

## High capacity layered oxides as positive electrode materials for Na-ion batteries.

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The search for positive electrode material for Na-ion batteries started back to the 1980's in parallel to Li based systems underlining the expected similarities between these two alkaline species. Though the potentialities of Li based systems obscured researches dedicated to Na ones for more than 30 years, the renewal of interest since 2010 prompted fast growing of reported works in this field. Without surprises, most of investigated family of compounds reflects the one already studied for Li-ion systems among which the layered oxides  $\text{Na}_x\text{MO}_2$  (M including at least one transition metal). Mainly two types of polymorph P2- $\text{Na}_{2/3}\text{MO}_2$  and O3- $\text{Na}_1\text{MO}_2$  differing by the oxygenated surrounding adopted by the Na cations (Prismatic or Octahedral) are easily prepared using conventional solid state reaction. The P-type structures exhibit better electrochemical performances than O-type essentially due to an easy diffusion of Na ions via face sharing prisms [1]. Unfortunately, P-type structure are Na deficient meaning that the capacity in full cell is restricted. To enhance the capacity of layered oxides we demonstrated the possibility to reach stoichiometric P-type  $\text{Na}_1\text{MO}_2$  via the use of ball milling with metallic Na. The investigation of the electrochemical behavior of this latter compound shows that the reversible capacity in full cell is twice that of the pristine material and that the other characteristics such as the good capacity retention upon cycling and rate performances are maintained [2]. However, the nearly stoichiometric P-type  $\text{Na}_1\text{MO}_2$  shows high sensitivity to moisture, which prevent an easy handling, in agreement with low voltage of the redox couple which limit the energy density that can be obtained. One way to enhance both capacity and energy density is to activate the anionic redox couple as demonstrated in Li-rich materials. We decided then to investigate the possibility of activating such anionic redox couple in Na-rich layered oxides. The study of the electrochemical behavior of different members of the  $\text{Na}_2\text{Ru}_{1-y}\text{Sn}_y\text{O}_3$  solid solution shows that like their Li-analogue, they present capacities that exceed theoretical capacity calculated from the cationic redox species [3]. The high capacity was found, by means of XPS analysis, to be associated to the accumulation of both cationic ( $\text{Ru}^{5+}/\text{Ru}^{4+}$ ) and anionic ( $\text{O}^{2-}/\text{O}_2^{n-}$ ) redox processes. The structural evolutions during cycling have been followed using in situ XRD and found to be associated with the cation disordering and loss of crystallinity on cycling. Therefore, in contrast to the Li series, such a formation of oxygen species is followed, for the Sn rich samples, by the irreversible loss of  $\text{O}_2$ .

These works which shows for the first time the feasibility of synthesizing nearly stoichiometric P-type layered oxides and obtaining high capacities due the anionic redox activity contribution, open the way to design new positive electrode materials for Na-ion batteries with the possibility to exchange at high voltage more than 1 electron per transition metal. It now remains to chemically manipulate these layered compounds to enhance their cycling behavior and stability against moisture so that they could be handled in air.

### References

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