the Li-ion conductivity. The highest Li-ion conductivity of 0.57 mS cm^{-1} was observed in samples produced by FAST, where the mean grain size was 10 μm and the relative density was 99.8% of the theoretical density (TD) [11]. For electrolytes prepared by conventional sintering of powder synthesized by solid state reactions, typical grain sizes in the range from 100 to 200 μm and 92%TD, a value of 0.2 mS cm^{-1} for the Li-ion conductivity were reported [10]. Conventional sintering of sol-gel powders leads to dense (96%TD) ceramics with Li-ion conductivity of 0.4 mS cm^{-1} and grain size of 260 nm [6], which is twice the value achieved by solid state reaction [10]. The reduction of the grain size of ceramics synthesized by solid state reaction to 4 μm and the increase of the density (98%TD) leads to a higher Li-ion conductivity [9], approaching the values reported for nano-grained ceramics (0.4 mS cm^{-1}). Decreasing the grain size of the sintered ceramics from 100 μm to a few microns does indeed lead to higher Li-ion conductivities [9,10], while a further reduction of the grain sizes does not necessarily lead to higher Li-ion conductivities [6]. Additionally, the decrease of the grain size improves the cycling performance. It was shown [10] that a fine microstructure enhances the homogeneity of the current distribution along the interface between the solid electrolyte and the metallic Li-electrode, thus suppressing the dendrite formation during cycling.

The approach of the present work is to combine the nebulized spray pyrolysis method (NSP) for powder synthesis with the field assisted sintering technology, also referred to as spark plasma sintering (SPS), in order to explore the influence of grain size and density on Li-ion conductivity of LLZO ceramics. NSP is an aerosol-based synthesis method, which is characterized by a high production yield (98%) and relatively high production rate (~0.3 g/h) on laboratory scale. This method is more attractive for industrial powder production than currently used solid state reaction procedure which requires repeated ball milling and heat treatment steps. Additionally, nanocrystalline powders with precise control of the chemical composition [12] are obtained.

In FAST processing, uniaxial pressure and pulsed direct electrical current are simultaneously applied to densify powder compacts. The heating rates achieved by this technique are an order of magnitude higher than those obtained using conventional sintering methods, leading to ceramic densities close to the theoretical values. Furthermore, the technique allows shorter sintering times at reduced sintering temperatures compared to conventional routes [13]. Presumably, this is attributed to the discharge generated at the particle contact points, which can lead to an enhancement of the sintering processes [14]. With regard to large-scale manufacturing, recent developments have led to a change from small lab-scale devices for batch production to larger furnaces suitable for industrial production [15].

In this study, NSP and FAST are combined for the first time, to obtain dense LLZO ceramics with grain sizes in the range of a few micrometers, in order to achieve high Li-ion conductivities and a low interfacial resistance to the Li-metal anode. In this respect, a new ceramic processing route and cell assembling process will be introduced. The electrochemical performance is studied using alternating current impedance spectroscopy (AC-IS) and galvanostatic cycling. The influence of the sintering technique on the phase composition, microstructure and microstrain is discussed and related to the electrochemical performance of the solid electrolyte.

2. Experimental

2.1. Powder synthesis and ceramic processing

$Li_{7-3x}La_3Zr_2Al_xO_{12}$ powders (x = 0.15, 0.17 and 0.20 mol) were synthesized using NSP. The synthesis procedure, process parameters and the experimental setup were reported elsewhere [12]. The procedure described here requires the use of excess lithium (30 wt %) to compensate for Li-loss at elevated temperatures [16]. The as-synthesized powders (consisting of a pyrochlore-related phase $La_{2+x}Zr_{2-x}O_{7+x/2}$ and Li_2CO_3) were annealed at 900 °C for 3 h in order to achieve nearly single phase cubic LLZO, with heating and cooling rates of 5 °C min^{-1} and 10 °C min^{-1}, respectively. The annealing process was conducted in air and the powders were removed from the furnace at 300 °C during cooling to avoid the uptake of water [17,18] and kept in an argon-filled glovebox. The annealing step is necessary since the formation of the desired phase of LLZO was not observed by only applying FAST on the as-synthesized powders. After annealing and achieving the desired phase composition the powder was consolidated and sintered using FAST (Dr. Sinter Lab 211-Lx). Graphite foils were used to isolate the specimen from the carbon die. The foils were coated with boron nitride spray to prevent any carbon diffusion into the sample. A carbon punch with a diameter of 7 mm was used and a uniaxial pressure of 25 MPa was applied. The voltage and current used in the process were controlled under automatic operation mode. The heating rate was set to 100 °C min^{-1} and the sintering temperature was held at 950 °C for 10 min, during which the pressure was increased to 50 MPa. The whole process was conducted under vacuum (1 Pa) to eliminate air inclusion inside the pores. The FAST process parameters are shown in Fig. 1. The densities of the sintered ceramics were determined based on their geometrical dimensions and masses. The final theoretical densities (ρ_t) were calculated based on the fraction (f) of the phases present in the sample (mean value of the two sides of the pellet determined by Rietveld analysis) and their theoretical densities (ρ):

$$\rho_t = (f \cdot \rho)_{\text{cubic}} + (f \cdot \rho)_{\text{tetragonal}} + (f \cdot \rho)_{\text{pyrochlore}}$$

2.2. Phase composition, structure and microstructure

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 diffractometer with Bragg-Brentano geometry equipped with an X-ray tube with Cu anode, and a Ni filter for the removal of the K_β radiation. A VANTEC detector and a fixed divergence slit (0.3°) were used. The measurements were performed with a step size of 0.015°

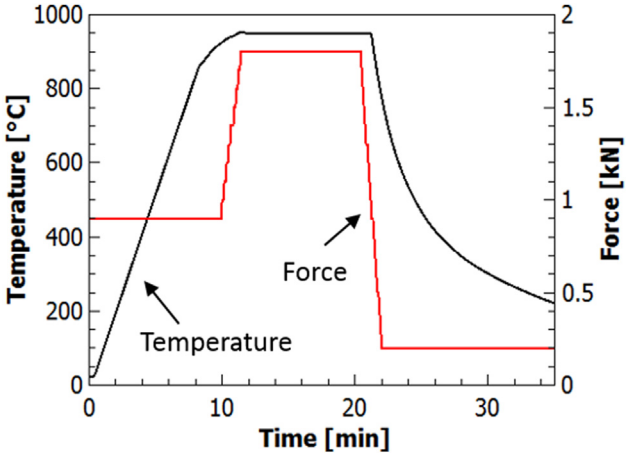

Fig. 1. Temperature and force profiles during the FAST-process.