Ultrafast Laser Spectroscopy of Electrode/Electrolyte Interfaces

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Direct chemical analysis of electrode/electrolyte interfaces can provide critical information on surface phenomena that currently limit the performance of Li-based battery systems [1-5]. In this work we introduce the use of *ex situ* femtosecond (fs) Laser Induced Breakdown Spectroscopy (LIBS) to probe compositional variations within the Solid Electrolyte Interphase (SEI) layer [6-8].

Nanometer-scale depth resolution was achieved for elemental and molecular depth profiling of SEI layers formed on Highly Oriented Pyrolytic Graphite (HOPG) electrodes in an organic carbonate-based electrolyte [9]. This work demonstrates the use of ultrafast laser spectroscopy as a highly versatile, light element-sensitive technique for direct, real-time chemical analysis of interfacial layers in electrochemical energy storage systems.

Unlike other analytical techniques, LIBS is extremely sensitive in the detection of lighter elements, making it ideal for the study of Li-based electrochemical energy storage systems. Although we have shown here that the technique can be used to probe interfacial phenomena, proper choice of irradiation conditions, including laser pulse duration and wavelength, can determine the exact sampling conditions to match the spatial and depth resolution requirements of a specific type of application. Chemical mapping, depth profiling and 3D sampling, either in situ or *ex situ*, are possible with this technique.

At the same time, because of the nature of the sampling and detection scheme, this technique can find use in different types of applications; remote sampling, in-line monitoring quality control and near-field laser ablation based chemical analysis are just a few of the potential applications of this technique in battery related research.

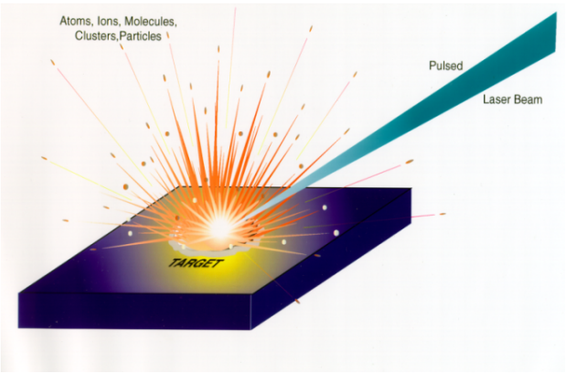

Figure 1. Interaction between the incoming laser beam and sample produces localized plasma that removes a thin layer of material in the form of atoms, ions, molecules, clusters and particles. Localized plasma provides excitation of the airborne species that results in light emission. It is the basis of the spectral identification of those species.

Here we studied the chemical composition of the SEI layer with a high depth resolution in He atmosphere. We were able to probe compositional variations within the SEI layer by studying the spectral emission of different elements and molecules as a function of depth at 7 nm resolution.

These results show that fs LIBS is a powerful tool for the real-time study of interfacial phenomena in battery systems and indicate the feasibility of using this all-optical technique for in situ analysis.

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