Formation and annihilation of defects is an intrinsic and inseparable part of alkali cation (de)intercalation from positive electrodes (cathodes) for metal-ion batteries. Here we discuss antisite disorder in the olivine-structured LiFePO$_4$, 3D framework or layered A$_2$MPO$_4$F (A = Li, Na, M = transition metal). We demonstrate that the bonding of the alkali metal cations to the semi-labile oxygen atoms is an important factor affecting electrochemical activity of alkali cations in the polyanion structures. Such semi-labile oxygens are not included into the M(O,F)$_6$ octahedra, being tetrahedrally coordinated by one P and three alkali cations and forming localized sp$^3$-hybridized states. Upon alkali cation deintercalation these oxygens experience severe undercoordination, causing an energy penalty for removing the alkali cations located in the proximity of such semi-labile oxygens. The importance of this semi-labile oxygens stems from their influence on the (de)intercalation mechanism, diffusion barriers and antisite defect formation. Dependence of the deintercalation potential of different alkali cation sites on the proximity to the semi-labile oxygens, charge compensation mechanism through the antisite Li/M disorder and associated changes in the deintercalation mechanism will be discussed. For LiFePO$_4$ we establish the relation between antisite Li/Fe disorder and chemical substitution in the polyanion sublattice leading to unusual “hydrotriphylite”-type solid solutions, altering the crystal structure and electrochemical capacity. The work was supported by RFBR (grant 17-03-00370).