Laser-Induced XUV Spectroscopy (LIXS) for High-Precision Lithium Analysis of Energy Materials

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Laser-induced breakdown spectroscopy (LIBS) is a powerful elemental analysis method thanks to the negligible sample preparation, rapid detection, and a spatially resolved sensitivity down to trace level, in any kind of sample matrix [1]. LIBS has also the ability for 2D spatially resolved mapping as well as depth profiling at a given location showing a local 3D mapping [2], such as 3D-mapping of an electrode in a lithium-ion battery. However, conventional LIBS is operated in the UV-visible spectral range (LIBS-OES), where the precision of LIBS is limited by the low stability and repeatability of the plasma emission [3]. This is particularly critical for spatially resolved analysis at nano-scale, where the sample heterogeneity is affected by the measurement precision. Utilization of the plasma emission in the extreme ultraviolet (XUV) wavelength range proved to fully overcome such limitations. Laser-Induced XUV Spectroscopy (LIXS) was applied to quantify lithium in energy materials, where the distribution of this element plays an important role for the functionality, for instance, in battery technology. The LIXS signal (7% RSD) is proved three times more stable than for LIBS-OES (23% RSD) by comparing the spectra of lithium fluoride (LiF) from 20 laser shots in single-shot mode. Moreover, a series of calibration samples Li_2O/Mn_xO_y were processed with LIXS to obtain the Li concentration calibration function for the quantitative analysis. By using the obtained calibration function, the 3σ-limit of detection of Li was calculated to be 0.12%. Depending on the level of LOD (limit of detection), LIXS can currently only be used for the analysis of non-trace elements in matrices, where the spatial distribution is the key information. There is an urgent need to optimize the instrumentation of LIXS to further improve its spectral intensity and sensitivity.

[1]   D. W. Hahn and N. Omenetto, "Laser-Induced Breakdown Spectroscopy (LIBS), Part II: Review of Instrumental and Methodological Approaches to Material Analysis and Applications to Different Fields," *Appl. Spectrosc.*, vol. 66, 347–419, 2012.

[2]   S. Imashuku *et al.*, "Quantitative lithium mapping of lithium-ion battery cathode using laser-induced breakdown spectroscopy," *J. Power Sources*, vol. 399, 186–191, 2018.

[3]   E. Tognoni and G. Cristoforetti, "Signal and noise in Laser Induced Breakdown Spectroscopy : An introductory review Optics & Laser Technology Signal and noise in Laser Induced Breakdown Spectroscopy : An introductory review," *Opt. Laser Technol.*, vol. 79, 164–172, 2015.