

**[o.m9.o3] The lithium layered oxides : from an intercalation reaction to a lithium-ion battery.** C. Delmas, *Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS and Ecole Nationale Supérieure de Chimie et Physique de Bordeaux, Av. Dr Schweitzer, 33608 Pessac Cedex (France).*

Keywords: layered oxides, intercalation, lithium batteries.

Lithium layered oxides with general  $\text{LiMO}_2$  formula can be used as positive electrode of lithium-ion batteries. During battery charge and discharge, lithium and electrons are reversibly deintercalated and then reintercalated.

The structures can be described from a packing of  $\text{MO}_2$  slabs, built up of edge-sharing  $\text{MO}_6$  octahedra. The orbital overlap leads, when M is a 3d cation, to metallic or semiconductor properties, while the 2D-character of the structure leads to a high lithium ion conductivity. The existence of several oxidation states allows changes in the material composition. All these properties allow reversible energy storage with a high power density.

When these compounds are used as positive electrode materials in lithium batteries, depending on M and on the lithium deintercalation amount, the layered structure can be preserved or not. In the case of the vanadium and manganese systems the layered structure is only maintained at the beginning of the lithium deintercalation, while an irreversible transition to a spinel related phase is observed when a too high amount of lithium is removed. Upon lithium deintercalation from  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ , the layered structure is maintained ; therefore these materials can be used in practical cells.

In order to understand the various processes involved during the lithium deintercalation and reintercalation and also to optimise the material properties a considerable fundamental research work has been carried out on these materials. A general overview of these studies will be presented.

A special attention will be devoted to the phase transitions which occur during the cycling ; they can result from lithium/vacancy orderings or to an insulator/metal transition.

In the case of the  $\text{LiNiO}_2$  system, which seems one of the most promising for large batteries (electric vehicle), partial substitution of several cations for nickel allows to monitor most of the properties. These effects will be discussed.

**Acknowledgements:** The author wish to thank L. Croguennec, M. Ménétrier and L. Fournès for their collaboration and SAFT, CNES, Union Minière and Région Aquitaine for financial support.

[1] C. Delmas, M. Ménétrier, L. Croguennec, I. Saadoun, A. Rougier, C. Pouillier, G. Prado; M. Grtine and L. Fournès. "An overview of the  $\text{Li}(\text{Ni},\text{M})\text{O}_2$  systems : syntheses, structures and properties." *Electrochemical Acta*, (1999), **45**: 243-253.

**[o.m9.o4] Crystal packing of intercalated layered structures.** P. Capková<sup>1,2</sup>, H. Schenk<sup>2</sup>. <sup>1</sup>*Faculty of Mathematics and Physics, Charles University Prague, Ke Karlovu 3, 12116 Prague, Czech Republic;* <sup>2</sup>*Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166; 1018WV Amsterdam, The Netherlands.*

Keywords: non graphitic lamellar compounds.

Intercalation of inorganic layered host compounds with organic species results in a hybrid organic/inorganic structure, where the two-dimensional supramolecular system of organic guest molecules in the interlayer space of host structure can exhibit the changes in conformation and consequently the changes in electronic properties. This modification of electronic properties due to the crystal field of host layers is used in development of new materials with interesting photofunctions<sup>1</sup> for (opto)electronic devices.

Using combination of molecular mechanics simulations with experiment (X-ray and synchrotron powder diffraction and IR spectroscopy) we determined the structure of the following intercalates with various organic guest species: phyllosilicates<sup>2</sup>, vanadyl phosphates<sup>3,4</sup> and zirconium phosphate<sup>5</sup>. This structure analysis based on the combination of modeling with experiment enables the structure determination, including the characterization of possible disorder. In addition we obtain the energy characteristics, such as the total sublimation energy, the host-guest and guest-guest interaction energy and their individual components (van der Waals, electrostatic and hydrogen bond energy) and the charge distribution on the host layers and guest species.

Crystal packing of intercalates is a result of the joint effect of several factors characterizing the mutual complementarity of the host structure and guest species such as: (1) the relationship between the structure parameters of the host layer, including the distances between active sites and size and structure parameters of guest species and (2) the relationship between the charge distribution on host and guest structure and the host-guest and guest-guest interactions. The results of structure analysis for series of intercalates enabled us to appoint some general criteria for the ordering of guest species and host layers and the classification of intercalates as to their interlayer ordering and layer stacking<sup>6</sup>.

[1] Ogawa M., Kuroda K. "Photofunctions of Intercalation Compounds", *Chem. Rev.* (1995), **95**, 399-438.

[2] Capková P., Burda J.V., Weiss Z., Schenk H. "Modelling of Aniline-Vermiculite and Tetramethylammonium-Vermiculite", *J. Mol. Model.* (1999), **5**, 8-16.

[3] Capková P., M. Trchová, V. Zima, H. Schenk "Structure analysis of Vanadyl Phosphate Intercalated with Acetone" *J. Sol.State Chem.* accepted for (2000).

[4] Capková P., Melánová K., Beneš L., Schenk H. "Modeling in Structure analysis of Vanadyl Phosphate Intercalated with 1-Alkanols" *J. Mol. Model.* (2000), **6**, 9-15.

[5] Capková P., Beneš L., Melánová K., H. Schenk, "Structure analysis of Intercalated Zirconium Phosphate Using Molecular Simulation", *J. Appl. Cryst.* (1998), **31**, 845-850.

[6] Capková P., Votinský J., "Molecular Mechanics Simulations of Intercalates", *Molecular Crystals and liquid Crystals*, Accepted in September 1999.