A new ceramic lithium solid electrolyte for rechargeable swing type batteries

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Abstract

BPO₄ is synthesized using a soft-chemical route. A substantial amount of lithium can be dissolved in the BPO₄ lattice, rendering solid solutions of $x\text{Li}_2\text{O}-\text{BPO}_4$ a lithium-ion-conducting electrolyte. Two syntheses are described to form $x\text{Li}_2\text{O}-\text{BPO}_4$ electrolytes, one resulting in the formation of ultrafine powders which can be used for dynamic compaction.

Keywords: Solid electrolytes; Ion conductivity; Lithium ion batteries

1. Introduction

During the past years a vast study is undertaken in search for Li⁺ ion conducting solids with potential use as electrolytes in, for instance, rechargeable batteries or smart windows. Unfortunately, a number of these solid electrolytes are not stable towards metallic lithium. Nevertheless, several interesting stable electrolytes were reported having good ionic conductivity, such as orthosilicates and germanates (Li₄SiO₄) [1,2], Li_(4-3x)Al_xGeO₄ [3], aluminates (Li₅AlO₄) [4], titanates Li₂Zr_(1-x)Ti_xO₃ [5], vanadates [6], and phosphates (Li_(1+x)Ti₂Si_xP_(3-x)O₁₂, Li_(1+x)M_xTi_(2-x)(PO₄)₃, M = Al, Cr, Ga, Fe, Sc, In, Lu, Y, or La) [7]. However, most of those electrolytes contain exotic and/or expensive metallic ions.

In this study we report on an inexpensive Li⁺ ion conducting solid electrolyte, lithia–boron phosphate, $\frac{1}{2}x\text{Li}_2\text{O}-\text{BPO}_4$ ($0.0 < x < 0.30$), which is synthe-

ized by a very simple synthesis using readily available precursor compounds.

BPO₄ is known as a SiO₂ (quartz) analogue [8–10]. However, at low temperatures it is claimed to crystallize in the tetragonal structure with lattice parameters $a = 4.34253 \text{ \AA}$ and $b = 6.6415 \text{ \AA}$ (JCPDS 34-132 [11]), a density of 2.802 g/cm^3 [11], an average index of refraction of 1.597 [11], and a thermal expansion coefficient of $9 \cdot 10^{-6} \text{ cm/cm per K}$ [12].

In addition, BPO₄ synthesized by B₂O₃ and P₂O₅ (or boric acid and phosphoric acid) has shown to be a good binder material for ceramic materials [13]. In fact, at our laboratory mixtures of concentrated boric acid and phosphoric acid proved to be a very good ceramic glue which can be used, for instance, to fire alumina chips together.

$\frac{1}{2}x\text{Li}_2\text{O}-\text{BPO}_4$ solid solutions are reported to be non-glass-forming [14] at x values below 1. Near $x = 1$ the solid Li₂BPO₅ is probably formed as an analogue of the synthesis of Primault (cited by Schulze [11]), who found Na₂BPO₅ as a side-prod-

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uct for the synthesis of pure BPO_4 using Borax and phosphoric acid.

In analogy with SiO_2 , BPO_4 is assumed to be stable towards metallic lithium. In addition, since certain glasses containing SiO_2 -matrices show potential use as conductive solids, the lithium containing boron phosphate was assumed to exhibit good electrical properties.

Besides the synthesis of lithium battery components, part of the research program is focused on the dynamic compaction of ceramic powders of solid state electrochemical device components. Dynamic compaction requires ultrafine powders. The present powders of $\text{Li}_2\text{O-BPO}_4$ are well suited for the dynamic compaction process.

In addition, it is shown that the use of ammonium ions in the wet-chemical synthesis leads to the formation of a foam, irrespective of whether pure BPO_4 or $\text{Li}_2\text{O-BPO}_4$ is formed. The electrical properties of solid electrolytes in the system $\text{Li}_2\text{O-BPO}_4$ are studied with impedance spectroscopy as a function of temperature and composition. The impedance spectroscopy measurements are performed at ambient atmosphere.

2. Experimental aspects

2.1. Synthesis of samples of BPO_4 from boric acid and phosphoric acid

Equimolar amounts of boric acid (H_3BO_3) and phosphoric acid (H_3PO_4) were mixed in water. To the white paste formed certain amounts of $\text{LiOH} \cdot \text{H}_2\text{O}$ were added. Several drops of the paste were used to form a uniform inner layer between two carbon platelets (15×15 mm). The samples were heated in air using a programmable oven (NEY 2-525 series II) with the following temperature program:

- heating from room temperature to 110°C at $2^\circ\text{C}/\text{min}$,
- keeping the samples at 110°C for 2 h,
- heating from 110 to 500°C at $4^\circ\text{C}/\text{min}$,
- keeping the samples at 500°C (the reaction temperature) for 6 h,
- allowing the samples to cool down in the oven to room temperature.

The thickness of the samples turned out to be about 0.5 mm. The samples were then used for AC impedance spectroscopy measurements.

2.2. Synthesis of the powders

Equimolar amounts of boric acid (H_3BO_3) and a phosphorus reactant (H_3PO_4 , $\text{H}_2\text{NH}_4\text{PO}_4$, or $\text{H}(\text{NH}_4)_2\text{PO}_4$) were mixed in water or $\text{NH}_3/\text{H}_2\text{O}$ mixtures in order to obtain a foam which results from the reaction. A maximum expansion of the foam is determined as a function of the phosphorus to nitrogen (NH_3 or NH_4^+) ratio. The reaction vessel used was a borosilicate test tube (inner diameter 14 mm and height 16 cm) covered with an aluminium foil cap, containing a small hole of about 1 mm diameter in order to release the volatile reaction products. The mixtures were heated in air using the following temperature program:

- heating from room temperature to 110°C at $1^\circ\text{C}/\text{min}$,
- keeping the mixtures at 110°C for 1 h,
- heating from 110 to 600°C at $2^\circ\text{C}/\text{min}$,
- keeping the mixtures at 600°C (the reaction temperature) for 10 h,
- allowing the mixtures to cool down in the oven to room temperature.

At the maximum expansion observed, several series of powders of $\text{Li}_2\text{O-BPO}_4$ were synthesized in about 1 g portions (10 mmol) at different reaction temperatures, i.e. 400 , 500 , 600 and 800°C . For the powders synthesized at 800°C a porcelain test tube was used. The white foamy reaction products were pulverized in a mortar and characterized by X-ray Diffraction (XRD) using a Philips PW 1840 Diffractometer equipped with a $\text{CuK}\alpha$ source operating at 40 kV and 50 mA. Scanning Electron Microscopy (SEM) is performed with a Philips SEM in order to obtain the primary particle size of the pulverized foam.

2.3. Impedance spectroscopy measurements

Impedance spectroscopy measurements were performed on two different samples, which are: (1) samples made by boric acid and phosphoric acid, using carbon substrates as electrodes (2) pellets of

pressed powders containing 10 w/o of binder material (Hoechst Micropulver). The pellets were heated at 600°C for 10 h prior to the AC impedance measurements. Platinum electrodes were sputtered with an Edwards sputter coater S150B.

The impedance measurements were executed with a Schlumberger Solartron 1260. The applied voltage amplitude is 100 mV and the frequency ranges from 0.01 Hz to 30 MHz. The measurements are performed between 22 and 90°C.

3. Results and discussion

3.1. BPO_4 samples from boric acid and phosphoric acid

The Li_2O-BPO_4 layers made by boric acid and phosphoric acid after firing show good contact with the carbon electrodes. The impedance spectra reveal the following results.

Fig. 1 shows a representative AC impedance spectrum of the cells $C|Li_2O-BPO_4|C$. The overall ionic resistivity is taken from the intercept of the Warburg impedance with the ordinate.

Fig. 2 shows the Arrhenius plot of the experimental bulk conductivities of a sample with $x = 0.1$. The activation energy is found to be 0.3 eV and appears to be almost independent on the lithium content x .

Finally Fig. 3 presents the room temperature

Fig. 1. Impedance spectrum of $0.035Li_2O-BPO_4$ synthesized from H_3BO_3 , H_3PO_4 and $LiOH \cdot H_2O$ with carbon electrodes. The spectrum is representative for all other samples. The frequency range is 0.1 Hz to 5 MHz and the temperature is 100°C.

Fig. 2. Arrhenius plot of $\ln(\sigma T)$ versus $1/T$ of $0.05Li_2O-BPO_4$ synthesized from H_3BO_3 , H_3PO_4 and $LiOH \cdot H_2O$ with carbon electrodes. Below 250°C the activation energy is 0.3 eV.

Fig. 3. Room temperature conductivity, $\sigma(298)$, of samples of $\frac{1}{2}xLi_2O-BPO_4$ synthesized from H_3BO_3 , H_3PO_4 and $LiOH \cdot H_2O$.

conductivities as a function of the lithium content x in the BPO_4 samples. At $x = 0.07$ a maximum is observed.

3.2. Synthesis and characterization of Li_2O-BPO_4 powders using ammoniumphosphate reactants

Fig. 4 presents the expansion ratio which is taken to be the ratio of the final volume of the foam and the starting volume of the reactants. From this figure it is clear that the expansion ratio reveals a plateau for N/P ratios (y) between 1 and 2. However, a rough maximum can be assigned at $y = 1$, and therefore, $H_2NH_4PO_4$ is used as phosphorus reactant in order to form the Li_2O-BPO_4 powders. During

Fig. 4. Volume expansion ratio as a function of the N/P ratio y . Actually, y is defined by the ratio $[\text{NH}_4^+]/[\text{PO}_4^{3-}]$.

the heating procedure all samples became completely transparent between 170 and 190°C, while the total reaction volume remains almost constant. Between 200 and 300°C the reaction mixture loses H_2O and NH_3 , upon which a vitreous compound is formed. At higher temperatures the mixture starts to foam. Initially the foam is transparent, then becomes opaque, and finally changes to a white foam.

The expansion ratio of the final volume and initial volume is about 15 to 30, but at certain lithium contents it even can reach a ratio of 30 to 50. Since NH_3 is lost only at temperatures higher than 200°C, it is assumed that formation of BPO_4 occurs between 200 and 300°C. $\text{H}_2\text{NH}_4\text{PO}_4$ is reported to melt at 190°C after which it decomposes [15]. It is also reported that BPO_4 occurs in two modifications summarized as 'soluble' and 'non-soluble' in water [16]. Note that soluble here means merely dispersible. The XRD patterns of the 'soluble' and 'non-soluble' BPO_4 are the same [16]. The 'soluble' to 'non-soluble' transition temperature lies between 400 and 500°C [16]. In addition to these BPO_4 compounds, BPO_4 exists also in hydrates written as $\text{BPO}_4 \cdot n\text{H}_2\text{O}$ with $1 < n < 6$. The XRD pattern of $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$ is reported by Gruner [16], and appears to have the same diffraction angles as H_3BO_3 . The BPO_4 powders synthesized at 400°C are very hygroscopic, and probably the 'soluble' BPO_4 product is formed here in accordance with Gruner [16]. The XRD patterns of all the other powders synthesized

above 400°C show after several days an extra peak in the XRD patterns near $d = 3.17 \text{ \AA}$, which results from either $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$ or from H_3BO_3 [16]. Drying the powder at 150°C for 2 hours prior to the XRD experiments results in a complete loss of the peak near $d = 3.17 \text{ \AA}$. Besides, since differential scanning calorimetry (DSC) measurements of H_3BO_3 show losses of water only at temperatures above 170°C, it seems unlikely that the $d = 3.17 \text{ \AA}$ results from H_3BO_3 . Therefore, it is plausible that $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$ is present as a side-fraction which is formed by water adsorption upon storage. For the powders synthesized at temperatures above 400°C, it is assumed that only the 'non-soluble' BPO_4 product is formed and that the powders are covered by a thin layer of $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$, which loses water already below 150°C. In some instances small traces of LiPO_3 and $\text{Li}_4\text{P}_2\text{O}_7$ are observed by XRD. SEM micrographs the pulverized foam are presented in Fig. 5. They show the primary particles to be about 100 nm (Fig. 5b). The particles are strongly agglomerated in spheres of about 2 μm . Due to the small primary particles, the powders are very sinter active.

3.3. Impedance spectroscopy measurements

Fig. 6 presents representative AC impedance spectra of the pellets recorded at several different temperatures. The results can be summarized as follows:

1. At low temperature (below 24°C) the spectra contain one (or two overlapping) semi-circles and sometimes a Warburg kind behaviour at low frequencies (below 0.1 Hz, which is not shown in Fig. 6).
2. Increasing the temperature, the total impedance of the overlapping semi-circles increases enormously. This results in an almost vertical straight line at higher temperatures (between 60 and 90°C).
3. At even higher temperatures (between 100 and 250°C), again a semi-circle is observed, with a diameter decreasing with increasing temperature.
4. When the pellets are cooled down to room temperature, the measured semi-circle is much larger compared to the starting situation (up to five times).
5. The spectra do not cross the origin.

Fig. 5. (a) SEM micrograph of $0.035\text{Li}_2\text{O}-\text{BPO}_4$ as synthesized. (b) SEM micrograph of the primary particles of $0.035\text{Li}_2\text{O}-\text{BPO}_4$ as synthesized.

Fig. 6. Impedance spectra of $0.075\text{Li}_2\text{O}-\text{BPO}_4$.

These observations can be well explained by the results obtained from XRD patterns. At low temperature (below 24°C) the powders (either pressed or not) contain $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$ at the surface. The water containing BPO_4 products are able to conduct the lithium ions quite easily, which means that the powders have a high surface conductivity, i.e. low resistivity in the AC impedance plots. By increasing the temperature water evaporates, and, thus, these very conductive surface regions disappear. Consequently this results in a lower overall conductivity probably determined by either the bulk or the grain boundaries, or both. Above 100°C all the water is lost, and, thus, at still higher temperatures, the conductivity increases according to the normal Arrhenius behaviour. A detailed study about these phenomena will be given in a forthcoming paper. If the pellet is allowed to cool down again to room temperature, the measured resistivity depends strongly on the amount of water again adsorbed at the surface of the grains. Remember that the impedance measurements were performed at ambient atmosphere. Therefore, ageing effects are an important feature in the conductivity of these powders. Hence, in order to measure the bulk conductivity, the samples should be dried prior to being used, and the measurements should be performed in dry atmosphere.

4. Conclusions

$\frac{1}{2}x\text{Li}_2\text{O}-\text{BPO}_4$ compounds can be used as lithium-ion-conducting electrolytes. Solid $\frac{1}{2}x\text{Li}_2\text{O}-\text{BPO}_4$ electrolytes can easily be formed in a one step process by boric acid and phosphoric acid to which $\text{LiOH} \cdot \text{H}_2\text{O}$ is added. The precursor mixture can be handled as a glue to paste certain objects. A maximum room temperature lithium-ion-conductivity is found to be $2 \cdot 10^{-6} \text{ S/cm}$ for $x = 0.07$, with an activation energy of about 0.3 eV.

Powders of $\frac{1}{2}x\text{Li}_2\text{O}-\text{BPO}_4$ are easily formed by addition of NH_3 to the precursor mixture. The reaction of this mixture results in foam formation, which, when pulverized, reveal ultrafine agglomerates with submicron primary particles.

The powders of BPO_4 have a hygroscopic surface which results in the formation of hydrates of BPO_4 ,

i.e., $\text{BPO}_4 \cdot 3\text{H}_2\text{O}$. This hygroscopic behaviour of the surface leads to a high conductivity state, which disappears at higher temperatures due to evaporation of water.

5. Comments

5.1. J. Fleig (Max-Planck-Institut, Stuttgart) asked the following questions:

(i) Is there an explanation for the deviation from Arrhenius behaviour at high temperature (Fig. 2)? Is it possible to reach again the starting value (cond. at 25°C) after heating (Fig. 2)?

(ii) Is it possible to explain the decrease of the conductivity for increasing Li concentration (Fig. 3)?

(iii) Could you observe a change in the conductivity due to annealing (powder samples)?

(iv) What was the low frequency limit in the measurements shown in Fig. 6?

(v) Did you obtain similar conductivity activation energies for the powders (above 100°C) and the other samples?

5.2. E.M. Kelder (Delft University of Technology) replied:

The conductivity plotted in Figs. 2 and 3 are derived directly from the intercept of the Warburg impedance with the ordinate as shown in Fig. 1. The observed value of the resistance becomes, therefore, a composed value of all the resistances present in the sample, for instance, bulk, grain boundary, and (hopefully not) electronic resistances. In order to derive the individual values of the resistances, an equivalent circuit should be used to which the data should be fitted. Unfortunately, at this moment we were not able to find such a circuit which covers all the data (both at different temperatures and different Li concentrations). The deviation from Arrhenius behaviour at high temperature could either be a transition in conduction mechanism or, what seems to be more realistic, a result of composite resistances, which behave differently as a function of temperature. A similar discussion can be held for question (ii) where the decrease of the conductivity for increasing Li concentration might be a result of an

increase in the grain boundary resistance. This might be plausible, since the samples with $x = 0.07$ appear to be sintered better, and are less brittle. The measurements presented in Fig. 1 are indeed fully reversible, thus, the deviation from Arrhenius behaviour is not coming from an irreversible reaction or process.

We indeed observe a change in conductivity due to annealing of the powder samples as suggested in question (iii). Physically adsorbed water results in an enormous increase in the overall conductivity. If the powders are annealed and stored in a dry box, the conductivity seems to become reversible, however, storage at ambient atmosphere leads to water adsorption, and, hence, a high overall conductivity. Recently, we measured a water adsorption between 50 and 200 mg per g BPO_4 , depending on the Li concentration.

The low frequency limit in the measurements shown in Fig. 6 is 0.1 Hz, however, for clearness of the high and low temperature data some data points are not shown.

All powders show a similar behaviour as a function of temperature. Up to now, we have not made AC impedance measurements on fully annealed powders in order to observe the bulk conductivities and activation energies. So, we are not in the position to compare the results of the two different sample materials. This will be done in the very near future.

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