Supporting Information

Stabilizing the Chemistry of NiO_x in Perovskite Solar Cells to Pass the Damp Heat Test

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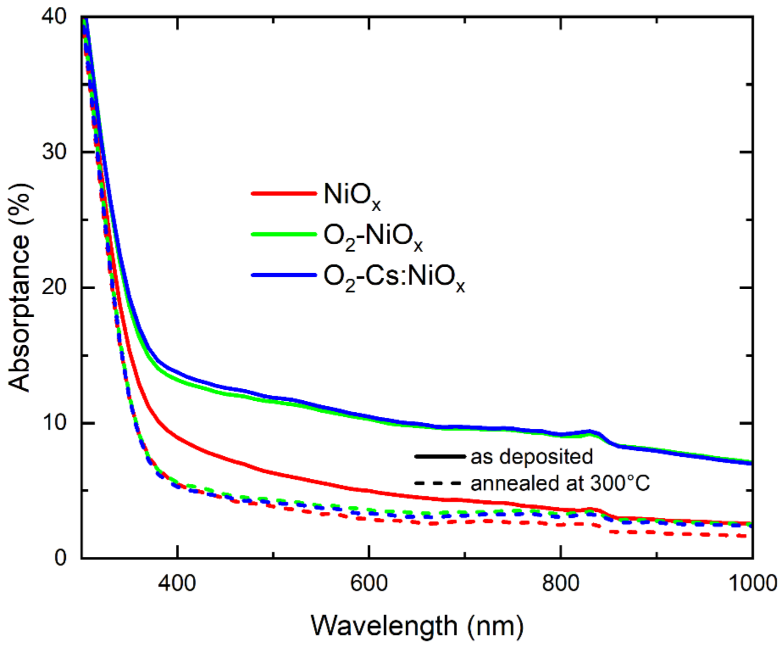


Figure S1: Absorptance spectra of NiO_x, O_2-NiO_x and O_2-Cs:NiO_x. *NiOx (red curves) O_2-NiO_x (green curves) and O_2-Cs:NiO_x (blue curves) films before (solid lines) and after annealing at 300°C in ambient air (dashed lines).*

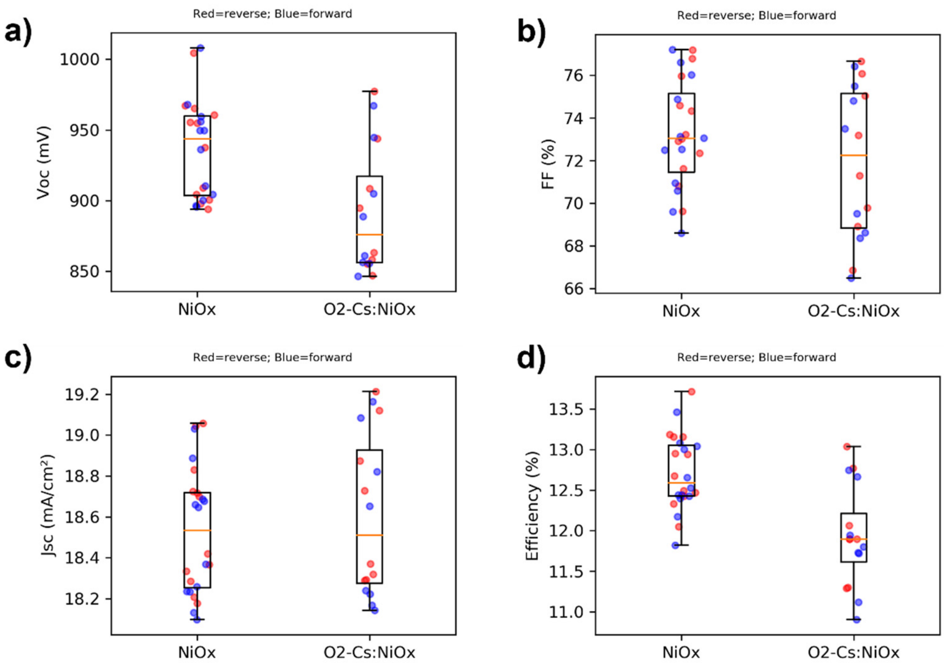


Figure S2: J-V parameters of as-deposited PSCs for NiO_x and O_2-Cs:NiO_x. *NiO_x (150 sccm Ar / 0 sccm Ar-O_2, NiO_x sputtering target) and O_2-Cs:NiO_x (120 sccm Ar / 30 sccm Ar-O_2 Cs:NiO_x sputtering target).*

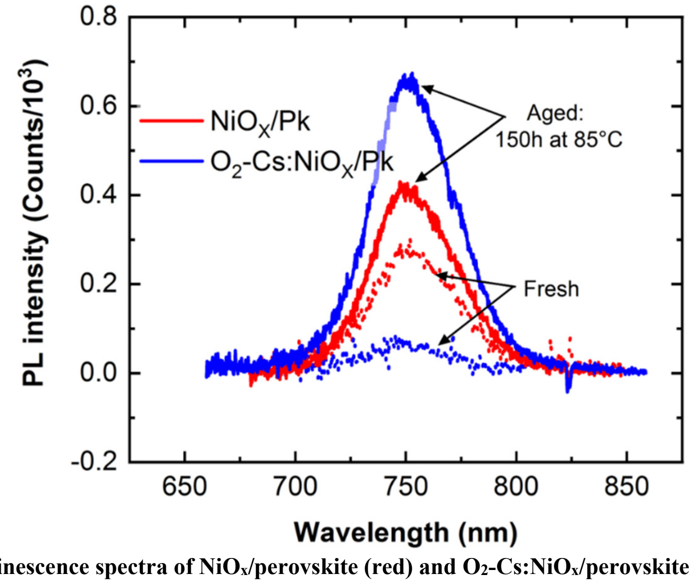


Figure S3: Photoluminescence spectra of NiO_x/perovskite (red) and O_2-Cs:NiO_x/perovskite (blue) films coated on glass/ITO substrates. *Fresh samples are represented with dashed lines while aged samples (after one week in N_2 at 85°C) are represented with solid lines.*

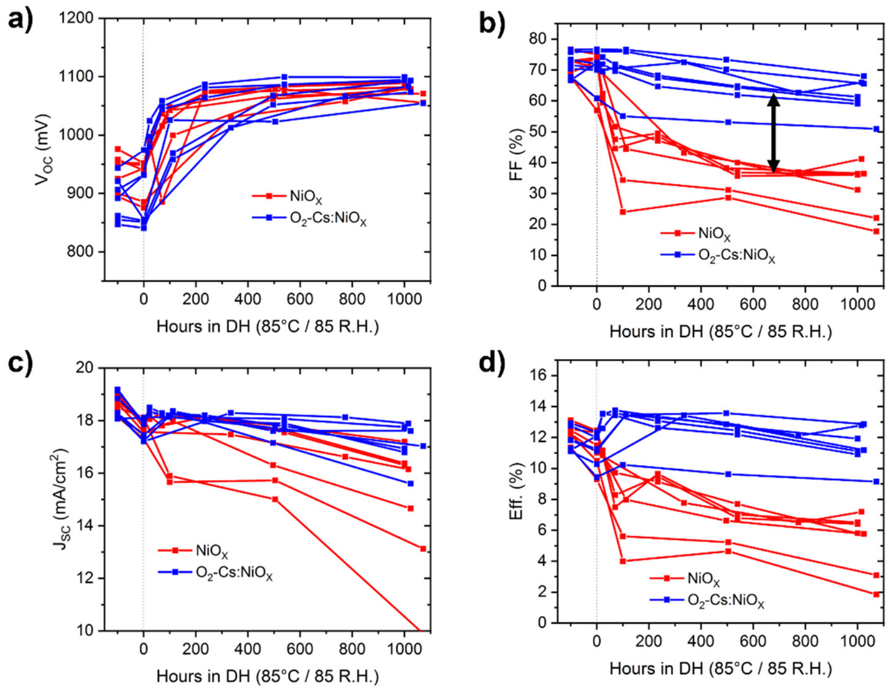


Figure S4: J-V performances of 1 cm^2 semi-transparent PSCs based on 20 nm NiO$_x$ and O$_2$-Cs:NiO$_x$ at different times of DH testing. *a) J_{SC}, b) FF, c) V_{OC}, d) Eff. To show statistics, 14 cells from 4 different batches are plotted here. The active area is 1cm^2.*

Note on Figure S4*: DH = -100h corresponds to the J-V measurement done on the as-finished device, whereas DH = 0h refers to the measurement after encapsulation. Right after the encapsulation, the devices show lower efficiencies due to lower J_{SC} and V_{OC}. This degradation caused by the encapsulation process is reversible after a few hours in the DH chamber, as it can be seen in Figures S4a and c. In more details, after encapsulation (DH = 0h), the device efficiency dropped by around 0.5 to 1% due to a decrease in J_{SC}. This J_{SC} variation could be caused by a combination of perovskite degradation due to the lamination process and the reflection of light at the front glass interface. After the first 160 hours in DH, the device efficiency increases as a result of a V_{OC} enhancement of up to 100 mV. The origin of this large increase in V_{OC}, observed in NiO$_x$-based devices (with and without an organic interlayer at the interface), and accompanied by an increased PL is not clear. However, it could be explained by the removal of Ni^{3+} traps at the interface during aging.*

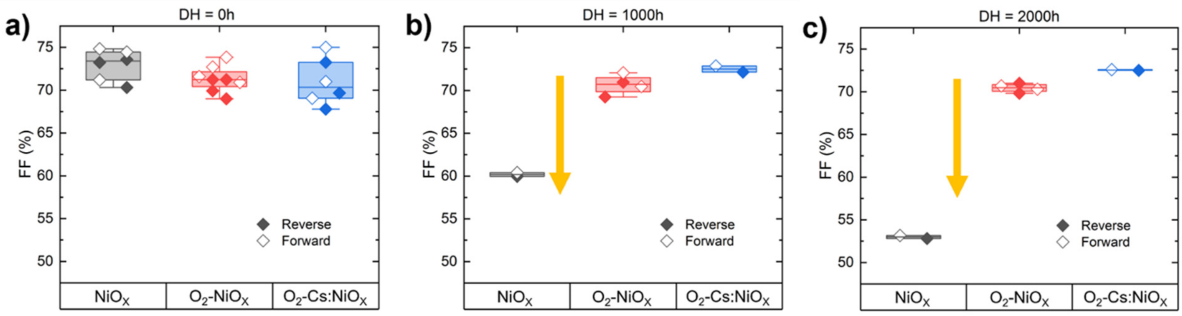


Figure S5: FF of NiO$_x$/MeO-2PACz-based PSCs presented in Figure 2 during damp heat testing. *After (a) encapsulation, (b) 1000 h and (c) 2000 h in DH chamber, for different HTMs. J-V of the devices after 2000h of DH are inserted in the (c).*

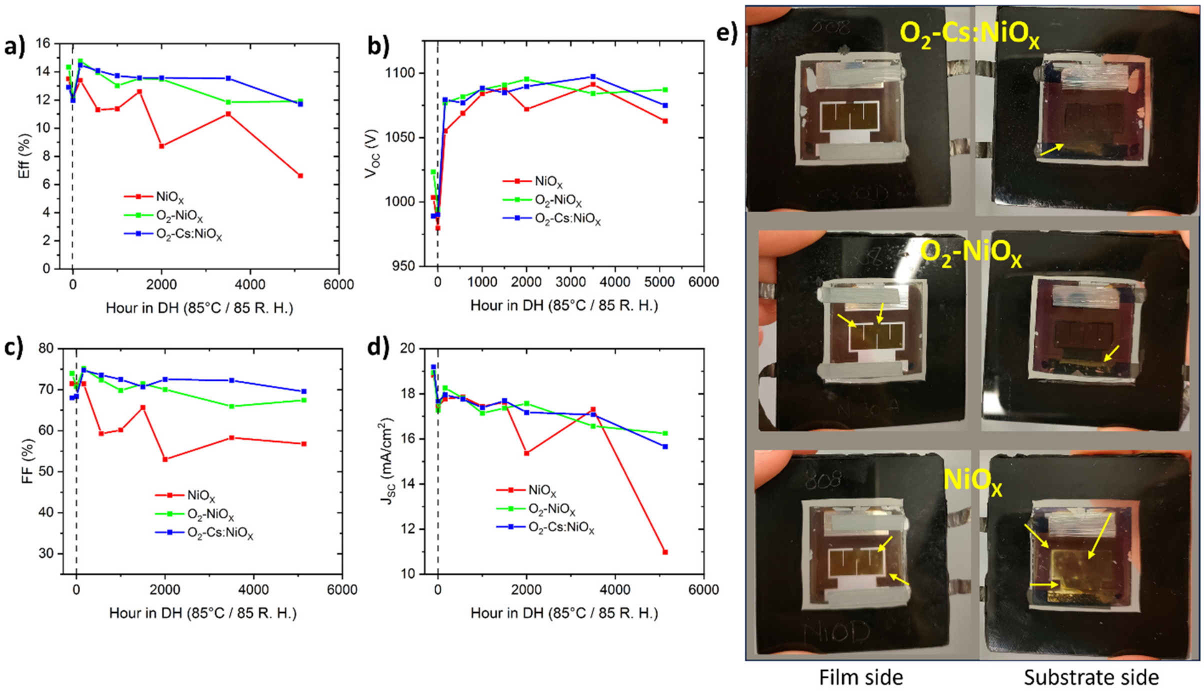


Figure S6: J-V parameters of NiO$_x$/MeO-2PACz-based PSCs presented in Figure 2 as a function of DH aging: *a) efficiency, b) V_{OC}, c) FF, d) J_{SC} and e) photos of each cell after more than 5100h in the DH chamber.*

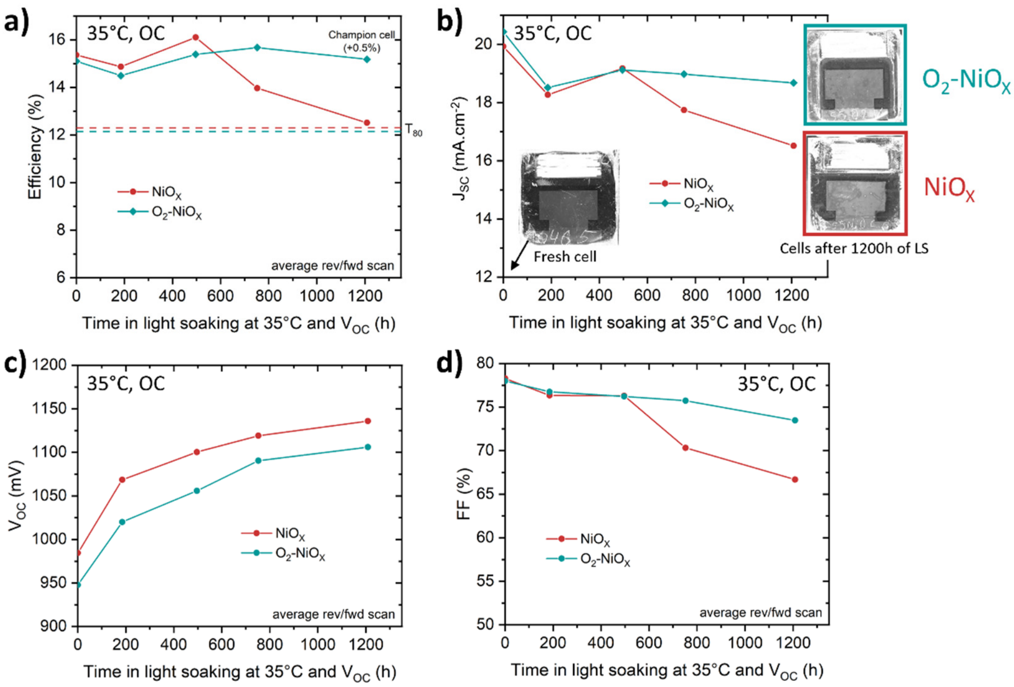


Figure S7: J-V parameters of PSCs based on NiO$_x$ and O$_2$-NiO$_x$ during light soaking at 35°C *and open-circuit conditions*: *a) Efficiency, b) J_{SC}, c) V_{OC} and d) FF of PSCs at different times during the light soaking test under 1 sun illumination, N_2 flow, 35°C and open-circuit conditions. Active area 1.04 cm^2.*

Since excess PbI_2 can cause perovskite degradation under light and heat [1], a perovskite solution approaching stoichiometric conditions (0.7% PbI_2 excess) was used for the light soaking degradation tests.

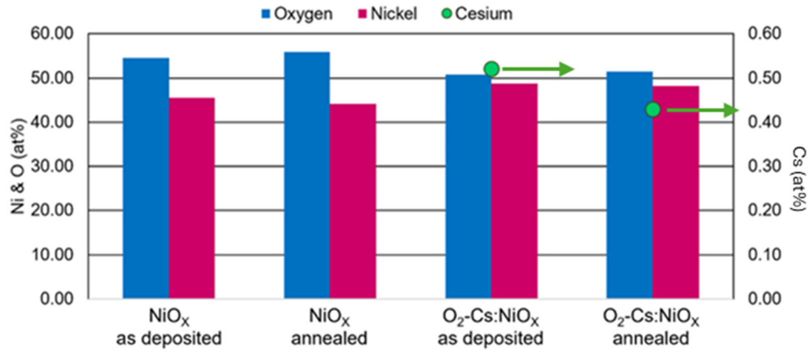


Figure S8: Atomic concentration of Ni, O, and Cs determined by STEM EDX for NiO_x and O_2-Cs:NiO_x 20 nm films. *For both materials, EDX measurements were done on both as-deposited and annealed films. Annealing was done in air at 300°C for 30 min.*

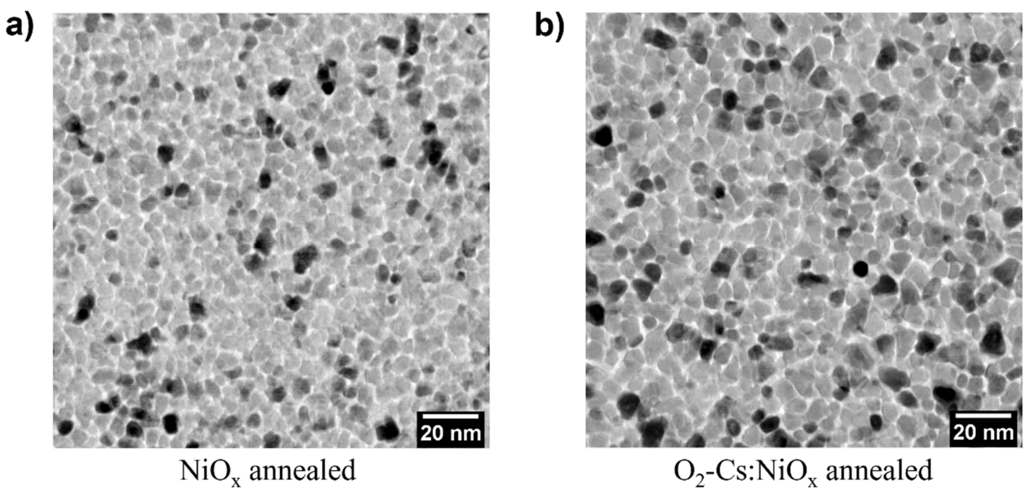


Figure S9: Microstructure of NiO_x and O_2-Cs:NiO_x thin films. *a) STEM bright-field image of annealed NiO_x and b) O_2-Cs:NiO_x film.*

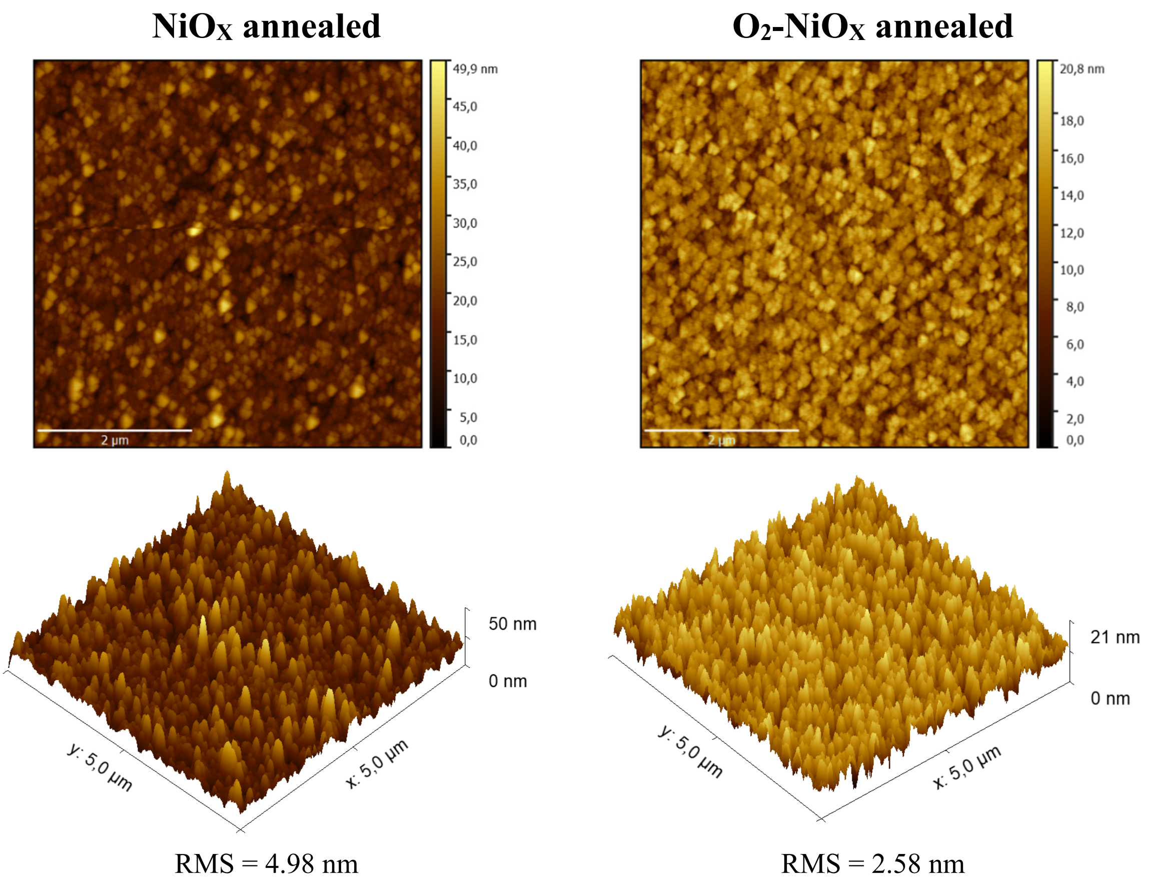
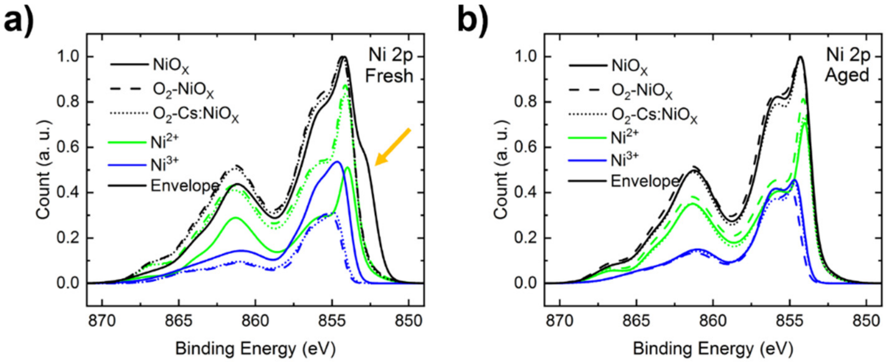


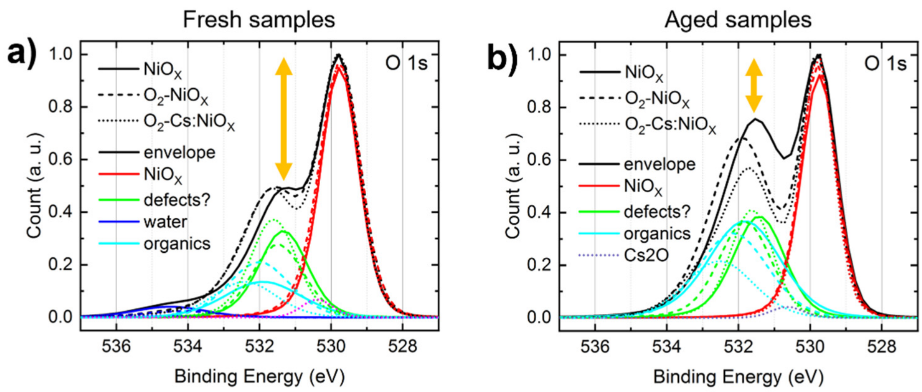
Figure S10: AFM images of both annealed NiO_x (left) and O_2-NiO_x (right) films. *The roughness of the O_2-NiO_x is two times lower than the one of the NiO_x. This result coincides with the observation that O_2-NiO_x is more compact thanks to improved stoichiometry (O_2-$NiO_{x=1.06}$, resulting in fewer Ni^{3+} species and $Ni_{vacancies}$) as well as a longer sputtering deposition.*



c)

Sample Names	Ni^0 (%)	Ni^{2+} (%)	Ni^{3+} (%)
NiO_X fresh	14	46	40
O_2-NiO_X fresh	0	79	21
O_2-Cs:NiO_X fresh	0	77	23
NiO_X aged	0	63	37
O_2-NiO_X aged	0	69	31
O_2-Cs:NiO_X aged	0	64	36

Figure S11: Ni 2p XPS surface analysis and deconvolution for each Ni oxidation state (Ni^0, Ni^{2+} and Ni^{3+}) for NiO_x, O_2-NiO_x and O_2-Cs:NiO_x films. *Ni 2p envelopes, Ni^{2+} and Ni^{3+}peaks deconvoluted for each a) fresh and b) aged HTM are plotted. Table c) presents the integrated values for each contribution, in the different HTMs, before and after aging at 85°C in an inert atmosphere. The Ni^0 contribution in the NiO_x film is shown by an arrow.*



c)

Sample Names	Ni 2p Ni^{2+} (%)	Ni 2p Ni^{3+} (%)	O 1s NiO %	O 1s defects %	O 1s orgs %
NiO_X fresh	23	20	31	16	10
O_2-NiO_X fresh	35	9	33	11	10
O_2-Cs:NiO_X fresh	36	11	31	14	7
NiO_X aged	22	13	27	16	22
O_2-NiO_X aged	25	11	29	16	18
O_2-Cs:NiO_X aged	25	14	31	17	14

Figure S12: XPS analysis of O 1s spectra for NiO_x, O_2-NiO_x, and O_2-Cs:NiO_x surfaces before and after aging at 85°C. *a) O 1s spectra of fresh samples and (b) aged one. Each O peak contribution is plotted in the same graph to highlight the shifts. Table c) presents the deconvoluted values obtained for each O and Ni contributions.*

References:

[1] F. Fu, S. Pisoni, Q. Jeangros, J. Sastre-Pellicer, M. Kawecki, A. Paracchino, T. Moser, J. Werner, C. Andres, L. Duchêne, P. Fiala, M. Rawlence, S. Nicolay, C. Ballif, A. N. Tiwari, S. Buecheler, *Energy Environ Sci* **2019**, 12, 3074.