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Application for beam time at ESRF – Experimental Method

IN OPERANDO LOCAL ELECTRONIC STRUCTURE OF NANOSCALE Li_xCoO_2 THIN FILMS

Proposal Summary (should state the aims and scientific basis of the proposal):

We aim to investigate the in-operando local electronic structure of nanoscale thin films LiCoO2 (LCO). LCO and related materials are extensively used in batteries as cathode materials and are expected to play a key role in neuromorphic computing in the near future. Understanding the mechanism of the delithiation process under operation conditions is a crucial step to improving performance and mitigating degradation. In particular, we pursuit to elucidate the depth of the spatial region where the spin state of Co is high (Co^{4+}) and how it is affected during the delithiation process.

Scientific background:

Rechargeable Li batteries is a robust technology because of a wide range of applications in energy storage for electronic devices. $LiCoO_2$ (LCO) has been the most important and most studied positive electrode material for Li ion batteries, and is an excellent model system for fundamental studies [1]. Introduced commercially by Sony in 1991, it is one of the most used cathodes for small portable electronics due to its good lithiation-delithiation reversibility and specific capacity, related to its ability to change its composition to Li_xCoO_2. LCO is also a critical material for neuromorphic computing applications [2]. Based in a resistance switching mechanism, A.A. Talin and coworkers have recently demonstrated the feasibility of a synaptic transistor based in LixCoO2 [3] suitable for neuromorphic applications [4]. The system is based upon the intercalation of Li-ion dopants into a channel of Li_xCoO_2.

LCO has been the subject of an impressive number of scientific and technological investigations [5]. However, the understanding of its electronic structure is still incomplete. LCO consists of CoO_2 layers and interlayers of Li atoms alternatively stacked along the c axis. It has been proposed that holes with strong O 2p character play a role in the electronic conductivity of the low spin state (Co^{3+})/high spin state (Co^{4+}) mixed valence and that the Li-ion flow can be stabilized via the oxygen hole. Such an oxygen hole state of LCO is unique and could be crucial for the performance of the batteries [6]. Nevertheless, despite of the enormous efforts made in the last decade, several aspects remain unclear. In particular, it has been recently proposed that there is a spatial phase separation and that the spatial region where Co presents a high spin state (Co^{4+}) is only some few nanometers from the surface, while bulk Co keeps a Co^{3+}configuration. The elucidation of the properties of this region is of importance, as the performance of any electrode relies on the knowledge of its structure and properties. Furthermore, the use of LCO in computing devices requires a deep understanding of the switching process – to allow fast switching of the devices – as well as long-term stability upon cycling – to avoid errors in the computing process.

X-Ray absorption spectroscopy (XAS) has been extensively used to probe the local changes in the electronic structure of several battery cathode materials [7]. We propose to use synchrotron radiation XAS experiments for operando characterization of LCO. We will concentrate in the changes induced in the electronic structure of LCO thin films – in particular, in the local environment of Co cations – during in-situ charge-discharge cycling. We will study two different processes. (1) changes in the local environment after a charge/discharge cycle and (2) the evolution of the local structure during cycling. These studies are particularly important for the application of LCO in neuromorphic computing.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantiy...etc):

The charge–discharge reaction of lithium ion batteries involves complex processes of Li ion migration between electrodes (Li ion transfer from the electrode to electrolyte, solvated Li ions in the electrolyte, etc). To avoid complexity of the composite electrode, it is highly advantageous to test an active material in the absence of a binder and conductive components. One of the ways to achieve this is to use a continuous thin film electrode on a conductive substrate that will act as collector. The samples will be previously grown by our collaborators and will be carried to the ESRF. Different samples will be prepared as a function of the LCO thickness, some formed by no-continuous islands, where we expect to achieve a more homogenous cationic state. Electrochemical cells will be prepared with polymeric separators soaked in the electrolyte and an anode disk that allows X-rays to reach the surface.

We will perform X-ray absorption spectroscopy (XAS and XANES) measurements at the Co K-edge to determine the atomic/electronic electron configuration and valence states of the LCO during the charge/discharge process. The peak position and the spectral line shape of the absorption spectra strongly depend on the local atomic and electronic structures of the ions. As mentioned before, two strategies will be followed:

(1) Evolution after cycling: in this case, after a charge (discharge) process, the electrochemical cell will be set in a stand-by state and spectra will be measured.
(2) For samples with clear and large changes in (1), XAS measurements will be carried out while a slow charge (discharge) process is performed.

Beamline(s) and beam time requested with justification :

The analysis of the oxidation states of Co can be achieved with a high-energy element-selective technique as hard X-rays XAS-NEXAFS. Considering the energy of the absorption lines, the SpLine-A beamline is the most suitable one to carry out our experiments. In addition, there is an electrochemical set-up for in-operando XAS available in this beamline that we have previously used in the experiment 25-01-987.

In order to measure all the data detailed, we estimate 15 shifts as the minimum time to obtain data with enough quality, based on the following calculations. Considering the length of the charge/discharge processes as well as the need of doing several cycling in each sample, we estimate that one day (24 hours) is needed for measuring each sample. When need 24 extra hours for test samples, mounting and aligning. So, 4 samples x 24 hours + 24 hours = 120 h (15 shifts).

Results expected and their significance in the respective field of research :

XAS-NEXAFS provides a unique opportunity to measure the spatial distribution of Co cationic state that could be crucial to understand and improve the performance of these electrodes. We also expect to examine the effect of the cyclability on the stability of the charge transfer behaviour. Previous experimental results assure the strength of this study by looking at XAS data, that could prove useful [6]

References

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[3] E.E. Fuller *et al*, Adv. Mat. 29, (2017) 1604310.
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[6] C. J. Patridge *et al*, J. Sol. Sta. Chem 203, (2013) 134
[7] J. R. Croy *et al*. Chem. Mater. 23, (2011) 5415 and references therein.