Is Li-doped $MgAl_2O_4$ a potential solid electrolyte for an all-spinel Li-ion battery?

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ABSTRACT

The ionic conductivity of Li-doped $MgAl_2O_4$ (LMAO), which is considered as a potential solid electrolyte for an all-spinel Li-ion battery, has not been investigated so far. Only NMR studies, which give information about the mobility or the Li-ion diffusion on local (microscopic) level, are performed on this system, but they do not give information about the long-range Li-ion diffusion, which is required for solid electrolyte application. Therefore, ionic conductivity study i.e., impedance spectroscopy, which provides insight into Li-ion diffusion on microscopic scale, is of great importance. The results reported here reveal for the first time ionic conductivity of LMAO ceramics and give insight into whether this material system has a potential for application as a solid electrolyte. The LMAO powders, with an average grain size of 55 nm, are synthesized by nebulized spray pyrolysis (NSP) and processed into dense ceramics (95–98% TD) using spark plasma sintering (SPS). The decrease of the lattice parameter with Li-doping indicates the incorporation of lithium into the spinel structure. X-ray diffraction structural analysis shows a systematic decrease of the occupancy of Al-octahedral ($16d$) sites with Li-doping, indicating that a fraction of the Li^+ ions are located on the octahedral ($16d$) sites, and at the same time in order to retain charge neutrality, some of the Al^{3+} ions are moved to the tetrahedral ($8a$) sites. The conductivity study reveals that even at a high temperature (~ 300 °C) the value of the Li-ion conductivity of LMAO, in the order of 10^{-7} S·cm^{-1} is poor and at room temperature it is substantially lower (~ 10^{-14} S·cm^{-1}). While the origin of this low conductivity remains unclear, it could be related either to the nano- and microstructure of the sintered ceramic or to the distribution of Li^+ ions inside the lattice. Nevertheless, the results presented here suggest that more conductivity studies have to be performed in order to draw a final conclusion about potential of LMAO ceramics for application as a solid electrolyte in Li-ion batteries.

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1. Introduction

Solid electrolytes conducting lithium ions at room temperature could potentially replace conventional liquid electrolytes in batteries and reduce the associated risks during operation, such as flammability and toxicity. In addition to the safety improvements, solid electrolytes could offer stability over a wider electrochemical potential as well as over a larger temperature range. However, achieving the required combination of the desired characteristics in solid electrolytes remains a major challenge. Even though several solid electrolytes have been synthesized [1–7], electrochemical cells based on solid electrolytes suffer from substantially lower power density compared to cells with a liquid electrolyte. Reasons for the reduced performance can be manifold: low ionic conductivity, instability of the electrolyte/electrode interfaces during cycling, limited kinetics of the electrodes and insufficient contact regions between electrode material and electrolyte [8].

Recently, a group of authors [9,10] introduced a novel concept of an all-spinel-type solid battery cell. The basis for their computational and NMR study was the experimentally not proven but patented idea of Thackeray and Goodenough [11]. In this all-spinel solid battery concept, which up to now is not experimentally demonstrated, all three major components (anode, cathode, and electrolyte) are spinel-based. As the interfacial compatibility between electrode and electrolyte is crucial for the performance of solid-state batteries, it is believed that this "lattice matching" concept could lead to a lower interfacial resistance between a spinel-based solid electrolyte and the well-known spinel electrode materials (cathode $LiMn_2O_4$ [12], and anode $Li_4Ti_5O_{12}$ [13]). Additionally, this concept would provide continuous pathways for Li-ion diffusion. The authors [9,10] suggested that two spinel systems $MgAl_2O_4$ and $ZnAl_2O_4$, which are otherwise known as electronic insulators [14], can become Li^+ ion conductors when doped with Li ($Li_xM_{1-2x}Al_{2+x}O_4$, M = Mg^{2+}, Zn^{2+}). These systems belong to a group of normal spinels (space group Fd-3 m) with Mg^{2+}/Zn^{2+} ions located

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in tetrahedral sites ($8a$), Al^{3+} ions located in octahedral sites ($16d$), and O^{2-} ions in $32e$ sites, while the remaining tetrahedral ($8b$) and octahedral ($16c$) sites are not occupied [15]. When doped with lithium, it is expected [9] that two Mg^{2+}/Zn^{2+} ions are replaced by one Li^+ and one Al^{3+} ion, in order to fulfill the charge neutrality. Despite Li-doping, both systems remain to be electronic insulators, which was experimentally validated by Rosciano et al. [9]. Based on the first-principle modeling [10], the Li-ion conduction in these materials is considered to take place by Li-ion hopping between tetrahedral and octahedral sites where $8a \rightarrow 16c \rightarrow 8a$ provides the shortest and energetically most favorable pathway for expected fast diffusion [9]. Based on a detailed NMR study [16], the Li-doped $MgAl_2O_4$ system showed higher Li-ion mobility than the Li-doped $ZnAl_2O_4$. However, it should be considered that NMR characterizes only the local Li^+ ion mobility or Li-diffusion, not the long-range diffusion needed for mass transport, as required for an electrolyte. Furthermore, it was found that the fraction of mobile Li^+ ions is well below 5%, raising the question whether this amount is sufficiently large for mass transport in the solid electrolyte.

The Li-ion conductivity in these proposed spinel-based solid electrolytes has so far not been reported despite the fact that the authors [9,10] have successfully synthesized the powders using a sol–gel technique. Most likely, the preparation of dense ceramics was not successful as spinel ceramics with high density can only be obtained at very high temperatures (above 1600 °C) and long sintering times [17,18]. For ceramics containing lithium, such conditions are not suitable due to the unavoidable Li-loss at high temperatures, especially if the ceramics are processed starting from fine powders [19]. In case of Li-containing powders the spark plasma sintering, SPS (also known as field assisted sintering, FAST) has been shown to be suitable as it enables processing of dense ceramics at substantially lower temperatures and shorter times than any other sintering technique resulting in a suppression of Li-loss.

As the ionic conductivity is the most crucial parameter for the practical application of the proposed materials in Li-ion batteries, the purpose of this study is to determine the ionic conductivity in Li-doped $MgAl_2O_4$ ceramics. Nebulized spray pyrolysis (NSP) was chosen for the preparation of Li-doped $MgAl_2O_4$ powders, as it allows for the direct synthesis of crystalline powders in a one-step process with a sufficiently high production rate in a laboratory setup (0.5 g·h^{-1}). In addition, the technique has the potential to be scaled up for industrial production. For the consolidation and sintering of the LMAO powders into dense ceramics for the conductivity studies, the SPS technique was employed.

2. Experimental

2.1. Material preparation

Li-doped $MgAl_2O_4$ (LMAO) nanopowders with the composition $(Li_xMg_{1-2x})Al_{2+x}O_4$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) were synthesized via nebulized spray pyrolysis (NSP). The experimental setup of NSP is illustrated in Fig. 1. A water-based precursor solution (total cation concentration 0.1 mol·l^{-1}), containing stoichiometric amounts of Li-, Mg- and Al-nitrates ($LiNO_3$, Sigma Aldrich, 99.99%; ($Mg(NO_3)_2$, Merck, 99%;

$Al(NO_3)_3 \cdot 9H_2O$, Merck, 98.5%), was nebulized inside a glass chamber using an ultrasonic generator (Dr. Hielscher UM20, 1.6 MHz). The mist of the precursor solution was transported by flowing oxygen (5 slm) into the hot-wall reactor consisting of an alumina tube inside a resistance furnace. A syringe pump was used for continuous precursor delivery at a rate of approximately 100 ml·h^{-1} to maintain a constant level of precursor solution inside of the nebulizer. The process pressure was held constant at 900 mbar using a Baratron absolute pressure gauge (MKS) and a butterfly valve (MKS) connected to a backing pump. Nanoparticles were synthesized at 1100 °C and collected using a filter-based collector kept at 120 °C to prevent water vapor condensation on the filter.

Dense LMAO ceramics were prepared by spark plasma sintering (Dr. Sinter Lab 211-Lx) using the as-synthesized powders filled into a graphite die with an inner diameter of 10 mm. During the heating up of the die at a rate of 100 °C·min^{-1}, a uniaxial pre-load pressure of 10 MPa was used. Sintering was carried out in vacuum (1 Pa) at 1050 °C for 10 min at a pressure of 100 MPa. During the cooling phase, the pressure was reduced at a rate of 4 kN·min^{-1}. The detailed SPS process conditions are provided in the Appendix (Fig. S1).

2.2. Characterization

Room temperature X-ray diffraction (XRD) patterns of the as-synthesized powders and sintered ceramics were recorded using a Bruker D8 diffractometer with Bragg–Brentano geometry equipped with an X-ray tube with a copper anode and a nickel filter. A VANTEC detector and a fixed divergence slit (0.3°) were used. A step size of 0.015° and a collection time of 1 s at 30 kV and 40 mA over the 2θ angular range between 10 and 120° were used. For high-temperature XRD (HT-XRD) the temperature stage (Anton Paar HTK 16, Bruker) was used to collect data in the temperature range 25–370 °C. All experimental parameters, with exception of the collection time (here 0.5 s), were the same as for the room temperature measurements. Rietveld analysis (TOPAS 3.0, Bruker) of the XRD patterns was used to determine phase composition of the as-synthesized powders, as well as phase composition and structural parameters (lattice parameters and Al-site occupancy) of the sintered ceramics. Results of the refinement are provided in the Appendix (Table S1, S2, Fig. S2). The instrumental contribution to the XRD patterns was eliminated from the experimental data based on a reference scan of LaB_6 (NIST 660a).

The microstructure of the as-synthesized powders and sintered ceramics was studied using a high-resolution scanning electron microscope, SEM (Philips XL30 FEG) operating at 10 kV. Prior to imaging, samples were coated with gold to prevent electrical charging. The microstructure of the sintered ceramics was studied at fractured surfaces. The particle and grain size distributions were obtained from the SEM micrographs by measuring the size of approximately 150 particles/grains (ImageJ 1.50a) and fitting the data by Gaussian distribution function [20].

The Li-ion conductivity of the sintered samples was determined using AC impedance spectroscopy. The data were collected in air in the temperature range 25–400 °C using a Solartron 1260 frequency response analyzer and SMaRT Software (Version 3.3.1, AMETEK) applying a 100 mV AC voltage signal over a frequency range from 1 MHz to 10 Hz. Prior to the measurement, the pellets were polished using diamond abrasive papers (final grade 800), Au-blocking electrodes (3 or 5 mm in diameter) were sputtered on both sides of the pellets and Pt-wires were attached to the sample using an in-house designed sample holder.

3. Results and discussion

3.1. Crystal structure and microstructure

X-ray diffraction patterns (Fig. 2a) of the as-synthesized powders with different Li-content ($x = 0$–0.4) show that the as-prepared
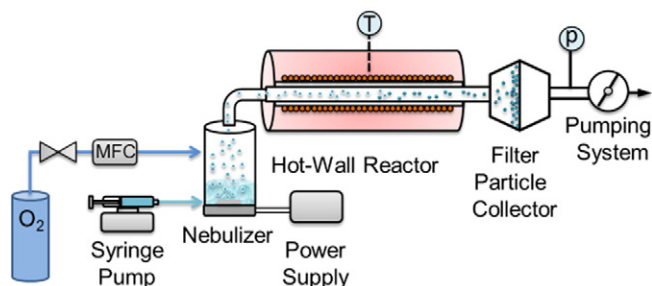

Fig. 1. Nebulized spray pyrolysis setup for synthesis of LMAO nanopowders.