

Influence of synthesis parameters on the electrical and structural properties of nanostructured $\text{BPO}_4\text{-Li}_2\text{O}$

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Abstract

Li-doped BPO_4 is a promising ceramic Li^+ -ion conducting electrolyte for all-solid-state Li-ion batteries. The influence of the synthesis conditions on the structural and electrical properties of nanostructured Li-doped BPO_4 was investigated. The particle size of the material can be changed by varying the synthesis parameters. In order to investigate the relation between the particle size and the Li^+ -ion conductivity a series of samples was synthesized for temperatures between 150 and 600°C for 1.3 to 10 h. Two different synthesis routes were used and the composition, phase(s), Li^+ -ion conductivity, particle size, and particle morphology have been determined. As a result, single-phase Li-doped BPO_4 with a particle size of 30 nm was obtained at a synthesis temperature as low as 150°C and synthesis time of only 5 h. Furthermore, a smaller particle size results in a higher Li^+ -ion conductivity. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the quest of finding an appropriate Li^+ -ion conducting ceramic electrolyte for Li-ion batteries, Li-doped BPO_4 seems to be a promising material. The advantages of all ceramic Li-ion batteries are widely recognized, but several hurdles have to be overcome. The hurdles to be surmounted are the relatively low Li^+ -ion conductivity and poor interfacial contacts with the ceramic electrodes. In previous papers [1–3], it was shown that the interface problems can be solved using dynamic compaction. The internal resistance of the Li-ion battery can be reduced by dynamic compaction of wound thin foils of active materials in a polymer binder. In this way sufficient interfacial contacts and large contact areas are obtained, resulting in a lower internal resistance. The Li^+ -ion conductivity as a function of the Li-doping level and the defect chemistry of this doped material were recently described by Jak et al. [4,5]. In this paper we focus on the optimization of the Li^+ -ion conductivity of Li-doped BPO_4 by changing the particle size at a fixed Li-doping level of 10 mole% Li,

i.e., $\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$, according to the defect model presented in Ref. [5]. One of the objectives of this work is to decrease the particle size and to study the influence of the size of the nanostructured particles on the ionic conductivity. In order to decrease the particle size, the synthesis parameters time and temperature were varied.

2. Experimental

Two series of Li-doped BPO_4 with 10 mole% Li ($\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$) were synthesized using different synthesis temperatures and times. Two synthesis methods were used: the $\text{P}_2\text{O}_5 + \text{H}_3\text{BO}_3 + \text{LiOH} \cdot \text{H}_2\text{O}$ synthesis method [6] and the $\text{H}_2\text{NH}_4\text{PO}_4 + \text{H}_3\text{BO}_3 + \text{LiOH} \cdot \text{H}_2\text{O}$ synthesis method [7]. In both synthesis methods, a few milliliters of CO_2 -free water were added and the precursors were used in a stoichiometrical ratio. Synthesis temperatures of 150, 300 and 600°C were used and synthesis times of 1.3, 2.5, 5 and 10 h. All syntheses were performed in air in a programmable furnace (NEY 2-525 series II). After synthesis, the samples were ball-milled using a planetary micro mill (Fritsch Pulverisette 7) in order to break up the agglomerates down to approximately 10 μm .

The dried powders were investigated using X-ray Diffraction (XRD, Siemens D500 diffractometer with inci-

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dent beam $\text{Co K}\alpha_1$ monochromator and position sensitive detector), Scanning Electron Microscopy (SEM, Jeol 5800 LV), Differential Scanning Calorimetry (DSC, Perkin-Elmer DSC 7), and Inductively-Coupled-Plasma Optical-Emission-Spectroscopy (ICP-OES, Perkin-Elmer Plasma 40). The Li^+ -ion conductivity was measured with AC-Impedance Spectroscopy (AC-IS, Schlumberger Solartron 1260) in a He-filled glove box.

From the XRD spectra the phase purity and particle size were deduced. Two spectra were recorded for each sample. One spectrum per sample was recorded within $20^\circ < 2\theta < 70^\circ$ with a step size of 0.050° and a counting time of 100 s. This spectrum was used to investigate the phase purity. The second spectrum was recorded within $73.5^\circ < 2\theta < 78.0^\circ$ with a step size of 0.020° and a counting time of 480 s. This second spectrum was used to calculate the integral peak width from the 75.5° (213) reflection. The particle sizes were calculated from fitting the spectra (EVA 3.10) and the derived integral peak width. The integral peak width was corrected using a SiO_2 and Al reference. The reflections of the references at 76.0° and 77.35° were used, respectively. The Scherrer equation [8] was used to calculate the particle size.

The calculated particle size from XRD spectra was cross-checked by SEM. Furthermore, SEM was used to compare particle morphologies of the powders. DSC was conducted on the powders in the temperature range from 50 to 700°C in order to investigate possible irreversible reactions and the eventual presence of precursor compounds left. The samples were placed in a platinum crucible and a heating rate of $20^\circ\text{C}/\text{min}$ was used. The experiments were performed under an argon atmosphere.

AC-IS measurements were performed at room temperature in a He-filled glove box with a voltage amplitude of 50 mV over a frequency range from 0.01 or 0.1 Hz to 10 MHz. The powders are pelletized by using Magnetic Pulse Compaction (MPC [3]) with a pressure pulse of about 1.0 GPa for 200 μs . As a result pellets with a diameter of 15.0 mm and a thickness of about 1.5 mm were obtained. The density of the pellets was about 65% of the theoretical density. Prior to the impedance measurements, the pellets were dried for several days at 80°C under vacuum. On both sides of the pellet, glass fiber membranes filled with a liquid electrolyte (1 M LiPF_6 in EC/DMC 1:2 volume ratio (Mitsubishi Chemical) and metallic Li electrodes were applied. To prevent leakage of the liquid electrolyte over the periphery of the pellet, the diameters of the glass fiber and Li electrodes were smaller than the pellet (10 mm instead of 15 mm). Subsequently, the symmetrical cell was placed in a gas tight cell holder.

3. Results and discussion

From Ref. [7], it is known that the $\text{H}_2\text{NH}_4\text{PO}_4$ synthesis results in a white ceramic foam of crystalline BPO_4 .

The P_2O_5 synthesis results in white solid material. However, at the low synthesis temperatures (150 and 300°C), the $\text{H}_2\text{NH}_4\text{PO}_4$ synthesis results in a mixture of foam and a glassy product. The P_2O_5 -synthesized materials look the same for practically all synthesis times and temperatures except for the 150°C 1.3 and 2.5 h syntheses. These two samples were still wet after synthesis and will not be discussed. XRD spectra of the P_2O_5 -synthesized material show identical spectra at all synthesis conditions. The spectra are concordant with literature data of undoped BPO_4 [9]. No peak shift as a function of the synthesis parameters is observed, only a change in peak width and intensity. No second phase is visible. In Table 1, the particle sizes are listed. An increase in particle size from 28 to 42 nm is found with increasing synthesis temperature. The synthesis time does not influence the particle size.

On the other hand the XRD spectra of the $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized materials show a strong dependency on the synthesis parameters. The material synthesized at 150°C is fully amorphous. The samples synthesized at 300°C for 1.3 and 2.5 h are amorphous, but the samples synthesized for 5 and 10 h show the presence of an amorphous phase with reflections of crystalline BPO_4 and $\text{H}_2\text{NH}_4\text{PO}_4$ (peaks A and D, Fig. 1). The XRD spectrum of the 300°C 1.3 h synthesis shows the presence of boron oxides and boron hydrates (peaks C and D). At a synthesis temperature of 600°C , the spectra are concordant with literature data [9] and no second phases are visible. A slight peak shift and a significant change in peak width and intensity as a function of the synthesis time are observed. In Table 1, the particle sizes are listed. The $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples at 150°C are not included since they are amorphous. The samples synthesized at 300°C are partially amorphous and, therefore, the calculated particle sizes are doubtful. The samples synthesized at 600°C show an increasing particle size with increasing synthesis time. The particle size increases from 18 to 33 nm and are smaller than the

Table 1
Particle sizes calculated from XRD spectra ((213) reflection)

Temperature [$^\circ\text{C}$]	Time [h]	Particle size [nm]	
		P_2O_5 -synthesis	$\text{H}_2\text{NH}_4\text{PO}_4$ -synthesis
150	5	30	–
150	10	28	–
300	1.3	29	15 ^a
300	2.5	33	29 ^a
300	5	31	67 ^a
300	10	30	13 ^a
600	1.3	41	18
600	2.5	40	24
600	5	39	27
600	10	42	33

^aAmorphous phase present.

Parameters used in Scherrer equation: $\lambda_{\text{Coka}} = 1.7890 \text{ \AA}$; $\beta_{\text{apparatus}} = 0.0022 \text{ rad}$; shape factor, $k = 0.9$.

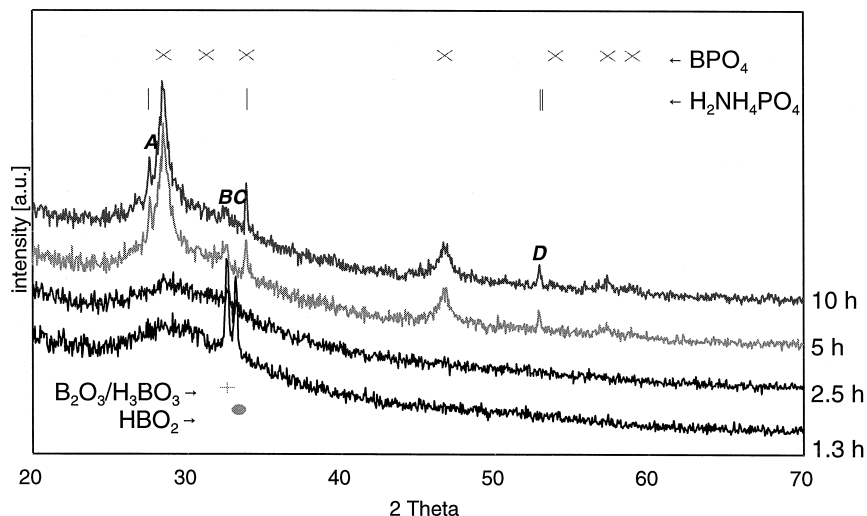


Fig. 1. XRD spectra $\text{H}_2\text{NH}_4\text{PO}_4$ -based synthesis (synthesized at 300°C). (Labels A–D see text).

particle sizes of the P_2O_5 -synthesized material at this temperature.

SEM analysis of the P_2O_5 -synthesized material shows agglomerates of spherical particles at all synthesis conditions used. The particle sizes estimated from SEM pictures agree with those calculated from XRD spectra. The $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples at 300°C show large glass-like particles (Fig. 2), which morphology is completely different from the samples synthesized at 600°C . The particles of the samples synthesized at 600°C are spherical and comparable with the P_2O_5 -synthesized material and the estimated particle size agrees with the XRD results.

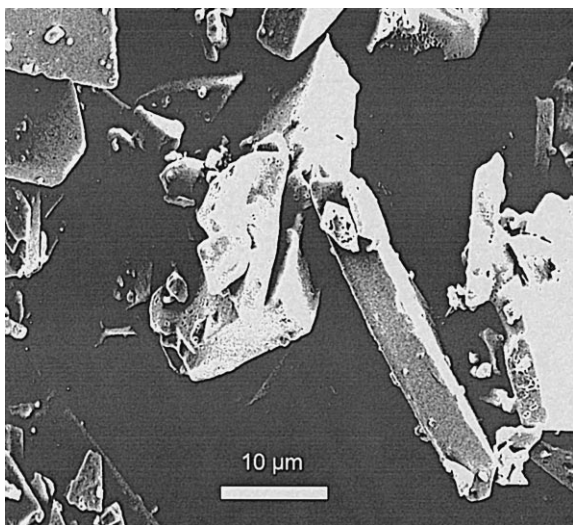


Fig. 2. SEM micrograph $\text{H}_2\text{NH}_4\text{PO}_4$ -based synthesis (synthesized at 300°C , 1.3 h).

From ICP-OES, the overall composition of the samples is calculated. All the P_2O_5 -synthesized samples have the correct stoichiometry ($\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$) in concordance with the defect model presented in Ref. [5]. The $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples made at 600°C reveal similar stoichiometry, but the samples synthesized at 300°C have a boron as well as a phosphorus deficiency.

DSC measurements of $\text{LiOH} \cdot \text{H}_2\text{O}$ show the release of physically bound water at 80 to 130°C and melting of LiOH at 450°C [10]. In the DSC spectrum of H_3BO_3 , the different dehydration steps are visible at 90 to 135°C (physically bound water), 170°C ($\text{H}_3\text{BO}_3 \rightarrow \text{HBO}_2$), 240°C (melting of HBO_2), and at 300°C ($\text{HBO}_2 \rightarrow \text{B}_2\text{O}_3$). These borates were also visible in the XRD spectra of the $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples at 300°C .

According to literature [11], P_2O_5 sublimates at 300°C . During mixing of the precursors and addition of cold water, a strong exothermal reaction takes place. When a few milliliters of cold water is added to a crucible with a few grams of P_2O_5 in which a thermocouple is placed, the temperature already exceeds 250°C , therefore, P_2O_5 probably sublimates already when water is added during synthesis. A synthesis temperature of 150°C is only necessary to dry the synthesized powder and is not important for the synthesis itself. The DSC spectra of all the P_2O_5 -synthesized samples do not show any clear peaks, except for some physically bound water at about 120°C . The absence of peaks in the DSC spectra recorded from 50 to 700°C proves that no precursor compounds are left at any synthesis time and temperature used, which is confirmed by the XRD results.

The DSC spectrum of $\text{H}_2\text{NH}_4\text{PO}_4$ shows melting at 195°C and boiling and/or decomposition in the temperature range of 300 to 340°C . The DSC spectra of the $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples at 300°C show two peaks

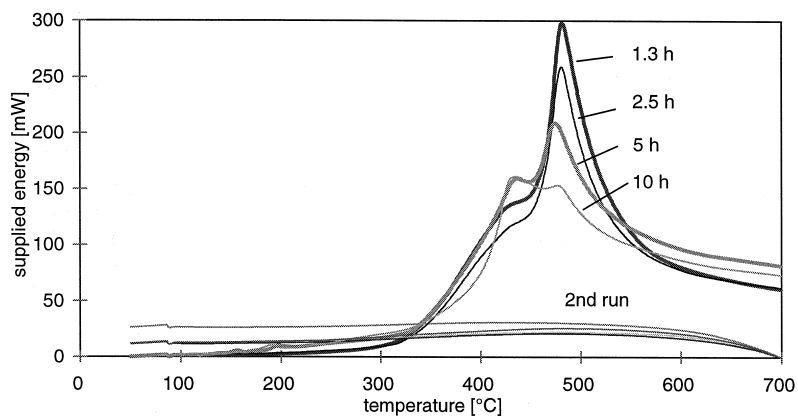


Fig. 3. DSC spectra $\text{H}_2\text{NH}_4\text{PO}_4$ -based synthesis (synthesized at 300°C , labels indicate synthesis time).

(Fig. 3). One peak starts at 330°C which increases with increasing synthesis time and one at 450°C which decreases with increasing synthesis time. The peak starting at 330°C can be attributed to decomposition of $\text{H}_2\text{NH}_4\text{PO}_4$ and/or the transition of HBO_2 to B_2O_3 . The peak starting at 450°C indicates melting of LiOH or B_2O_3 [10]. When the DSC results are combined with the XRD results, one can distinguish which transitions take place. In the XRD spectra, a decrease in peaks B and C is observed with increasing synthesis time. These two peaks are attributed to borates. In the DSC spectra, a decrease of the 450°C peak is visible. Combination of these results indicate that the DSC peak at 450°C is a result of melting of B_2O_3 instead of LiOH . A similar approach can be used for the 330°C DSC peak and the XRD peaks A and D. Peaks A and D increase with increasing synthesis time and the 330°C peak in the DSC spectra also increases. Peaks A and D are attributed to $\text{H}_2\text{NH}_4\text{PO}_4$, and, therefore, the 330°C

peak is most probably due to decomposition of $\text{H}_2\text{NH}_4\text{PO}_4$.

The presence of these two peaks proves that crystalline Li-doped BPO_4 cannot be synthesized below 300°C . After cooling down to room temperature, a second run is performed. In the spectra of the second run, all peaks are absent. The DSC spectra of the $\text{H}_2\text{NH}_4\text{PO}_4$ -synthesized samples at 600°C do not show any peaks, indicating a complete transformation of the precursor materials into Li-doped BPO_4 .

Preliminary results of the total Li^+ -ion conductivity of the MPC samples are obtained from AC-IS measurements. In Fig. 4, the total Li^+ -ion conductivity as a function of the particle size is presented for the P_2O_5 -based synthesis. Here, the total ionic conductivity represents the sum of the grain boundary and the bulk conductivity. A decrease in total ionic conductivity with increasing particle size is observed.

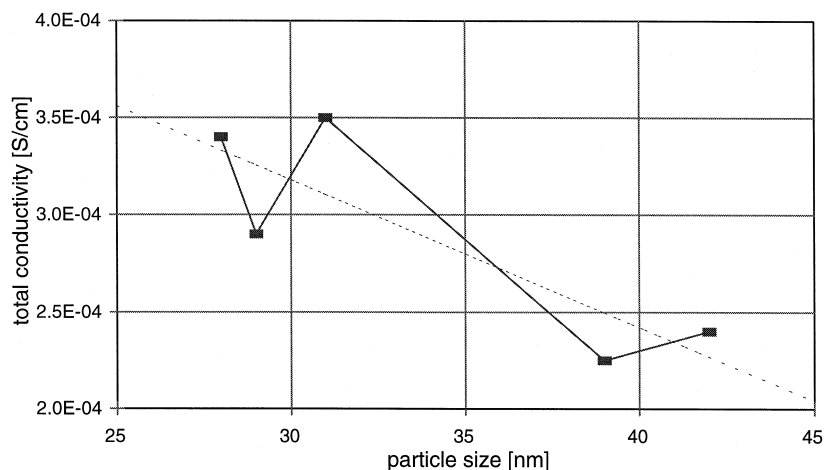


Fig. 4. Total ionic conductivity at room temperature as a function of the particle size. Cell: Li glass fiber + LiPF_6 BPO_4 (P_2O_5 -based synthesis) glass fiber + LiPF_6 Li.

4. Conclusions

Crystalline single-phase Li-doped BPO_4 with 10 mole% Li ($\text{Li}_{0.1}\text{B}_{0.967}\text{PO}_4$) can be obtained by synthesizing a mixture of $\text{P}_2\text{O}_5 + \text{H}_3\text{BO}_3 + \text{LiOH} \cdot \text{H}_2\text{O}$ at 150°C for 5 h in air. With these synthesis parameters, the resulting particle size is 30 nm. With increasing synthesis temperature, the particle size increases to 42 nm. When $\text{H}_2\text{NH}_4\text{PO}_4$ instead of P_2O_5 is used, a synthesis temperature of at least 450°C is necessary. At 300°C , there are still considerable amounts of $\text{H}_2\text{NH}_4\text{PO}_4$ and borates present. At 600°C , the particle size increases from 18 to 33 nm with increasing synthesis time, which is smaller than obtained with the P_2O_5 -based synthesis.

Preliminary impedance spectroscopy measurements show an increasing total Li^+ -ion conductivity with decreasing particle size. Assuming a similar bulk conductivity of the samples, this dependency may be attributed to grain boundary conductivity, as smaller particles result in a larger number of grain boundaries per unit of volume, and hence, an increased conductivity.

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