Study of positive electrode materials for lithium-ion batteries by experimental and theoretical soft and hard X-ray photoemission spectroscopy

PhD thesis in CEA Grenoble, France

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A few hours by train from Paris to the north and the Mediterranean to the south, and a stone’s throw from Lyon, lies Grenoble. Nestled at the foot of the French Alps, with Italy and Switzerland just over the mountains, the Grenoble area offers up arts and culture and sports and outdoor activities and is also home to an impressive sci-tech community. Live in Grenoble and enjoy the best of both worlds—all the benefits of city life, combined with easy access to the outdoors. With stunning mountain landscapes all around, nature is an intrinsic part of the city’s identity.

Grenoble is a major center for both technology and higher education. The city is home to more than 62,000 students, and around 15% of the student population is international. Together, Grenoble's government and private-sector labs employ 22,000 researchers. CEA is a pillar of this ecosystem. The research center also enjoys a prime location near exceptional scientific instruments like the European Synchrotron Radiation Facility or ESRF (one of the world's most powerful synchrotrons), and Institut Laue-Langevin (ILL), home to extremely brilliant neutron beamlines used for spectroscopy.

Photoemission spectroscopy (X-ray, XPS, or ultraviolet, UPS) is one of the direct probes of the changes in the electronic structure of materials during redox processes involved in lithium ion-batteries at the atomic scale. However, it is limited by the extreme surface sensitivity, with a typical photoelectron path length of a few nanometers for the energies usually available in the laboratory[1,2]. Moreover, the spectra interpretation requires the ability to model accurately the electronic structure, which is particularly delicate in the case of transition metal based electrode materials. Upon lithium insertion and de-insertion, the charge transfer toward cations and anions induces local electronic structure changes that require an adapted model that takes into account electronic correlations.

In this thesis, we propose to use these limitations to our advantage to explore the electronic surface structure including the solid electrolyte interphase (SEI), and the bulk of the active cathode particle. Thanks to the first lab-based hard X-ray photoemission spectrometer in France (HAXPES), the electronic structure of two prototypical electrode materials ($LiCoO_2$ and $LiNiO_2$) have been studied up to about 30 nanometers[3,4]. To widen our picture on the role of cations and anions from surface to bulk in lamellar metal oxide electrodes for lithium-ion battery, this thesis will focus on the mixed lamellar metal oxide $Li(Ni_{1-x-y}Mn_xCo_y)O_2$ (NMC), currently one of the leading material in industrial applications.

The comparison between the Soft-XPS and HAXPES spectra, during battery operation (*operando*) and post-mortem, will allow decoupling the surface and core spectra for different NMC compositions and at different stages of the battery life cycle. The interpretation of the photoemission spectra will be done by direct comparison with ab-initio calculations combining density functional theory (DFT) with dynamical mean field theory (DMFT)[5,6]. This coupled approach will allow to go beyond the usual techniques based on cluster models, which do not take into account long-range screening, and to validate the quality of theoretical predictions on the effects of electronic correlations (effective mass, potential transfer of spectral weight to Hubbard bands)[7].

The thesis will include an instrumental (in particular, calibration of Scofield factor on model systems) and theoretical (prediction of core photoemission spectra based on DFT+DMFT calculations) development. The performance of electrochemical systems based on different cathode materials (NMC with different compositions) in combination with liquid and solid electrolytes and a Li metal anode will be studied in the frame of combined experimental and theoretical soft and hard X-ray photoemission spectroscopy.

The candidate will be hosted at the PFNC in the Laboratory of Characterization for Energy of CEA Grenoble under the direction of Dr. Anass BENAYAD (Department of Materials) and LMPS (Department of Electricity and Hydrogen for Transportation) under the supervision of Dr. Ambroise VAN ROEKEGHEM.

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