

ABSTRACT - POSTER

Controlled synthesis of LiVOPO₄ polymorphs: from hydrothermal precursor design to phase control and morphology optimisation

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Polyanion compounds have emerged as promising cathode materials for lithium-ion batteries, combining high theoretical energy density with excellent thermal and electrochemical stability owing to their rigid structure.¹ Among these, LiVOPO₄ stands out for its ability to utilize two vanadium redox couples, offering a high theoretical capacity.² However, LiVOPO₄ exists in multiple polymorphic forms, including metastable phases, each exhibiting distinct electrochemical behavior, making phase-pure synthesis a critical challenge. Beyond phase control, particle size and morphology equally govern electrochemical performance, as they determine ion diffusion pathways and the accessible active surface area.

In this work, a systematic hydrothermal synthesis approach was employed to better understand the formation of LiVOPO₄ polymorphs. Phase transitions from the hydrothermal precursor to the final crystalline polymorphs were mapped using thermogravimetric analysis (TGA) and *in-situ* X-ray diffraction (XRD), revealing that the α1-phase forms upon calcination above 280°C, while the β-phase requires temperatures exceeding 550°C. This thermal mapping enabled reproducible formation of distinct phase-pure polymorphs. To address the challenge of large particle agglomerates, which are unfavorable for battery performance, two strategies were explored: ball milling, with systematic variation of milling speed and duration, yielded a twofold increase in specific capacity for the α1-phase at low current rates, demonstrating the benefit of reduced particle size and improved surface accessibility. In contrast, ball milling of the β-phase resulted in a deterioration in electrochemical performance, an effect attributed to differences in structural sensitivity between the two polymorphs, as the β crystal structure appears more susceptible to mechanically induced disorder. Secondly, direct modification of the hydrothermal synthesis conditions, including precursor concentration and reaction time, revealed a transition between homogeneous and heterogeneous nucleation regimes that influenced particle morphology and size during crystallization.

Together, these findings establish structure-property relationships linking synthesis and processing parameters to the structural and electrochemical behavior of LiVOPO₄. This mechanistic understanding provides a rational basis for further optimization of this promising cathode material.

References

1. Gong, Z., Yang, Y. *Energy and Environmental Science*, 2011, Vol. 4 (9), 3223-3242.
2. Hildago, M.F.V. et al. *Journal of Materials Chemistry*, 2019, Vol. 7 (14), 8423-8432.