

Unravelling the multivalent charge-storage mechanism of NASICON $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ for rechargeable Zn-ion batteries

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Research on “beyond lithium-ion” has initiated significant efforts in exploring multivalent (MV) ion storage, which include but are not limited to Mg^{2+} , Zn^{2+} , and Ca^{2+} . For nearly a century, zinc metal has been considered as an ideal anode, as demonstrated in commercial batteries (e.g. Zn– MnO_2 , Ni–Zn, etc.), because of its high volumetric capacity (Zn: 5855 mAh cm^{-3} vs. Li: 2061 mAh cm^{-3}), low toxicity, and natural abundance. For cathodes, the basis of charge-storage has relied on the intercalation of positively-charged cations into a host crystal framework. In the field of Zn^{2+} -based batteries, lingering questions regarding Zn^{2+} intercalation remain due to the complex processes that occur concomitantly during cycling, such as proton-driven reactions, irreversible phase transformations, and electrolyte degradation. In the present study, we investigate the MV charge-storage properties of a robust Na^+ superionic conductor (NASICON) structure based on $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) coupled with X-ray synchrotron techniques to unravel potential-dependent structure–property relationships. Although previous reports have demonstrated reversible cycling of NVP in Zn^{2+} -based electrolytes, we hypothesize that a two-stage intercalation mechanism of Na^+ and Zn^{2+} may be responsible for the achievable high specific capacity rather than relying solely on Zn^{2+} . Two-electrode cells were first constructed where carbon-composite electrodes of NVP and zinc foil served as the cathode and anode, respectively, separated by a glass fiber separator soaked in 0.5 M zinc acetate. The initial charging profile at a slow C-rate of C/20 indicates Na^+ extraction from $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ to $\text{NaV}_2(\text{PO}_4)_3$ observed by a single plateau in the galvanostatic charge/discharge curve, while subsequent discharge at the same rate results in two plateaus at 1.35 and 1.2 V. *Operando* X-ray diffraction of the cells were collected to examine the changes associated with the first charge-discharge cycle, which indicated reversible behavior based on the shifting of X-ray reflections associated with the NVP structure. To examine subtle changes linked with Na^+ and Zn^{2+} two-stage intercalation, electrodes were cycled to a desired potential and collected for *ex situ* X-ray diffraction analyses. Rietveld refinement of these samples was performed to understand the changes in the crystal structure when accommodating both Na^+ and Zn^{2+} . Furthermore, the changes in V oxidation state, V-O coordination, and the presence of Zn^{2+} was studied by X-ray absorption spectroscopy. The results of this work present a thorough analysis of the complex charge-storage mechanism of MV Zn^{2+} insertion/de-insertion of a well-established NASICON structure.