

Matching Electrochemical Properties and Phase Transformations in NASICON-type Electrode Materials for Na-ion batteries

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NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode materials are considered as promising candidates for high-performance Na-ion batteries due to extremely long cyclic stability and an outstanding ability to operate at high (dis)charge rates. However, its cost-effectiveness can still be improved using transition metals cheaper than vanadium, which could also increase the energy density compared to that in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

The replacement of V with Mn and Cr in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ lowers the cost of the materials and enhances the operation voltage. Substitution of V by electrochemically inactive Mg and Sc allows studying vanadium redox processes without contributions from these metals (Figure 1).

Na content x in $\text{Na}_x\text{MM}'(\text{PO}_4)_3$ (MM' = MnCr, MgV, ScV, MnV, V₂)

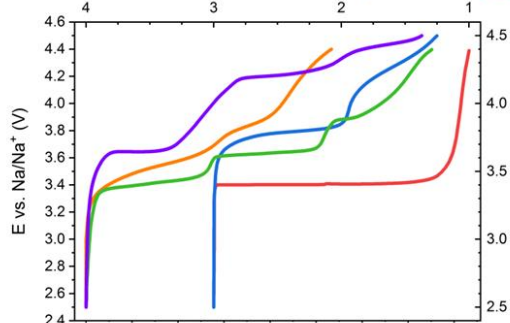


Figure 1 Comparison of galvanostatic charge curves of NASICON compounds with different composition.

When the voltage window above 3.8 V is utilized, Mn^{2+} substitution enhances the energy density of $\text{Na}_{3+x}\text{Mn}_x\text{V}_{2-x}(\text{PO}_4)_3$ compounds for up to 10% compared with the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. The evolution of the transition metal oxidation states in $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ during charge and discharge was studied by X-ray absorption spectroscopy (XAS) in *ex situ* and *operando* regimes using an electrochemical cell with X-ray transparent windows.

In order to link electrochemical features with the phase transformations in NASICON samples *operando* X-ray powder diffraction was carried out (Figure 2). The crystal structure changes on charge and discharge were studied as

well as the electrode performance in narrow (2.5-3.8 V), wide (2.5-4.5 V) and extra wide (1.0-4.5 V) potential windows.

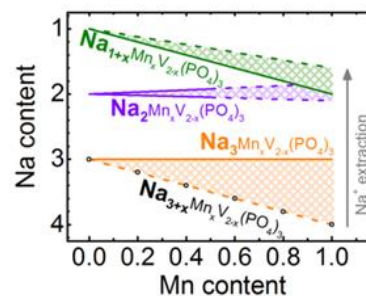


Figure 2 Schematic illustration of the Na^+ deintercalation regimes from $\text{Na}_{3+x}\text{Mn}_x\text{V}_{2-x}(\text{PO}_4)_3$ ($0 \leq x \leq 1$).

The results indicate that in case of narrow voltage window the Na^+ (de)intercalation reaction is reversible, however for the V-substituted compounds charging above 3.8 V increases energy density, but leads to the loss of reversibility and capacity fade. However, for some compounds an overdischarge below 2.5 V suppresses the capacity fade [1].

The experimental results indicate the benefits of vanadium-substituted compounds and ability to outperform the unsubstituted materials in terms of rate-capability. Therefore they should be preferred for high-power applications.

Acknowledgements

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References

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