In-situ ED-XRD studies of iron incorporation limits in Na-based post-spinel type compounds

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Abstract

Over the last decade, research on sodium-ion based batteries has greatly accelerated. Sodium batteries are indeed now considered as viable alternatives to Li-based systems due to the plentiful availability and low cost of sodium. The most widely studied positive electrode materials for Na-battery technologies today are sodium layered oxides, polyanionic compounds, or Prussian blue analogs. Each class of these materials presents unique challenges. Therefore, with an aim of identifying optimized electrode materials for sodium-ion batteries, it is interesting to pursue fundamental new explorations of oxide systems with inherently more stable three-dimensional structures and higher mass fraction ratios of electrochemically active species. Among known sodium oxide phases exhibiting electrode materials appropriate qualities (i.e. reasonable electronic and ionic conductivity plus framework stability during cycling), a family of compounds with a post-spinel $CaFe_2O_4$-type structure appear promising.

In this context, the structural evolution and properties of the system $NaFe_xMn_{2-x}O_4$ have been examined. In theory, the three-dimensional atomic structure offers wide diffusion channels for sodium ions, and the introduction of abundant iron could improve the energy density due to the high redox potential of the $Fe^{4+/3+}$ couple. However, the synthesis of certain post-spinel phases – including $NaMn_2O_4$ - requires high-pressure conditions. In this presentation, the recent results of our in-situ energy-dispersive X-ray diffraction (ED-XRD) studies performed at the SOLEIL beamline Psiché will be presented. In particular, we have examined how the role of Fe substitution in $NaFe_xMn_{2-x}O_4$ impacts the required pressure for synthetic formation (up to 5 GPa and 1000 ^oC) and the metastability of the targeted post-spinel structures on decompression. Conclusions will be discussed concerning how fundamental insight from our work can help guide the further exploration of alternative NaM_2O_4 type positive electrode materials based on similar structure types.