

Single particle approach to Raman study of LiFePO₄: spatial resolution and laser-induced decomposition

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Raman spectroscopy (RS) is one of the most promising candidates for industrial quality control tool for lithium battery industry. But there is a gap between chemical and physical aspects of materials characterization.

Despite the abundance of publications focused on solid-state chemistry and electrochemistry, there is an lack of research on physics of laser-particle interaction. To correctly interpret the experiment results, it is required to understand from what area the signal is received and what processes light can induce in the sample.

To define the RS resolution, we examined a 72 single LiFePO₄ (LFP) particles of different sizes on a Raman-active Si substrate. The ratio of intensity of Si band near 521 cm⁻¹ to one for major LFP band near 951 cm⁻¹ was used as a main characteristic parameter.

We showed that the probing depth of micro-Raman spectroscopy can greatly exceed instrumental estimation and reach several microns due to the particle morphology and variation of local optical properties conceivably caused by a variation of defect concentration. At the same time the edges of microscale particles and pores block Raman response from underneath layer more effectively than particles of transparent LFP. As a result, the μ RS measurement in a small pore can be attributed to superficial probing.

Six of 72 particles altered during RS probing and revealed a heterogeneity in pathways and products of laser-induced degradation of LFP. Some decomposed particles kept their form, while others became spherical, possibly due to melting. The disordered α -Fe₂O₃ phase was observed for all the decomposition products, but the second phase differs. For two of six particles, the second

phase is γ -Li₃Fe₂(PO₄)₃, which is typical for complete oxidation. The second phase with characteristic triplet 940-1015-1080 cm⁻¹ remained unidentified.

We hope that this work can help to organize relatively non-destructive RS measurements, properly interpret the obtained results, and take another step towards a better understanding of physicochemical processes, induced in microscale particles, regardless of the driving force origin – laser irradiation, heating, or cycling.

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