

# Effects of Mn-doping on the Structural and Electrochemical Properties of $\text{Na}_3\text{Ni}_2\text{SbO}_6$ for Sodium-Ion Battery



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Invited for this month's cover picture is the group of Prof. Shigeto Okada. The cover picture shows 2 kinds of synthesized Mn-doped  $\text{Na}_3\text{Ni}_{2-x}\text{Mn}_x\text{SbO}_6$  layered oxide cathode materials for Na-ion batteries. The heavily doped ( $x=0.5$ ) sample in the right side suffers from large polarization, corresponding to the reduced two-phase reaction range and a large volume change of the unit cell upon sodium extraction. On the other hand, the lightly Mn-doped ( $x=0.25$ ) sample in the left side shows enhanced O'3-P'3 phase transition kinetics due to the smaller volume change of the unit cell. Read the full text of the Article at 10.1002/batt.201900166.

## *What prompted you to investigate this topic/problem?*

Up to now, doping to the cathode for Li-ion battery has been very well developed during the last two decades to fine-tune their properties. Actually, the most widespread lithium-ion battery cathodes  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) and  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  (NCM) are  $\text{LiCoO}_2$ -derivatives where Co has been partially replaced by other transition (Ni and Mn) or non-transition (Al) metals. Layered Na-ion hosts borrow the same operation principle, i.e., reversible intercalation of Na into (predominantly) layered transition metal oxide structures. However, Na-ion hosts have specific properties originating from the larger size of  $\text{Na}^+$ . In general, sodium hosts show more complex phase transitions with more intermediate phases, emerging during the electrochemical desodiation. According to the recent literature reports  $\text{Na}_3\text{Ni}_2\text{SbO}_6$  is a promising new cathode material because the distance between the  $\text{Ni}_2\text{SbO}_6$  slabs is almost perfect to sustain reversible reinsertions of up to two sodium ions per formula unit. There is also a purely aesthetic aspect of this work, because  $\text{Na}_3\text{Ni}_2\text{SbO}_6$  structure is not just layered, but it has honeycomb structure, where one Sb in the transition metal layer is surrounded by 6 Ni. To us, it was quite natural to ask the question whether Ni could be partially replaced by other transition or non-transition metals. Such dopants inevitably would break the perfect honeycomb symmetry because after doping into the Ni site not all atoms surrounding Sb will be Ni. Preliminary DFT calculations revealed that even light Mn doping decreases the band gap, which is believed to improve the electrochemical performance of battery cathode materials. Another interesting aspect was to investigate how Mn doping would affect phase transition

kinetics upon repeated Na reinsertions. Most part of the current investigation aimed to answer the latter question.

**Batteries & Supercaps**

Front Cover  
S. Okada and co-workers  
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**What was the biggest surprise (on the way to the results presented in this paper)?**

This work revealed the existence of a clear threshold between enhanced and worsened battery performance induced by Mn-doping. It was a little bit surprising that Mn and Mg doping reported in a separate previous study have equivalent influence on the battery performance, namely lightly doped  $\text{Na}_3\text{Ni}_{1.75}\text{M}_{0.25}\text{SbO}_6$  ( $\text{M}=\text{Mn}$  or  $\text{Mg}$ ) show enhanced O'3-P'3 phase transition kinetics. Our initial expectation was that Mg could play the role of just a structure stabilizer (similar to Al in  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ) whereas Mn might act as either redox couple and/or reduce band gap and improve electrical conductivity. Another surprise was that preparing phase-pure  $\text{Na}_3\text{Ni}_2\text{SbO}_6$  is relatively difficult and requires double calcinations with intermediate grinding. It is therefore surprising that doping might offer more convenient and repeatable synthetic procedures despite the apparently broken honeycomb symmetry of the doped  $\text{Na}_3\text{Ni}_{2-x}\text{M}_x\text{SbO}_6$  phases.

**Does the research open other avenues that you would like to investigate?**

We believe and hope the answer to this question is yes. The work done so far actually only unveil the complexity and beauty of this material. In the relatively short time, we could devote to this project we could not answer many important

questions. For example, it is not clear in detail yet whether Mn could act as a major redox couple, or it would act only as electrochemically inert element similar to the case of  $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$  where Ni and Co redox couples are active, but Mn is inactive. In case Mn becomes electrochemically active, Jahn-Teller distortion would play a role and might explain enhanced phase transition kinetics and suggest optimal Mn doping levels. Lighter doping (e.g.,  $x=0.05$ , or 0.10) could be even more beneficial, but harder to study theoretically because the need of larger supercells and many possible Mn-doping configurations. It might be anticipated that  $\text{Na}_3\text{Ni}_2\text{SbO}_6$  would allow multi-element doping and even higher levels of fine tuning than the layered Li-ion hosts. Taking into account that developing  $\text{LiCoO}_2$  derivatives NCA and NCM took more than a decade to fine tune and commercialize, most of the work regarding Na-ion host materials remains to be done. From this perspective primary goal of our work is actually to show the possibility for fine tuning of  $\text{Na}_3\text{Ni}_2\text{SbO}_6$  and thus open new avenues for further, more detailed studies.

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