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Solid State Ionics

The influence of water on the electrical conductivity of aluminum-substituted lithium titanium phosphates

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ABSTRACT

$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0.1 \leq x \leq 0.6$) powders were prepared by a novel sol-gel method with high phase purity, densification activity and conductivity. Diffraction analyses showed that the solubility limit of Al^{3+} was reached at $x = 0.5$. The highest ionic conductivity was obtained for $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$, which reached $1.0 \times 10^{-3}\,S\,cm^{-1}$ at $25\,°C$ when tested in ambient air. However, measurements in dry argon resulted in a conductivity of only $5 \times 10^{-4}\,S\,cm^{-1}$ at $25\,°C$. Hence, the influence of moisture or water on microstructure and grain-boundary conductivity was investigated by impedance spectroscopy, scanning electron microscopy, Raman spectroscopy, X-ray and neutron diffraction. An ion exchange of Li^+ by protons could not be unambiguously achieved by exposure of LATP powder in water. Neutron diffraction of humidified samples did not clearly indicate the presence of water or protons in the crystal structure of LATP, whereas μ-Raman measurements confirmed the presence of water/protons on the sample surface and in the bulk material. A higher signal of the vibrational modes of H_2O was measured on grain boundaries than in the grain interior on the sample surface as well as on the fractured surface of sintered specimens. Therefore the higher apparent conductivity of LATP samples may predominantly result from adsorbed water from ambient air at grain boundaries. Hence, the conductivity tested in dry argon represents the correct conductivity of LATP samples. The highest density after sintering is not necessarily leading to high conductivity but rather the microstructure plays the dominant role.

1. Introduction

Aluminum-substituted lithium titanium phosphate (LATP) is one of the most promising candidates for solid-state electrolytes in lithium-based batteries. LATP was first reported in the late 1980s [1]. It belongs to the NASICON (Na super-ionic conductor) family [2], which crystallizes in rhombohedral structure (space group $R\bar{3}c$). It shows high ionic conductivity ($5–13 \cdot 10^{-4}\,S\,cm^{-1}$ at room temperature) [3–6], chemical stability in ambient atmosphere, water, and even basic or acidic solutions [7–11], and high mechanical strength [12]. It has been frequently applied in advanced lithium-based batteries [7,13–15].

Although LATP has been developed for almost 30 years, there are still fundamental questions that have not been clearly answered. One of the most important questions is the optimized amount of Al-substitution in the $LiTi_2(PO_4)_3$ structure. Aono et al., the discoverers of LATP, claimed the optimal amount of Al substitution in $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATPx) is $0.3 < x < 0.4$ (prepared by solid state reaction) [3], which

corresponds to the upper limit of Al substitution in LATPx. Further substitution results in Al-rich secondary phases. Since normally the conductivity of a material is directly proportional to the amount of charge carriers [16], $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP0.3) or $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP0.4) should show the highest conductivity in the series because the Li^+ concentration in the unit cell reaches a maximum. Until today, almost all of the subsequent related work focused on these two compositions. Although Cretin et al. indicated that better synthesis routes like the sol-gel method can shift the limit of Al substitution up to $x = 0.6$ [17], the reported conductivity of LATPx in their study was rather low ($1–6 \cdot 10^{-5}\,S\,cm^{-1}$ at room temperature).

Another important fundamental question is the influence of water (or moisture) on LATP. Many studies discuss the stability of LATP in different solutions [7–13]. These reports mainly focus on phase changes or chemical decomposition of LATP, mainly related to the grains of polycrystalline materials before and after contact with different solutions. The conclusion of the authors, stating that LATP is stable in

ambient atmosphere or in aqueous solutions, only means that the grains of LATP samples or crystal structure show no obvious changes (e.g. phase transformations) in the above-mentioned conditions. However, the total conductivity, σ_{total}, of a polycrystalline material includes grain (bulk) conductivity (σ_b) and grain-boundary conductivity (σ_{gb}). The conditions at the grain boundaries may therefore largely influence the properties of a polycrystalline material. Particularly for LATP, it was reported that the total conductivity ($\sigma_{total} = \sigma_b + \sigma_{gb}$) of LATP is actually mainly influenced by σ_{gb} because σ_b can be 1 to 2 orders of magnitudes higher than σ_{gb} [12]. The conductivity tests in almost all former reports were performed directly in ambient air, without any consideration of a possible influence of moisture on the apparent conductivity of LATP materials. Takahashi et al. [18] reported that the apparent conductivity of LATP immersed in a LiCl aqueous solution decreased by one order of magnitude when the material was moved from ambient air into a dry glove box, indicating the possible impact of moisture on σ_{gb}. Moreover, even when only grain conductivity is considered, phase changes or chemical decomposition are not the only possible reasons causing the properties of LATP to alter in contact with water. Zhang et al. [19] investigated H^+ ionic diffusion from water and acidic solution into LATP glass using both cyclic voltametric experiments and modeling approaches and revealed that the diffusion of H^+ into the glassy LATP structure is negligibly low. In contrast, Thangadurai et al. confirmed an exchange between H^+ and Li^+ ions in water-treated $Li_5La_3Nb_2O_{12}$ polycrystalline samples using neutron diffraction (ND) experiments [20].

In this report, LATPx samples ($0.1 \leq x \leq 0.6$) were prepared by an aqueous solution-based sol-gel method [21,22], which can be used for large-scale powder preparation. The limit of Al substitution in this LATPx series is discussed. The influence of moisture or water on LATPx is investigated with respect to both bulk and grain-boundary properties. The crystal structures of dry and moisturized LATPx are studied by ND in detail in order to elucidate the Li^+ ion conduction pathway and to validate the incorporation of protons, e.g. by ion exchange for Li^+, into the structure of the moisturized sample.

2. Experimental

For the preparation of LATPx powders, titanium (IV) isopropoxide (97%, Aldrich) was added to deionized water while stirring. A titanium hydroxide precipitate was formed immediately. The precipitate was filtered and washed. Deionized water and nitric acid (65%, Aldrich) was then added to the titanium hydroxide precipitation. When a clear TiO^{2+} nitrate solution was formed, a twofold molar amount of citric acid was added to form coordination compounds with TiO^{2+} and in this way the solution was stabilized.

Stoichiometric amounts of $LiNO_3$ (99%, Alfa Aesar) and $Al(NO_3)_3 \cdot 9 H_2O$ (99%, Alfa Aesar) were weighed and added to the TiO^{2+} nitrate solution while stirring. After the salts were dissolved, a corresponding amount of $NH_4H_2PO_4$ (99%, Merck) was then added to the solution and a sol was immediately formed. After about 1 h, a stiff gel was spontaneously formed. More detailed information on the synthesis can be found elsewhere [21,22].

The gel was dried at 80 °C for 24 h. The dried gel was then calcined at 600 °C for 3 h. The calcined powder was milled in ethanol with zirconia balls on a milling bench for 48 h. After drying, the powder was then put into a cylindrical pressing mold with a diameter of 13 mm and pressed at a uniaxial pressure of 100 MPa. The pressed pellets were sintered at 850–1050 °C for 5 h. Pure white samples were obtained after sintering. The XRD patterns of the sintered LATPx powder were collected with a Siemens D4 diffractometer using CuKα radiation.

The prepared dense LATPx pellets were sputtered with Au on both sides and sealed in Swagelok cells inside an Ar-filled glove-box to avoid continuous contact with moisture. The impedance spectra of the samples were recorded from −30 °C to 70 °C using a commercial electrochemical system (VMP-300, Bio-Logic SAS, with AC frequency range

from 3 MHz to 1 Hz). For comparison, samples stored in ambient air for 72 h (~20 °C, relative humidity (RH) ~ 50%) were also tested in ambient conditions. A typical $Li_{1.5}Al_{0.5}Ti_{1.5}(PO_4)_3$ (LATP0.5) sample with Au electrodes was immersed into deionized water for 24 h. After wiping off the surface water, the conductivity was tested in air. The sample was then stored in a drying oven (VOT, Memmert) at 70 °C in vacuum and after another 24 h, the conductivity was tested in dry Ar. The wet-dry cycles were repeated 5 times. Microstructures of the samples were investigated by scanning electron microscopy (SEM; Ultra55, Zeiss). The elemental content of Li, Al, Ti, and P in the water in which the sample had been immersed was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).

Room temperature μ-Raman spectra of dry and humidified polycrystalline samples were recorded in quasi-backscattering geometry under excitation of the 488 nm and 514.5 nm lines of a mixed Ar − Kr ion gas laser. The maximum laser power was 10 mW at the sample surface. A long working distance objective (Olympus, with a magnification 80×) with high numerical aperture (N.A. = 0.75). was used to focus the laser beam onto the sample surface in the form of a circular spot of about 2 μm in diameter, and to collect the scattered light. The scattered radiation was dispersed by a triple-monochromator (Horiba-Jobin Yvon, model T64000), set in double subtractive/single configuration and equipped with holographic gratings (1800 lines/mm). The detection of the filtered radiation was provided by a multichannel detector, which is an open-electrode CCD, consisting of a matrix of 1024×256 pixels, and nitrogen-cooled at −134 °C. The CCD maximum efficiency occurred in the green/yellow region. The spectral resolution was better than $0.6 \, cm^{-1}$/pixel (for 514.5 nm) and $0.8 \, cm^{-1}$/pixel (for 488 nm) within the whole spectral range of interest. The micro-probe setup was also coupled to a camera which allowed for the exploration and selection of the sample region to be measured. All the spectra were calibrated in wavenumber using the emission lines of an Ar spectral lamp and the Raman peak of an O_2 molecule in air, occurring at $1550.5 \, cm^{-1}$, as well. The spectra reproducibility was monitored by means of repeated micro-Raman measurements carried out under the same experimental conditions from several grains, both in the middle and at the boundaries, of the densified LATPx pellets. In general, the spectra recorded from corresponding regions of different grains were matched perfectly.

In order to investigate possible proton substitution of Li, two samples with composition LATP0.5 were selected for X-ray powder diffraction (XRD) and ND experiments: one sample was handled and kept in dry Ar (hereafter named LATP_dry) and another sample was immersed in deionized water for 24 h and subsequently stored in air (LATP_wet). The diffraction experiments were carried out on a Bruker D4 diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å) and the time-of-flight (TOF) diffractometer POWGEN at the Spallation Neutron Source at the Oak Ridge National Laboratory. Unit cell parameters of both samples were determined with the program Powder cell [23]. For the ND experiments, the samples (~3 g) were placed in vanadium cans with 10 mm diameter. Data were collected in the TOF range between 6780 μs and 205,000 μs with two different wavelength bands of 1.066 Å and 2.665 Å at low temperature (10 K) and room temperature (300 K).

For structural Rietveld analyses and the calculation of Fourier difference maps to locate Li and H atoms, a combination of the programs FullProf [24] and Jana2006 [25] was used. The background was fitted by manually set points and linear interpolation. Peak profiles were modeled using pseudo-Voigt functions with back-to-back exponentials. Both samples showed one weak reflection of a minor amount of a secondary phase, which was identified as $AlPO_4$ and was only observed by ND. Rietveld analyses on phase fractions of $AlPO_4$ resulted in amounts of < 0.5 wt%. Hence, for the refinements with full-matrix least-square against F^2 only the NASICON-type structure was considered.