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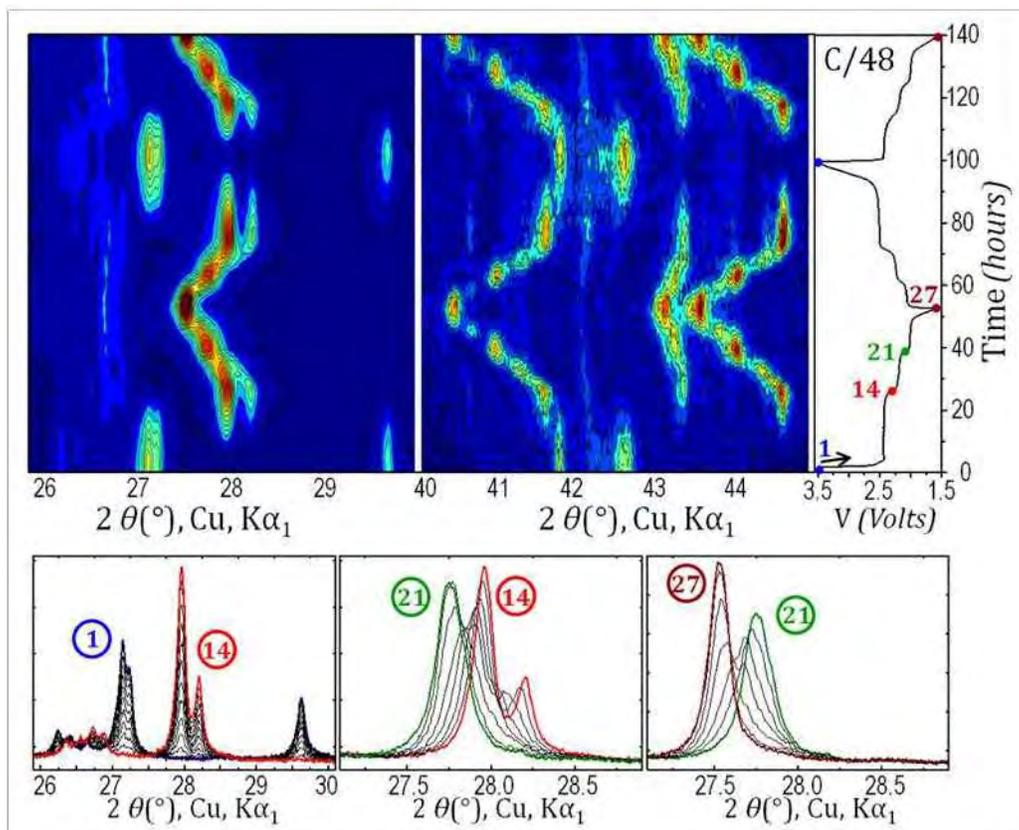
Diffraction studies of Tavorite-based polyanionic materials for Li-ion batteries

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Polyanionic materials attract great interest in the field of Li-ion batteries thanks to the wide range of possible available compositions, resulting in a great amount of different properties (1). For instance, the high working potential together with a capacity of 156 mAh/g (leading to a theoretical energy density of 655 Wh/g) made Tavorite LiVPO₄F a widely studied material and a suitable candidate for commercial exploitation. Here we will focus our interest on the homeotype structure of LiVPO₄O. This oxy-phosphate shows the ability to exploit two redox couples, V⁵⁺/V⁴⁺ at 3.95 V vs. Li⁺/Li and V⁴⁺/V³⁺ at an average potential of 2.3 V vs. Li⁺/Li upon Li⁺ extraction and insertion, respectively (2). The two domains show marked differences both in the electrochemical signature and in the phase diagram, which is extremely rich. In particular, while the high-voltage domain shows a relatively simple two-phase transformation between LiVPO₄O and ε-VPO₄O, the low-voltage domain is more complicated and it shows a series of three apparent biphasic reactions while Lithium is inserted in the Tavorite structural framework. To elucidate this reaction, we performed in-situ X-Ray diffraction (Kα₁), i.e. we recorded the whole process in real time during battery discharge. The end member Li₂VPO₄O was also isolated ex-situ and its crystal structure determined for the first time thanks to neutron diffraction measurements (3). Both the phase diagram and the different crystal structures will be discussed.

[1] C. Masquelier, L. Croguennec, *Chemical Reviews*, 2013, 113, 6552, [2] J.-M. Ateba Mba, C. Masquelier et al., *Chemistry of Materials*, 2012, 24 (6), 1223, [3] M. Bianchini, J.-M. Ateba Mba et al., *Energy and Environmental Sciences*, submitted



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