

# Phosphate framework materials for ion insertion batteries: Understanding, performance, degradation

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Various phosphate and mixed phosphate framework materials are attracting a lot of interest as structurally and electronically diverse materials. Due to their stability they are suitable for various electrochemical applications. Na SuperIonic Conductor (NASICON) structure type  $A_xMe_2(PO_4)_3$  ( $A = Li, Na, K; Me = Ti, V, Mn$  etc.) compounds, in addition to being archetypical solid electrolytes, are also interesting electrode active materials for various devices such as batteries and faradaic deionization cells. However, there is still a number of issues to be solved before their full potential could be utilized. This involves not only finding the right composition of different transition metals but also improving the stability of the electrolyte/electrode interface especially in the aqueous case. Aqueous stability and electrochemical degradation of electrode materials is related to complex acid-base equilibria, material dissolution, metal leaching etc. Some of our recent contributions in terms of understanding and enabling of Ti-, Mn- and V-based phosphate framework materials for the use in aqueous electrochemical systems is reviewed [1-12]. The role of parasitic reactions such as oxygen reduction (ORR) and hydrogen evolution (HER) and their relation to local pH changes towards the stability of  $NaTi_2(PO_4)_3$  are determined [3,10]. The results show that local alkalinity is responsible for most of its degradation which is only accelerated at high rates. Several mitigation strategies by the use of conformal atomic layer deposited electrode coatings and oxygen scavenging by the use of strongly reducing additives are suggested [4,5,10]. The dissolution of transition metals as the main aqueous degradation mechanism for  $Na_{1+2x}MnTi_{2-x}(PO_4)_3$  and  $Na_{3-x}V_{2-x}Ti_x(PO_4)_3$  positive electrodes is established [1,8,9]. However, the results suggest that in Mn- and V-based positive aqueous battery electrodes it is not the material degradation which is responsible for most of the observed capacity fade per se but rather the loss of contact between particles and the conductive phase [1,8]. Various modification and metal substitution strategies leading to superior stability in half- and full-cells are presented [2,6,7,11].

## References

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