

Quantitative electron diffraction tomography for the structure solution of cathode materials for Li-ion batteries

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Quantitative electron diffraction tomography (EDT) is a perfect tool for studying electrode materials for Li-ion batteries due to its ability to obtain diffraction data from submicron crystals (typically 100-200 nm), sensitivity to “light” atoms as Li and reduced dynamical effects (enhanced by the intrinsic property of the electrode materials to comprise only lightest possible elements to maximize the capacity). Here we demonstrate applications of EDT to the crystal structure analysis of polyanion cathodes, including location and occupancy refinement of the Li positions.

We applied EDT for monitoring the deintercalation process in $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ (LMFP) olivine [1]. We investigated a pristine and two delithiated phases (mid (3.7 V vs. Li/Li^+) and fully-charged (4.2 V), since upon charge two first-order phase transformations take place). All structures keep the *Pnma* space group and unit cell metrics and no sign of local ordering was found. The difference Fourier maps of the electrostatic potential calculated from EDT data, allow to localize the Li atoms (Fig 1). The refined occupancies of the Li positions for all samples are in excellent agreement with the Li contents measured from the E-x dependence obtained with galvanostatic cycling. Regarding the role of Jahn-Teller distortion due to Mn^{3+} in the delithiation mechanism, this effect is not of cooperative nature, since the octahedral distortions in pristine and fully-charged samples vary insignificantly (5%).

EDT sheds light on the family of (Li,A)-ion cathode materials that are obtained by subsequent chemical or electrochemical exchange of Na/K by Li. This allows obtaining new polymorphs that are not attainable by direct synthesis due to thermodynamic reasons. We synthesize new KVPO_4F fluorophosphates with KTiOPO_4 (KTP) structure, having a 3D system of continuous spatial cavities and two potassium positions [2]. Upon charge up to 5.0 V vs Li/Li^+ the K1 site becomes empty whereas residual potassium (17%) resides in the K2 site (Fig. 2). At the same time, the structure changes from noncentrosymmetric (*Pna2₁*) to centrosymmetric (*Pnan*). After lithiation, the K2 sites are shared by K and Li but K1 still remains empty. Li occupies a new Li3 position having [4 + 2] coordination with four short 1.99–2.14 Å Li3-O bonds. Both Li sites reside in the channels along the *b* axis and form a row of Li atoms.

The discussed examples show that EDT is a reliable technique for the crystal structure solution and refinement. It can be used as a routine method for the study of cathode materials, since no special sample preparation is required. Furthermore, EDT provides valuable information of the lithium atom positions and occupancies.

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[1] O.A. Drozhzhin, V.D. Sumanov, O.M. Karakulina, A.M. Abakumov, J. Hadermann, A.N. Baranov, K.J. Stevenson, E. V Antipov, *Electrochim. Acta* 191 (2016) 149.

[2] S.S. Fedotov, N.R. Khasanova, A.S. Samarin, O.A. Drozhzhin, D. Batuk, O.M. Karakulina, J. Hadermann, A.M. Abakumov, E. V. Antipov, *Chem. Mater.* 28 (2016) 411.

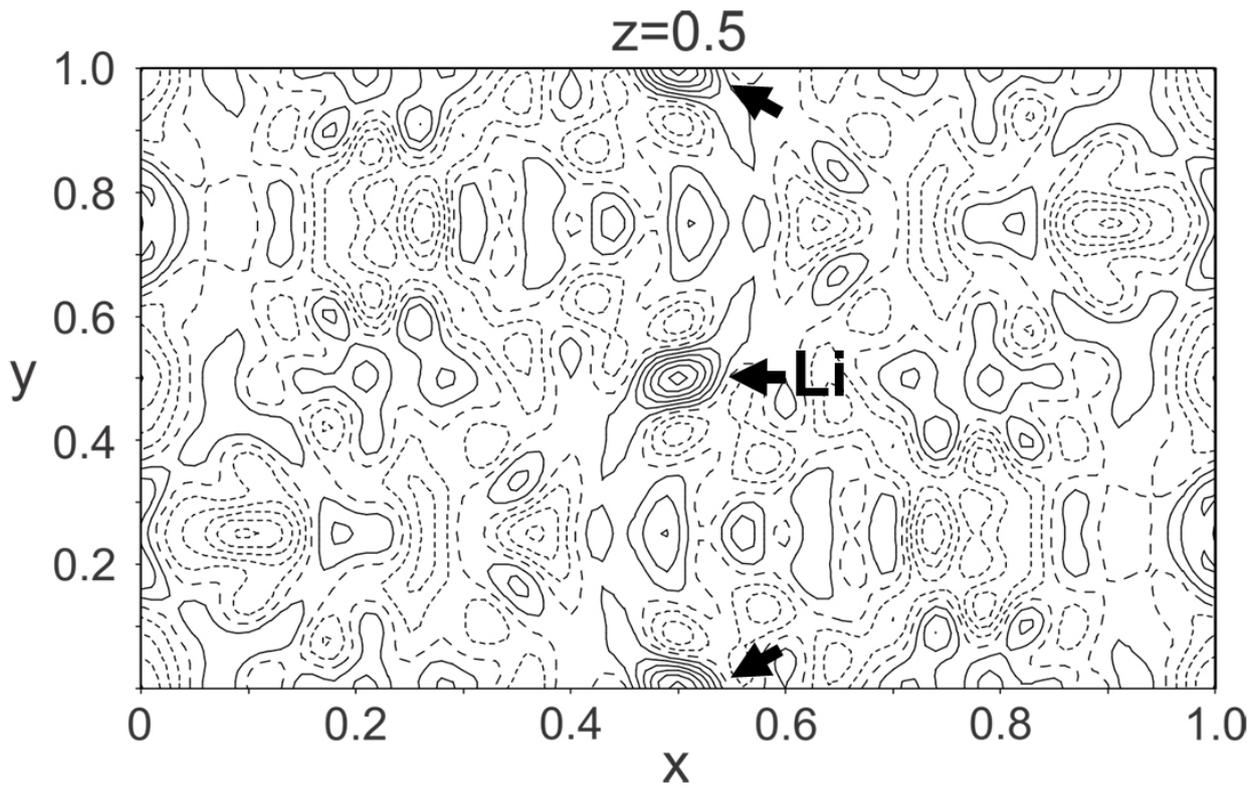


Fig. 1. Difference Fourier map around the Li position for the $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ calculated from EDT data. Note the presence of a clear maximum of scattering density (marked by arrows).

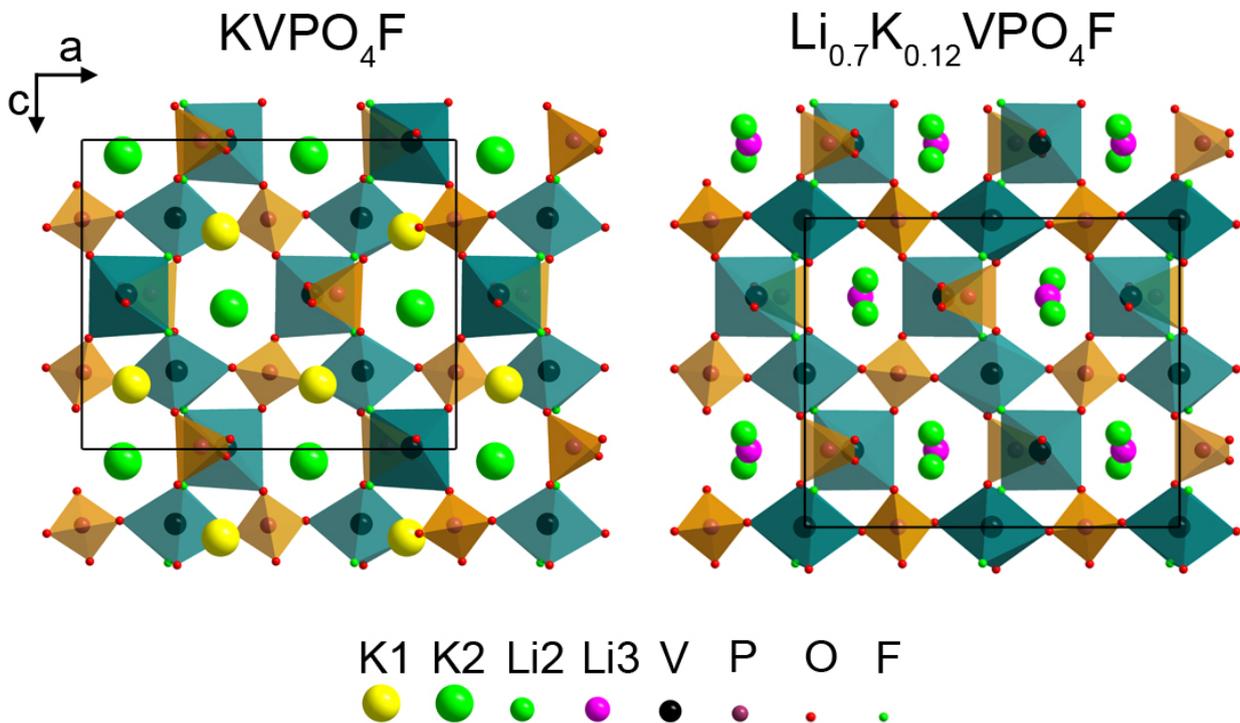


Fig. 2. Crystal structures of pristine KVPO_4F and lithiated $\text{Li}_{0.7}\text{K}_{0.12}\text{VPO}_4\text{F}$ shown along $[010]$ direction.