

New insights into the kinetics of Na insertion and extraction into the $\text{FePO}_4/\text{NaFePO}_4$ system

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Sodium-ion batteries are considered an attractive alternative to lithium-ion batteries as could potentially be much less expensive, safer and environmentally benign [1]. Similarly to Li-ion cells, in Na-ion batteries 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 NaFePO_4 . Olivine NaFePO_4 is (meta)stable under normal operation conditions and, contrary to the electrochemically inactive maricite form, can reversibly insert/extract Na ions, with a theoretical capacity of 154 mAh/g. This materials present intriguing differences with its Li-ion counterpart. Indeed, contrary to LiFePO_4 which presents a reversible biphasic transformation [3], distinct phase transformation mechanisms are observed during Na insertion and extraction into NaFePO_4 [4]. Moreover, the cell polarization is significantly higher in the case of Na-ion which suggests a less favorable kinetics of Na diffusion compared to Li, in accordance with previous theoretical previsions. However, despite of a high volume mismatch between end members (more than 17,6% for $\text{FePO}_4/\text{NaFePO}_4$ while 6,9 % for $\text{FePO}_4/\text{LiFePO}_4$), which seems to play an important role in the phase transformation mechanisms [5], olivine FePO_4 presents good stability upon charge and discharge.

This work will present new insights into the kinetics of intercalation and de-intercalation of Na into FePO_4 and NaFePO_4 , respectively, and its correlation with the mechanisms of phase transformation upon battery operation. In situ X-ray diffraction, electrochemical impedance spectroscopy and galvanostatic intermittent titration technique, performed upon Na^+ and Li^+ insertion and extraction into the same host material, allowed us to precisely follow the kinetics of phase transformation and ion/vacancies diffusion during charge and discharge and contrast the differences between the two type of ions.

The obtained results will be discussed in terms of physical and mechano-chemical aspects of the charge and discharge reactions and will be contrasted with the mechanism of the lithium counterpart.

References:

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