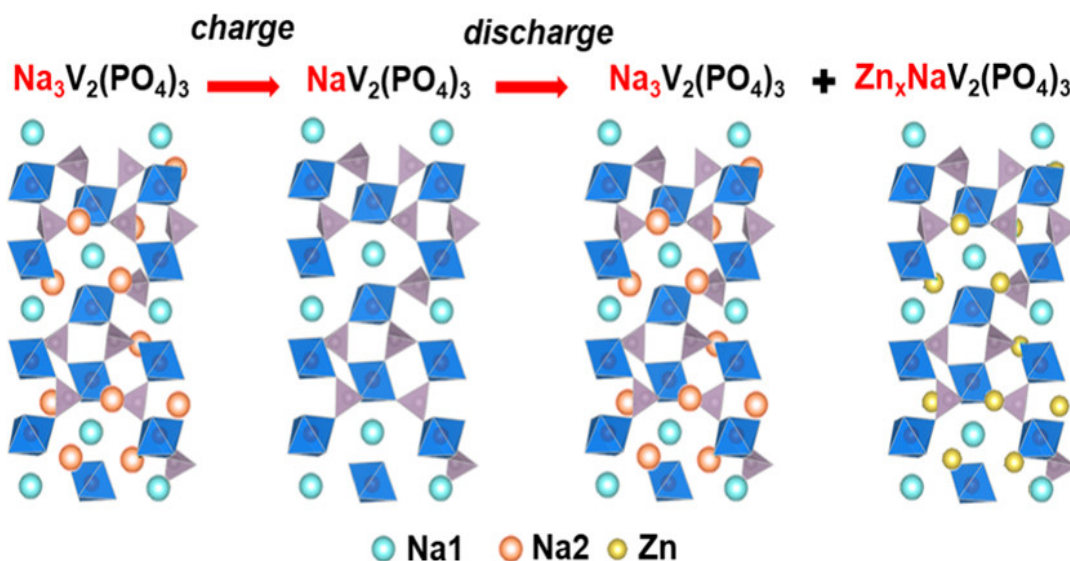


## Cathode Enables Quasi-Two-Stage Intercalation for Multivalent Zinc Batteries

Widespread applications for electrochemical energy storage based on lithium-ion batteries now demand higher performance in terms of energy and power density, coupled with robust cycle life. Despite major advancements in lithium-ion batteries, a shortage of precious metals, such as cobalt, which is typically used in the cathode in lithium-ion batteries and is sourced from only a few countries globally, is predicted. This shortage has driven the energy storage community to develop “beyond lithium-ion” technology, based on earth-abundant metals, such as monovalent sodium and potassium or divalent calcium, magnesium, and zinc. Divalent metals, if used directly as a metal anode, can provide high capacity density compared to lithium because each ion carries twice the charge. They are also relatively cost-effective. However, challenges remain in identifying a cathode material capable of high capacity, stable cycling, and balancing the capacity of multivalent metal anodes. Moreover, a critical challenge in developing cathode materials for multivalent charge storage lies in addressing sufficient multivalent cation mobility required for reversible intercalation.

In a recent study, researchers from SSRL investigated the potential-dependent structure–property relationships, along with chemical changes, of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , a vanadium phosphate-based cathode for a Zn-metal battery (Figure). The  $\text{Na}^+$  superionic conductor (NASICON) structure has  $\text{Na}^+$  occupying two different crystal lattice sites: the Wyckoff 6b (Na1) and 18e (Na2) sites. It has been used earlier as a cathode material for sodium-ion batteries and showed promise in accommodating Zn-ions in the 18e sites after Na-ions are extracted. Researchers investigate the potential-dependent structure–property relationships, along with chemical changes, of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  using x-ray synchrotron-based methods to correlate crystal structure changes with the charge/discharge operation.



**Figure.** Schematic of the potential-dependent crystal structures associated with the charge and discharge cycle of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  determined from x-ray diffraction.

With a combination of *operando* and higher resolution *ex situ* x-ray diffraction measured at beam lines 11-3 and 2-1 at SSRL, researchers revealed a quasi-two-step insertion process with both  $\text{Na}^+$  and  $\text{Zn}^{2+}$  reversibly filling the 18e sites of the NASICON structure (Figure). The oxidation-reduction reactions associated with this quasi-two-stage electrochemical process and the presence of ionic  $\text{Zn}^{2+}$  was verified by x-ray absorption spectroscopy at the Zn and V K-edges. The results provide an exciting direction for utilizing a polyanionic framework for multivalent ion insertion and may be applicable to other divalent ions such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

### Primary Citation

J. S. Ko, P. P. Paul, G. Wan, N. Seitzman, R. H. DeBlock, B. S. Dunn, M. F. Toney and J. N. Weker, "NASICON  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  Enables Quasi-Two-Stage  $\text{Na}^+$  and  $\text{Zn}^{2+}$  Intercalation for Multivalent Zinc Batteries", *Chem. Mater.* **32**, 3028 (2020) doi: [10.1021/acs.chemmater.0c00004](https://doi.org/10.1021/acs.chemmater.0c00004)

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