# Amorphization/Recrystallization Mechanism in the Ternary $Li_xMPn_4$ Phases (M=Ti,V; Pn=P,As) : A DFT Study

M.-L. Doublet[a], F. Lemoigno[a], L.Monconduit[b], F. Favier[b]
a : CNRS-LSDSMS b: CNRS-LAMMI
Université Montpellier II – Place E. Bataillon
F-34095 Montpellier, Cedex 5

We present a computational study of the electrochemical reactivity of the ternary transition metal pnictides $Li_xMPn_4$ (M=Ti, V ; Pn = P, As) towards elemental lithium. These phases have been recently proposed as promising negative electrode materials[1] for the design of new Li-Ion batteries. They show high specific capacities ($500< C <1000 mAhg^{-1}$) in their first charge/discharge cycle which are holded on to 80% after 20 cycles. To get more insigths into the Li insertion/deinsertion mechanisms involved in these materials, electronic structure calculations and structural relaxations have been performed, using the density functional theory formalism (codes VASP, WIEN).

## 1. Crystal Structure and Electrochemical reactivity of the $Li_xMPn_4$

As shown in figure 1, the $Li_xMPn_4$ phases crystallize in a cubic symmetry. The pnictogen atoms form a *f.c.c.* bulk in which the tetrahedral and octahedral Pn-coordinated cationic vacancies are filled by Li/M in a statistical manner, and by Li, respectively.

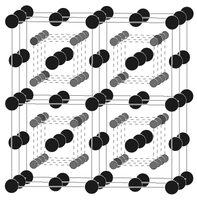

**Fig.1** : 2x2x2 Crystal structure of $Li_7MPn_4$. The transition metal atoms (red) are statistically distributed over the tetrahedral Pn-coordinated sites of the *f.c.c.* bulk of Pn atoms (blue).

A study of the electrochemical reactivity of these materials towards elemental lithium, through the assembly of $Li/Li_xMPn_4$ half cells (M=Ti, V, Mn, Pn=P, As)[2] has revealed that a large number of lithium per formula unit can be reversibly extracted/inserted from/in the $Li_xMPn_4$ networks (up to 10 lithium for $Li_xVAs_4$). Galvanostatic measurements show that a two-phase process occurs upon charge (flat potential profiles) whereas a more complex mechanism is involved upon discharge. Recently, *In situ* X-ray diffraction patterns collected upon cycling have shown that the *f.c.c.* peaks of the starting lithiated and crystallized phases progressively vanish upon charge (delithiation) while they partially reappear upon discharge (lithiation). This suggest a reversible amorphization/recrystallization process upon cycling.

## 2. Electronic Structure Calculations

To elucidate the electrochemical reaction mechanism, we performed electronic structure calculations, with full structural relaxations, on the $Li_xMPn_4$ (M=Ti,V ; Pn=P,As) bulk for various lithium compositions. As shown by the electron density maps given in figure 2, the electronic structure of these materials describes weakly interacting $MPn_4$ tetrahedra. This leads to a wide charge vacancy between the tetrahedra (*i.e.* inside the cubic cell) that favours the lithium diffusion.

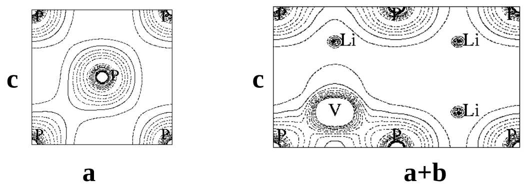

**Fig.2 :** Electron density maps for the $Li_7VP_4$ phase in the (**a,c**) plane (face of the *f.c.c.* cell) and in the (a+b,c) plane.

Moreover, our calculations show that the stability of the $MPn_4$ tetrahedra is not that affected by the loss of charge when lithium content goes from 7 to 3.

As depicted in figure 3, the M-Pn bonds are slightly shortened (by no more than 5%) when $4Li^+$ are extracted from $Li_7MPn_4$. This leads to a small contraction of the tetrahedra within the cell and to a new charge distribution along the M-Pn bonds. As a consequence, the total anionic charge of each $MPn_4$ tetrahedra (which decreases with the number of lithium) keeps on being efficiently compensated by the remaining $Li^+$ cations, through electrostatic interactions. In addition, due to $Li^+$-$Li^+$ destabilizing interactions, the unit cell parameter of the initial cubic lattices does not follow the M-Pn bond contraction when lithium is extracted from the $Li_7MPn_4$ phases. The main consequence of this is a loss of the *f.c.c.* symmetry for the relaxed $Li_3MPn_4$ unit cells, in full agreement with *in situ* XRD.

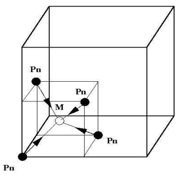

Fig. 3 : M-Pn bondlength contraction of the $MPn_4$ tetrahedra for $Li_3MPn_4$.

The high reversible charge/discharge process evidenced for the ternary $Li_xMPn_4$ phases is then associated with a destruction/recovering of the long-range cubic order. This has been rationalized by means of a contraction/elongation of the strongly bonded $MPn_4$ tetrahedra. Because the contraction is not larger than 5% the total unit cell volume remains nearly unchanged. This is a crucial point since materials that combine a small volume expansion together with a wide range of lithium are highly requested in the lithium rechargeable battery field.

[1] M.-L. Doublet, F. Lemoigno, F. Gillot and L. Monconduit *Chem. Mat.* 14 **2002** 4126.
[2] L. Monconduit, F. Gillot, M-L. Doublet, F. Lemoigno *Solid State Ionics* **2002** In press