"Crystallo-Chemistry": A wonderful tool to study Energy Related Materials

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Crystal structure determination is obviously widely used in science and especially in chemistry or Materials Science. Energy Materials (or more precisely Battery Materials) are of course no exception to this rule. In order to follow the different mechanisms involved during the charge and discharge of a battery for instance, *"operando"* technics are essentials.

X-Ray diffraction measurements combined with other technics such as XAS can help us in understanding what is actually going on during operation of batteries.

As an example, my presentation will be mainly focused on NaSICon type material. Although they have been known for decades, these materials never cease to amaze us (me) and there is still room for discoveries.

Firstly known for their high ionic conductivity (hence the name: NA SuperIonic CONductor) [1], their chemical versatility allow them to be used as electrode materials (anode or cathode) as well as as coating materials for different battery technologies (Li-ion, Na-ion, multivalent-ions and all-solid-state batteries) by tuning its composition [2-4]. Indeed, the NASICON crystal structure of general formula $A_xMM'(XO_4)_3$, allows a wide range of chemical substitutions. The Alkali "A" atom can either be $Li^+/Na^+/K^+$, and the M/M' sites can basically be filled with any combination of 3d or 4d transition metals.

Among them, the vanadium phosphate $Na_3V_2(PO_4)_3$ (NVP) is of particular interest because of its fantastic rate capacity and thermal stability, with a theoretical capacity of 117.6 mAh/g at 3.4 V vs. Na^+/Na by the V^{3+}/V^{4+} redox couple yielding an energy density of 396 Wh/kg [4]. Because of the wide oxidation range of Vanadium, NVP can be used either as an anode or a cathode.

NASICON materials have also proven to be among the best solid electrolyte material for sodium All-Solid-State-Batteries (ASSBs). As an example, $Na_{3.4}Zr_2Si_{2.4}P_{0.6}O_{12}$ attains ionic conductivity as high as 10 mS/cm [5-6] with 3D diffusion path.

I will show the astonishing diversity of the crystal chemistry of the NASICON materials (both as electrode or electrolyte) mostly studied through *operando X-Ray Diffraction* as well as its use in ASSBs.

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