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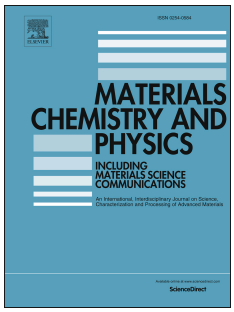

A first-principle study of NaMPO$_4$ (M= Mn, Fe, Co, Ni) possible novel structures as cathode materials for sodium-ion batteries: Structural and electrochemical characterisation

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A first-principle study of NaMPO$_4$ (M = Mn, Fe, Co, Ni) possible novel structures as cathode materials for sodium-ion batteries: structural and electrochemical characterisation.

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Abstract

Transition metal containing polyanion compounds are effective excellent electrode materials for sodium-ion batteries due to their high intrinsic electrochemical potentials and to the resulting high energy density. Iron sodium phosphates, in particular, are attractive due to the large natural abundance of both Na and Fe. These materials have been extensively studied in their most common olivine structures: maricite and triphylite. In this work, we expand the current knowledge of this class of materials by investigating the structural properties and the energetics of a series of modification exhibiting different coordination for the intermetallic atom M = Mn, Fe, Co, Ni by means of density functional theory calculations. An expanded-volume NaFePO$_4$ configuration with the zeolite ABW structure is predicted to be stable at high temperature. This type of structure, presenting a tetrahedral Fe–O coordination geometry, has been previously reported only for the NaCoPO$_4$ case. A semi-amourphous phase is predicted to be a possible metastable intermediate configuration between the known octahedral coordinated structures and the novel tetrahedral-coordinated one. The electrochemical characterisation of the latter reveals a similar deintercalation potential with respect to triphylite, and a higher diffusion barrier caused by the incompressibility of the PO$_4$ tetrahedra along the diffusive path. This result offers important insight about the correlation between the diffusive properties of ions and their local chemical environment.

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