Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information.

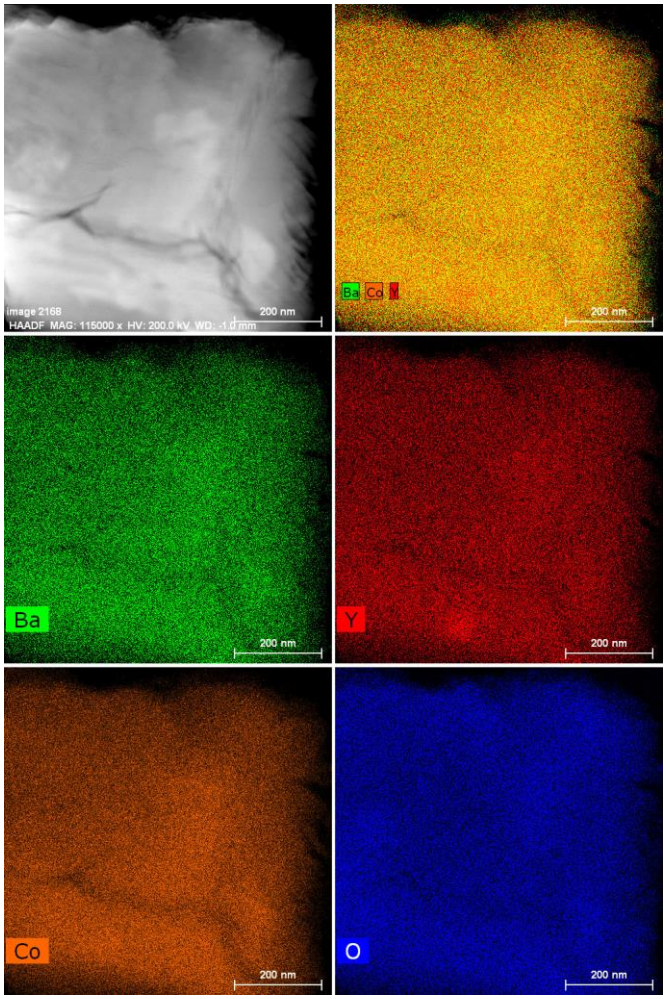

Figure S1. HAADF-STEM image of the $YBaCo_4O_{7.3}$ crystallite, compositional EDX maps of Ba, Co, Y and O and the mixed color-coded map.

Table S1. Crystallographic parameters for $YBaCo_4O_{7.3}$ from the Rietveld refinement from PXRD data ($CoK\alpha_1$, λ = 1.789Å), space group *P*6$_3$*mc*, *a* = 6.30038(3) Å, *c* = 10.24280(6) Å, R_F = 0.031, R_P = 0.025, R_{wP} = 0.034.

Atom	Position	*x/a*	*y/b*	*z/c*	U_{iso}, Å^2
Y1	2*b*	2/3	1/3	0.8745(2)	0.0146(9)
Ba1	2*b*	2/3	1/3	0.5014(1)	0.0215(7)
Co1	2*a*	0	0	0.4369(6)	0.0144(6)
Co2	6*c*	0.1708(1)	-*x*	0.6846(3)	0.0151(4)
O1	6*c*	0.5122(5)	-*x*	0.7369(5)	0.0199(12)*
O2	2*a*	0	0	0.2420(11)	0.0199(12)

O3	6*c*	0.1638(5)	-*x*	0.5008(7)	0.0199(12)

*ADPs for O1, O2, and O3 were kept identical during the refinement.

Table S2. Main interatomic distances for $YBaCo_4O_{7.3}$, Å.

Y1-Ba1	3.824(2)
Y1-O1	2.200(6)
Y1-O3	2.256(6)
Co1-O2	1.964(12)
Co1-O3	1.908(6)
Co2-O1	1.941(4)
Co2-O2	1.962(3)
Co2-O3	1.885(8)

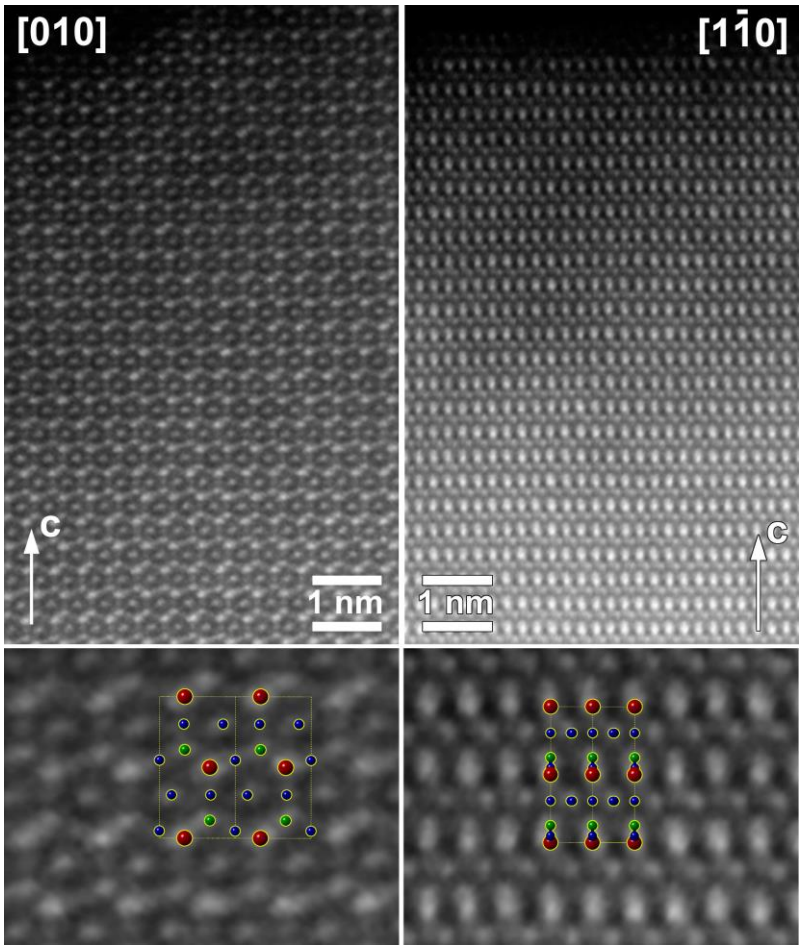

Figure S2. [010] (left) and [1$\bar{1}$0] (right) HAADF-STEM images of $YBaCo_4O_{7.3}$. The inserts below show the enlarged parts of the images with the overlaid projections of the cation sublattice of the *P*31*c* structure. The Ba, Y and Co atoms are shown as brown, green and blue spheres, respectively. The oxygen atoms are omitted for clarity. In the [010] image the prominent distorted hexagons are

formed by two interpenetrating triangles of the Ba columns (the brightest) and Y columns (less bright), respectively. In the $[1\bar{1}0]$ image these columns form the dumbbells being closely projected and overlapping with the Co1 columns. The layers of the dumbbells are separated by the layers of weaker dots corresponding to the Co2 columns.

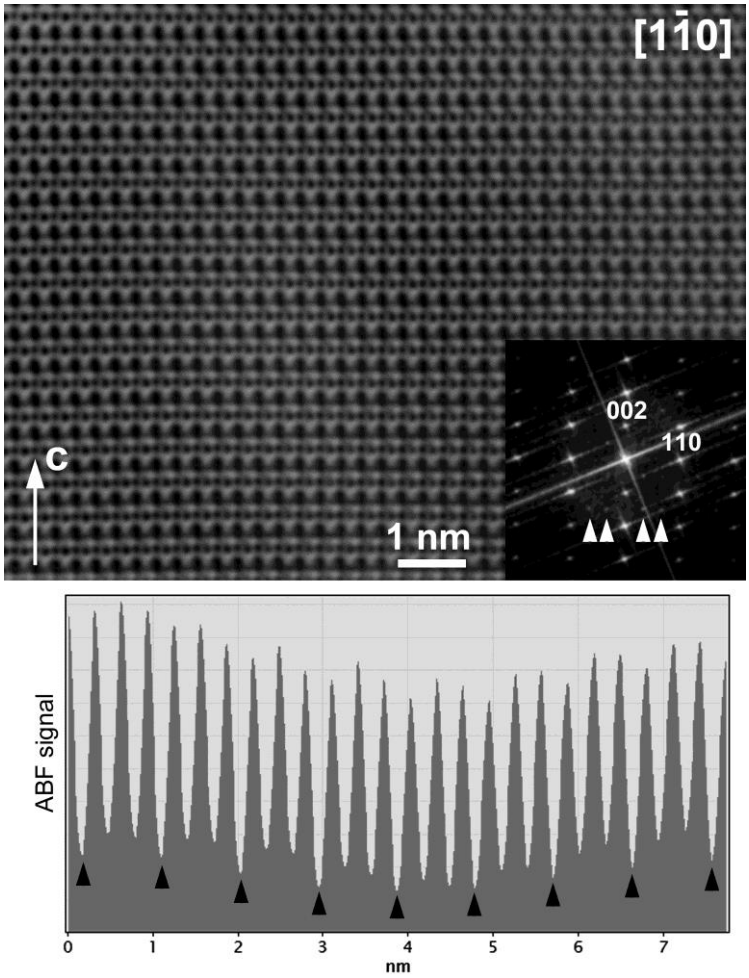

Figure S3. Fourier-filtered $[1\bar{1}0]$ ABF-STEM image of $YBaCo_4O_{7.3}$ (top). Fourier transform (insert) demonstrates the presence of the satellite reflections (marked with white arrowheads). The intensity profile (bottom) along the Ba/Y/Co1 triangular layers shows tripled periodicity along the {110} direction corresponding to the **q** = 1/3(**a*** + **b***) + **c*** modulation (marked with black arrowheads).

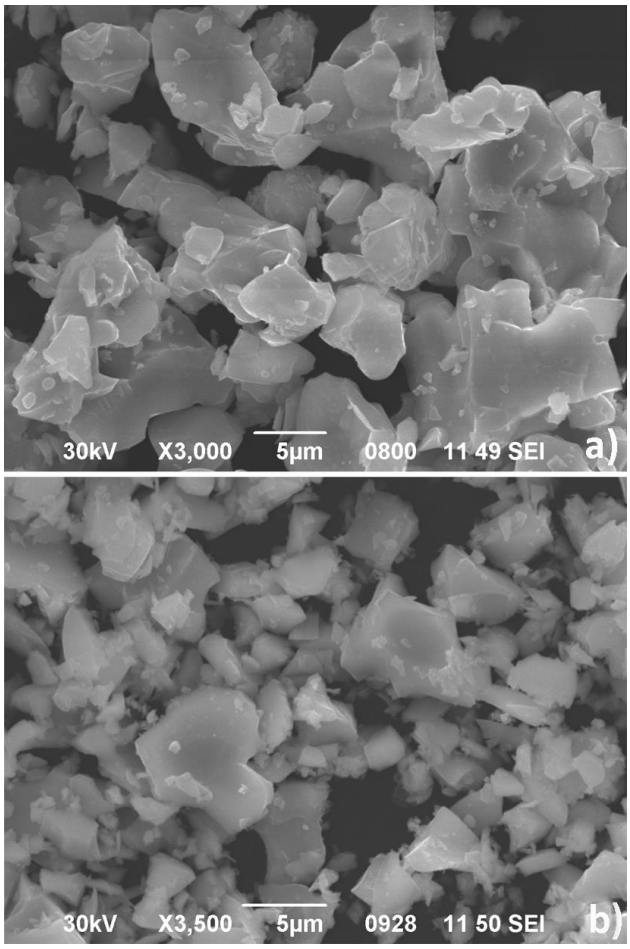

Figure S4. SEM images of the $YBaCo_4O_{7.3}$ crystallites before (a) and after (b) ball milling.

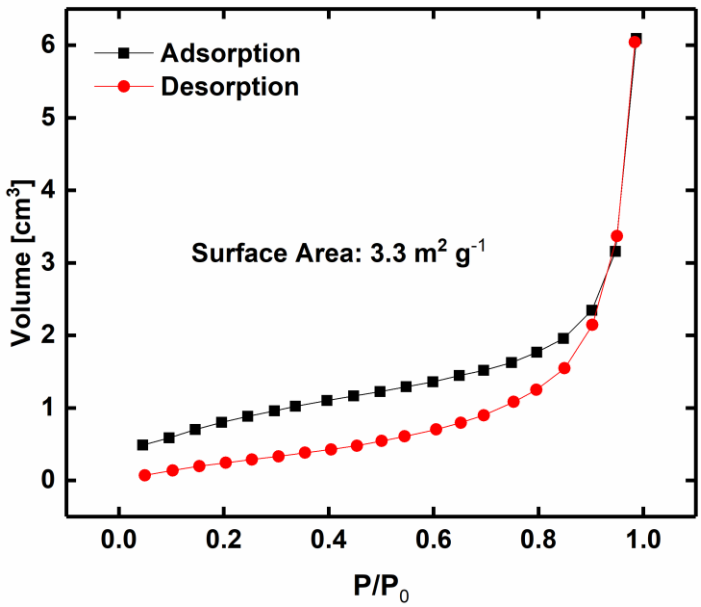

Figure S5. Nitrogen sorption isotherms for BET surface area analysis for $YBaCo_4O_{7.3}$.

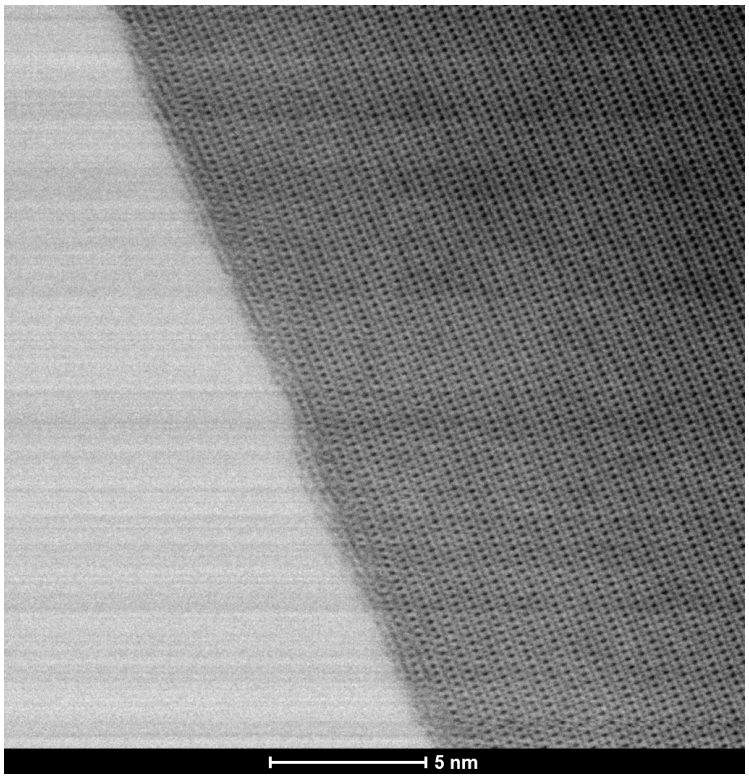

Figure S6. $[1\bar{1}0]$ ABF-STEM image of of $YBaCo_4O_{7.3}$ showing surface crystallinity.

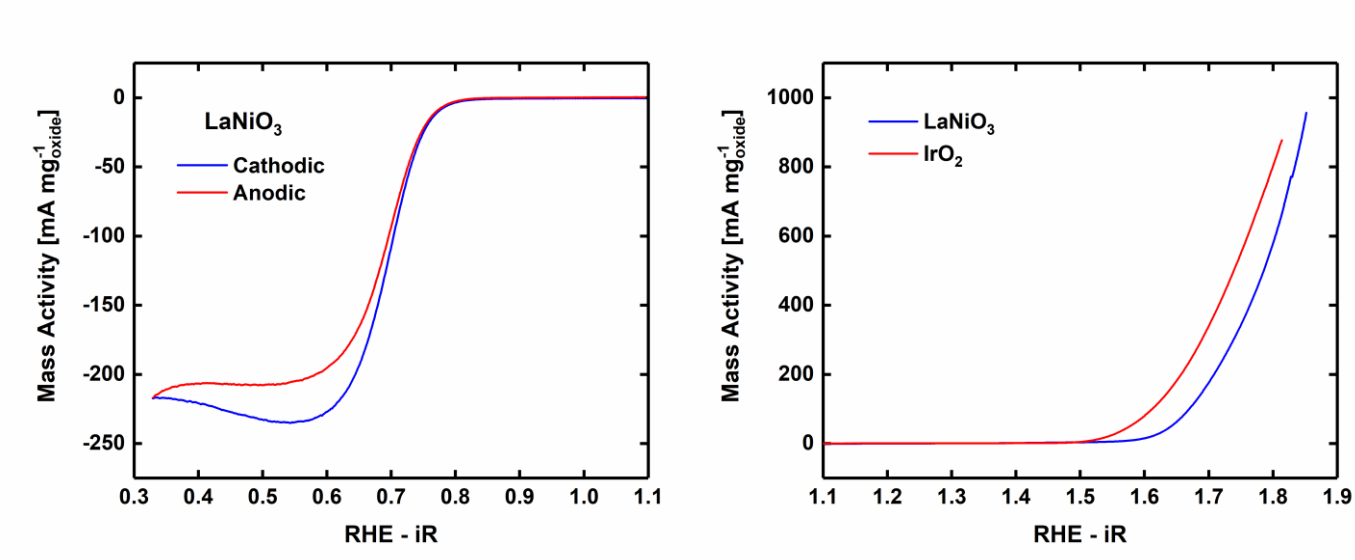

Figure S7. Electrochemical characterization of benchmark catalysts. (a) ORR spectrum of $LaNiO_3$ supported at 30 wt% on VC. ORR measurements were performed in O_2 saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} and a rotation rate of 1600 rpm. (b) Averaged OER spectra of benchmark catalysts. $LaNiO_3$ was supported at 30 wt% and IrO_2 at 20 wt% on VC. OER measurements were performed in O_2 saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} and a rotation rate of 1600 rpm.

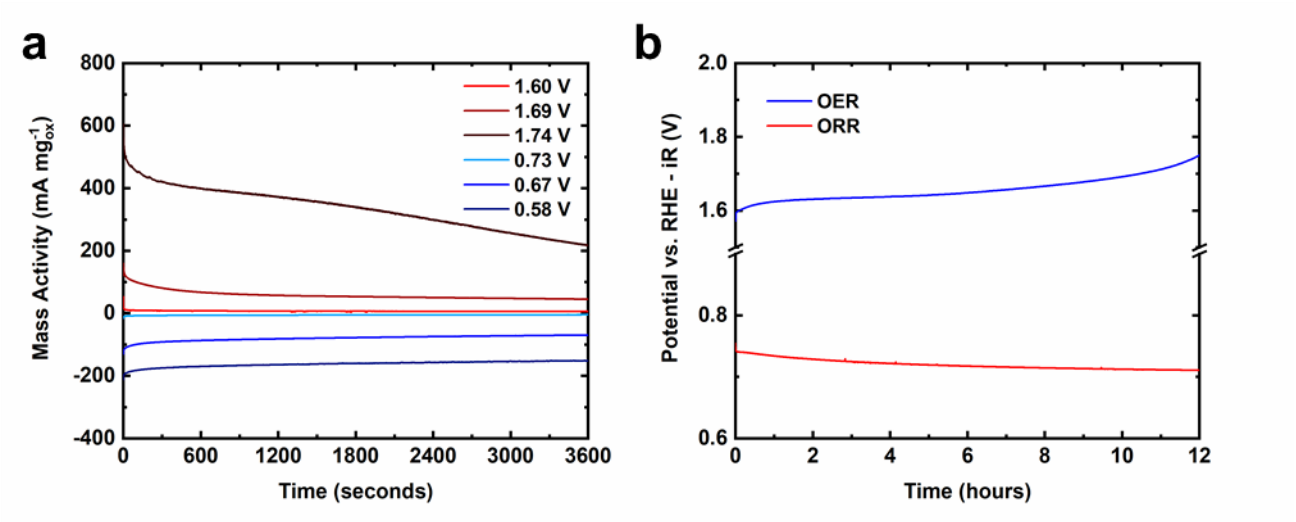

Figure S8. Electrochemical stability experiments for $YBaCo_4O_{7.3}$ supported at 30 wt% on Vulcan carbon XC-72 and dropcast on 5 mm glassy carbon electrodes at a mass loading of 51µg/cm^2 and tested in O_2-saturated 0.1 M KOH while rotating at 1600 rpm. a) Chronoamperometry experiments performed for one hour each. b) Constant current stability tests in which the catalyst was made to maintain 10 mA/mg for both the OER and ORR.

Table S3. Electrochemical characterization of $YBaCo_4O_{7.3}$, other selected benchmark materials and metal oxides that have previously been studied in the same experimental setup.

Composition	OER potential (V) vs RHE @ 10 mA/cm2	ORR potential (V) vs RHE @ −3 mA/cm2	ΔE (V)	OER Tafel Slope (mV/dec)	ORR Tafel Slope (mV/dec)	source
$LaCoO_3$	1.64	0.64	1.00	51	-	*
$LaNi_{0.75}Fe_{0.25}O_3$	1.68	0.67	1.01	44	-	*
$LaNiO_3$	1.66	0.64	1.02	91	63	this work
20 wt% IrO_2	1.61	0.69	0.92	82	-	this work
20 wt% Pt	2.02	0.86	1.16	-	59	*
$YBaCo_4O_{7.3}$	1.68	0.68	1.00	58	66	this work

* Forslund, R. P.; Hardin, W. G.; Rong, X.; Abakumov, A. M.; Filimonov, D.; Alexander, C. T.; Mefford, J. T.; Iyer, H.; Kolpak, A. M.; Johnston, K. P.; et al. Exceptional Electrocatalytic Oxygen Evolution via Tunable Charge Transfer Interactions in $La_{0.5}Sr_{1.5}Ni_{1-x}Fe_xO_{4\pm\delta}$ Ruddlesden-Popper Oxides. *Nature Commun.* **2018**, *9*, 3150.