

Mn-Based NASICON: correlation between synthesis method, morphology, and conductivity

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Sodium-ion batteries (SIBs) are seen as a sustainable alternative to lithium-ion batteries (LIBs). This is due to several factors: the low cost and earth abundance of sodium, and the comparable electrochemical properties of SIBs and LIBs. The advancement of SIBs technology necessitates the development of novel, high-performance electrode materials utilizing earth-abundant elements. Furthermore, optimizing experimental methodologies, e.g., particle design, doping, and carbon coating is crucial to enhance the electrochemical properties of the electrode materials [1]. In recent decades, NASICON phosphates with general formula $\text{Na}_{3+x}\text{MnM}(\text{PO}_4)_3$ (M = transition metal) have been intensively researched, especially as cathode material owing to the environmental-friendly and cost-effective of Mn, as well as the high redox voltage of $\text{Mn}^{2+/3+}$ (3.6 V) and $\text{Mn}^{3+/4+}$ (4.0 V) [2]. In our work, we presented the synthesis, structure and conductivity of an earth abundant Mn/Fe-based NASICON phosphate, $\text{Na}_4\text{MnFe}(\text{PO}_4)_3$ (NMFP). This material was successfully synthesized by solution-assisted solid-state reaction (SS), sol-gel (SG) and Pechini methods (P). From refined X-ray diffraction data, the prepared phosphate found to crystallize in trigonal symmetry with space group R-3c. The synthesis-related effects on microstructure and conductivity were examined using scanning electron microscopy (SEM), atomic force microscopy (AFM) and impedance measurements. The smaller particle size and regular distribution of the powder were achieved through the Pechini route, resulting in a dense pellet with enhanced grain boundary conductivity (Table.1). This contributes significantly to the total conductivity of the material, demonstrating the profound influence of the synthesis method on conductivity. Additionally, this compound shows low activation energy below 90 °C, suggesting its potential as a promising candidate for future energy storage applications.

Table 1. Conductivities of NMFP pellets at 30 °C and the relative density.

Pellets	σ_g (S/cm) $\times 10^{-7}$	σ_{gb} (S/cm) $\times 10^{-7}$	σ_t (S/cm) $\times 10^{-7}$	Relative density (%)
NMFP/SS	3.370	0.647	0.543	92.260
NMFP/SG	3.230	0.760	0.626	93.568
NMFP/P	3.590	2.640	1.520	97.907

- [1] J. Hou, M. Hadouchi, L. Sui, J. Liu, M. Tang, W.H. Kan, M. Avdeev, G. Zhong, Y.K. Liao, Y.H. Lai, Y.H. Chu, H.J. Lin, C. Te Chen, Z. Hu, Y. Huang, J. Ma, Unlocking fast and reversible sodium intercalation in NASICON $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ by fluorine substitution, *Energy Storage Mater.* 42 (2021) 307–316. <https://doi.org/10.1016/j.ensm.2021.07.040>.
- [2] R. Thirupathi, V. Kumari, S. Chakrabarty, S. Omar, Recent progress and prospects of NASICON framework electrodes for Na-ion batteries, *Prog. Mater. Sci.* 137 (2023) 101128. <https://doi.org/10.1016/j.pmatsci.2023.101128>.