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Iron and Sulfate Based Positive Electrode Materials for Na-ion Batteries

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Concept of Na-ion batteries is among the most promising battery technologies to deal with the issue of critical and scarce elements used in Li-ion batteries. Portable applications demand high energy density, favoring V- and Mn-based Na-ion positive electrode materials. In contrast, for stationary applications where battery weight is less critical, component cost becomes a more compelling factor. Stable polyanionic frameworks ensure longer cycling life as well as greater safety in comparison to layered oxides. In 2023 Mn has been classified as a critical raw material by EU committee, which promotes search and development of new materials based on abundant Fe. For the polyanionic part, phosphates are widely studied, leaving space for investigation of pure sulphate phases and in parallel for mixed phosphate-sulphates.

From this point of view, we revisited already reported $\text{NaFe}_2\text{PO}_4(\text{SO}_4)_2$ (NFPS), which crystallizes in NaSICON structural type [1-4]. High-purity samples of NFPS were synthesized and studied by means of X-ray, neutron and electron diffractions, scanning electron microscopy and electrochemical methods. A new description of the structure was proposed and the relationship between synthesis conditions, stoichiometry, structure, and electrochemical performance will be discussed. Optimization of morphology and electrode formulation allowed us to obtain theoretical capacity at C/30 cycling rate (mass loading 20 mg/cm²). Step-by-step up-scaling led to synthesis of 8 g of NFPS per batch.

Attempts to synthesize sodiated compound of the same element compositions as NFPS via easy up-scalable solid-state synthesis result in new alluaudite-type series of phases. Challenges of the synthesis linked to control of stoichiometry and promising electrochemical performance will be presented.

A new phase based on only abundant elements, such as Na, Fe and S, obtained via simple ball-milling procedure, could be suggested as a cheap and efficient positive electrode material for stationary storage. Its synthesis requires only two easily-available precursors and no heating is required. One of the main advantages of this material is excellent stability of cycling. Structure and electrochemical experiments would also be presented.