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Understanding Properties of Functional Materials with Atomic-Resolved Electron Energy Loss Spectroscopy

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The recent improvements in electron microscopy instrumentation have lead to the adoption of electron energy loss spectroscopy (EELS) beyond the traditional fields of applications related to chemical analysis of materials and biological structures. EELS is increasingly attracting the attention of the solid-state physics and nano-optics communities due to the unparalleled spatial and energy resolution of this technique. This growing interest is supported by recent publications showing the realization of atomic-resolved spectroscopy in complex solids and over ten years of research by several groups around the world probing surface-plasmon resonances. In this presentation, we focus on examples of applications of spatially resolved EELS for the study of energy-related materials, mainly Li-based layered compounds, and complex oxides with potential electronic applications, showing how atomic resolved measurements provide insight into the macroscopic properties of these materials.

The experimental work was carried out with an FEI Titan (80-300 Cubed) microscope equipped with an electron energy loss spectroscopy (EELS) system (Quantum 966) and a monochromator. Samples were prepared using a combination of focused ion beam milling (Zeiss NVision 40 FIB/SEM) with low energy Ar ion final polishing (Fischione "NanoMill" system), and more conventional methods such as grinding powders into electron transparent samples. We have probed the structure of Li-based layered compounds used for energy storage applications and a variety of oxides, some superconducting compounds, either in single crystal forms or produced as ultrathin films grown by pulsed laser deposition methods. For Li-based compounds, inert atmosphere handling procedures were followed for transferring samples from a glove box system to the transmission electron microscope using a vacuum transfer holder.

We have investigated a number of technologically relevant structures based on the $LiNi_xMn_yCo_{1-x-y}O_2$ (known as "NMC") cathode materials, high-Li content phases (the so-called "high-energy" NMC phases), and cathode materials with coatings produced by Atomic Layer Deposition (ALD) method. In these systems, we have shown that the valence of transition metal ions, and the charge compensation mechanisms, can be effectively probed in pristine materials and cathodes that have been electrochemically cycled [1]. We demonstrate that the valence can be mapped effectively using a combination of spectra from reference compounds and statistical methods implemented to extract "phase" information with much reduced noise level in the spectra. From a practical point of view, we also show that this approach can be used to understand the evolution and degradation of these electrode materials under different electrochemical cycling conditions [2]. In the high-energy NMC compounds, we highlight how atomic-resolved mapping can be used to detect the presence of few atomic layers surface segregation of the transition metal atoms and changes in the local electronic structure of this material based on the O-K edge. These results are interpreted in light of the valence changes, the Li and oxygen loss on the cathode material.

In hole-doped high-temperature superconductors in the $YBa_2Cu_3O_{6+\delta}$ system and in a chain-ladder compound of the $Sr_{14-x}Ca_xCu_{24}O_{41}$ family, we have investigated the localization of holes at atomic resolution. Probing the O-K and Cu-L edges, we show that real-space measurements in these compounds provide detailed insight into the formal valence of Cu atoms as a function of oxygen content in $YBa_2Cu_3O_{6+\delta}$ [3]. We also investigated how detailed atomic-resolved maps can be used to identify sub-oxide phases in thin films of these materials [4]. In the chain-ladder compound $Sr_3Ca_{11}Cu_{24}O_{41}$, we highlight how EELS fine structure measurements at the O-K edge, combined with electron probe propagation calculations, provide detailed quantitative determination of the holes distribution [5]. These results on fine structures analysis are contrasted with the electron-doped high-temperature superconductors where local changes in the composition, generated upon doping, are observed.

In light of these studies, the limitations of EELS measurements for the detection of single atoms and their bonding environment are discussed [6].

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