



Experiment title: <i>Operando</i> X-ray absorption spectroscopy to understand the switching mechanisms in TiN/La ₂ NiO _{4+δ} /Pt memristors for neuromorphic computing	Experiment number: MA-5230	
Beamline: ID12	Date of experiment: from: 26/04/2022 to: 03/05/2022	Date of report:
Shifts: 18	Local contact(s): Dr. Fabrice Wilhelm wilhelm@esrf.fr	<i>Received at ESRF:</i>
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Report:

Objective

This experiment aimed to 1) experimentally measure valence changes of Ni and Ti in the resistive switching (RS) behaviour of TiN/La₂NiO_{4+δ}(L2NO4)/Pt memristors under *operando* conditions (*in situ* electrical bias of the device under the x-ray beam). 2) carry out XANES measurement on an identical sample at different regions of interest. 3) Perform XANES measurement on L2NO4 films with different oxygen over-stoichiometry.

Experimental

The photon source is the APPLE-II type helical undulator HU-38 at the fundamental harmonic of its emission. The annealed samples were measured in the 2nd experimental hutch (EH3) under vacuum and at T = 298K in a top-up 7/8+1 multibunch filling mode for better beam stability and nearly constant beam current of 130 mA. The intensity detector used was a silicon photodiode and the total fluorescence yield (TFY) was collected in backscattered geometry (detector plane at 90° respect the beam vector). Particularly, the Ni K-edge and Ti K-edge were measured in grazing incidence configuration.

The *operando* measurements were performed in the 3rd experimental hutch (EH4) (with the chopper stopped) at atmospheric pressure in open air and at T = 298K. Two silicon drift detectors¹ (SDD) were used to collect the partial fluorescence yield (PFY) in backscattering configuration. A 20 μm thick Co foil was inserted in front of the SDD to reduce elastic scattering for Ni K-edge. Beam spot size of ~5 μm was achieved using 2 Be parabolic lenses with a radius of curvature of 50 μm (focal image distance ~1.6 m) and it was used for precise XANES mapping. Spot size of 200 μm was set with the secondary slits and it was used for low-photon density XANES over large areas. Polyscans were done in the 6521.9 – 6622.9 eV energy range. In order to improve sensitivity and for time-resolved *operando* measurements (scale of seconds), spectra were also acquired at fixed energy close to the Ni K-edge and Ti K-edge inflection points. A Keithley 2410 sourcemeter was used to apply bias to the device (voltage applied on Pt contact and TiN contact grounded).

Results

The data presented in the following section serves as proof of trend. Further data analysis and careful data treatment will be carried out to precisely determine the Ni and/or Ti oxidation states.

¹ Each silicon drift detector is a SiriusSD with an on-chip active area of 100 mm² equipped with a low capacitance primary amplification device (RaySpec) coupled to Falcon-X processors (XIA LLC).

1. Mapping of TiN/pristine-L2NO4/Pt devices

By moving the beam to another region without TiN electrode, a XANES spectrum was measured (red line in Figure 1), which is compared to the spectrum of a region with a TiN electrode (black line) the same figure. It is worth noting that the black XANES spectrum was measured prior to any applied DC sweeps in *operando* measurements. In the inset, it is clearly seen that the shift of the Ni-K edge towards lower energy, suggesting Ni is spontaneously reduced when putting contact L2NO4 with TiN. Thus, a TiNO_x interlayer might be formed spontaneously after evaporating TiN on top of L2NO4. This could be due to the uptake of oxygen from L2NO4 layer into TiN.

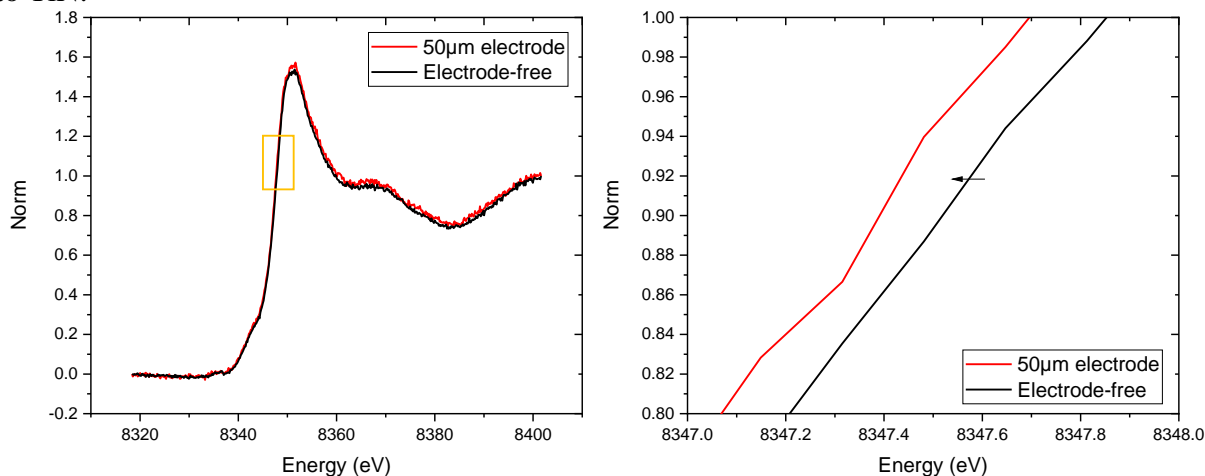


Figure 1: (Left) XANES spectra of L2NO4 film with electrode (red line) and without electrode (black line). (Right) similar to (Left) but in higher magnification of the region marked in yellow square of the left figure.

2. Operando XANES measurements of TiN/pristine-L2NO4/Pt device

Ni-K edge:

The experimental setup is illustrated in Figure 2a. Beforehand, a XANES spectrum was carried out to find the Ni-K edge energy (8347.81 eV). The Ni-K edge is determined by the first derivative method. Next, the $50 \times 50 \mu\text{m}^2$ beam focused on a $50 \times 50 \mu\text{m}^2$ device to collect the X-ray absorbance at the Ni-K edge energy (8347.81 eV) vs time, while DC sweeps of ± 2.7 V were applied to the device. The collected signals of the Ni-K edge position were then averaged and presented as a function of applied voltage in Figure 2b. The corresponding I-V characteristics of the device-under-test are plotted in Figure 2c. Only the first and the 10th sweeps are depicted, showing no major difference between them.

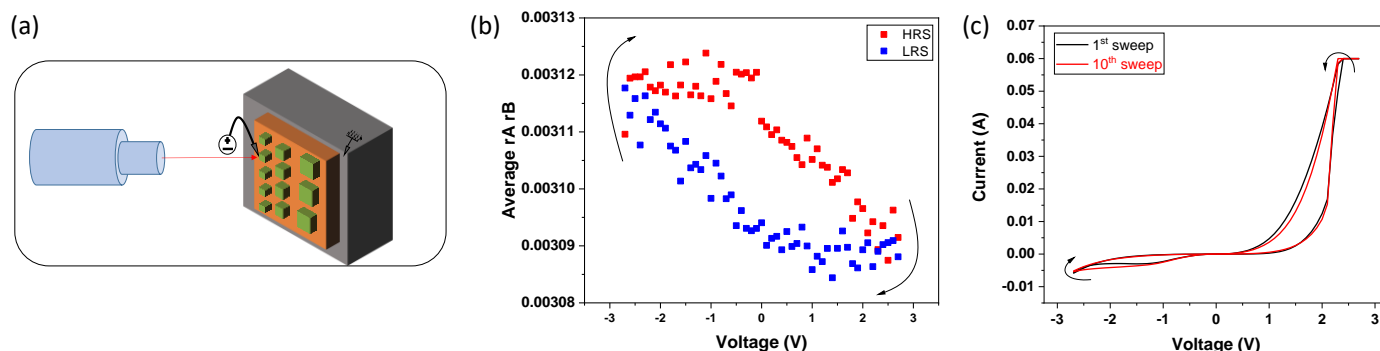


Figure 2: (a) Experimental setup of operando XANES performed on a TiN/L2NO4/P device. (b) Evolution of averaged intensity of Ni-K edge position (8347.81 eV) measured while biasing the device (10 cycles). (c) The corresponding I-V characteristics obtained during the measurements (only the first and the last sweeps are shown)

Ti-K edge:

A similar setup was used (as seen in Figure 2a). A XANES spectrum was carried out to find the Ti-K edge position (4980.63 eV). The X-ray absorbance was recorded at the energy corresponding to the Ti-K edge energy, while the device was submitted to bipolar voltage sweeps at ± 2.7 V. The collected data from ten switching cycles were then averaged and plotted in Figure 3a. This graph shows a closed loop and reversible switching. However, if we observe the first three cycles separately (Figure 3b), there seems to be a time-dependent intensity shift, which might be related to electron injection during the measurements. The individual cycles do not show

a complete and reversible process. It should be noted that, in terms of RS behaviour, the device worked in standard regime as usual, as seen in Figure 3c.

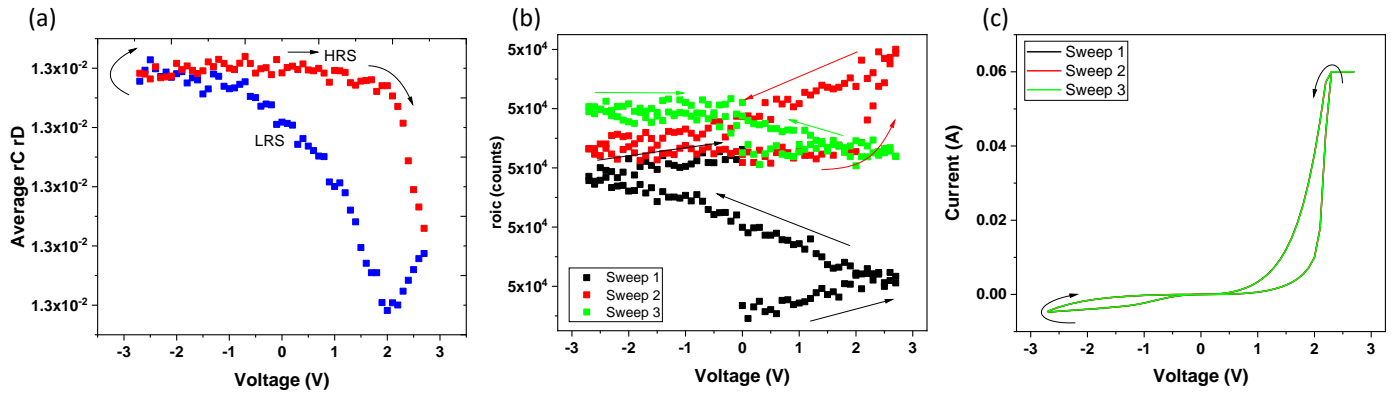


Figure 3: Evolution of intensity of Ti-K edge position (4980.63 eV) (a) average values obtained by ten cycles and (b) values recorded during the first three voltage sweeps. (c) The corresponding I-V characteristics of these three cycles in (b).

3. Ex situ XANES measurements

3.1. L2NO4 films with different oxygen stoichiometry

To prepare for an upcoming beamtime at the ESRF (MA-5239), preliminary XAS measurements were performed on dense La_2NiO_4 thin films on YSZ substrates to verify that

- I. diffraction peaks of the single crystal substrate do not interfere with the film signal
- II. the expected changes in oxidation state can be resolved.

XANES measurements of L2NO4 films with different oxygen stoichiometry were carried out.

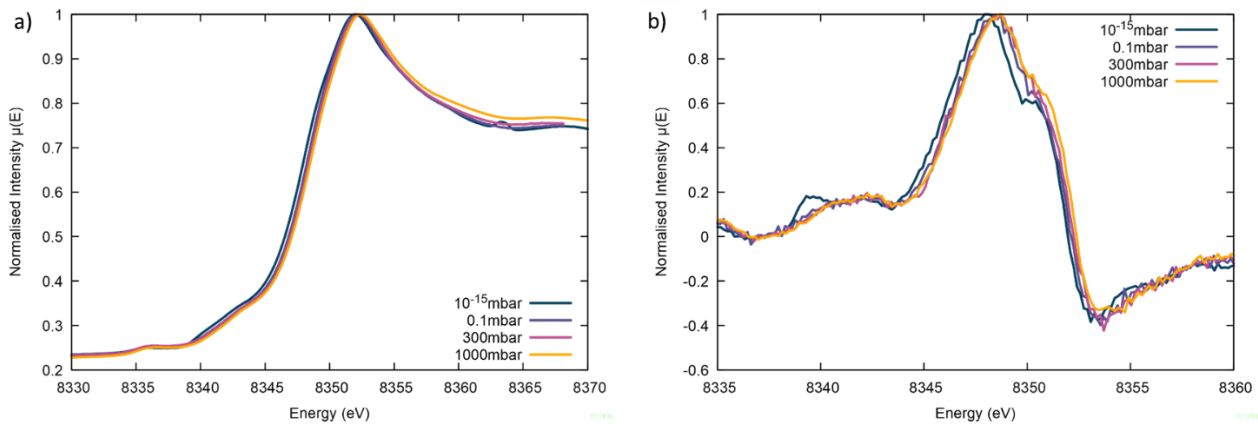


Figure 4: XANES spectra (a) and first derivative of dense L2NO4 thin films annealed under different $p\text{O}_2$ conditions.

L2NO4 thin films were annealed ex ante in different oxygen partial pressure conditions, corresponding to different charging levels and the shift of the Ni-K edge was measured, as shown in Figure 4a. The inflection point, obtained via the first/second derivative method, shifts by about 0.7 eV (Figure 4b) continuously from the hydrogen to the oxygen annealed sample. This correlates to a change in the oxygen off-stoichiometry of about 0.15, which makes this material an interesting candidate for the use in oxygen ion batteries.

3.2. Ti/L2NO4/Pt devices with different thermal annealings

Rapid thermal annealing (RTA) is an additional process to further oxidize TiO_x interlayer at the Ti/L2NO4 interface. RTA step is required to trigger the RS in Ti/L2NO4/Pt devices. Three Ti/L2NO4/Pt samples were submitted to three RTAs with different durations. The XANES measurements focused on Ni-K edge and Ti-K edge were performed on these three samples, as seen in Figure 5a and Figure 5b, respectively. In Figure 5a, the first/second derivative of full XANES spectra was added at the bottom to determine the Ni-K edge energy for each sample. The Ni-K edge of the sample annealed for 3 minutes is shifted towards lower energy, suggesting Ni is more reduced. The sample annealed for 10 minutes of RTA shows the lowest Ni-K edge energy, suggesting the most reduced Ni in L2NO4 film. This observation can be attributed to the loss of oxygen, which was diffused to Ti electrode and further oxidized TiO_x interlayer can be formed. Figure 5b is XANES measurements at Ti-K edge of those three samples with TiO_2 power (Ti^{4+}) and Ti foil (Ti^{0+}) added for comparison. The first/second derivative was also used to determine the Ti-K edge (not shown, similar to Figure 5a). The Ti-K edge energy of

each sample is indicated in each spectrum. The pristine sample and 3-minute sample show the intermediate valence of Ti^{3+} , while the 10-minute sample shows the valence of Ti^{4+} (edge position is close to TiO_2 powder (Ti^{4+})). This observation is consistent with the Ni-K edge XANES in Figure 5a, suggesting that 3 minutes are not long enough to further oxidize TiO_x interlayer, while 10 minutes lead to too much oxidized TiO_x (mostly TiO_2).

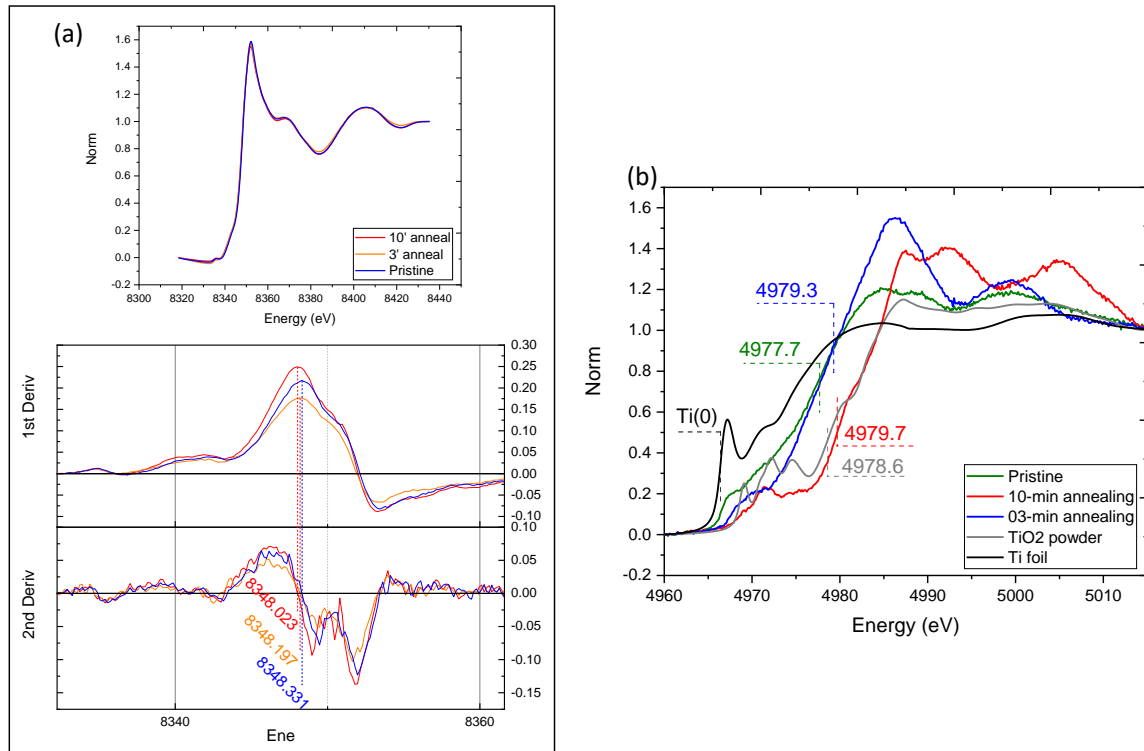


Figure 5: *Ex situ* XANES measurements of three Ti/L2NO4/Pt devices with different duration of annealing. (a) XANES spectra at Ni-K edge. (b) XANES spectra at Ti-K edge.

Conclusions

The XANES experiments carried out in beamline ID12 have allowed for observing the variation of the Ni-K edge position (valence state change) in *operando* mode and mapping mode. These results suggest that oxygen movement could play a key role in RS behaviour. First, oxygen could be spontaneously uptaken when TiN is evaporated on top of L2NO4. Next, the reversible change of Ni oxidation states (due to the oxygen ion drift) during the RS process could be related to the switching mechanism. However, this observation was not able to obtain for Ti-K edge position where the individual cycles did not close.

For *ex situ* XANES measurements of L2NO4 films with different oxygen stoichiometry, thanks to the large shift and the absence of major diffraction peaks, the device architecture and materials choice can be used for further XANES measurements. Additionally, the obtained large shift is promising for planned *in situ* measurements under different temperatures, atmospheres and polarization in the upcoming beamtime to be able to investigate the cation valence state with spatial resolution.

Ex situ XANES measurements of Ti/L2NO4/Pt devices with different RTA duration confirm the role of the RTA process in the formation of TiO_x interlayer. The displacements of Ni-K edge and Ti-K edge were observed between different RTA samples, suggesting Ni decreased towards lower valence state and Ti increased towards higher valence after being exposed to RTA, being in agreement with the further oxidation of TiO_x (oxygen migrated from L2NO4).