

## Experiment report

Experiment number: 20217084 (CERIC-ERIC)/A08-1 1090 (ESRF)

Beamline: BM08 LISA Beamline

Title: Unravelling the Lithium Storage Mechanism at low Potentials in Pure and Bismuth doped Niobium Oxide Anodes for Lithium-Ion Batteries

### Achievements:

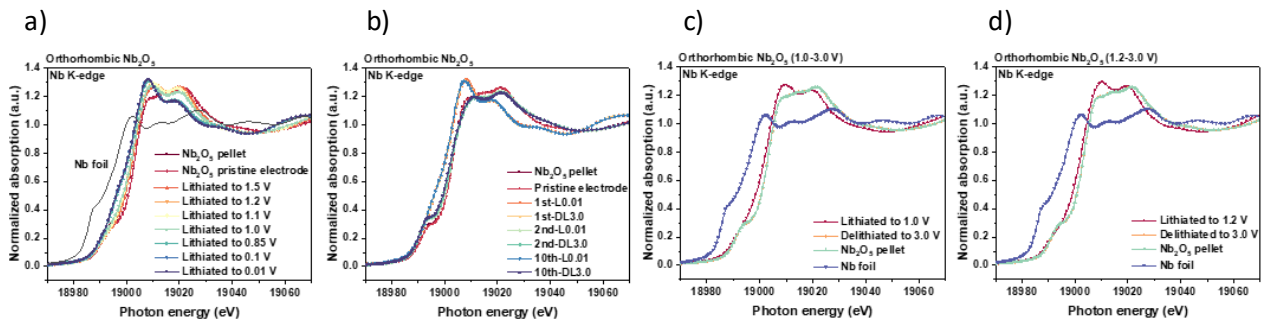
A complete set of *ex-situ* specimens has been explored for pure and Bi-doped orthorhombic Nb<sub>2</sub>O<sub>5</sub> as well as monoclinic Nb<sub>2</sub>O<sub>5</sub> cycled electrodes, complemented by an *in-situ* XANES study for pure Nb<sub>2</sub>O<sub>5</sub> in the voltage range of 1.0 -3.0 V. For the abovementioned materials, the Nb K-edge and Bi L<sub>3</sub>-edge were investigated. A so far preliminary analysis of the results signifies that: i) The Nb K-edge for orthorhombic Nb<sub>2</sub>O<sub>5</sub> shows an evident change in structure and local environment during the initial cycle, and the structure remained stable in the next few cycles; ii) the Bi in the Bi-doped samples shows a reduction to the metallic state and, possibly, alloying with lithium, which may be the reason for the higher capacity; iii) monoclinic Nb<sub>2</sub>O<sub>5</sub> retains its original structure in the first cycle, which can explain the high initial Coulombic efficiency. We anticipate that these findings, following a detailed analysis, will provide us with an in-depth understanding of the structural transformations that are contributing to the electrochemical processes in orthorhombic/monoclinic Nb<sub>2</sub>O<sub>5</sub> as well as the role of the bismuth dopant and, thus, help with the development of high-performance anodes for lithium-ion batteries.

### Report:

The realization of high-performance lithium-ion batteries has been a hot spot of intense research in order to satisfy the inevitable tendency towards a net-zero carbon emission landscape. Graphite, the state-of-the-art commercial anode, is limited by its intrinsic sluggish kinetics, which leads to lithium plating during fast charging, especially at low temperatures. Considering the fast charging properties, insertion-type anodes, such as Nb<sub>2</sub>O<sub>5</sub>, are ideal candidates for next-generation batteries. However, the reported specific capacity of Nb<sub>2</sub>O<sub>5</sub>, cycled in a rather narrow voltage range, remained relatively low so far. When the voltage window of orthorhombic Nb<sub>2</sub>O<sub>5</sub> is extended to 0.01 – 3.0 V, the specific capacity can be doubled while retaining promising cycling performance. Bi doping increases the capacity even further compared with pure orthorhombic Nb<sub>2</sub>O<sub>5</sub>. Moreover, another crystalline type – monoclinic Nb<sub>2</sub>O<sub>5</sub> – displays a better initial Coulombic efficiency. Therefore, to unveil the lithium storage mechanism in the extended voltage range of different Nb<sub>2</sub>O<sub>5</sub>-based materials, we have performed a detailed X-ray absorption spectroscopy study. Pellets of the pristine materials and model compounds as well as several cycled electrodes upon the first cycled and after several cycles were prepared and measured for all three materials. We also prepared pouch cells with the same electrodes for *operando* experiments. Even though we managed to run the pouch cells in the narrow voltage of 1.0 – 3.0 V, we have experienced issues with the extended voltage range. These issues have not been observed in our previous experiments and were, therefore, not anticipated. Currently, we are investigating the reasons for the bad electrochemical performance. At present, most likely are different properties of the carbon-based current collector owing to a new supplier or issues with the lithium metal due to some power failure of the dry room prior to the experiment.

Anyhow, the results of the *ex-situ* study of electrodes prepared in an Ar-filled glove box with the O<sub>2</sub> and H<sub>2</sub>O levels below 0.1 ppm have provided detailed insights into the structural transformation in the initial cycle for orthorhombic and monoclinic samples and provide the information of the role of bismuth doping to some extent. Overall, the analysis so far has been rather qualitative and so is the discussion herein, whereas a more detailed interpretation of the EXAFS data sets requires more time.

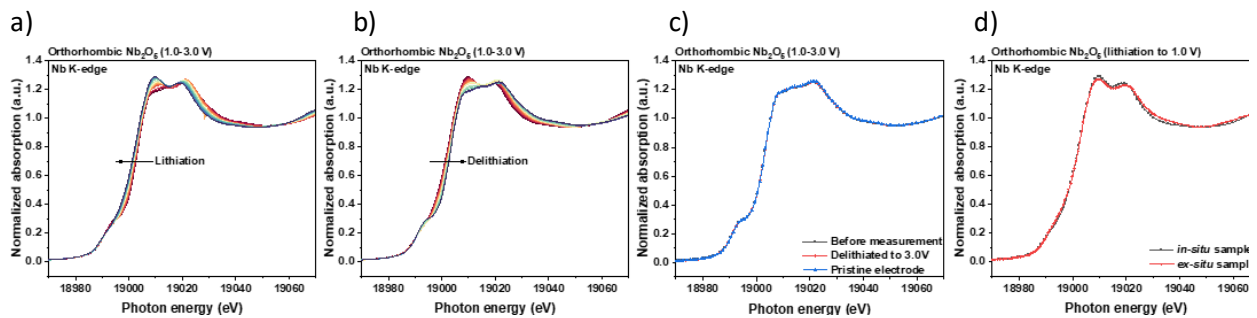
Starting from orthorhombic Nb<sub>2</sub>O<sub>5</sub> samples, we can see from Figure 1a that, upon lithiation, the position of Nb main edge shifts to lower energy, confirming that the oxidation states of niobium is reduced during lithiation. Upon delithiation, the oxidation state of Nb shifts back to higher energy; however, the XANES features of Nb K-edge are different after the first de-lithiation process, suggesting that an irreversible structural change occurs. Figure 1c and 1d shows how the structure maintains almost identical when the electrodes were cycled in narrower voltage ranges.



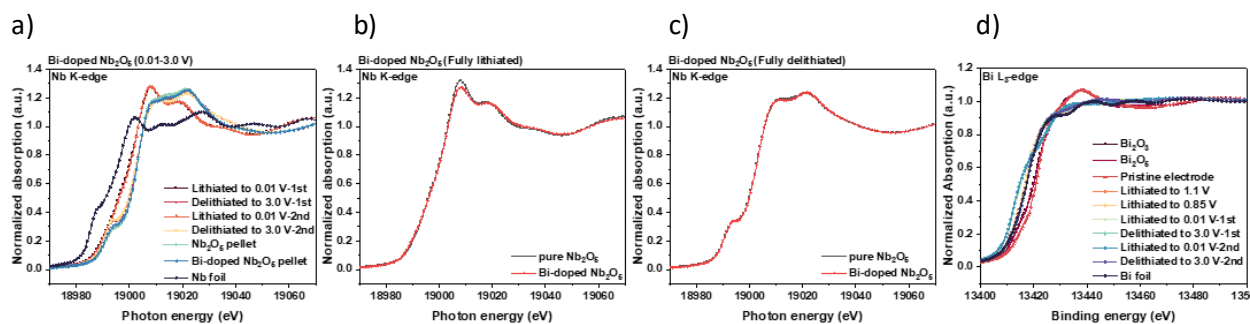
**Figure 1.** Ex-situ spectra of orthorhombic Nb<sub>2</sub>O<sub>5</sub> during lithiation and delithiation in the voltage range of (a) 0.01 - 3.0 V, (c) 1.0 – 3.0 V, (d) 1.2 – 3.0 V, (b) comparison of orthorhombic Nb<sub>2</sub>O<sub>5</sub> in the 1<sup>st</sup>, 2<sup>nd</sup>, and 10<sup>th</sup> cycles.

*Operando* XAS data are shown in figures 2a-2d, the results are coherent with the *ex-situ* spectra. However, the precise determination of the oxidation states and coordination nature of Nb requires a more detailed analysis, which is currently underway.

Figure 3a-3c indicate that, qualitatively speaking, the evolution of Nb in Bi-doped Nb<sub>2</sub>O<sub>5</sub> is quite similar to pure Nb<sub>2</sub>O<sub>5</sub>. Interestingly, the Bi L<sub>3</sub>-edge (Figure 3d) reveals that the bismuth is reduced to the metallic state during lithiation, probably leading to the increased capacity of this system. The reversibility of this alloying process, however, needs to be better understood and investigated.

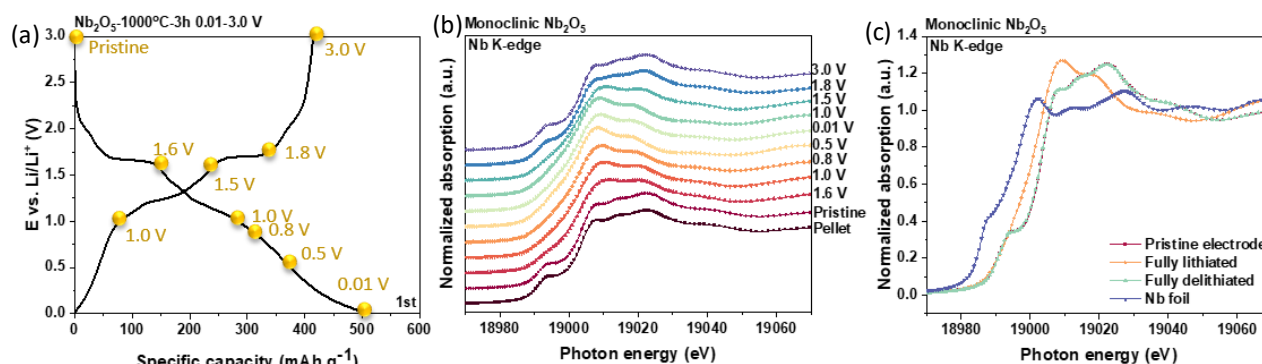


**Figure 2.** *Operando* spectra of orthorhombic Nb<sub>2</sub>O<sub>5</sub> during lithiation in the voltage range of 1.0 – 3.0 V (a) lithiation, (b) delithiation; Comparison of *operando* and *ex-situ* samples (c) delithiated to 3.0 V, (d) lithiated to 1.0 V.



**Figure 3.** Ex-situ spectra of Bi-doped  $\text{Nb}_2\text{O}_5$  cycled electrodes (a) Nb K-edge spectra in the first two cycles, comparison between pure orthorhombic  $\text{Nb}_2\text{O}_5$  and Bi-doped (b) at fully lithiated state, (c) at fully delithiated state, (d) the evolution of Bi  $L_{3-}$ edge upon de-/lithiation.

Lastly, Figure 4a describes the first cycle voltage profile of monoclinic  $\text{Nb}_2\text{O}_5$  based on different “hold” voltages. Figure 4b and 4c show a reversible feature in the first cycle.



**Figure 4.** (a) 1<sup>st</sup> cycle voltage profile of monoclinic  $\text{Nb}_2\text{O}_5$  with distinct voltages for ex-situ spectra analysis. (b-c) Normalized ex-situ XANES spectra of cycled electrodes based on distinct voltages.

To summarize, the analysis of data collected from this experiment is still at an early stage, but given the insightful information from ex-situ spectra, we consider that the experiment was successful. The preliminary data analysis illustrates that: i) the structural change happens in the first cycle and then become stable upon cycling for orthorhombic  $\text{Nb}_2\text{O}_5$ ; ii) the alloy process of bismuth doping upon lithiation contributes to higher capacity; iii) the unchanged structure of monoclinic  $\text{Nb}_2\text{O}_5$  somewhat results in initial Coulombic efficiency and good cycling performance. Accordingly, the collected data bear important information for the further improvement of anodes based on insertion-type mechanism for next-generation lithium-ion batteries. A further step yielding a deeper insight into these systems is the collection of *operando* data which could not be measured during the experiment due to issues probably related to the cell preparation. We would like to mention that we are very satisfied with the high-quality spectra collected at the LISA beamline and professionalism of the beamline scientists and staff.