

Vanadium-based NASICON Cathode Materials with Enhanced Performance for Sodium Ion Batteries

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There is a significant need for cost effective, safe, and high performance energy storage technologies for an ever increasing variety of applications. Sodium ion batteries (NIBs) are one such type of battery chemistry sharing many similarities to their lithium counterparts with regard to fundamental operation and materials used. The argument for NIBs is one of cost and responsible resource use, with a focus on shifting away from materials traditionally used in lithium systems, such as cobalt-based cathodes and copper current collectors for the graphite anode. Sodium-containing prismatic layered oxides (1-3), open framework phosphates (4- 6) & ferrocyanides (7, 8) have been reported as possible electrode materials for NIB systems.

NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is one such open framework material that can host up to four sodium ions per unit. But as cathode, it has only a useable capacity of about 120 mAh g^{-1} at 3.4V vs. Na/Na^+ , i.e. one sodium ion per vanadium. Improvements in energy density are required to make this material more attractive for battery applications. In this presentation we will report on the enhancements that can be achieved via a partial substitution of vanadium by various transition metals.

Figure 1 shows the PXRD pattern of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with and without partial iron substitution of vanadium. Through this process, the material remains phase-pure and the rhombohedral structure (R3-c) is preserved with only slight shifts in peak positions and changes in relative intensities. The change in reaction mechanism of the material obtained by metal substitution is investigated by cyclic voltammetry (Figure 2). The pristine material shows a single redox reaction around 3.4V , as is known for the $\text{V}^{3+/4+}$ redox couple. In the case of partial vanadium to iron substitution, two new components in CV curve are observed: first is the appearance of $\text{Fe}^{2+/3+}$ peaks located at 2.5V ; second is an additional redox couple appearing at 4.0V for $\text{V}^{4+/5+}$. Since a certain amount of vanadium has been allocated now to iron, we can thus force some of the remaining vanadium to become redox active at this higher voltage, in a facile and stable manner.

In our presentation, we aim to shed more light on the electrochemical enhancement observed by optimizing the amount and type of transition metal substitutes in the

NASICON structure. This will include a thorough analysis of the physical and chemical effects of the respective substitutions, with a special focus on the electrochemistry of the sodium intercalation process.

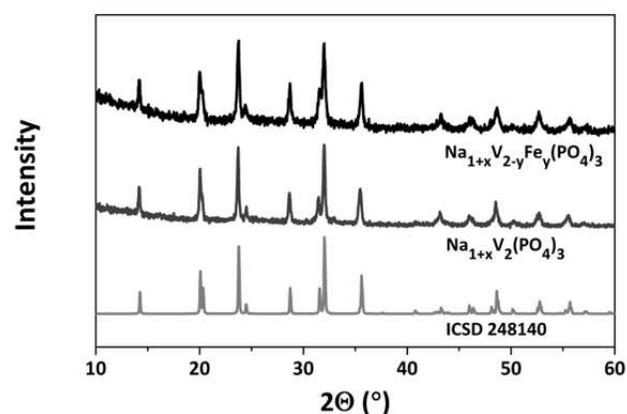


Figure 1. XRD pattern of reference, pristine, and substituted materials.

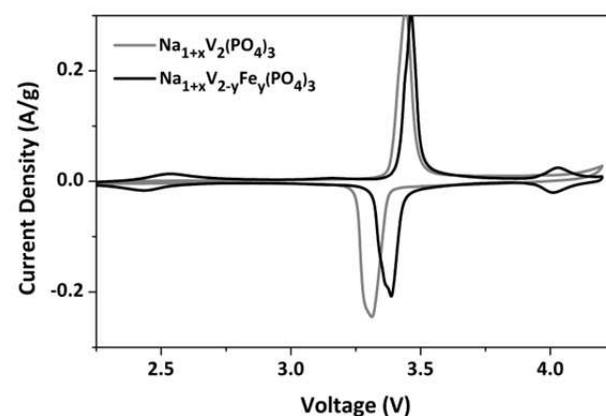


Figure 2. Cyclic voltammogram of pristine and substituted materials.

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