

The demand for Li-ion batteries worldwide has experienced substantial growth in recent years, primarily driven by the increasing adoption of electric vehicles (EVs), portable electronic devices, and renewable energy storage systems. The automotive industry played a particularly significant role as automakers strive to transition toward electric and hybrid vehicles to reduce carbon emissions. Additionally, the broad worldwide adoption of renewable energy sources, such as solar and wind power, has contributed to the need for efficient energy storage solutions. In all cases, until now, Li-ion batteries were a preferred choice due to high energy storage density (both gravimetric and volumetric) as well as relatively long cycle life, in comparison to other energy storage technologies. Moreover, ongoing advancements in Li-ion technology, coupled with efforts to improve the energy density and cost-effectiveness are likely to further boost their demand across various industries. As the world seeks cleaner and more sustainable energy solutions, the demand for Li-ion batteries is expected to grow in the foreseeable future, which will pose certain challenges, e.g. materials availability issues. Therefore, sodium-ion batteries (Na-ion) are considered to address some of these challenges, mostly due to broader availability of sodium in comparison to lithium, as well as relatively lower price. However, Na-ion technology is not free of challenges though. Due to high ionic radius and relatively high atomic mass of sodium, Na-ion batteries show lower energy density and power output in comparison to Li-ion counterparts. Above issue can be hindered by developing materials with crystal structure tuned for high reversibility of charge/discharge processes that would allow for longer battery lifetime resulting in reduced cost of batteries replacement in large-scale storage systems. That's why studies in the field of Na-ion batteries are mostly focused on solutions for large-scale energy storage systems that aim to balance the demand and supply of electric energy in case of both conventional power plants and renewable energy sources.

The electrochemical characteristics of the battery hinge to a high degree on the careful selection and through investigation of electrode materials as well as the electrolyte. Given that the cathode material accounts for roughly 30% of the overall battery cost, the project will focus on the obtaining and optimising of polyanionic compounds with NASICON and alluaudite crystal structures, that may be cathodes for Na-ion batteries. Besides influence on capacity and reversibility of the whole cell, these materials should exhibit chemical and thermal stability, be reasonably priced and also safe to use. Among the compounds presented in the available literature, the materials NASICON- $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  and alluaudite- $\text{Na}_2\text{M}_3(\text{PO}_4)_3$  (M = transition metal) seem to be good candidates. While these materials possess high structural and thermal stability, their development is impeded by the limitation in electrical conductivity. In the present literature regarding both of these materials groups, there are still significant knowledge gaps ranging from the selection of the elements in M sublattice, through the choice of the best electrolyte, to optimization and enhancement of the transport and electrochemical properties by the substitution in  $\text{PO}_4$  and Na sublattice.

The scientific aim of the project is to elucidate how chemical composition and structural features affect physicochemical properties of 3-dimensional (NASICON, alluaudites and derivatives) cathode materials for next generation Sodium-ion batteries (SiBs) with superior energy storage capability, which might partially replace commonly used Lithium-ion batteries (LiBs). For this purpose the following materials were selected:

- NASICON-related compounds with general formula  $\text{Na}_{3-x}\text{K}_x\text{M}_2(\text{PO}_4)_3$  and  $\text{Na}_{3-x}\text{K}_x\text{M}_2(\text{PO}_4)_{3-y}\text{F}_y$  (M = transition metal: V, Fe, Mn, Cu, etc.);
- Alluaudite materials, with general formula  $\text{Na}_{2-x}\text{K}_x\text{M}_3(\text{PO}_4)_3$  and  $\text{Na}_{2-x}\text{K}_x\text{M}_3(\text{PO}_4)_{3-y}\text{F}_y$  (M=transition metal: V, Fe, Mn, Cu, etc.).

The author plans to accomplish these objectives by synthesis and comprehensive analysis of aforementioned cathode materials. The studies will include a diverse array of advanced experimental techniques, which will mainly focus on the structural aspect of materials properties; its influence on the electrical conductivity, sodium ions diffusion and electrochemical performance in test cells, as well as evolution of these properties with changing chemical composition and state of charge/discharge in test cells. Transport properties measurements and electrochemical analysis will also be accompanied by structural analysis with the goal to reveal the mechanisms and relations that impact the effectiveness of materials operation in Na-ion cells.