4th International Symposium on
Energy Challenges & Mechanics
- working on small scales

11-13 August 2015
Aberdeen, Scotland, UK

High voltage mixed transition metal lithium phosphor olivines as positive active materials for lithium ion batteries

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Accepted for publication on 21st April 2015

Lithium transition metal phospho olivines $LiMPO_4$ (M = Fe, Mn, Co) are attractive candidates as cathode materials for lithium ion batteries. The electrochemical utilization is restricted to the one-electron step $M(II) \rightarrow M(III) + e^-$ with theoretical specific capacities from 167 to 171 mAh/g. Redox-potential and theoretical energy density increase in the series Fe, Mn, Co, Ni.

While $LiFePO_4$ is commercialized, the cobalt and manganese analogues are still under development. In spite of their structural similarity the materials show distinct differences in their electrochemical performance. Structural and chemical stability in the delithiated state are controlled by the transition metal as well as the mechanical stress resulting from the moving phase boundary during the electrochemically driven phase transition. Nano–sizing, ion doping and substitution and application of conductive coatings have been proven to be effective techniques to improve the electrochemical behavior. As substituents redox-active as well as inactive divalent metals can be introduced.

The presentation starts with a brief overview on synthesis and characterization and fundamental aspects of pure materials $LiFePO_4$, $LiMnPO_4$ and $LiCoPO_4$ and their properties. Lithium mixed transition metal phosphates have been synthesized and characterized. The investigated systems contain electrochemically active transition metals as well as inactive magnesium. They all form a solid solution series $Li[M1_{1-x-y}M2_xM3_y]PO_4$.

In the mixed systems the electrochemical process is governed by the transition metals proceeding stepwise according to the sequence of their individual redox-potentials. Small potential shifts of the plateaus have been observed depending on the particular composition.

Magnesium primarily influences the electrochemical properties by structural effects. In the case of magnesium substituted $LiMnPO_4$ a significant potential shift and increased utilization are observed. Furthermore a new voltage step at 4.8 V has been observed by inducing the utilization of the Mn(III)/Mn(IV) redox–pair. Common strategies to further improve these materials will be presented and discussed including their implications for future applications.

Keywords: Lithium ion battery, cathode materials, olivine, lithium mixed metal phosphates