Electronic Supplementary Information

# Chromium nitride as stable cathode current collector for thin film all-solid-state Li-ion batteries

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## Experimental

The coin cells used in this work were assembled according to the scheme presented in Fig. S1.

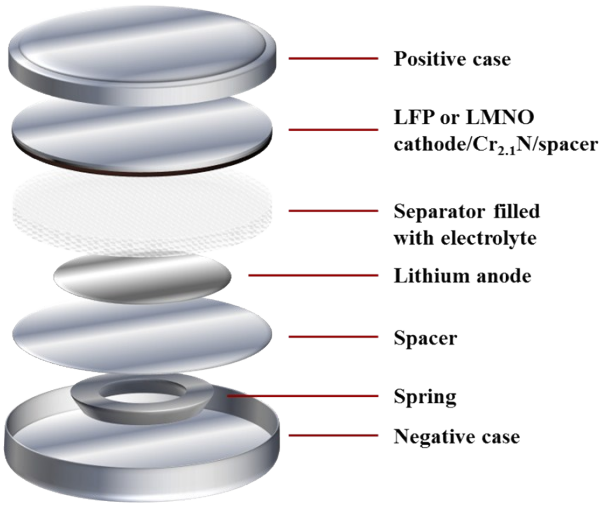


**Figure S1.** Scheme of the coin cells assembly.

## Results and discussion

The thickness of the $Cr_xN$ films with varying $N_2$/Ar content is presented in Fig. S2. The thickness was calculated from SEM cross sections (Fig. S4).

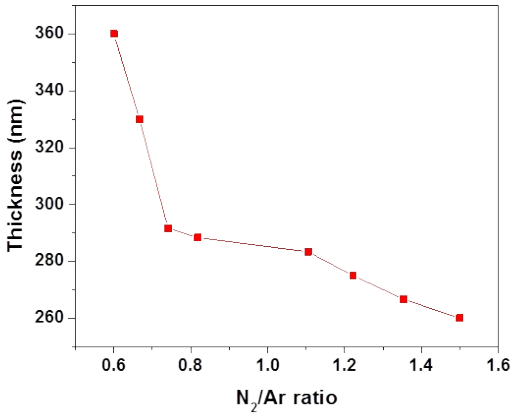


**Figure S2**. $Cr_xN$ thin film thickness determined by SEM as a function of the $N_2$/Ar ratio.

**Table ST1**. Quantification values of the different $Cr_xN$ samples from the EDX spectra. The penetration depth of the electrons is larger than the $Cr_xN$ films, therefore we observe aluminum, sodium, magnesium and silicon signals which originate from the soda lime glass used as substrate.

| $N_2$/Ar ratio | Element | Atomic. Number | Netto | Mass (%) | Mass Norm. (%) | Atomic (%) | Abs. error (%) | Rel. error (%) |
|---|---|---|---|---|---|---|---|---|
| **1.50** | Nitrogen | 7 | 42815 | 19.24 | 18.28 | 40.01 | 2.32 | 12.06 |
| | Oxygen | 8 | 15432 | 5.48 | 5.20 | 9.97 | 0.75 | 13.68 |
| | Sodium | 11 | 2789 | 0.61 | 0.57 | 0.77 | 0.07 | 10.75 |
| | Silicon | 14 | 26892 | 5.18 | 4.92 | 5.38 | 0.24 | 4.63 |
| | Chromium | 24 | 64405 | 73.51 | 69.84 | 41.17 | 2.78 | 3.78 |
| | Carbon | 6 | 2014 | 1.00 | 0.95 | 2.42 | 0.21 | 21.42 |
| | Magnesium | 12 | 1281 | 0.22 | 0.21 | 0.27 | 0.04 | 17.77 |
| | Aluminium | 13 | 138 | 0.02 | 0.02 | 0.02 | 0.00 | 11.21 |
| | | | Sum | 105.26 | 100.00 | 100.00 | | |
| **1.35** | Nitrogen | 7 | 33793 | 18.34 | 17.79 | 39.65 | 2.26 | 12.31 |
| | Oxygen | 8 | 11318 | 4.84 | 4.69 | 9.16 | 0.69 | 14.28 |
| | Sodium | 11 | 1648 | 0.47 | 0.45 | 0.61 | 0.06 | 12.41 |
| | Silicon | 14 | 17464 | 4.60 | 4.46 | 4.96 | 0.22 | 4.74 |
| | Chromium | 24 | 53197 | 73.58 | 71.38 | 42.85 | 2.79 | 3.79 |
| | Carbon | 6 | 1605 | 0.95 | 0.92 | 2.40 | 0.22 | 22.61 |
| | Magnesium | 12 | 895 | 0.20 | 0.20 | 0.26 | 0.04 | 19.16 |
| | Aluminium | 13 | 460 | 0.10 | 0.09 | 0.11 | 0.03 | 33.38 |
| | | | Sum | 103.08 | 100.00 | 100.00 | | |
| **1.22** | Nitrogen | 7 | 33415 | 16.88 | 16.44 | 37.82 | 2.08 | 12.34 |
| | Oxygen | 8 | 11383 | 4.41 | 4.30 | 8.65 | 0.63 | 14.32 |
| | Sodium | 11 | 1674 | 0.46 | 0.45 | 0.63 | 0.06 | 12.43 |
| | Silicon | 14 | 16509 | 4.12 | 4.02 | 4.61 | 0.20 | 4.81 |
| | Chromium | 24 | 58872 | 75.74 | 73.74 | 45.71 | 2.87 | 3.79 |
| | Magnesium | 12 | 748 | 0.16 | 0.16 | 0.21 | 0.04 | 22.79 |
| | Carbon | 6 | 1620 | 0.89 | 0.87 | 2.34 | 0.20 | 22.73 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Aluminium | 13 | 156 | 0.03 | 0.03 | 0.04 | 0.00 | 10.72 |
| | | | Sum | 102.71 | 100.00 | 100.00 | | |
| **1.11** | Nitrogen | 7 | 39105 | 16.20 | 15.61 | 36.60 | 1.97 | 12.18 |
| | Oxygen | 8 | 16235 | 5.12 | 4.93 | 10.12 | 0.70 | 13.63 |
| | Sodium | 11 | 2534 | 0.56 | 0.54 | 0.77 | 0.06 | 11.13 |
| | Silicon | 14 | 24053 | 4.87 | 4.69 | 5.48 | 0.23 | 4.68 |
| | Chromium | 24 | 71261 | 76.37 | 73.59 | 46.47 | 2.89 | 3.78 |
| | Magnesium | 12 | 1273 | 0.22 | 0.21 | 0.29 | 0.04 | 17.87 |
| | Aluminium | 13 | 510 | 0.08 | 0.08 | 0.10 | 0.03 | 38.01 |
| | Copper | 29 | 637 | 0.36 | 0.35 | 0.18 | 0.12 | 32.82 |
| | | | Sum | 103.78 | 100.00 | 100.00 | | |
| **0.82** | Nitrogen | 7 | 36722 | 13.93 | 13.51 | 33.46 | 1.71 | 12.27 |
| | Oxygen | 8 | 14033 | 3.85 | 3.73 | 8.10 | 0.54 | 14.03 |
| | Sodium | 11 | 857 | 0.17 | 0.16 | 0.25 | 0.04 | 22.54 |
| | Silicon | 14 | 16707 | 3.19 | 3.09 | 3.82 | 0.16 | 4.99 |
| | Chromium | 24 | 83468 | 80.59 | 78.18 | 52.15 | 3.04 | 3.77 |
| | Copper | 29 | 975 | 0.51 | 0.49 | 0.27 | 0.14 | 27.75 |
| | Magnesium | 12 | 931 | 0.15 | 0.14 | 0.21 | 0.04 | 23.64 |
| | Aluminium | 13 | 903 | 0.14 | 0.14 | 0.17 | 0.03 | 24.23 |
| | Carbon | 6 | 1350 | 0.56 | 0.55 | 1.58 | 0.14 | 25.32 |
| | | | Sum | 103.09 | 100.00 | 100.00 | | |
| **0.74** | Nitrogen | 7 | 28915 | 12.61 | 12.63 | 31.96 | 1.58 | 12.55 |
| | Silicon | 14 | 12844 | 2.55 | 2.55 | 3.22 | 0.13 | 5.23 |
| | Chromium | 24 | 69667 | 80.42 | 80.49 | 54.88 | 3.04 | 3.78 |
| | Oxygen | 8 | 10175 | 3.21 | 3.22 | 7.13 | 0.47 | 14.74 |
| | Sodium | 11 | 1065 | 0.23 | 0.23 | 0.35 | 0.04 | 18.60 |
| | Magnesium | 12 | 619 | 0.10 | 0.10 | 0.15 | 0.03 | 31.87 |
| | Carbon | 6 | 1533 | 0.78 | 0.78 | 2.31 | 0.18 | 23.42 |
| | | | Sum | 99.90 | 100.00 | 100.00 | | |
| **0.66** | Nitrogen | 7 | 29381 | 12.19 | 11.74 | 30.76 | 1.53 | 12.54 |
| | Silicon | 14 | 8880 | 1.64 | 1.58 | 2.06 | 0.10 | 5.85 |
| | Chromium | 24 | 80302 | 86.18 | 83.01 | 58.57 | 3.25 | 3.77 |
| | Oxygen | 8 | 11414 | 3.32 | 3.20 | 7.33 | 0.48 | 14.50 |
| | Carbon | 6 | 816 | 0.37 | 0.36 | 1.09 | 0.11 | 30.73 |
| | Sodium | 11 | 554 | 0.11 | 0.11 | 0.18 | 0.03 | 30.44 |
| | | | Sum | 103.82 | 100.00 | 100.00 | | |
| **0.60** | Nitrogen | 7 | 30319 | 10.95 | 10.75 | 28.70 | 1.37 | 12.53 |
| | Silicon | 14 | 10259 | 1.73 | 1.70 | 2.26 | 0.10 | 5.74 |
| | Chromium | 24 | 92638 | 85.00 | 83.40 | 60.01 | 3.20 | 3.77 |
| | Oxygen | 8 | 13007 | 3.09 | 3.04 | 7.10 | 0.44 | 14.32 |
| | Copper | 29 | 1189 | 0.60 | 0.59 | 0.35 | 0.15 | 25.76 |
| | Carbon | 6 | 1253 | 0.50 | 0.49 | 1.52 | 0.13 | 26.34 |
| | Aluminium | 13 | 388 | 0.05 | 0.05 | 0.07 | 0.03 | 56.56 |
| | Magnesium | 12 | 0 | 0.00 | 0.00 | 0.00 | 0.00 | 3.05 |
| | | | Sum | 101.92 | 100.00 | 100.00 | | |

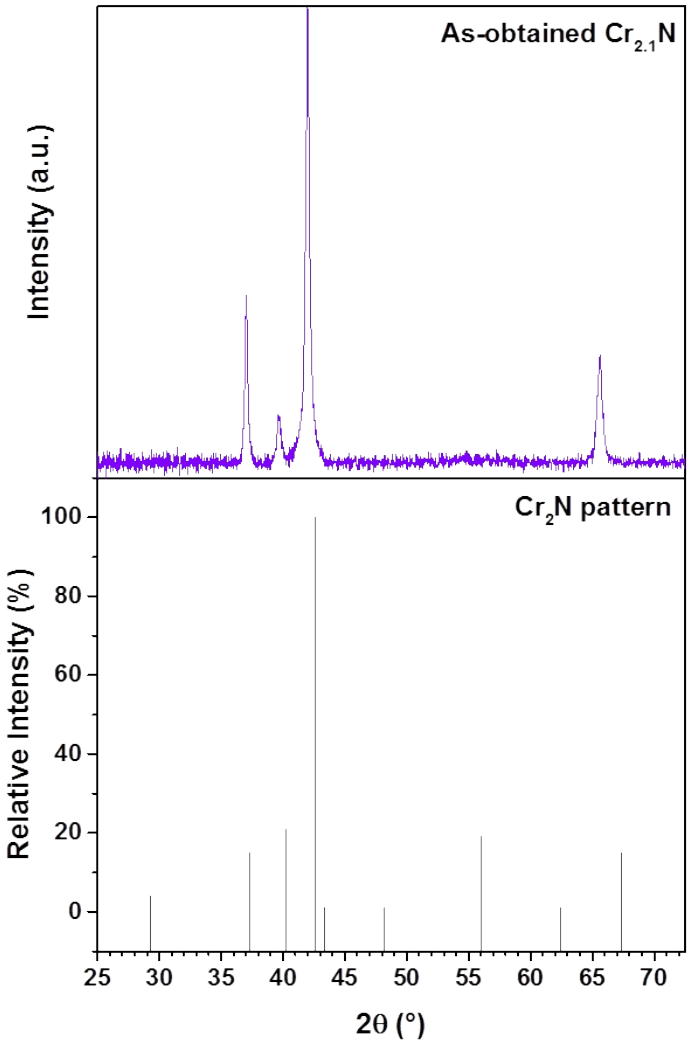


**Figure S3**. Relative peaks intensities of as-prepared $Cr_{2.1}N$ (top) and the $Cr_2N$ pattern.

The SEM cross sections in Fig. S4 were obtained by mechanical cleaving of the silicon substrate.

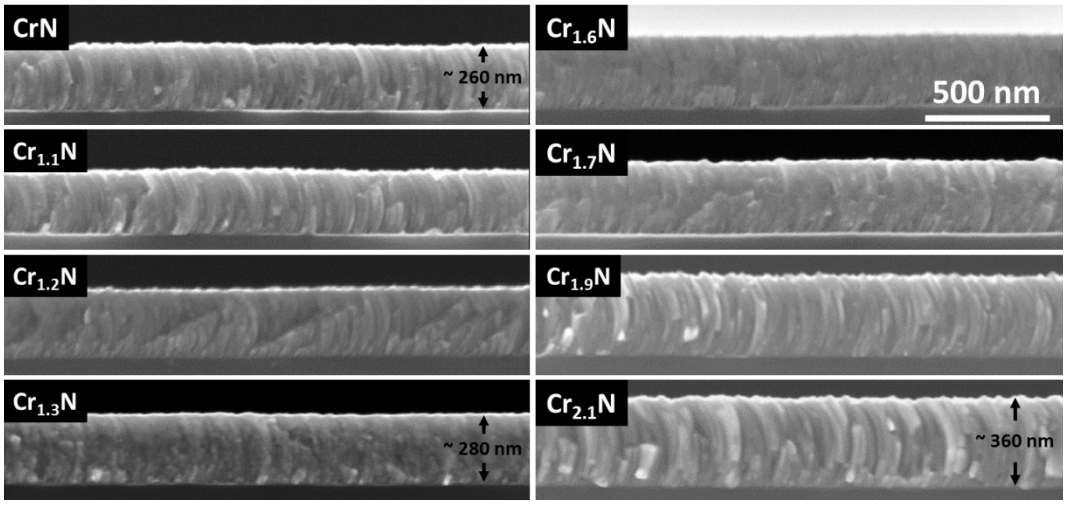


**Figure S4.** SEM cross sections of $Cr_xN$ thin films on Si(100).

The change in surface microstructure for CrN-$Cr_{2.1}N$ is presented in Figure S5.

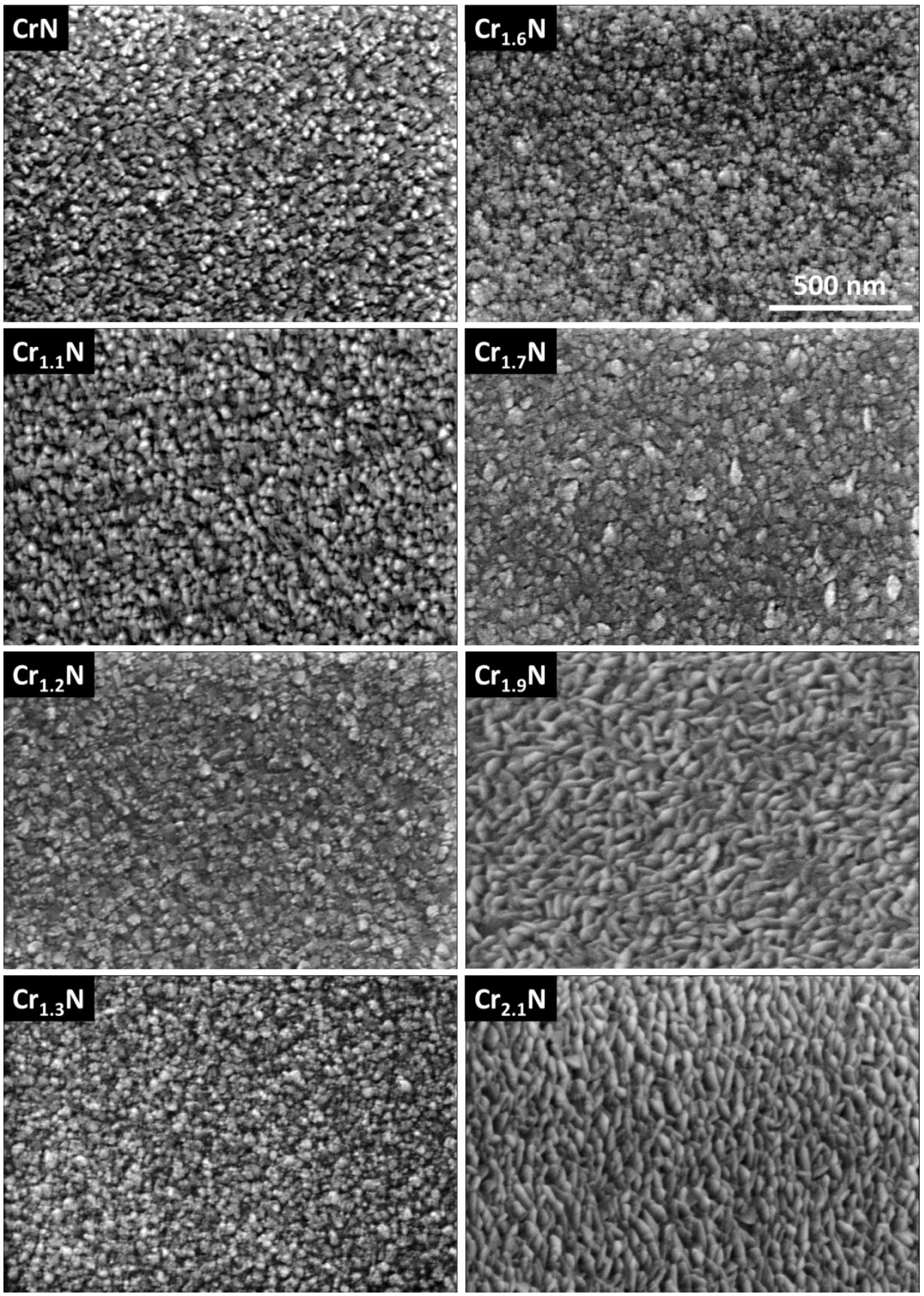


**Figure S5.** SEM normal views of $Cr_xN$ thin flims (the scale is the same for all images).

For the $Cr_{2.1}N$ composition, the thickness of the film was swept between 45 nm and 489 nm, Fig. S6, and the sheet resistance measured as shown in Fig. S6a), obtaining an exponential trend for the sheet resistance that approximately obeys the equation $sh = 2.79 + 39.56 \times e^{-0.01 \times th}$ [$R^2$ = 0.992], where *sh* is the sheet resistance and *th* the thickness. Even for the thinnest film prepared of 45 nm the sheet

resistance remains relatively low and from the SEM micrographs of Fig. S7(b-d) no macroscopic voids are observed, although this low thickness region is characterized by the presence of discontinuities or islands in the film.

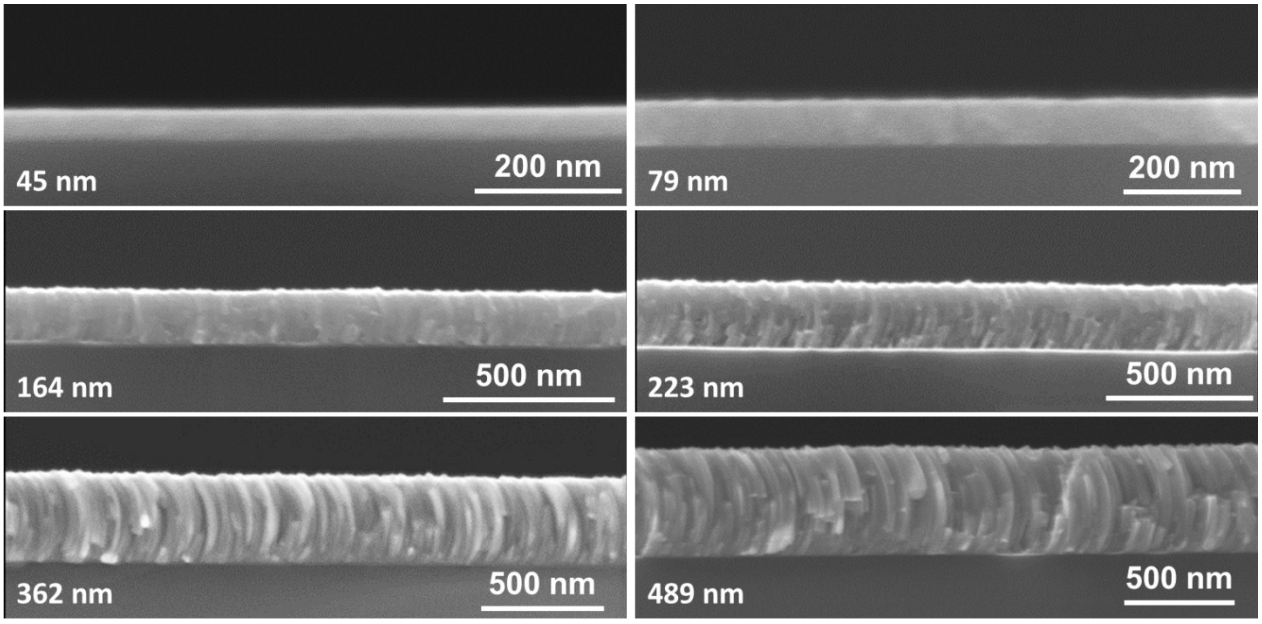


**Figure S6**. SEM cross sections of $Cr_{2.1}N$ with different thicknesses.

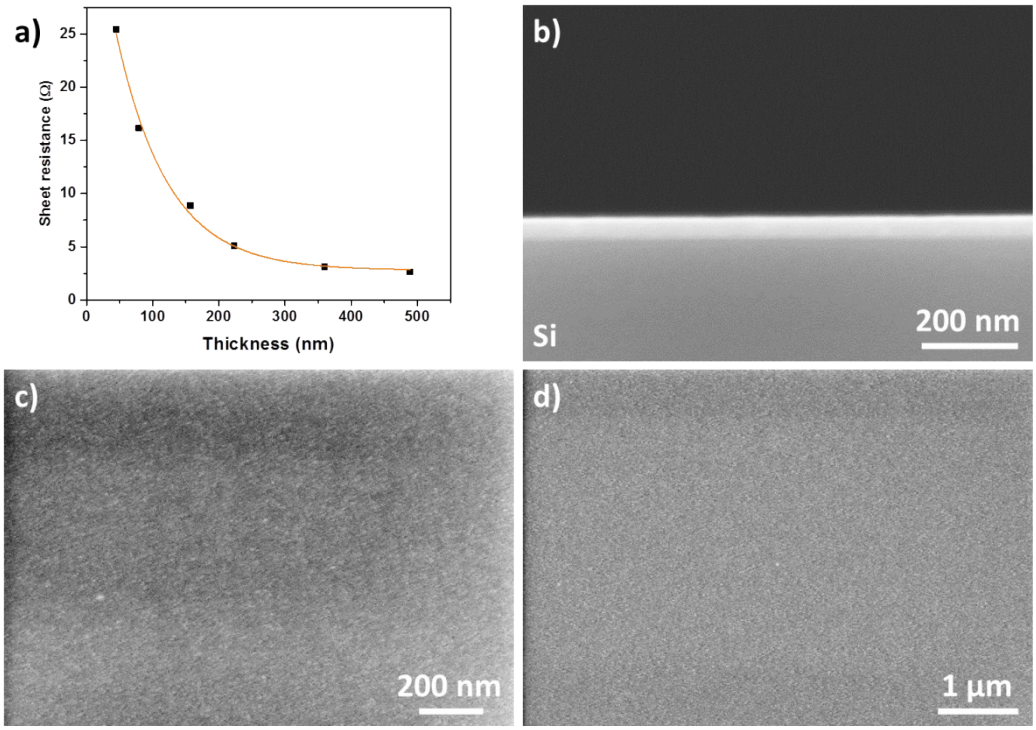


**Figure S7**. a) Evolution of $Cr_{2.1}N$ sheet resistance with thickness. b)-d) SEM micrographs of a 45 nm thick $Cr_{2.1}N$ film.

The change in surface microstructure for $Cr_{2.1}N$ thin films of 79 nm to 489 nm is presented in Fig. S8.

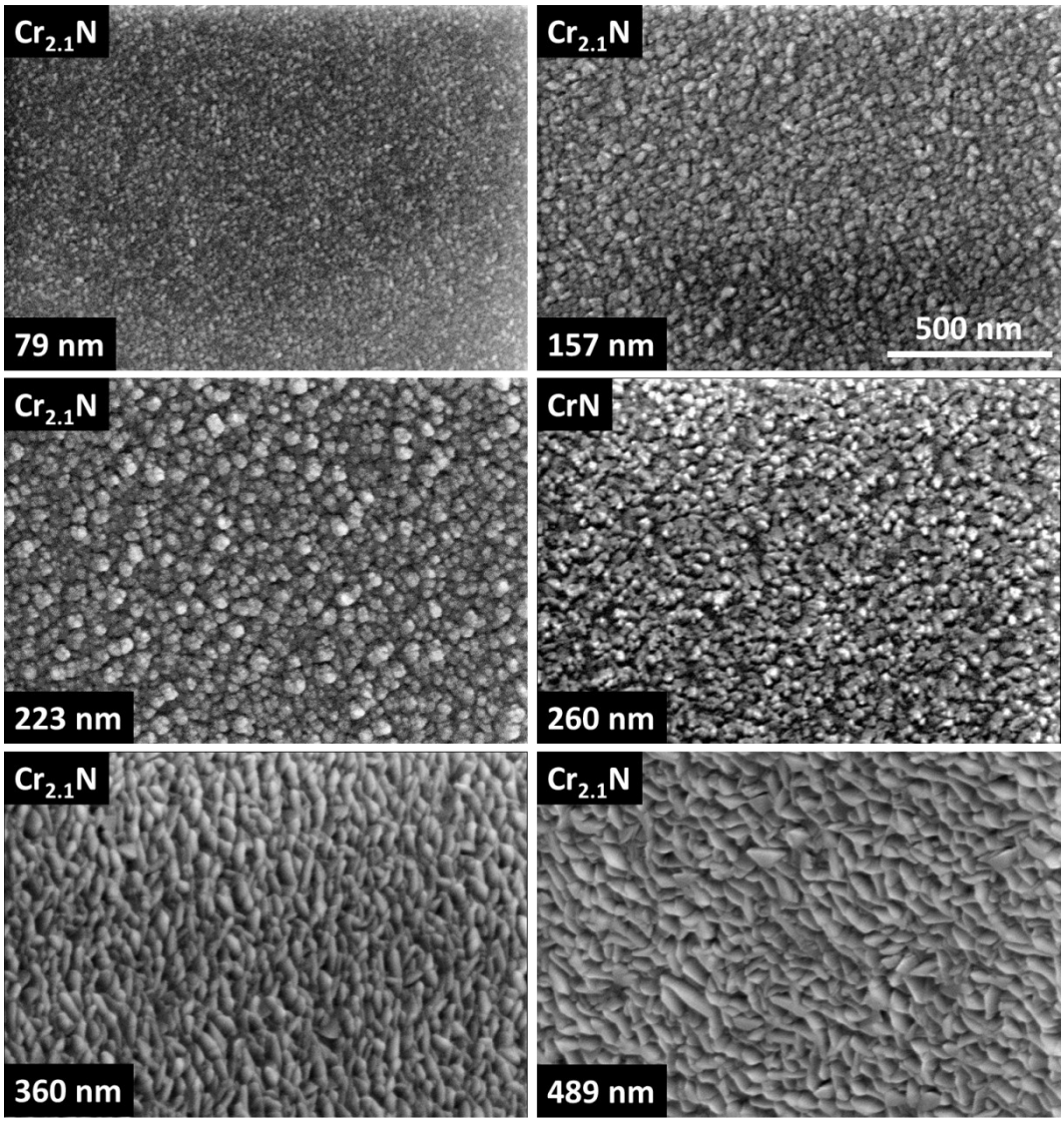


**Figure S8**. SEM normal views of $Cr_{2.1}N$ with different thicknesses. A 260 nm thick CrN film has been included for comparison.

The morphology of as-prepared LMNO/$Cr_2N$/Si samples can be seen in Fig. S9.

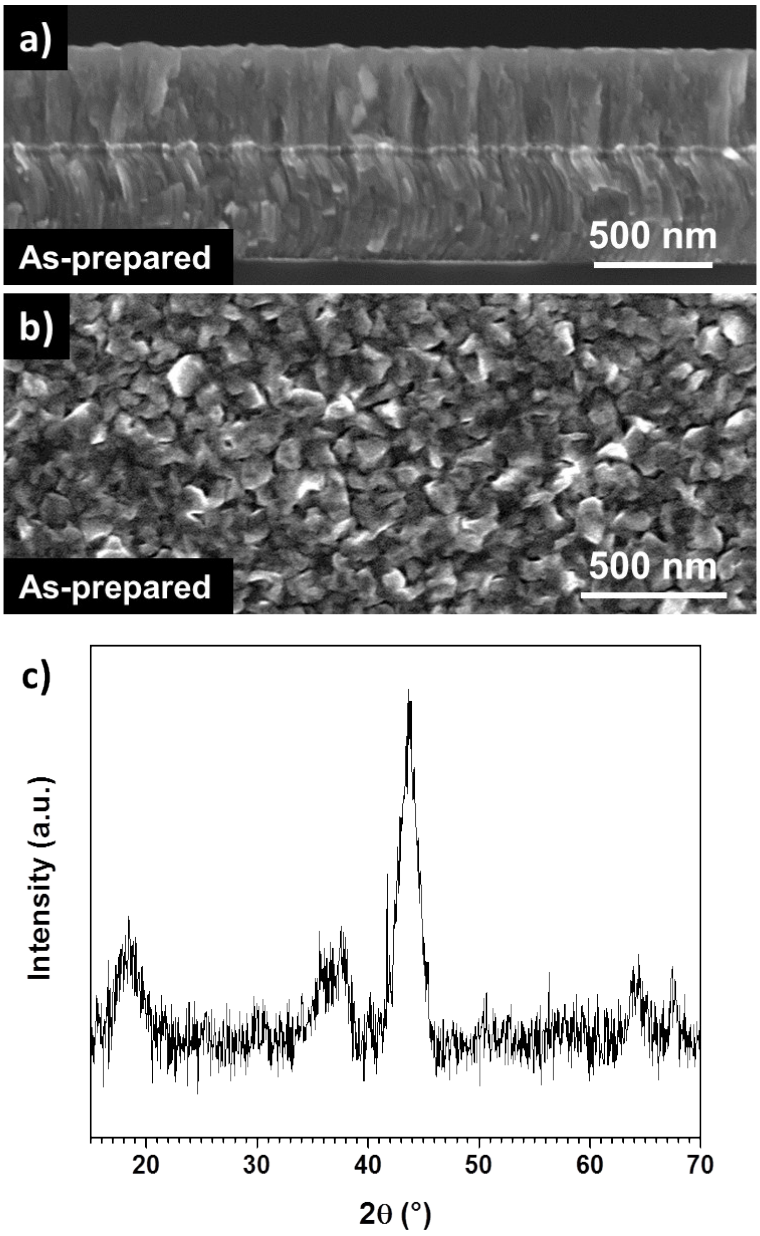


**Figure S9**. SEM normal view of as-prepared LMNO(500) on $Cr_2N$(500 nm)/Si (a) and its cross section (b). c) GIXRD of as-prepared LMNO(500 nm)/$Cr_2N$(500 nm)/SS at ω = 1°.

Upon annealing the surface of the samples develops crystals which size depends on the annealing temperature, observing the largest crystal for the 700 °C 1 hour treatment, which might be attributed to the large surface segregation of chromium (Fig. S10).

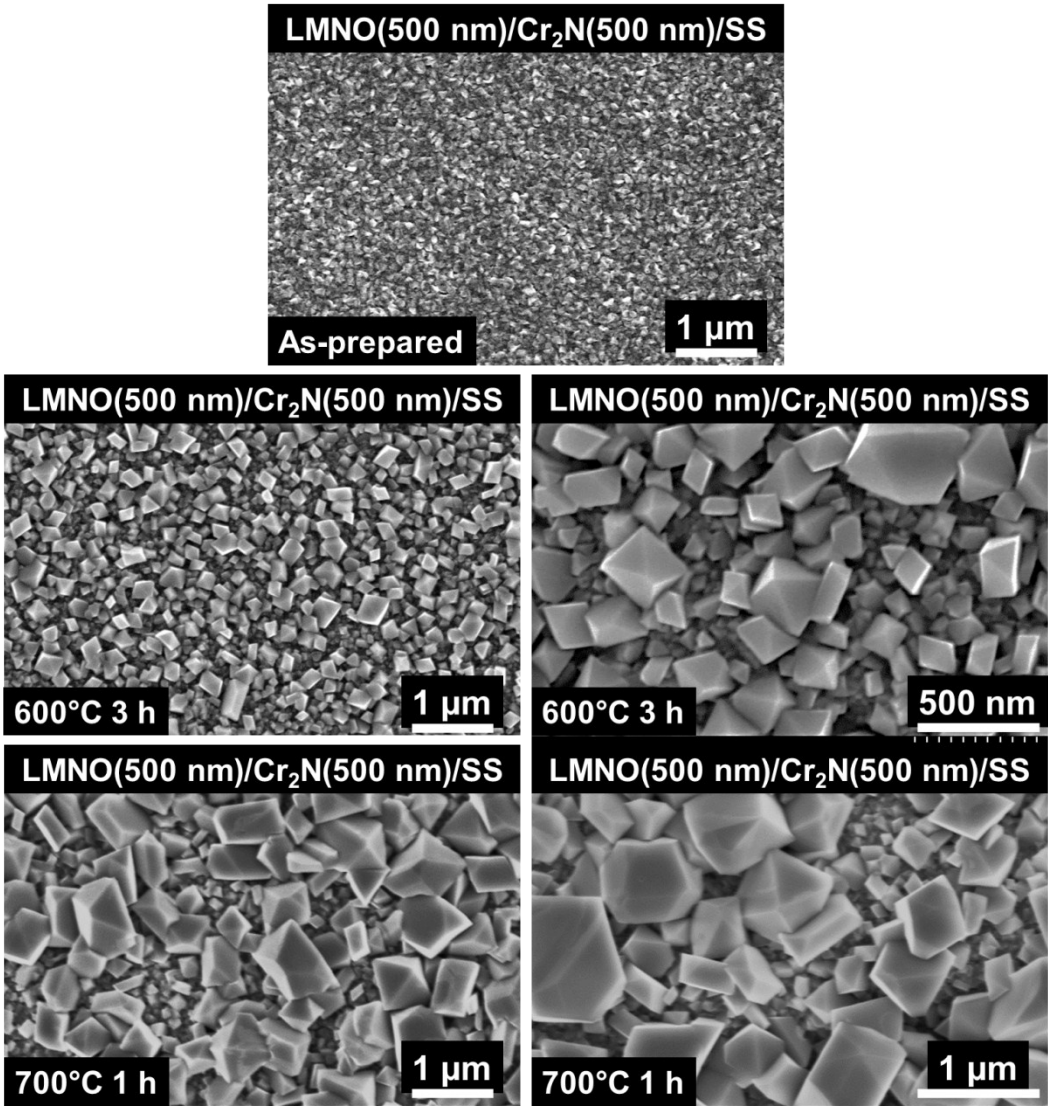


**Figure S10**. SEM normal views of LMNO(500 nm)/$Cr_2N$(500 nm)/SS for the as-prepared (top), 600 °C 3 h (middle) and 700 °C 1h (bottom) cases.

The morphology of LMNO/$Cr_2N$/Si annealed at 700 °C for 1 hour can be seen in Fig. S11.

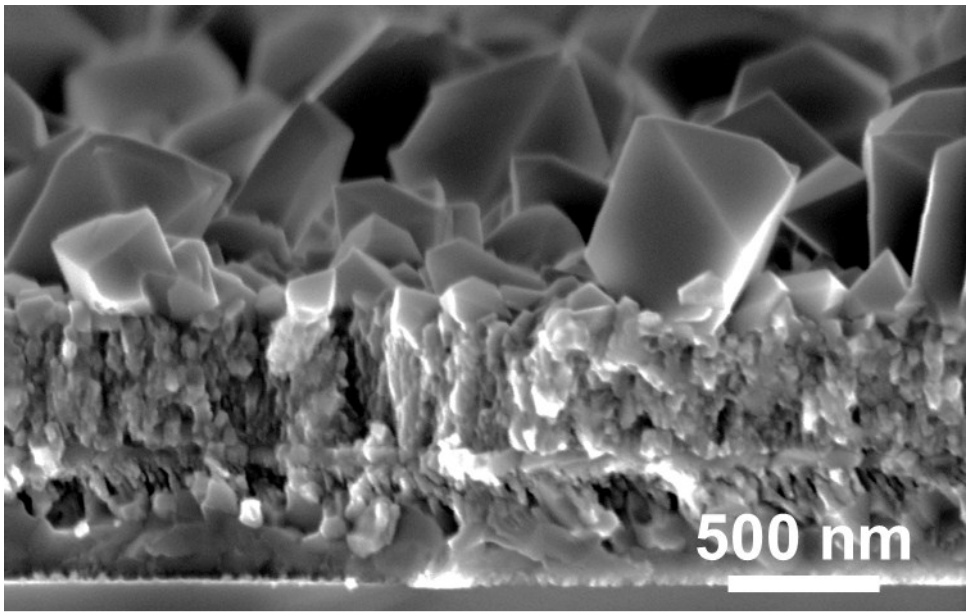


**Figure S11**. SEM cross section of LMNO(500 nm)/$Cr_2N$(500 nm)/Si annealed at 700 °C 1 hour.

Figure S12 gathers the XPS surveys for some relevant samples. Please notice that the Na and Ca originally present in the survey of sample LMNO(500 nm)/$Cr_2N$(500 nm)/Si at 600 °C is due to impurities in the first target that decreased upon target usage.

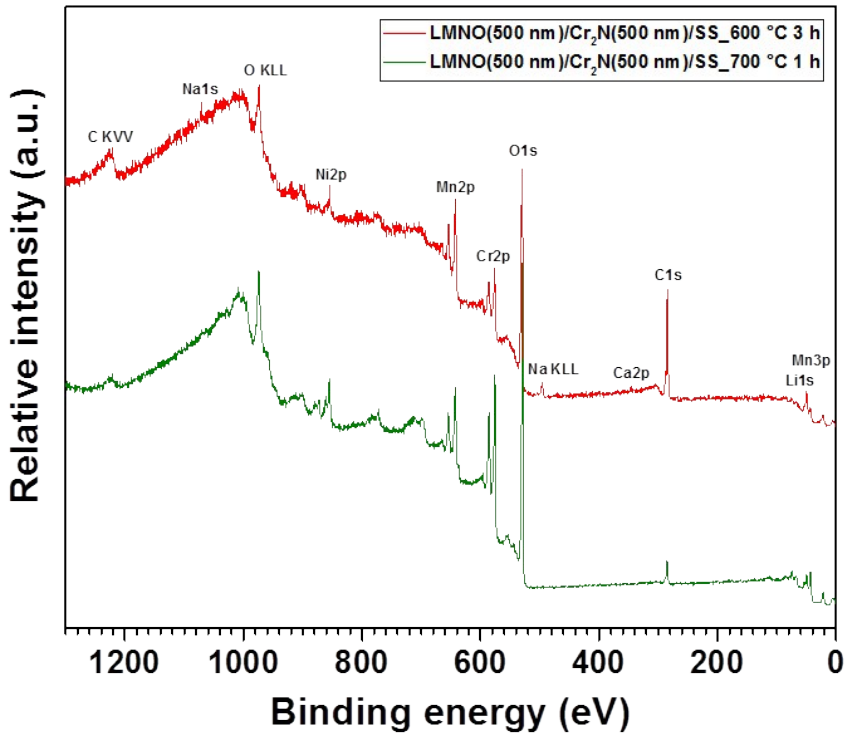


**Figure S12**. XPS surveys of the samples LMNO(500 nm)/$Cr_2N$(500 nm)/SS annealed at 600 °C for 3 hours and annealed at 700 °C 1 hour.

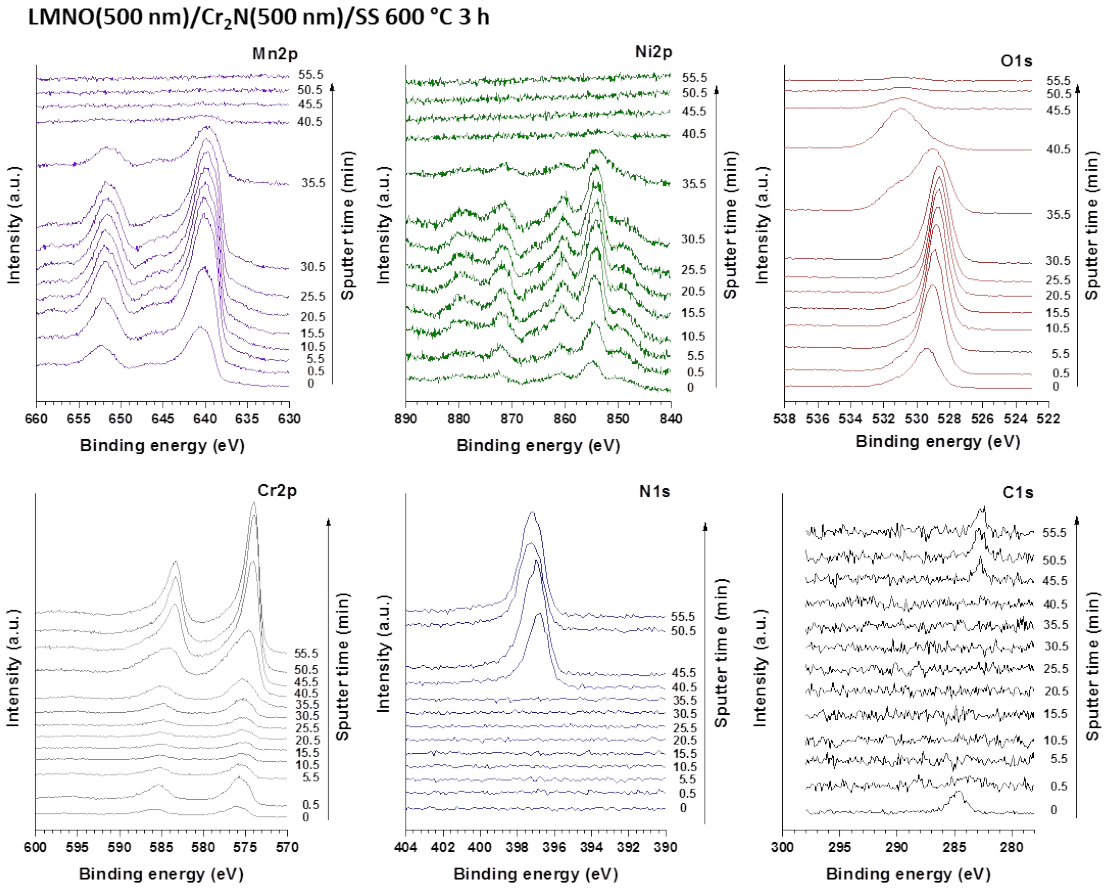


**Figure S13**. XPS peaks for several elements in the sputter-depth profile of LMNO(500 nm)/$Cr_2N$(500 nm)/SS, annealed at 600 °C for 3 hours.

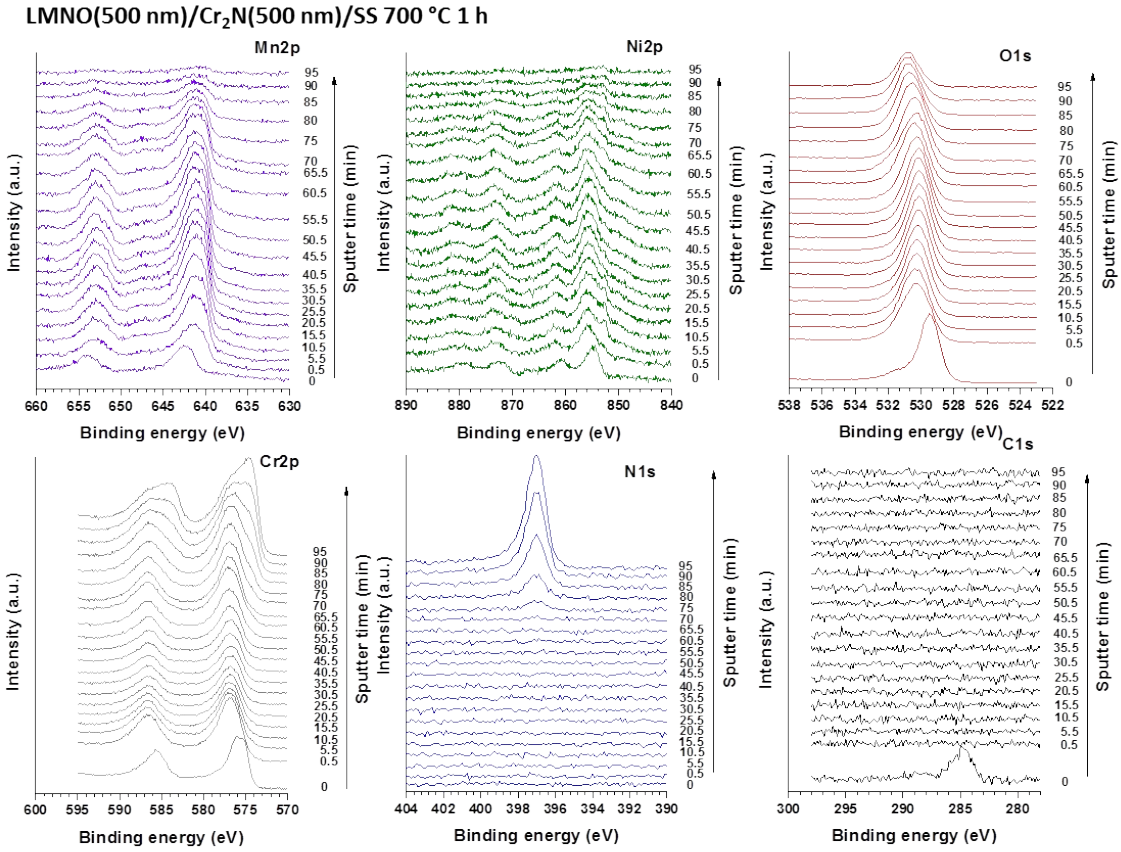


**Figure S14**. XPS peaks for several elements in the sputter-depth profile of LMNO(500 nm)/$Cr_2N$(500 nm)/SS, annealed at 700 °C for 1 hour.

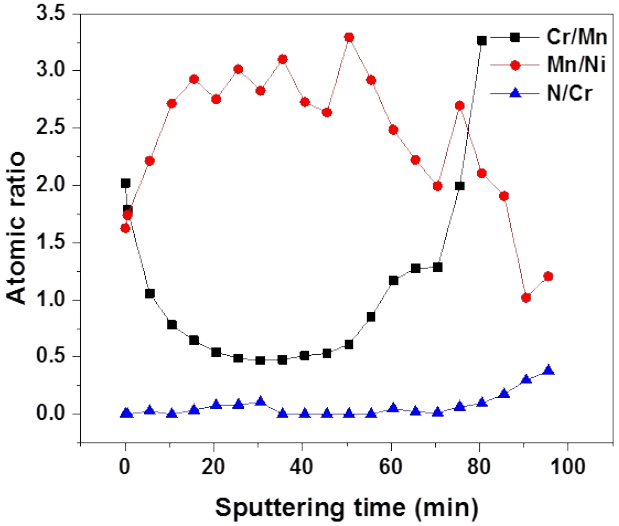


**Figure S15**. Mn/Cr, Mn/Ni and N/Cr atomic ratios for LMNO(500 nm)/$Cr_2N$(500 nm)/SS after annealing at 700 °C 1 hour calculated from Fig. S17.

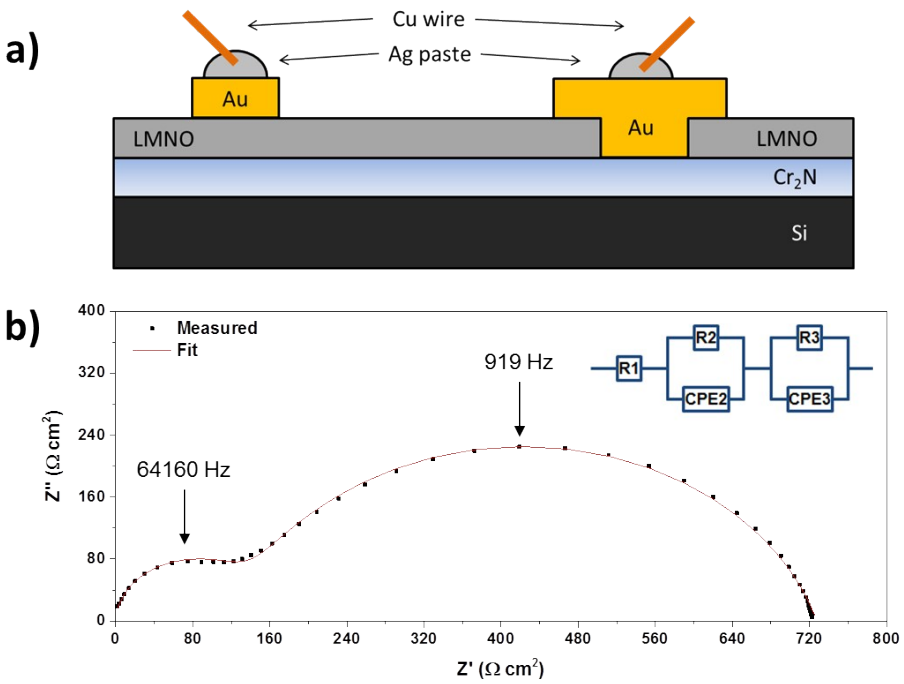


**Figure S16**. a) Scheme of the multilayer and contacts used for EIS. b) Nyquist plot at room temperature of LMNO(500 nm)/$Cr_2N$(500 nm)/Si after annealing at 600 °C 3 hours, frequency range 1 MHz to 10 mHz. The fit of the data is shown in red. The inset depicts the equivalent circuit, used to fit the data, consisting of resistors and constant phase elements.