Hydrothermal synthesis of $LiFePO_4$

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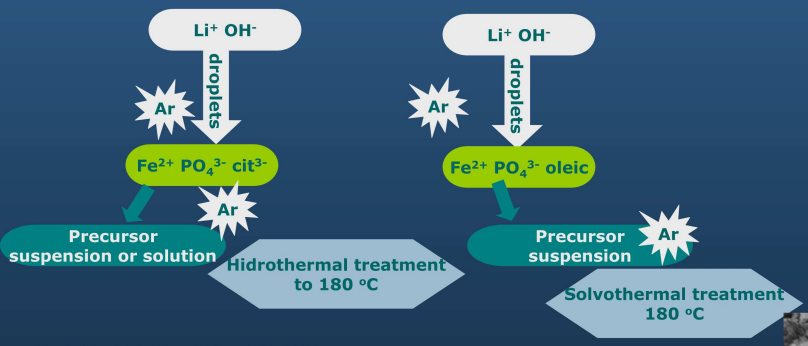
INTRODUCTION

High capacity storage of electric energy is technology of strategic importance for modern society. As lithium-ion batteries with their high capacity and generated power can improve electrical storage for electric vehicles and portable devices; they became a one of the major topics of research today. One of most perspective cathode material for lithium-ion batteries is $LiFePO_4$. Superior characteristics of this material are high Li storage capacity, stability, non-toxicity and low price, major disadvantage is low electronic conductivity.



METHODS & MATERIALS

$LiFePO_4$ was prepared by hydrothermal process starting from $FeSO_4*7H_2O$, 85% H_3PO_4 and $LiOH*H_2O$. H_3PO_4 and $FeSO_4$ was dissolved in water or water-i-propanol mixture (3:2), LiOH solution was added subsequently. Used solvents were previously deoxygenated. The molar ratio of Li:Fe:P was 3:1:1 in all experiments. For Fe^{2+} stability to form mild reduction conditions citric acid were added in experiments with water as reaction media. Oleic acid was also added as surfactant in experiments with water-alcohole mixture used as reaction medium. Amount of citric acid was varied through experimets in order to examine influence of additive concentration, as well as pH value on phase purity and particle sizes. After hydrothermal synthesis precipitated powders were centrifuged and washed with distilled H_2O and dried for several hours on 60 °C in air.

Phase composition is determined by XRPD measured on Philips PW 1050 diffractometer and PANalytical X'Pert PRO with Cu $K\alpha_{1,2}$ radiation , morphology of particles by FE-SEM SUPRA 35 VP (Carl Zeiss) and particle size distribution from light scattering measurements on Malverns Mastersizer 2000 equipped with HeNe 633 nm wavelenght laser and blue light source of 455 nm wavelenght.

RESULTS & DISCUSSION

After synthesis yellowish green, dark green or gray powders are collected.

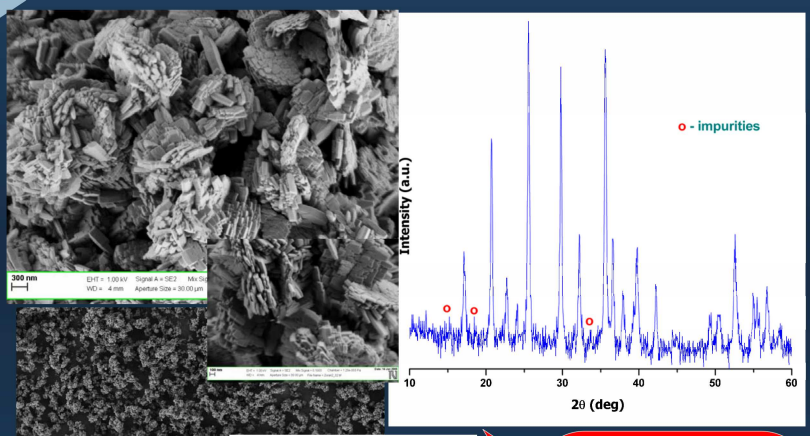
Starting concentration of Fe^{2+} ions were 0.03 mol/l in precursor. On lower synthesis temperatures of 150 and 160 °C with citric acid addition after 4 h amorphous powders were produced with very fine plate like particles. Starting pH of precursor solutions in these reactions was 5.

Increasing synthesis temperature to 180 °C and times to 72 h crystalline aggregated powder was obtained with some impurities mainly due adsorption of Fe^{2+} ions from solution and latter oxidation on the surfaces of the particles.

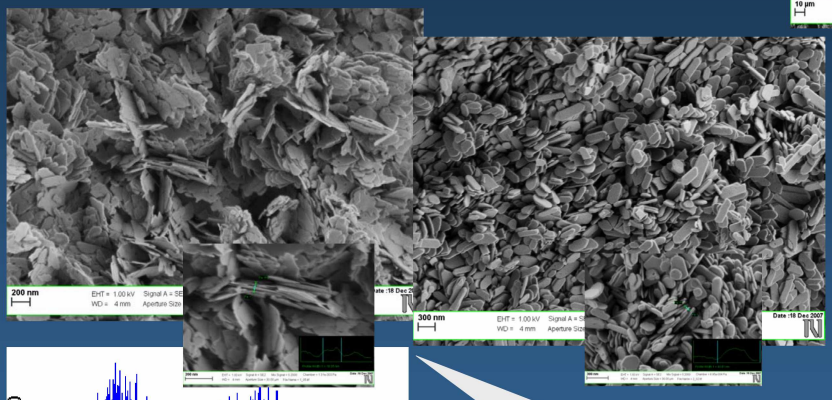
Citric acid in this case act as reducing agent and stabilize specific plate shape of crystals.

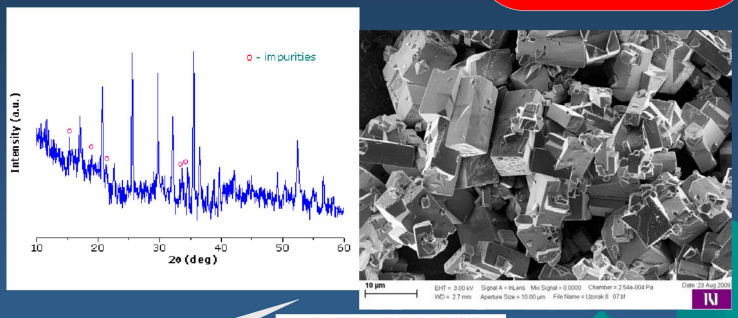
Using the mixture of water and isopropanol solubility of ferrous salt is decreased and concentrations in precursor suspensions were lowered to 0.015 mol/l of Fe^{2+}. pH value of suspension was set to 5 by adding ethanoic acid. After 24 h of reaction crystalline product was collected.

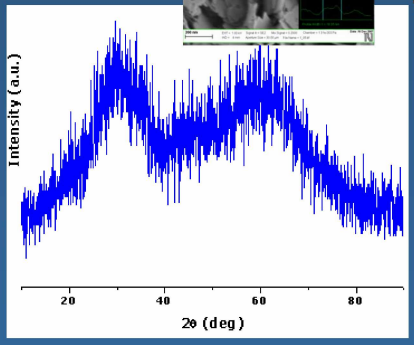
In solvothermal conditions crystallization kinetics are improved. Powders are also aggregated in 30 μm large blocks, formed of rectangular shaped particles of few μm long. Product contains impurities mainly from hydrated ferrous and ferric phosphates.



$LiFePO_4$ synthesized by hydrothermal reaction using precursor solution pH 5 at 180 °C for 72 h. Citric acid was added as reducing agent. Impurities originated from oxidated unreacted Fe^{2+} adsorbed on surface of particles.

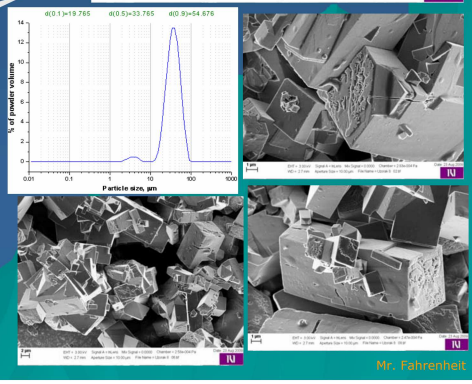






Amorphous powders Synthesized at 150 and 160 °C after 4 h. Diffraction data of sample produced on lower temperature

$LiFePO_4$ synthesized in water – i-propanol at 180 °C 24 h with addition of oleic acid as surfactant.



Conclusion

$LiFePO_4$ is possible to produce by hydrothermal and solvothermal processes using different organic additives that acts as reducing agents and shape control of particles. Advances of this approach are possibility to synthesize composite (carbon) or hybrid particles suitable for further processing.

Mr. Fahrenheit