

New insights into the kinetics of Na insertion and extraction into the FePO₄/NaFePO₄ system

D. Saurel^a, H. Anne^a, M. Galcerán Mestres^a, B. Acebedo^a, M. Lepoitevin^a, T. Rojo^{a,b} and M. Casas Cabanas^a

^a *CIC Energigune - Parque Tecnológico, C/Albert Einstein 48, 01510 Miñano, Spain*

^b *Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, 48080 Bilbao, Spain*

dsaurel@cicenergigune.com

Sodium-ion batteries (SIB), which were studied in parallel to Li-ion batteries (LIB) in the early days of the research on insertion secondary batteries, are subject to a renewed interest in recent years as a potential lower cost alternative to LIB [1]. Similarly to LIB, in SIB Na⁺ ions are shuttled between the positive and negative electrodes during charging and discharging, with an electrolyte acting as the transportation medium for those ions. Fundamental differences related to phase stability, volume expansion, ionic diffusivity or voltage between the insertion of lithium versus insertion of sodium in the same host compound have been observed in several materials, resulting in successive phase transitions that are less common in the lithium counterparts [2].

A material that well illustrates these differences is olivine NaFePO₄. This (meta)stable material under normal operation conditions can reversibly insert/extract Na ions with a theoretical capacity of 154 mAh/g at an average voltage of 2.9V [3]. This material presents intriguing differences with its Li-ion counterpart. Indeed, contrary to LiFePO₄ which presents a reversible biphasic transformation [4-5], distinct phase transformation mechanisms are observed during Na insertion and extraction into NaFePO₄ [6-8]. Moreover, the cell polarization is significantly higher in the case of sodium which suggests a less favourable kinetics of Na diffusion compared to Li, confirmed by larger diffusion coefficient for lithium as deduced from impedance spectroscopy performed at x=0.9 [9]. However, to our knowledge the diffusion coefficient remains unknown for intermediate sodium compositions. Furthermore, a discrepancy is observed in the theoretical predictions of activation energy of ionic diffusion in the end members,[10-11] while to our knowledge no experimental value has been yet reported.

Using ex-situ and in operando X-ray diffraction, galvanostatic intermittent titration technique and electrochemical impedance spectroscopy we have been able to follow the kinetics of phase transformation and ion/vacancies diffusion during charge and discharge and contrast the differences between the two types of ions inserting and extracting into/from the same host structure.

References:

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