Morphology-Controlled Synthesis of Olivine-type $LiMnPO_4$ as a Cathode in Lithium-Ion Batteries

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Lithium transition metal phosphates, $LiMPO_4$ (M = Fe, Mn, Co, Ni), with olivine-type structure have attracted the research interest as promising cathode materials for high-power lithium ion batteries with potential application in HEV. The main drawback of phospho-olivines is their low electronic conductivity, which determines the lower rate capability. To improve the rate capability, it is necessary to elaborate specific methods that allow controlling the morphology and nano-crystallinity of the phospho-olivines.

In this contribution we report new methods for the preparation of nano-crystalline $LiMnPO_4$ with controlled morphology. The first method is based on the formation of homogeneous precursors by freeze-drying of mixed phosphate-formate solutions. The thermal decomposition of the precursors at temperatures above 400 °C yields pure $LiMnPO_4$ with isometric particles and close particle distribution in the range of 60–120 nm, which do not form aggregates. The Rietveld analysis evidences that $LiMnPO_4$ are characterized with a low extent of Li-to-Mn disorder (below 1%). The particle sizes of $LiMnPO_4$ are varied by the concentration of the solutions subjected to freeze-drying and by the annealing temperature.

The second method is based on ion-exchange reactions using dittmarite-type host matrices with composition $MMnPO_4.H_2O$ (M = NH_4 and K). The structural similarity between the dittmarite- and olivine-type structures facilitates the ion-exchange process at low-temperatures. The ion exchange reaction was performed at 270 ^oC in an eutectic mixture $LiCl:LiNO_3$ for a short time (90 min). The exchange of potassium with lithium results in the formation of $LiMnPO_4$ with platelet-like aggregates composed by nearly isometric nano-particles (about 90 nm). The exchange of NH_4^+ with Li^+ takes places with NH_3 release, which destroys the pristine dittmarite particles. As a result, nearly isometric particles with dimensions in the range of 70 - 110 nm are formed. The particle shape and dimensions are preserved during further annealing up to 500 ^oC.

The results obtained demonstrate that the ion-exchange and the phosphate-formate methods are effective for the synthesis of nano-sized $LiMnPO_4$ with a controlled morphology, which is favourable for its application as cathode material in lithium-ion batteries.

Acknowledgment

Authors are grateful to the financial support from the National Science Fund of Bulgaria (Ch 1701/2007 and National Centre for New Materials DO-02-82/2008).