Soft X-ray Emission Spectroscopy of Crystalline and Amorphous Li_xSi Alloys in Lithium-Ion Batteries: A Theoretical Study

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It is demonstrated that methods of the soft X-ray emission spectroscopy (SXES) can be used as a powerful tool for the comprehensive analysis of the electronic and structural properties of lithium silicides Li_xSi forming in lithium-ion batteries (LIB) anode upon Si lithiation [1]. On the basis of density functional theory (DFT) and massive molecular dynamics (MD) simulations it is shown that coordination of Si atoms in Li_xSi decreases with increase in Li concentration both for the crystalline and amorphous phases. In amorphous a- Li_xSi alloys Si tends to cluster forming Si-Si covalent bonds even at the high lithium concentration. It is demonstrated that the Si-$L_{2,3}$ emission bands of the crystalline and amorphous Li_xSi alloys show different spectral dependencies reflecting the process of disintegration of Si-Si network into Si clusters and chains of the different sizes upon Si lithiation. The Si-$L_{2,3}$ emission bands of Li_xSi alloys become narrower and shift towards higher energies with an increase in Li concentration. The shape of the emission band depends on the relative contribution of the X-ray radiation from the Si atoms having different coordination. This feature of the Si-$L_{2,3}$ spectra of Li_xSi alloys can be used for the detailed analysis of the Si lithiation process and LIB's anode structure identification. The computations were performed at the Resource Center "Computer Center of SPbU", St. Petersburg, Russia and the Research Institute for Information Technology at Kyushu University, Japan.

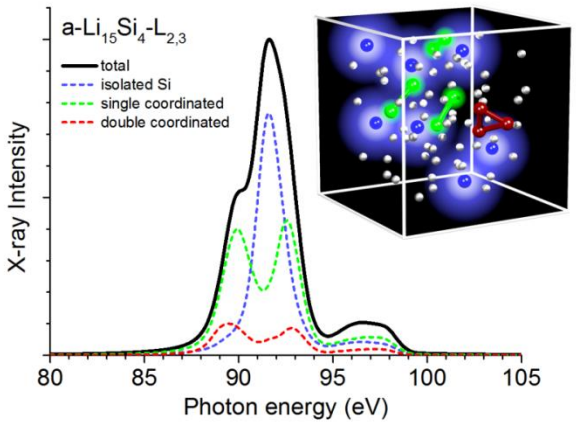

Figure 1. Soft X-ray Si-$L_{2,3}$ emission spectrum calculated for the amorphous $Li_{15}Si_4$ structure.

References:

[1] A. Lyalin, V. G. Kuznetsov, A. Nakayama, I. V. Abarenkov, I. I. Tupitsyn, I. E. Gabis, K. Uosaki, T. Taketsugu, arXiv:1801.01983 [physics.chem-ph] (2018).