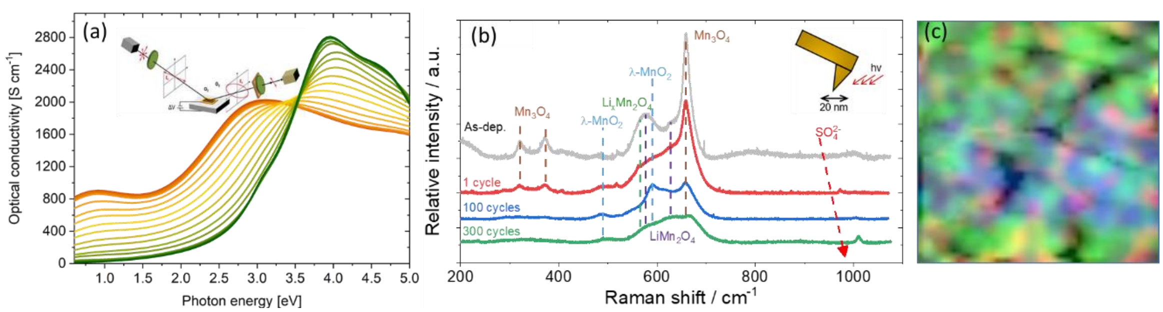
Operando ellipsometry and Tip-enhanced Raman spectroscopy (TERS) applied to li-ion battery materials

Alex Morata[1], Juan Carlos Rosillo[1], Yunqing Tang[1], Valerie Siller[1], Francesco Chiabrera[1], M. Stchakovsky[2], Marc Nuñez[1], Nerea Alayo[1], Marc Chaigneau[2], Albert Tarancón[1,3]

1. Department of Advanced Materials for Energy Applications, Catalonia Institute for Energy Research (IREC), Jardins de les Dones de Negre 1, 08930 Sant Adrià del Besòs, Barcelona, Spain
2. HORIBA Scientific, Avenue de la Vauve, Passage Jobin Yvon, 91120 Palaiseau, France
3. ICREA, Passeig Lluís Companys 23, 08010, Barcelona, Spain

Ion-based devices such as batteries, fuel cells and electrolyzers will play a major role in the future carbon-free energy systems. Many efforts are being dedicated to find techniques that allow understanding interfacial and ion diffusion phenomena occurring during operation, as these are often limiting overall performance. The sophistication of some of the most powerful techniques, such as isotopic ion exchange methods, in situ TEM and synchrotron radiation based techniques, limits the routine access to essential information for developing next-generation cells. In addition, commonly available techniques have also been explored including X-ray diffraction, atomic force microscopy, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) showing different compromises between spatial and time resolutions.

In this talk, we will discuss the development of procedures based on two optical techniques: spectroscopic ellipsometry (SE), and tip-enhanced Raman spectroscopy (TERS). Despite the well-known capabilities of Spectroscopic Ellipsometry (SE) to infer the properties of thin film and multilayers, such as thickness, crystallinity, materials ratio in mixtures, roughness, structure of the interfaces, electronic band structure etc., the use of this affordable, non-destructive technique for the study of ion-transport under operation is very so-far limited. We will illustrate the potential of SE with several examples on the field of lithium-ion batteries and solid oxide cells. In a first example, we will show the use of SE to monitor Li^+ transport properties and degradation phenomena through real-time tracking of the oxidation-state and volume changes associated with lithium insertion and extraction along $LiMn_2O_4$[1] and $Li_4Ti_5O_{12}$[2] thin-film electrodes in different liquid electrolytes ($LiSO_4$ and $LiPF_6$, respectively). In a second example, we use SE for studying the concentration of point defects in $La_{1-x}Sr_xFeO_{3-\delta}$ (LSF) thin films as a function of equivalent oxygen partial pressure, temperature and Sr concentration[3]. Finally, we present our recent advances in the utilization of Tip-Enhanced Raman Spectroscopy (TERS) for the study of the distribution of species in the surface of Li-ion battery cathodes. We show the high potential of TERS for studying phase evolution at grain boundaries thanks to the combination of the chemical sensitivity of Raman spectroscopy with high spatial resolution of scanning probe microscopy (SPM).



Evolution of optical conductivity as a function of the photon energy obtained by spectroscopic ellipsometry in $La_{1-x}Sr_xFeO_{3-\delta}$ layers (a). Overall spectra from TERS on $LiMn_2O_4$ layers with increasing number of cycles (b). Topographic map of the sample operated for 100 charge-discharge cycles (c). Colors indicate the presence of LiMn2O4 (green), Mn3O4 (blue) and SO_4^{2-} (red).

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