

### Supporting information:

In case of the plasma deposited  $\text{CoO}_x/\text{Ti}$  XRD patterns were recorded for  $\text{pl\_CoO}_x/\text{Ti\_4}$  and  $\text{pl\_CoO}_x\text{OH}_2/\text{Ti\_7}$ . A successful deposition of  $\text{CoO}_x$  was confirmed additional with XPS spectra for the here shown samples. All XRD measurements were recorded symmetric and additionally with an incidence angle of  $3^\circ$  for a higher surface sensitivity. Figure S1 shows the comparison of the recorded GIXRD and XRD for  $\text{pl\_CoO}_x\text{OH}_2/\text{Ti\_7}$ . As expected the intensity for the  $\text{TiO}_2$  reflexes is increased compared to the reflexes of Ti in case of the GIXRD but there are no reflexes for either  $\text{Co}_3\text{O}_4$  nor  $\text{CoO}$  or  $\text{Co}(\text{OH})_2$  detected. These results confirm that the plasma deposited  $\text{CoO}_x/\text{Ti}$  and  $\text{CoO}_x\text{OH}_2$  are X-ray amorphous.

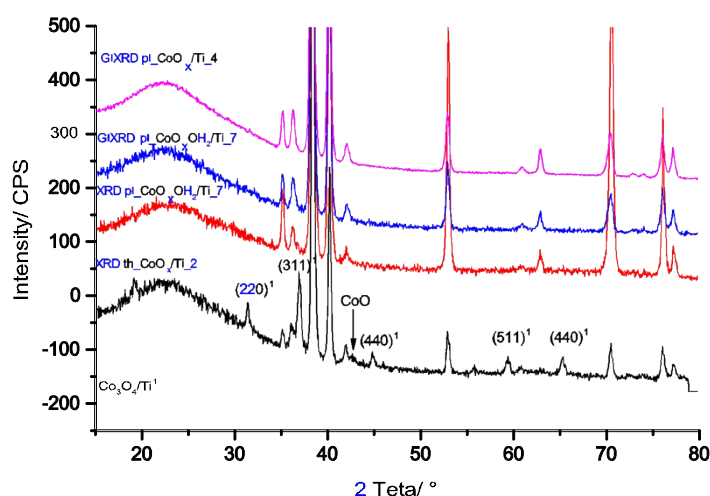


Figure S1. GIXRD pattern of  $\text{pl\_CoO}_x/\text{Ti\_4}$  (pink), as well as GIXRD of  $\text{pl\_CoO}_x\text{OH}_2/\text{Ti\_7}$  (blue) in comparison to the XRD pattern (red) and XRD of a conditioned  $\text{th\_CoO}_x/\text{Ti\_2}$  (black). GIXRD patterns were recorded using an incident angle of  $3^\circ$ .

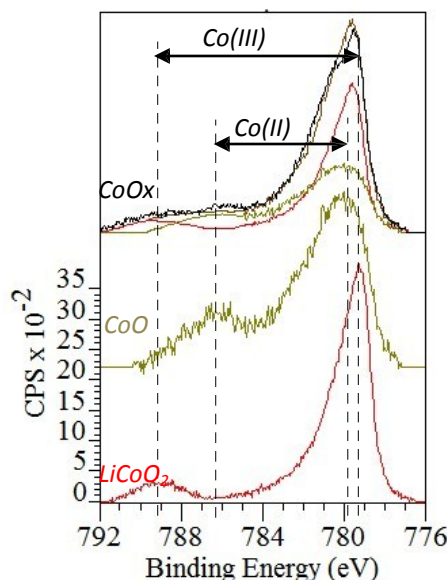


Figure S2. XPS spectra of  $\text{LiCo}_2$  and  $\text{CoO}$  used as line curve fit for the  $\text{Co 2p}$  spectra of  $\text{Co(II)Co(III)O}_x$ .

**Table S3. Electron Binding Energies for several peak fits of the Co 2p<sub>3/2</sub> line of the as deposited and the conditioned samples th\_CoO<sub>x</sub>/Ti.**

Sample	Conditioning [min]	Fit I [eV]	Fit II [eV]	Co(III) [%]	VB [eV]	Φ [eV]	η at 2 mA/cm <sup>2</sup> [V]	η at 5 mA/cm <sup>2</sup> [V]
th_CoO <sub>x</sub> /Ti_2	0	0	780	0	0.58	4.63	0.51	0.55
	2	779.5	780.4	52	0.47	5.41	0.39	0.43
	12	779.4	780.5	62	0.36	5.44	0.39	0.42
	27	779.6	780.2	77	0.34	4.85	0.38	0.43
th_CoO <sub>x</sub> /Ti_1	0	779.5	780.6	10	0.53	4.55	0.5	X
	2	779.5	780.4	52	0.57	5.17	0.45	0.48
	12	779.4	780.5	71	0.52	5.22	0.45	0.48

**Table S4. Electron Binding Energies for several peak fits of the Co 2p line of the as deposited and the conditioned samples plasma deposited samples.**

Sample	Conditioning [min]	Fit I [eV]	Fit II [eV]	Co(III) [%]	VB [eV]	Φ [eV]	η (2 mA/cm <sup>2</sup> ) [V]	η (5 mA/cm <sup>2</sup> ) [V]	η (10 mA/cm <sup>2</sup> ) [V]
pl_CoO <sub>x</sub> /Ti_3	0	779.5	780.8	60	0.49	4.67	0.43	0.45	0,47
	15	779.8	781.0	55	0.35	4.73	0.43		
pl_CoO <sub>x</sub> /Ti_9	0	779.6	780.1	62	0.42	4,73	0.39	0.45	n.d
	15	779.5	780.1	77	0.34	4.88	0.45		
pl_CoO <sub>x</sub> OH <sub>2</sub> /Ti_6	0	779.3	780.8	37	0.43	4.58	0.37	0.4	0,41
	15	780.2	780.5	90	0.38	4.0	0.37		
pl_CoO <sub>x</sub> OH <sub>2</sub> /Ti_8	0	x	780.5	0	0.21	3.9	0.33	0.34	0,37
	5	779.6	780	90	0.35	5.5	0.33		