One year Post-doctoral position

Theoretical study of $LiMPO_4X$ (M = transition metal and X = F, OH, O) with tavorite structure

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Since the evidence of good performances of $LiFePO_4$ as positive electrode in Lithium batteries, the search for other phosphates materials, that would lead to higher potential (> 3.45 V vs. Li^+/Li), is intense. In this context, the transition metal fluorophosphates seem to be promising, as the electronegativity of F, leads to an increase if the M-O(F) bonds and therefore to an increase of the energy difference between the transition metal redox couple and Li+/Li. Among the materials that are presently studied, the tavorite $LiMPO_4X$ (M = Fe, V, Ti,… et X = F, OH, O) family is very interesting. Thus, the $LiVPO_4F$ phase was recently studied [1-4]. It exhibits a 4.25 V (*vs.* Li^+/Li) for the V^{4+}/V^{3+} redox couple and a 130 $mAh.g^{-1}$ as reversible capacity. Other tavorite phases as LiFePO4F and LiTiPO4F were also studied [5-7]. In parallel at ICMCB, we worked on the $LiFePO_4$.OH and $HFePO_4$.OH homeotypic phases [8-9]. In this context, a PhD student at ICMCB is presently working in collaboration with the LRCS lab in Amiens on the $LiMPO_4X$ (M = Fe, V, Ti) fluoro-and oxyphosphates with the tavorite structure: synthesis, characterization and mechanism involved in the intercalation/deintercalation of Li ions.

The post-doctoral position proposed here concern the theoretical study of these phases with X = F, OH, O using DFT first principles calculations and Monte Carlo simulations.

In a first part, the research subject will be focused on the theoretical study of the initial phases: determination of the most stable Li sites, calculations of the expected average voltages and analysis of the change in chemical bonds while changing the TM ion or the X group. VASP and WIEN2k codes will be mainly used.

In a second part, structural modifications implied in the intercalation/deintercalation process will be studied from a theoretical point of view in strong link with the experimental studies: Li sites, intermediate phase formation …

In a last part, diffusion properties will be studied theoretically in collaboration with Anton Van der Ven (University of Michigan, USA), using DFT calculations and Monte Carlo simulations: diffusion coefficient and diffusion paths will be determined.

Candidates should have a strong expertise in DFT calculations on inorganic solids (VASP, WIEN2k codes).

References:

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[3] J. Barker, R.K.B. Gover, P. Burns, A. Bryan, M.Y. Saidi and J.L. Swoyer, *J. Electrochem. Soc.* **152**, A 1776 (2005).
[4] Barker et al., *Patent No.: US 6,855,462 B2* (2005).
[5] N. Recham, J-N. Chotard, J-C. Jumas, L. Laffont, M. Armand, and J-M. Tarascon, *Chem. Mater.* **22**, 1142 (2010).
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[7] T.N. Ramesh, K.T. Lee, B.L. Ellis, and L.F. Nazar, *Electrochemical and Solid-State Letters* **13**, A43 (2010).
[8] N. Marx, L. Croguennec, D. Carlier, A. Wattiaux, F. Le Cras, E. Suard and C. Delmas, *Dalton Transactions*, **21**, 5108-5116 (2010).
[9] N. Marx, L. Croguennec, D. Carlier, L. Bourgeois,F. Le Cras and C. Delmas., *Chem. Mater.* **22**, 1854-1861 (2010).