

Determination of the enthalpy of mixing in the binary system $\text{LiFePO}_4\text{--FePO}_4$ at 25 °C

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Lithium iron phosphate (LiFePO_4) is known for its capability to deintercalate lithium ions reversibly [1] as well as for its high thermal stability. Thus, LiFePO_4 is discussed to be a promising cathode material for the application in lithium ion batteries (LIB). In comparison with other cathode materials, such as LiCoO_2 and $\text{Li}(\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3})\text{O}_2$ [2], lithium iron phosphate possesses several benefits: low price, low toxicity, small volume change of about 7 % and a high theoretic specific capacity of 170 mAh g^{-1} .

During the cycling process of a battery LiFePO_4 undergoes a sequence of complex chemical reactions. The group of Yamada [3] proved that LiFePO_4 and FePO_4 are partly miscible into each other at room temperature. Thus, solid solution phases are formed while charging (delithiation cathode reaction) or discharging (lithiation cathode reaction) a LIB [4] until phase separation takes place. The width of the miscibility gap in this system depends on both temperature [5] and the primary crystallite size [6, 7]. Nevertheless, besides these phenomenological considerations a detailed calorimetric investigation focussed on the thermodynamics of the mixing behaviour of this binary system is still missing.

This contribution focuses on the determination of the enthalpy of mixing in the system $\text{LiFePO}_4\text{--FePO}_4$ via isothermal titration calorimetry (ITC) by applying a thermal activity monitor system (TAM 2277) from Thermometric at 25 °C. In order to account for the influence of the particle size on the mixing enthalpy, two samples with significantly different particle size distributions are investigated. The lithiation reaction of FePO_4 is carried out by adding of the dissolved reducing agent lithium iodide stepwise into a dispersion of the solid in acetonitrile. All of the calorimetric results are generally in good accordance with additionally conducted equilibrium cell potential measurements.

The ITC method turns out to be a new promising research tool in order to investigate redox reaction induced phase transition processes of lithium intercalating compounds as well as the enthalpy of mixing in the $\text{LiFePO}_4\text{--FePO}_4$ system. Compared to cell potential measurements, it offers an opportunity to access enthalpic changes directly. Thus, it complements results gained by electrochemical studies and provides new insights for a better understanding of electrode reactions in LIB.

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