

Phosphate cathode materials for lithium-ion batteries: on the way from LiFePO_4 to LiMnPO_4

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Phosphate cathode materials are a major alternative to oxide compounds as lithium-ion battery (LIB) cathodes, primarily due to the success story of lithium iron phosphate LiFePO_4 , often referred to as LFP. The main difference between phosphate and oxide materials is the presence of phosphate (PO_4) or pyrophosphate (P_2O_7) groups, which form a reliable structural framework and "bind" oxygen anions. Due to these factors, phosphate-based materials show stable cycling over thousands of charge-discharge cycles, the ability to charge or discharge quickly, and increased thermal stability, i.e. safety of use. At present, LFP has become the basis of a whole area both in research activities and in the field of the LIB industry - an actively developing and extremely promising.

In the course of our work, we have studied many options for the synthesis of LFP, with an emphasis on the solvothermal synthesis method. The report will discuss the features of the structure of phosphate materials and the effect of various defects on their electrochemical properties, the relationship between synthesis methods, the morphology of materials and their characteristics, as well as the prospects for alternative LFP compositions to further improve the performance of LIB batteries. As an example, so-called Li-rich olivines obtained by means of solvothermal method will be discussed.

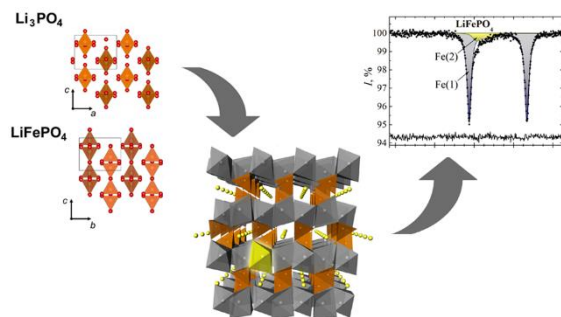


Figure 1. Li-rich olivines: origin of formation and MS spectra "signature".

We observed that presence of a certain amount of Li^+ in M2 position in the crystal structure of the initial phosphate leads to

appearing of additional component in Mössbauer spectroscopy (MS) spectra of all studied compounds, corresponding to ferric ions in the same position with distorted second coordination sphere. Evolution of MS spectra during charge/discharge revealed clear connection between relative contribution of this component and the mechanism of Li^+ (de)intercalation. Extended single-phase regions with large Li^+ non-stoichiometry in triphillite and heterosite phases of $\text{Li}_{1-x}\text{FePO}_4$ observed by means of synchrotron X-ray powder diffraction (SXPD) appear due to Li-Fe defects existing in Li-rich olivines and acting as a "diluting" agent preventing two-phase spinodal decomposition. These features can be regarded as an additional merit of Li-rich olivines [1] as a promising cathodes for high-power Li-ion batteries.

In addition, the main difficulties that arise when trying to increase the energy intensity of cathode materials by completely or partially replacing iron with manganese, as well as possible ways to overcome them, will be considered.

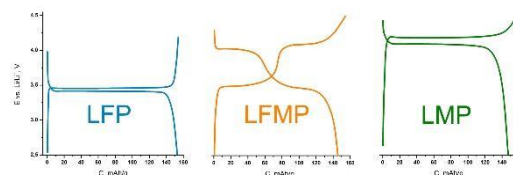


Figure 2. Charge-discharge curves of the LiFePO_4 (LFP), $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ (LFMP) and LiMnPO_4 (LMP) cathode materials.

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References

- [1] Drozhzhin Oleg A., et al., Exploring the Origin of the Superior Electrochemical Performance of Hydrothermally Prepared Li-Rich Lithium Iron Phosphate $\text{Li}_{1+d}\text{Fe}_{1-d}\text{PO}_4$, Journal of Physical Chemistry C, 124 (2020) pp. 126-134.



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