Positron annihilation at grain boundaries in lithiated and delithiated Li_xFePO_4 battery material

J. Kuriplach[1*], A. Pulkkinen[2], and B. Barbiellini[2,3]

[1] *Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, CZ-180 00 Prague 8, Czech Republic*
[2] *Department of Physics, School of Engineering Science, LUT University, FI-53851, Lappeenranta, Finland*
[3] *Physics Department, Northeastern University, Boston, MA 02115, USA*

The $LiFePO_4$ battery cathode material [1] is employed in various devices, including electric cars and bicycles, (mobile) home appliances, path/security lights, *etc*. This material possesses some advantages over frequently used $LiCoO_2$-based materials, except slightly lower energy density. Nevertheless, $LiFePO_4$ materials can be further optimized and as a help in this process studying the structure and other properties of grain interfaces in cathodes made of small grains (powders) is necessary. The point is that Li ions are diffusing in and out of the grains – via the grain interfaces, which is an important aspect of the battery operation (discharging and charging).

The selected grain boundaries (GBs) in $LiFePO_4$ and $FePO_4$ were constructed by means of the coincidence site lattice geometrical concept [2] adapted to (Li)$FePO_4$ orthorhombic crystal system. Initial atomic configurations/supercells containing up to 200 atoms were then relaxed using a pseudopotential electronic structure code based on the density functional theory considering the magnetism of the studied system. Positron characteristics such as lifetime and positron binding energy to GBs were determined using relaxed configurations. The bulk positron properties of $LiFePO_4$ and $FePO_4$ were calculated already earlier [3]. Structural and positron calculations show that studied grain boundaries exhibit free volumes where positrons can be trapped. The GBs in $FePO_4$ have longer lifetimes. The comparison with positron lifetime data for a powdered $LiFePO_4$ sample (grain size ~100 nm) [4] suggests that one lifetime component could originate from the GBs. This indicates that positron annihilation spectroscopy could in principle be used to study grain interfaces in Li_xFePO_4 system and probably also in other Li-ion battery cathode materials. Possible ways of Li diffusion at GBs in the studied material are also discussed.

References

[1] A.K. Padhi *et al.*, *J. Electrochem. Soc.* **144**, 1188 (1997).
[2] M.L. Kronberg and F.H. Wilson, *Trans. AIME* **185**, 501 (1949).
[3] J. Kuriplach and B. Barbiellini, *Defect Diffus. Forum* **373**, 35 (2016).
[4] P. Zhang *et al.*, *J. Electrochem. Soc.* **159**, A402 (2012).

*Corresponding author, Email: jan.kuriplach@mff.cuni.cz