Preparation and characterization of three dimensionally ordered macroporous 
Li₅La₃Ta₂O₁₂ by colloidal crystal templating for all-solid-state 
lithium-ion batteries

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Abstract

Three dimensionally ordered macroporous (3DOM) membranes of Li₅La₃Ta₂O₁₂ (LLTO) for all-solid-state lithium-ion batteries were prepared by using colloidal crystal templating of mono dispersed polystyrene (PS) spheres combined with sol–gel synthesis of LLTO precursor. During the sol–gel synthesis, the appropriate mixtures of CH₃COO Li, La(NO₃)₃·6H₂O and Ta(OC₂H₅)₅ were dissolved in two different solvents to prepare garnet-type LLTO. Various sizes of mono dispersed (1, 3 and 5 μm) PS beads were used as a template to investigate the size effect of template on the network formation of LLTO membranes. The transformation from precursor solutions, which are added onto the PS template, to crystalline phase, was investigated by TG analysis and X-ray powder diffraction (XRPD). The morphology of the PS templates and the 3DOM garnet membranes were investigated by Scanning Electron Microscopy. The templates made from 5 μm PS spheres were found to be the most suitable template to obtain 3DOM membranes of LLTO.
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1. Introduction

Rechargeable lithium-ion batteries are nowadays widely used as energy power supplies in various electronic devices due to their high energy density [1]. However, the conventional rechargeable batteries contain hazardous and flammable organic liquid electrolytes, making them potentially unsafe and reducing the cycle life due to formation of an irreversible solid electrolyte interface [2]. For these reasons, replacement of the liquid electrolyte with a safer and stable solid-electrolyte is necessary to improve the safety by preventing the risk of liquid electrolyte leakage and improving the cycling stability. Research efforts were directed towards finding suitable solid electrolytes for lithium ion batteries with high lithium ion conductivity as well as good chemical stability with commonly used intercalation materials for battery applications [3]. A wide range of compounds with different crystal structure types has been investigated, such as Li₄SiO₄, Li₂SO₄, Li₁₄ZnGe₂O₁₆, Li₁⁺ₓTi₂₋ₓMₓ(PO₄)₃ (M = Al, Sc, Y, La), Li-β-alumina and Li₀.₃₄La₀.₅TiO₂.₹₈ with perovskite crystal structure. Some of the reported ionic conductivities are in between 10⁻³ and 10⁻⁷ S/cm [4–10]. In addition to the above mentioned compounds, new classes of compounds with garnet-type structure have attracted great interest as potential solid-state lithium-ion conductors in the last few years. Compound series with the chemical formula Li₅La₃M₂O₁₂ (M = Nb, Ta),...
2. Experimental

2.1. Preparation of polystyrene (PS) colloidal crystal templates

Colloidal crystal templates of PS spheres were formed using gravitational settling in combination with evaporation to prepare the 3DOM Li$_5$La$_3$Ta$_2$O$_{12}$ solid electrolyte combined with sol–gel method. For gravitational settling in combination with evaporation, 2 ml water suspensions of 50 mg PS/ml (Sigma Aldrich) with various mono-dispersed PS bead sizes (1, 3, 5 μm) were prepared and placed inside a syringe (20 ml PE/PP BD Biscardit II) that was cut in half. Those were left to dry overnight at 333 K under atmospheric conditions. Finally, the PS templates were removed by pushing the plunger of the syringe.

2.2. Preparation of 3DOM Li$_5$La$_3$Ta$_2$O$_{12}$

Sol–gel synthesis of Li$_5$La$_3$Ta$_2$O$_{12}$ was done using two different solvents. In the first solution, lithium(I) acetate (99.95%, trace metal basis Aldrich Chemistry) was dissolved in ethanol (99.9%, Technisolve) whereas in the second solution it is dissolved in ethylene glycol (EG) (99% Merck KGaA) and glacial acetic acid (HAc) (100% Merck KGaA) used as chelating agent while stirring and heating at 343 K for 1 h under reflux conditions. The molar ratio of HAc and EG was kept as 3:2. Lanthanum(III) nitrate hexahydrate (99.999%, trace metal basis, Aldrich Chemistry) and tantalum(V) ethoxide (99.999%, Alfa Aesar) were added with molar ratio (Li:La:Ta) 6:3:2 in both solutions. A 20% excess amount of lithium was used to compensate for lithium evaporation and the concentration of the mixture solution was approximately 0.05 M. The whole mixture was stirred and heated at 343 K for 1 h under reflux conditions. Solvent evaporation was induced by heating the mixture to 393 K without refluxing and the concentration of the solutions was increased up to 0.1 M upon evaporating of the solvents. The mixture was left to cool at room temperature, yielding a low viscosity transparent precursor solution. The precursor solutions were added to the previously obtained PS templates using vacuum impregnation. Four drops of solution were added to the PS deposits after which the sample was heated to 303 K for 15 min under vacuum. This was repeated three times. Finally, the samples were heated at 973 K for 1 h under static air atmosphere to decompose the PS particles and to form the solid electrolyte.

2.3. Characterization

Thermogravimetric (TG) analysis using a Mettler Toledo TGA/SDTA 851 instrument was carried out on PS template filled with precursor solution in 70 μl Al$_2$O$_3$ crucibles from 300 to 1273 K with a heating rate of 5 K/min in flowing air (50 ml/min). X-ray powder diffraction (XRPD) analysis was performed to investigate the phase purity and crystal structure of the resulting porous membranes. Data were collected at room temperature with a Bruker Endaur D4 diffractometer using CuKα radiation in the 2 theta range 5° to 90° with a step size of 0.01° and a counting time of 1 s. The morphology of the PS templates as well as the porous membranes was investigated by Scanning Electron microscopy (SEM) using a Quanta 3D FEG instrument (FEI Company).

3. Results

3.1. Formation of colloidal crystal templates

Mono-dispersed polystyrene spheres with 1, 3 and 5 μm bead size were used to form the crystal templates by using gravitational settling in combination with evaporation to prepare the 3DOM Li$_5$La$_3$Ta$_2$O$_{12}$ solid. Fig. 1 shows the SEM pictures of the templates prepared by using various PS sphere sizes. It can be seen in the SEM micrographs that long range ordered templates with some stacking faults was prepared for further manipulations.
3.2. Decomposition of PS templates filled with precursor solution

PS templates were filled with garnet sol–gel precursors and dried at room temperature in a vacuum chamber. The dried samples were annealed under flowing air from room temperature to 1200 K at a rate of 5 K/min. During the removal of polystyrene templates and the crystallization of the garnet phase, the reaction mixtures undergo several processes, such as combustion of the PS template, decomposition of precursor solution, and oxidation. After the addition of precursor solutions onto the templates, the removal of PS and the formation of garnet compound were monitored by thermal analysis (TG/DTA) which is shown in Fig. 2. On the basis of thermal analysis of the sample prepared using HAc/EG as solvent, the weight decreases between 300 and 400 K and between 450 and 600 K are assigned to loss of residual solvents, HAc and EG, respectively. While, when PS is impregnated with EtOH containing precursor, the solvent evaporation is minor due to the low temperature evaporation of EtOH. At around 600 K, the weight loss accelerates for both precursor solutions, till it reaches 650 K due to combustion of the polystyrene. A slow and steady weight loss from 650 K to 950 K can be attributed to decomposition and oxidation of residual organics from the sol–gel precursors. There is no significant weight loss higher than 950 K for both types of precursors which is indicating that the transformation of the precursor to oxides starts above this temperature followed by crystallization of pure LLTO phase. This has also been verified by XRPD analyses.

3.3. Phase formation

Fig. 3 shows the XRPD patterns of calcined 3DOM LLTO prepared with two different solutions at 973 K. The PS template was filled with precursor solutions separately and
they are annealed at 973 K for 1 h reaction time. The
diffraction peaks of the 3DOM LLTO samples at 973 K match
very well with those of the corresponding garnet phase
Li$_5$La$_3$Ta$_2$O$_{12}$ without any other additional peaks. The crystal-
lite sizes of those samples were estimated from the line
broadening of the main peaks by using Scherrer equation. [21]

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray, $k$ is the constant (0.9),
$\theta$ is the diffraction angle and $\beta$ is the full width at half
maximum (FWHM). According to the calculations, the 3DOM
LLTO prepared using HAc/EG have larger crystallite size
(\approx 35 nm) than the EtOH used sample (\approx 24 nm). This can
be seen from the sharper X-ray diffraction peaks. These results
show that the precursor solutions are completely transformed
into garnet-type LLTO phases at 973 K.

3.4. Morphology of 3DOM LLTO

Figs. 4 and 5 show several SEM images of 3DOM LLTO
with various colloidal crystal templates sizes (1, 3, 5 μm) by
addition of EtOH based or HAc & EG mixture based precursor
solutions, respectively. All differently sized PS templates were
very well aligned as discussed in Section 3.1 in detail. As can
be seen in Fig. 4a and Fig. 5a, starting with very well aligned
1 μm PS template, this is yielding very dense LLTO materials.
This can be explained by the fact that the grains of the garnet
compound are growing too large and destroy the interstitial
space of the 1 μm PS template, which further prevents
the formation of the porous network. In addition, Gao et al.
showed that the HAc/EG mixture based solutions first decom-
pose to the LiLa$_2$TaO$_6$ phase with a crystal structure different
from garnet at 923 K, while above 973 K it is fully trans-
formed into the garnet phase in the sol–gel synthesis of
Li$_5$La$_3$Ta$_2$O$_{12}$ [22]. So the coalition and phase transformation
to the garnet compound of the intermediate phase above 923 K
could lead to agglomeration and result in large grains for
garnet phase LLTO. For 3DOM garnet-type LLTO originating
from 3 μm PS template, porous network formation is observed
as shown in Fig. 4b and Fig. 5b but there is some irregularity
in the long range order and there are break downs in the
network due to the shrinkage during calcinations. Significantly
improved network formation is obtained with the 5 μm PS
template compared to the other template sizes (Fig. 4c and
Fig. 5c). Moreover, it can be clearly seen in Fig. 4c and
Fig. 5c, that when HAc/EG mixture is used for the precursor
solution the network formation is further improved compared
to the EtOH based precursor. The alternating layers as well as
the long range order were obtained with combination of 5 μm
PS template and HAc/EG based LLTO precursor solution.

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**Fig. 4.** SEM image of 3DOM LLTO prepared using mono-dispersed PS templates (a) 1 μm, (b) 3 μm and (c) 5 μm combined with EtOH based precursor solution and annealed at 973 K for 1 h.

**Fig. 5.** SEM image of 3DOM LLTO prepared using mono-dispersed PS templates (a) 1 μm, (b) 3 μm and (c) 5 μm combined with HAc/EG based precursor solution and annealed at 973 K for 1 h.
(Fig. 6). In general, using HAc/EG as a solvent has a positive effect by increasing the grain size which enhances the interconnectivity of the network.

4. Conclusion

Three dimensionally ordered Li$_3$La$_3$Ta$_2$O$_{12}$ membranes with garnet-type structure were prepared by the colloidal crystal templating method using various sizes of mono-dispersed PS spheres, combined with two different sol–gel synthesis methods. Experiments were performed with both ethanol based LLTO precursor solutions as well as an acetic acid and ethylene glycol mixed-base solution. All of above mentioned different PS size templates yielded pure and crystalline garnet phase when they are annealed at 973 K. As we discussed before, three-dimensionally ordered macroporous (3DOM) structures can be used to enlarge the contact area between the solid electrolyte and electrode material when they are impregnated by electrode material. This can be achieved with porous and very well ordered 3DOM materials. Using 1 μm mono-dispersed PS template yielded an undesired dense LLTO membrane which is due to the large grains of the LLTO garnet phase. Porous 3DOM LLTO membranes were obtained with 3 μm spheres with absence of long range order and many defects. Our findings also showed that PS template with 5 μm beads is the optimum size for highly ordered and porous membranes. Further improvement in terms of long range order in network formation is also possible when the ethanol-based precursor solution is replaced with acetic acid and ethylene glycol mixture-based LLTO precursor solution. Unfortunately the mechanical properties of the 3DOM garnet-type LLTO membranes are poor and the membranes are very fragile which currently prevents us to perform the lithium ion conductivity measurements but the impregnation of electrode material would increase the mechanical properties of porous electrolyte materials.

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References

[14] V. Thangadurai, W. Weppner, Investigations on electrical conductivity and chemical compatibility between fast lithium ion conducting garnet-like Li$_5$Ba$_5$Al$_2$Ta$_2$O$_{12}$ and lithium battery cathodes, J. Power Sources 142 (2005) 339–344.