
Comprehensive electrochemical characterization of an LTO anode for an all-solid state thin-film microbattery

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Despite continuous improvements, lithium-ion batteries (LIB) struggle to meet the ever-increasing performance and safety requirements set by the modern consumer. All-solid-state batteries (ASSB) have recently been considered as a viable alternative, however, there are still multiple obstacles preventing broader commercialization of ASSBs. One of the major remaining challenges is the insufficient understanding of the electrochemical processes taking place on the electrode-solid electrolyte interface, which in turn leads to poor long-term battery performance. A scaled-down version of an ASSB, all-solid-state thin-film microbatteries (ATFB) have proven to be a valuable tool for studying interfacial processes, as well as finding practical use in different small-scale electronic devices. Proper characterization of such systems generally proves to be more difficult than for batteries with liquid electrolyte, as it is difficult to access the solid-solid interface without severely damaging the delicate thin film electrodes. The ability to employ *in-situ* characterization techniques therefore plays a key role in enabling a deeper understanding into the working principles of an ATFB. One of the most common *in-situ* electrochemical characterization techniques in battery research, electrochemical impedance spectroscopy (EIS) provides a non-destructive way to analyze the electrochemical behaviour of an electrode material in an already assembled ATFB.

One of the more widely used ATFB anode materials, spinel lithium titanate or LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) exhibits little volume change (0.2–0.3 %) and high stability during electrochemical cycling, which makes it an excellent candidate for use in ATFB model systems [1]. Our research encompasses the fabrication of a thin-film LTO anode with the pulsed laser deposition technique, and its subsequent structural and electrochemical characterization in different ATFB configurations, including a full-cell ATFB. One of our main goals is to perform a somewhat broader EIS characterization of such a system by employing a transmission line model (TLM), which is commonly used in LIB impedance modelling. Such a model could be used to obtain certain physically meaningful battery parameters, which are otherwise difficult to extract using less broadly applicable equivalent circuit models [2].

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How can we fabricate passive electronic components in a greener way?

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Going green and more efficient is the key to better living. In the electronic era, dielectric ceramics are widely used in wireless communication systems and various electronic devices. Even so, their large-scale production still requires high temperatures and negatively contributes to high energy consumption. One of the incentives to reduce the processing temperatures is Room Temperature Fabrication (RTF) of “upside-down” composites, which constitute of high loading of functional ceramic filler and a small amount of binder admixed to the ceramic particles in the form of a solid and saturated aqueous solution[1]. In this way, bulk ceramic upside-down lithium molybdate-strontium titanate (LMO-ST) composites were fabricated at room temperature [2]. As the LMO binder is deposited on the surface of ST filler particles during pressing and drying, composites densify. In our research, we were stepping through different stages of the process, to gain a deeper insight into and optimize the densification process. Up-to-now composites resulted in a sufficient binding with 76 to 85% relative density, relative permittivity in the range of 65–120 and dielectric loss tangent values of 0.002–0.05 at 1 MHz. By the fact that the connectivity of a composite plays a key role in its properties, we shed light on the investigation of the surface modification of ST, wetting, and the crystallization of the LMO. Results of mathematical predictions highlighted the influence of remaining porosity which has a detrimental effect on dielectric and mechanical properties. By addressing this, the fiber-reinforcement and impregnation post-treatment are under investigation. The implementation of different materials in multicomponent composites widens the range of functional properties prominent for electronic applications.

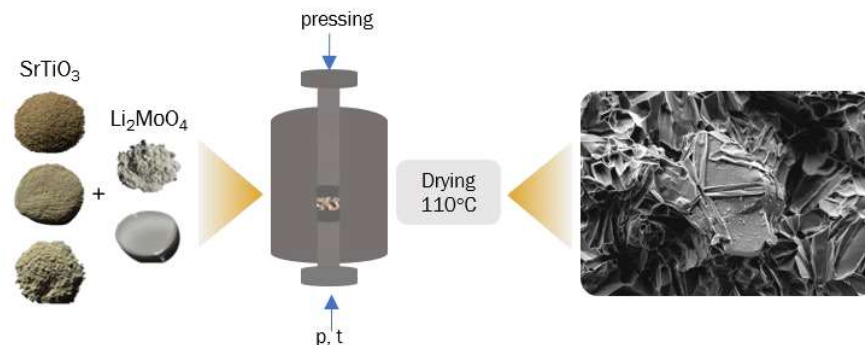


Figure 1. RTF processing of LMO-ST composites.

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Steering the Hydrothermal Topotactic Epitaxy of SrTiO₃ on Bi₄Ti₃O₁₂ Platelets by Supersaturation

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Engineering of functional materials, including photocatalysts, with improved properties, is possible when it is based on a detailed understanding of the reaction mechanisms and nucleation-crystallization processes. We are attempting to contribute to solutions for energy-related problems by the development of H₂ evolution photocatalysts based on heterostructures with improved charge carrier separation. Due to the favorable band edge positions and the similarity of crystal structures, the proposed candidates are epitaxially intergrown SrTiO₃/Bi₄Ti₃O₁₂ heterostructures. However, their formation under alkaline hydrothermal conditions is not straightforward and an understanding of the transformation process is needed. X-ray diffraction and electron microscopy techniques help us to understand this process, which occurs by Bi₄Ti₃O₁₂ dissolution and SrTiO₃ epitaxial growth until complete transformation into SrTiO₃ platelet. Nanoscale examination of the individual phases and the SrTiO₃/Bi₄Ti₃O₁₂ interface using a high-resolution transmission electron microscope (HR STEM) enabled us to determine the {110} Bi₄Ti₃O₁₂ || {100} SrTiO₃ orientation relationship and develop the understanding of the process at the atomic level. To be able to exert control over the nucleation crystallization process the interplay between interfacial free energy and supersaturation was investigated. For that purpose, we determined the lattice mismatch between {110} plane in Bi₄Ti₃O₁₂ and {100} in SrTiO₃. The misfit was found to be 1.78 %, which is an unavoidable contribution to interfacial free energy. On the contrary, our results accord with the theory and we can influence the nucleation and growth of SrTiO₃ by supersaturation and therefore, control the process by changing the molarity of NaOH and the initial Sr:Ti molar ratios. For example, at conditions with the initial stoichiometric Sr:Ti molar ratio and lower (2M) NaOH concentration the supersaturation is not large enough to enable SrTiO₃ overgrowth over the whole Bi₄Ti₃O₁₂ basal surface planes. Instead, SrTiO₃ island growth prevails. As the supersaturation increases by increasing the initial Sr:Ti molar ratio, the number of SrTiO₃ nuclei is becoming larger and their size is becoming smaller. Finally, at a 12-times higher Sr:Ti initial molar ratio than needed for theoretical SrTiO₃ formation, the layer-by-layer growth mechanism prevails over the island formation mechanism causing the intermediate SrTiO₃/Bi₄Ti₃O₁₂ and final SrTiO₃ nanostructures retain the platelet shape of the template. Understanding this particular transformation mechanism provides general design principles for the preparation of two-dimensional nanoheterostructures with epitaxial contact.

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Tailoring the microstructure of $\text{Li}_{0.33}\text{La}_{0.56}\square_{0.11}\text{TiO}_3$ through exaggerated grain growth

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Increasing demand for energy requires safe, stable, and powerful energy storage. One of the promising solutions are rechargeable Li-ion batteries with solid electrolyte and in particular perovskites such as $\text{Li}_{0.33}\text{La}_{0.56}\square_{0.11}\text{TiO}_3$ (LLTO) with excellent ionic conductivity [1], [2]. While LLTO grains may reach ionic conductivities as high as 10^{-3} S/cm, the grain boundaries exhibit orders of magnitude lower values that decrease the total ionic conductivity of the electrolyte. Our strategy to reduce the contribution of grain boundaries was to prepare coarse-grained LLTO by triggering exaggerated grain growth of LLTO grains, as previously reported in several other perovskite-based systems [3]. The samples with La:Ti ratios from 0.56 to 0.62 by systematically lowering the addition of TiO_2 were prepared via a conventional solid-state approach and sintered at 1250 and 1350 °C. The stoichiometric sample shows a typical uniform microstructure with an average grain size of ~ 5 μm , whereas the sample with La:Ti ratio of 0.61 has bimodal grain size distribution composed of elongated grains measuring up to 100 μm in length and surrounded by smaller grains. In this sample, we observed the presence of polytypic lamellae with structural characteristics of Ruddlesden-Popper type $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ phase and the elongation of the grains in the direction of the lamella. The presence of polytypic lamellae accelerates the growth of the matrix LLTO grains in the initial stages of grain growth (up to 1250 °C). The lamellae are thermally unstable at higher sintering temperatures (1350 °C) and recrystallize to perovskite LLTO. The result is LLTO ceramic microstructure with extremely large grains, measuring even more than 100 microns in diameter. To our best knowledge, a microstructure with so large grains has not been reported in LLTO ceramics before.

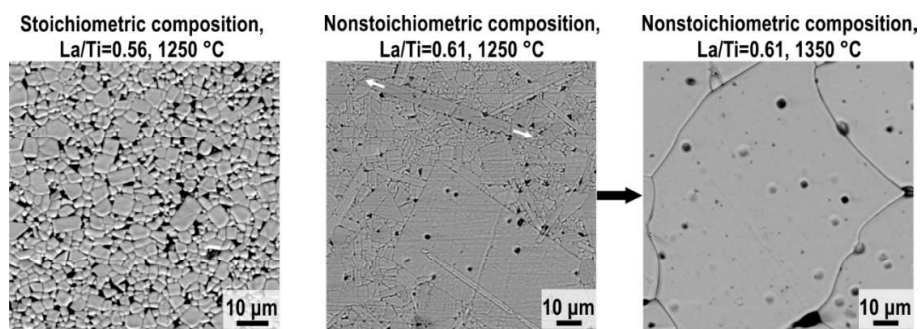


Figure 1. LLTO microstructure at different sintering temperatures and La/Ti ratio.

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Thin-film lithium manganese oxide cathodes synthesized by pulsed laser deposition

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Thin-film lithium-ion batteries have shown great potential for investigating properties of the intrinsic material and pursuing development of solid-state batteries. In order to study intrinsic properties of the material, additive-free cathodes are synthesized with pulsed laser deposition technique. One of the promising materials to use as a thin-film cathode is lithium-rich manganese oxide Li_2MnO_3 (LMO), due to its high specific capacity of 458 mAh/g. Nevertheless, the mechanism of lithium intercalation/deintercalation for Li_2MnO_3 is not fully understood; it has been reported that is intrinsically inactive because of high valence state of Mn^{4+} , still nanosized LMO is activated upon initial cycle and appears to have high specific capacity [1]. Significant amount of work was done on LMO thin-films, prepared with pulsed laser deposition technique, where the influence of deposition parameters on structure, morphology and electrochemical properties is thoroughly studied. In order to achieve high-quality thin-films with desired composition and crystal structure, one should carefully control an amount of lighter elements that can be scattered during plasma expansion, so thin-films of LMO often result in lithium and oxygen deficiency. To challenge this problems, lithium enriched targets are used to synthesize stoichiometric thin-film [2]. The aim of our research is understanding the influence of experimental parameters on final properties of synthesized thin films. In our work we synthesized LMO thin-films from home-made target with composition $\text{Li}_{3.2}\text{MnO}_3$ (60% lithium excess) on single crystal 0,5%wt Nb-doped SrTiO_3 (Nb:STO) substrates with (001) and (111) crystal orientation. We analysed synthesized thin-films using XRD to study the influence of Nb:STO substrate orientation on thin-film growth direction and AFM to determine morphological properties of the film.

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