

Single-phase Na⁺/Li⁺ co-insertion mechanism within olivine FePO₄

Marie Lachal^{a,b}, Renaud Bouchet^{a,b*}, Charles Delacourt^c, Cécile Rossignol^{a,b}, Fannie Alloin^{a,b}, Saïd Obbade^{a,b}

^a Université Grenoble Alpes, LEPMI, F-38000 Grenoble, France

^b CNRS, LEPMI, F-38000 Grenoble, France

^c Université de Picardie Jules Verne, LRCS, 80039 Amiens, France

*marielachal@hotmail.fr

Olivine LiFePO₄ (de)lithiation mechanism has been largely studied over the past 10 years and is usually observed and interpreted as a two-phase transition. However, recent publications demonstrated that the dynamic transformation from LiFePO₄ to FePO₄ (and reverse) would go through a metastable solid solution Li_xFePO₄, especially in the case nanoparticles at high charging rate [1-3]. Olivine NaFePO₄ (de)sodiation mechanism appears even more complex with the existence of the intermediate phase Na_{2/3}FePO₄, leading to two charging plateaus and extended solubility limits [4-6]. This work presents the peculiar (de)insertion mechanism during chemical delithiation and electrochemical sodiation observed by *operando* XRD. Firstly, *ex situ* XRD performed on partially chemically delithiated Li_xFePO₄ powders have shown a stabilized solid solution at equilibrium state, which is usually observed under dynamic conditions [3]. Secondly, the Li_{0.6}FePO₄ phase obtained by chemical delithiation has been electrochemically characterized in Na half-cell. Associated *operando* XRD displays a progressive shift of the diffraction peaks (Figure 1), revealing a Li⁺/Na⁺ co-insertion mechanism via a complete solid solution. These results, reported for the first time, bring new insights on Li⁺/Na⁺ insertion mechanisms within olivine FePO₄ structure.

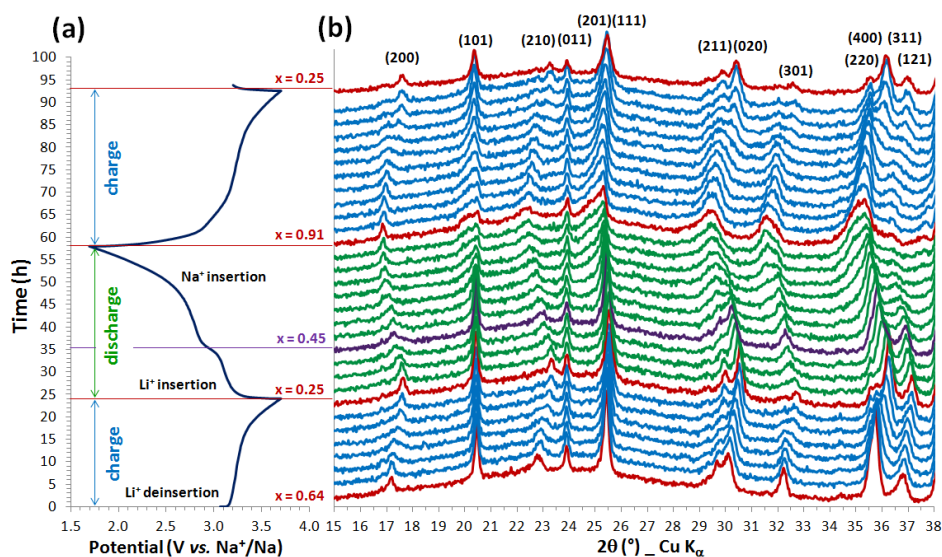


Figure 1: Electrochemical and structural characterizations of Li_{0.6}FePO₄ in Na half-cell : (a) Charge/discharge galvanostatic curve at C/60 rate, (b) *operando* XRD patterns at different states of charge/discharge.

- [1] R. Malik, F. Zhou, G. Ceder, Nat. Mater. 10 (2011) 587–590.
- [2] Y. Orikasa, et al. J. Am. Chem. Soc. 135 (2013) 5497–5500.
- [3] H. Liu, et al. Science 344 (2014) 1252817.
- [4] P. Moreau, D. Guyomard, J. Gaubicher, F. Boucher, Chem. Mater. 22 (2010) 4126–4128.
- [5] M. Galceran et al. Phys. Chem. Chem. Phys. 16 (2014) 8837–8842.
- [6] J. Gaubicher et al. Electrochem. Commun. 38 (2014) 104–106.