Alternative Cathode materials: beyond one-electron reaction

New target for Li-ion batteries: high energy cathode materials

The future generation of high energy density Li-ion batteries is strongly related to the development of safe and cheap cathode materials with either higher capacity and/or higher working potential than currently used active materials. The Li insertion reaction in the cathode structure normally involves one-electron transfer per transition metal atom, and this represents the main limitation in terms of specific capacity. The development of cathode active materials able to reversibly insert more than one Li per formula unit would be a breakthrough in the advancement of high energy Li-ion battery systems. Constraints on electrolyte systems stability at high voltages and structural stability of cathode materials have to be overcome. With the aim of exploring the feasibility of multi-electron reaction concept in Li-ion battery, different classes of materials that potentially can exchange more than one lithium ion per transition metal have been synthesized and characterized from structural, morphological and electrochemical point of view, namely lithium manganese silicate $\text{Li}_2\text{MnSiO}_4$, lithium vanadium monophosphosphate $\text{LiV}_2(\text{PO}_4)_3$ and $\text{LiMn}_9\text{H}_6\text{O}_8$ spinel.

Monophosphate $\text{LiV}_2(\text{PO}_4)_3$: a novel cathode material

Pyrophosphate based polyoxoanions
- Estimated: possible exchange of 6 Li$^+$, Th. Capacity 173 mAh g$^{-1}$
- Robust three-dimensional ($\text{PO}_4$)$^{3-}$ and ($\text{PO}_4$)$^{2-}$ framework with multiple sites for alkali ions
- High chemical and thermal stability
- 2D ionic conductive pathways

Orthorhombic $\text{Li}_2\text{MnSiO}_4$: stability in different electrolyte systems

- Low cost, Intrinsic thermal stability (strong Si-O bonds)
- Possible exchange of 2 Li$^+$, Th. Capacity 333 mAh g$^{-1}$ at high working potential (> 4V)
- Low electronic conductivity
- Poor cycling stability (irreversible structural changes upon Li$^+$ removal)

Nanosized, carbon coated $\text{Li}_2\text{MnSiO}_4$ (Prist), space group with first cycle discharge capacity of ~200 mAh g$^{-1}$ has been synthesized by solid-state method. Scanning tests on powder and electrodes revealed reactions of $\text{Li}_2\text{MnSiO}_4$ with HF generated by degradation of standard fluorinated electrolytes (LiPF$_6$-based) especially at relatively high temperatures and/or in the presence of traces of water. Consequent Mn dissolution and decomposition of the orthorhombic structure is confirmed. XRD, IR and XPS results confirm formation of Li$_2$SiF$_6$. Corrosion of active material in standard electrolyte system, together with irreversible structural changes upon Li$_x$ extraction, electrochemical reactions are considered as the main reason for the poor capacity retention upon cycling of the $\text{Li}_2\text{MnSiO}_4$-based cathode. Alternative F- free electrolytes have been investigated.

Spinel $\text{Li}_2\text{Ni}_x\text{Mn}_{1-x}\text{O}_4$: high-voltage and high-capacity cathode material

- Spinel structure facilitates the Li$^+$ diffusion
- The working potential is ca. 4.7 V vs. Li/Li$^+$
- Low production cost and easy to obtain
- Theoretical specific capacity 147 mAh g$^{-1}$
- $x=0$ stoichiometric $\text{Li}_2\text{Mn}_2\text{O}_4$ is present as Mn$^{4+}$ (electrochemically inactive at high potential)
- Mn$^{4+}$ can be reduced to Mn$^{3+}$ at potentials below 3 V theoretically inserting up to 2.5 Li$^+$ per formula unit
- Theoretical specific capacity reaches 267 mAh g$^{-1}$
- The overall process involves 3 cubic (at high potentials) and 2 tetragonal phases (at low potentials), resulting in high structural stress

Conclusions and future work

Different structures of alternative cathode materials allowing multielectron reactions have been successfully synthesized and characterized. The feasibility of practical use is explored and different aspects have been investigated including the study of the Li$^+$ insertion/extraction mechanism, the reversibility of involved structural transformations and the compatibility of cathode materials with possible degradation products of standard electrolytes. Further analysis are in progress, in collaboration with project partners, in order to design and optimize future generation of cathode materials for high energy density Li-ion batteries.