

Effective Doping Engineering of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ as a High-Performance Cathode Material for Sodium-Ion Batteries

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Abstract : Sustainable batteries are possible through the development of cheaper and greener alternatives whose most feasible option is epitomized by Sodium-Ion Batteries (SIB). $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ (NVPF) an important member of the Na-superionic-conductor (NASICON) materials, has recently been in the spotlight due to its interesting electrochemical properties when used as cathode namely, high specific capacity of 128 mA h g^{-1} , high energy density of 507 W h Kg^{-1} , increased working potential at which vanadium redox couples can be activated (with an average value around 3.9 V), and small volume variation of less than 2%. These traits grant NVPF an excellent perspective as a cathode material for the next generation of sodium batteries. Unfortunately, because of its low inherent electrical conductivity and a high energy barrier that impedes the mobilization of all the available Na ions per formula, the overall electrochemical performance suffers substantial degradation, finally obstructing its industrial use. Many approaches have been developed to remediate these issues where nanostructural design, carbon coating, and ion doping are the most effective ones. This investigation is focused on enhancing the electrochemical response of NVPF by doping metal ions in the crystal lattice, substituting vanadium atoms. A facile sol-gel process is employed, with citric acid as the chelator and the carbon source. The optimized conditions circumvent fluorine sublimation, ratifying the material's purity. One of the reasons behind the large ionic improvement is the attraction of extra Na ions into the crystalline structure due to a charge imbalance produced by the valence of the doped ions (+2), which is lower than the one of vanadium (+3). Superior stability (higher than 90% at a current density of 20C) and capacity retention at an extremely high current density of 50C are demonstrated by our doped NVPF. This material continues to retain high capacity values at low and high temperatures. In addition, full cell NVPF//Hard Carbon shows capacity values and high stability at -20 and 60°C. Our doping strategy proves to significantly increase the ionic and electronic conductivity of NVPF even at extreme conditions, delivering outstanding electrochemical performance and paving the way for advanced high-potential cathode materials.

Keywords : sodium-ion batteries, cathode materials, NASICON, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, Ion doping

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