Lasers and batteries

Laserlab-Europe, with its 45 national laser research infrastructures in 22 European countries, plays an essential role in the development of new battery technologies with ultra-high performance through its cutting-edge laser spectroscopy and materials-processing technologies, as well as device prototyping and know-how, which drive forward research and technology in this field.

A key asset for the development of lithium and post-lithium battery technologies is the understanding of the dynamical processes occurring in functioning materials during multiple charging and discharging cycles, both in real time and in real space. In specific, the tracking of the physical mechanisms that lead to the degradation of electrodes is of particular interest.

Linear and nonlinear optical spectroscopies provide a very powerful toolbox for studying these fundamental processes and optimizing material and device architecture design for improved performance, as they are non-destructive, non-invasive and with fast acquisition times and exquisite chemical and surface sensitivity.
A battery can be decomposed in the following components: i) electrodes (anode and cathode); ii) electrolyte; iii) auxiliary materials required for the device, such as current collectors and separators.

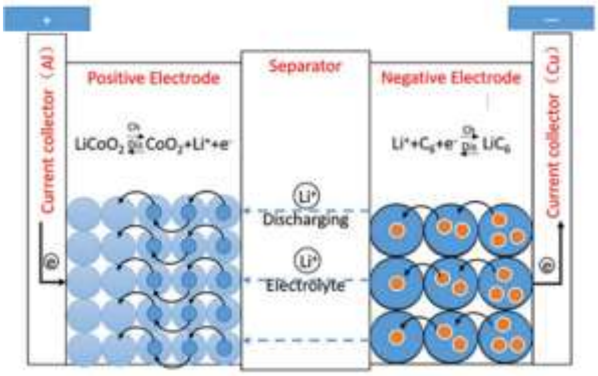

Figure 1 Battery components

Spectroscopic studies help to investigate and improve all aspects in three experimental situations of growing complexity and realism: i) *ex situ* on the electrode materials without the electrolyte; ii) *in situ* in a model system which reproduces the operating conditions of the complete device; iii) *operando* in a working device.

In the following we summarize the optical techniques which are commonly used for battery studies and the information that they can provide.

- **UV-visible spectroscopy can be used to study anodic intercalation processes into anodes and cathodes** for both lithium and post-lithium technologies[1]. Recently, interferometric scattering optical microscopy has been used to study nanoscopic lithium-ion dynamics in battery materials and apply it to follow cycling of individual particles for the archetypal cathode material Li_xCoO_2[2]. The same characterization has also been applied *operando* to commercial operating batteries using fiber optic evanescent wave spectroscopy[34]. **Spontaneous Raman spectroscopy** has been used to study the structural changes induced by ion intercalation[5] and *operando* Raman microscopy has allowed to visualize the evolution of the grain structure of the material[6] . Raman spectroscopy has also been used to monitor reversible oxygen redox processes in low-cobalt high energy density cathodes for lithium-ion batteries[7].
- **Optical spectroscopies** have been used to monitor the **morphological and chemical changes at the electrode-electrolyte interface**. Visible/infrared sum-frequency generation (SFG) spectroscopy has been employed to detect the specific adsorption of electrolyte molecules at the electrode surface[8]. *Operando* video microscopy has been used to visualize in real time dendrite formation and evolution in Li metal electrodes[9]. Surface Enhanced Raman Spectroscopy (SERS) and

Electroreflectance Spectroscopy (ERS) have been used to visualize *in situ* zinc electrodeposition on a gold electrode[10]. Moreover, the solid-electroyte interphase has been studied by ATR-FTIR[11][12], Raman[13][14] and SFG[15].

- **Optical spectroscopies can also be applied to the study of the electrolytes**. Stimulated Raman scattering (SRS) microscopy, combining chemical sensitivity and high speed, has been used to visualize in 3D and in real time the Li^+ ion distribution in the electrolyte and to relate it to shape changes in electrode[16]. IR transient absorption and 2DIR spectroscopy have been employed to study microscopic solvation structures of Li^+ ions, their intermolecular interactions with neighboring solvent molecules and understand their transport mechanisms[17]. Fourier-transform infrared (FTIR) spectroscopy and coherent anti-Stokes Raman scattering (CARS) microscopy have been used to study Li^+ distribution in a gel electrolyte[18].
- Finally, **X-ray photon-in photon-out spectroscopies and microscopies**, both a synchrotrons/FELs and using tabletop sources, are very useful for battery studies. X-ray diffraction (XRD) is employed to follow structural evolution of electrodes during charge-discharge cycles[19], nanoscale transmission X-ray microscopy (TXM) combined with X-ray absorption near-edge spectroscopy (XANES) allows *operando* tracking of phase transformations during delithiation processes[20], X-ray nano-computed tomography (CT) reveals microstructural heterogeneities in electrodes[21], and coherent diffractive imaging (CDI) ptychography is used to monitor dynamic electrochemical processes[22].

Laserlab-Europe offers outstanding research opportunities to the battery community by providing expertise and access to world-class laser research facilities with different and complementary technical specifications and areas of expertise, covering all aspects of excellent forefront laser-based science.

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