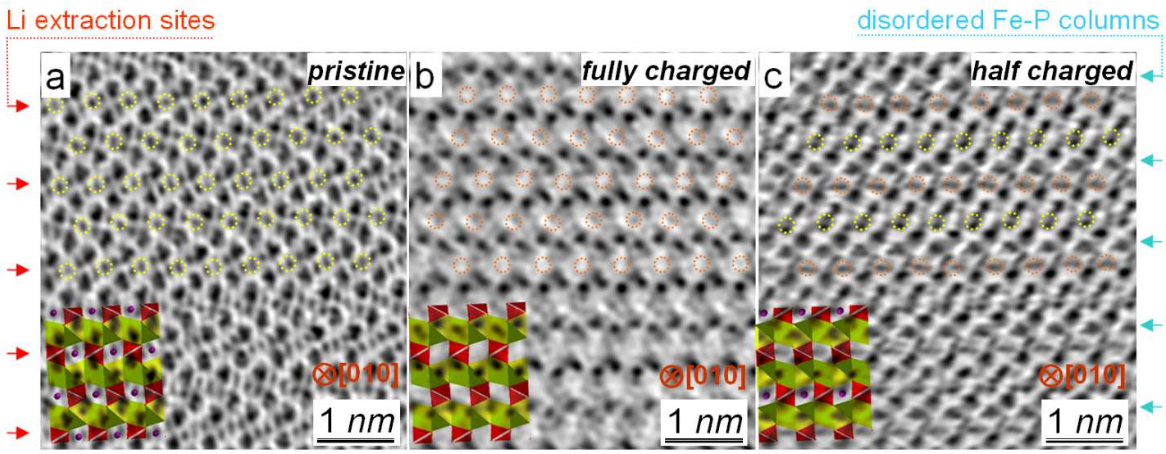
Theoretical and experimental characterization of Li transport in $LiFePO_4$ cathode and thio-LISICON electrolytes for next generation rechargeable Li-ion batteries

Nicola Marzari, THEOS, Ecole Polytechnique Fédérale de Lausanne
Joachim Maier, Max-Planck Institute for Solid State Research, Stuttgart
Bettina Lotsch, Max-Planck Institute for Solid State Research, Stuttgart



Li_xFePO_4 is rapidly emerging as one of the most promising and already widely used cathode materials for rechargeable Li-ion batteries, in particular for applications requiring high-rate performance. However, no general consensus has yet been achieved on the microscopic mechanisms governing Li-ion transport in its interior. Furthermore, available electrolytes still challenge performance and safety, and novel solid lithium electrolytes are highly sought after. A careful characterization of Li diffusion during the charge/discharge transients, both through the cathode and suitable solid electrolytes, is thus crucial to develop new strategies to improve the performance of Li-ion batteries. Central questions to be addressed in this project include i) the nature and existence of intermediate phases forming in the cathode at or near the interface between Li-rich and Li-poor materials (see Figure), ii) their role in the (de)lithiation processes, iii) the conditions under which different Li transport regimes are reached, and iv) the search for suitable solid electrolytes compatible with a Li_xFePO_4 cathode. These questions will be addressed using a combination of computational and experimental techniques. First-principles calculations using novel Hubbard functionals will be performed to evaluate the relative stability of various configurations and to compute kinetic barriers in the cathode; first-principles molecular dynamics will be used to screen and the characterize novel chalcogenide-based solid electrolytes of the tetragonal LGPS-type family. The experimental activity will focus on materials synthesis and characterization, impedance spectroscopy, cyclic voltammetry, pulse field gradient NMR and Li relaxometry. The long term goal of this project is twofold: reaching a precise characterization of the Li transport mechanisms under various operative conditions, and identifying viable materials design strategies for the cathode and the electrolyte to optimize performance for target applications.

1. L. Gu et. al., *JACS* 133, 4661 (2011); Zhu et al., *Adv. Funct. Mat.* 24(3), 312–318 (2014)