Effective Ca-doping in $Y_{1-x}Ca_xBaCo_2O_{5+\delta}$ Candidate Cathode Materials for Intermediate Temperature Solid Oxide Fuel Cells

Zhihong Du[a,b], Chunlin Yan[a], Hailei Zhao[a,b,*], Yang Zhang[a], Chunyang Yang[a], Sha Yi[a], Yao Lu[a], Konrad Świerczek[c,d]

[a]School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China
[b]Beijing Municiple Key Lab for Advanced Energy Materials and technologies, Beijing 100083, China
[c]AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Hydrogen Energy, al. A. Mickiewicza 30, 30-059 Krakow, Poland
[d]AGH Centre of Energy, AGH University of Science and Technology, ul. Czarnowiejska 36, 30-054 Krakow, Poland

Supplementary Information

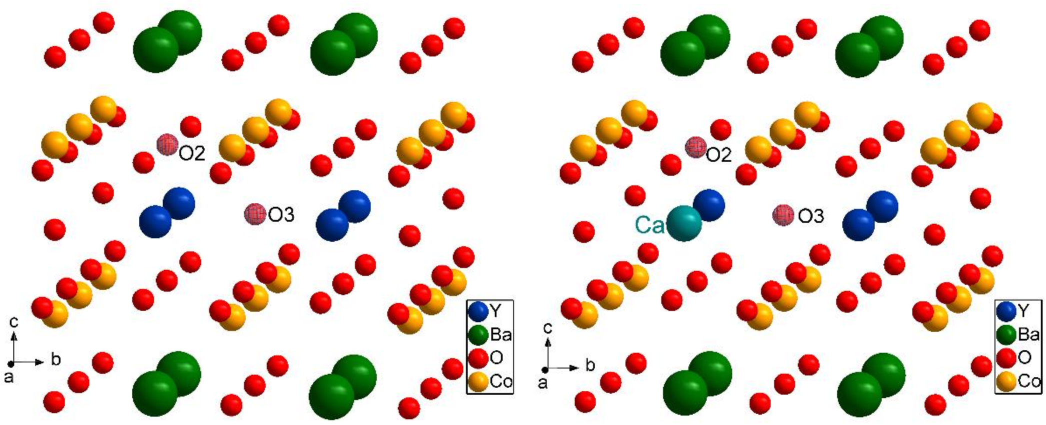

Fig. S1. Structural model of the YCBC materials used for *ab initio* calculations. Tetragonal cell with 38 atoms $Y_4Ba_4Co_8O_{22}$ (left) and $Y_3CaBa_4Co_8O_{22}$ (right) corresponds to a 2×2×1 supercell of the $YBaCo_2O_{5.5}$.

*Corresponding author at: School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China. Tel.: +86 10 82376837; Fax.: +86 10 82376837;
E-mail address: hlzhao@ustb.edu.cn (H. Zhao).

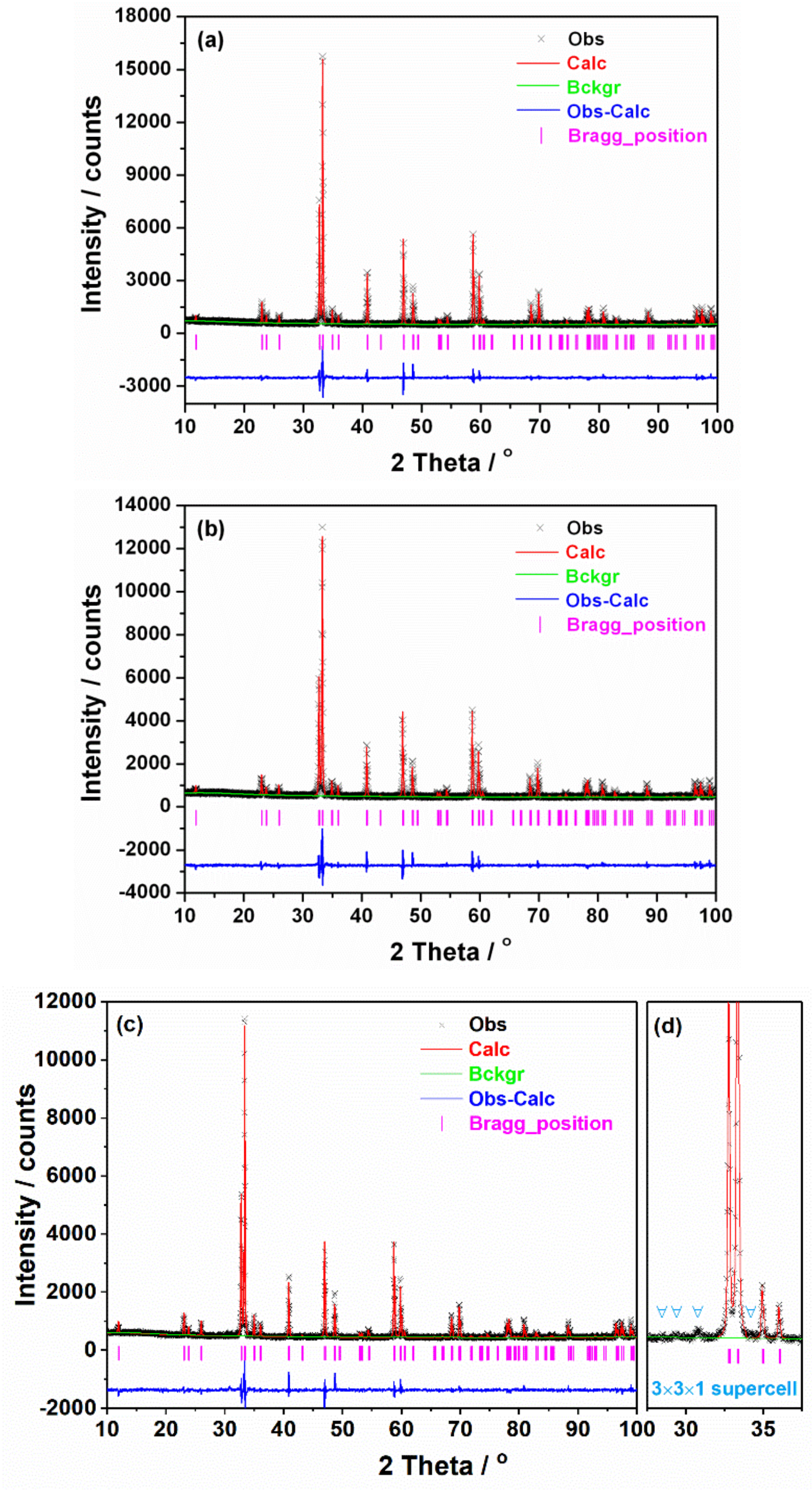

Fig. S2. Rietveld refinement of room temperature XRD patterns of the $Y_{1-x}Ca_xBaCo_2O_{5+\delta}$: (a) x = 0, (b) x = 0.1 and (c) x = 0.2. (d) presents the very weak reflections originated from the oxygen vacancy-ordered 3×3×1 supercell.

Tab. S1. Structural parameters derived from Rietveld refinements for the considered $Y_{1-x}Ca_xBaCo_2O_{5+\delta}$. Space group is *P4/mmm*; Y 1*c* (0.5, 0.5, 0); Ba 1*d* (0.5, 0.5, 0.5); Co 2*g* (0, 0, *z*); O1 1*b* (0, 0, 0.5); O2 4*i* (0, 0.5, *z*); O3 1*a* (0, 0, 0). Here O1 corresponds to the oxygen in BaO plane, O2 in CoO_2 plane, and O3 in YO_δ plane. The refined occupancy factor Occ(O3) is also given.

	x = 0	x = 0.1	x = 0.2
z(Co)	0.245(1)	0.245(1)	0.244(1)
U_{iso} (Co)	0.010(1)	0.011(1)	0.010(1)
z(O2)	0.199(1)	0.197(1)	0.195(1)
Occ(O3)	0.44(2)	0.42(2)	0.38(2)
U_{iso} (O1 = O2 = O3)	0.023(2)	0.025(2)	0.028(2)
U_{iso} (Ba)	0.010(1)	0.012(1)	0.011(1)
U_{iso} (Y = Ca)	0.025(1)	0.022(1)	0.020(1)
$d_{Ba–O2}$ (Å)	2.977(5)	2.988(5)	2.997(5)
$d_{Ba–O1}$ (Å)	2.7388(1)	2.7404(1)	2.7425(1)
$d_{Ba–Co}$ (Å)	3.339(2)	3.344(3)	3.347(2)
$d_{Y–O2}$ (Å)	2.443(4)	2.436(4)	2.431(4)
$d_{Y–O3}$ (Å)	2.7388(1)	2.7404(1)	2.7425(1)
$d_{Y–Co}$ (Å)	3.300(2)	3.298(3)	3.298(2)
$d_{Co–O1}$ (Å)	1.910(4)	1.917(5)	1.919(4)
$d_{Co–O2}$ (Å)	1.968(2)	1.971(2)	1.974(2)
$d_{Co–O3}$ (Å)	1.841(4)	1.835(5)	1.832(4)
$d_{O2–O3}$ (Å)	2.444(4)	2.437(4)	2.431(4)

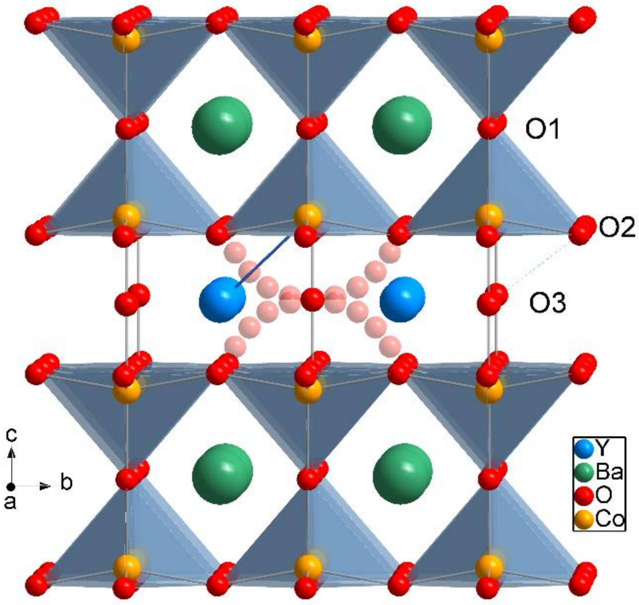

Fig. S3. Refined crystal structure of $YBaCo_2O_{5+\delta}$ at room temperature in *P*4/*mmm* space group. The oxygen migration path between O2 and O3 sites in the Y-O3 layer is shown.

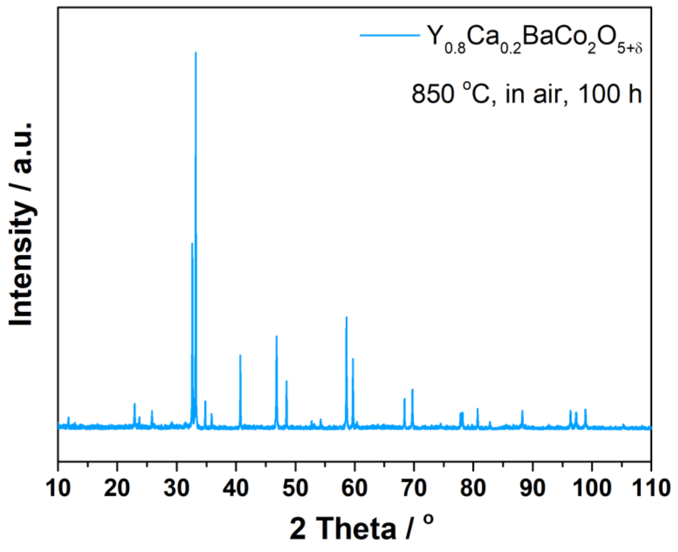

Fig. S4. XRD pattern of $Y_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ after annealing at 850 °C for 100 h in air.

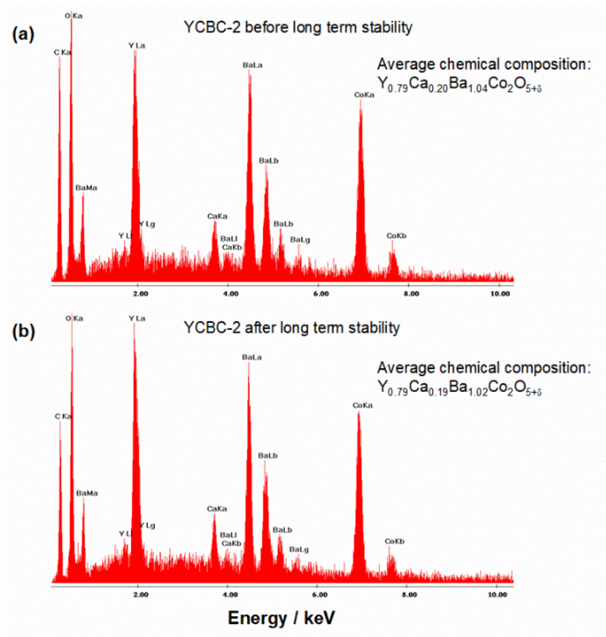

Fig. S5 EDX analysis of YCBC-2 cathode (a) before and (b) after the long term stability test. The average chemical composition were calculated.

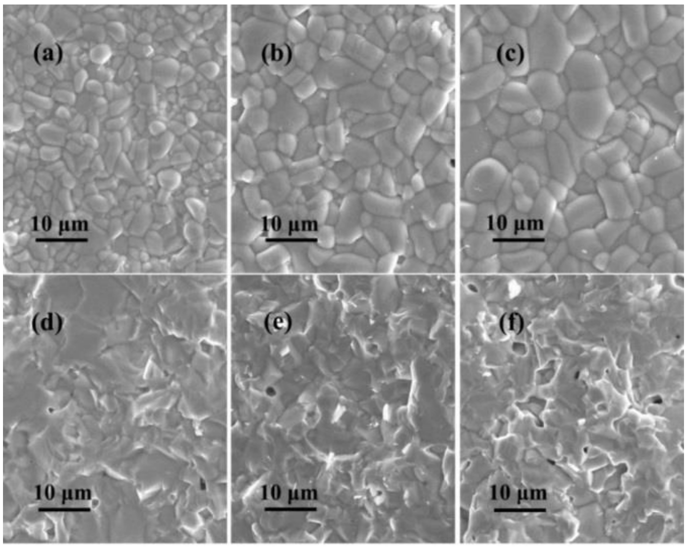

Fig. S6. SEM micrographs of $Y_{1-x}Ca_xBaCo_2O_{5+\delta}$ (surface and cross-section): (a), (d) x = 0; (b), (e) x = 0.1 and (c), (f) x = 0.2 samples used for electrical conductivity measurements.

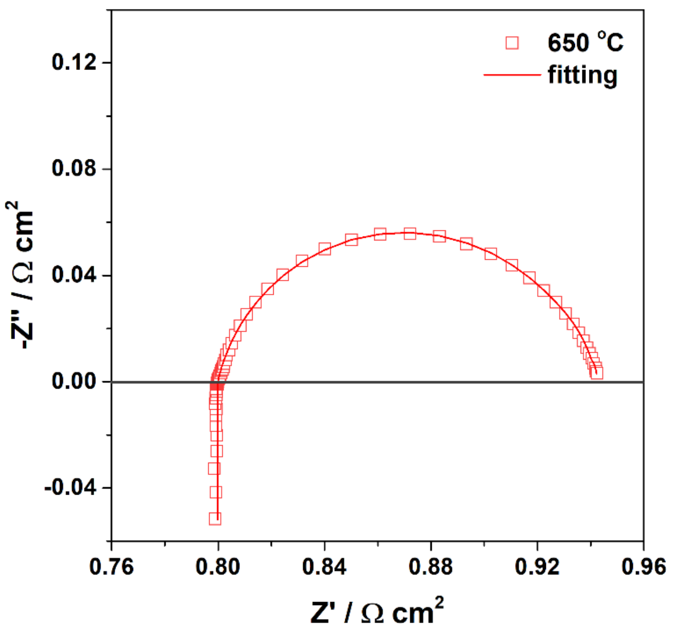

Fig. S7. Exemplary impedance spectra for symmetrical cell with YCBC-2 cathode in air at 650 °C. Data were fitted using L-R_s-(QR) equivalent circuit. Due to the symmetrical configuration, equation ASR = $R \times S/2$ is used to evaluate the values of area specific resistance, where R is the refined polarization resistance from the equivalent circuit, S is the active area of the YCBC cathode (as shown in the figure).

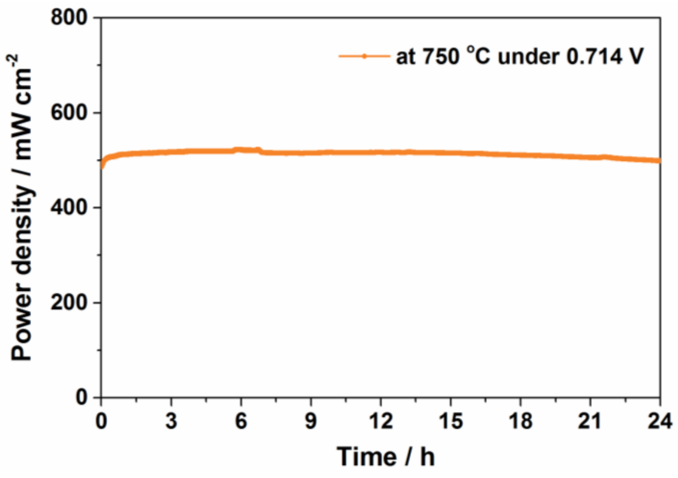

Fig. S8. Short term stability of YCBC-2-GDC/LSGM/LDC/$Sr_2FeMo_{0.65}Ni_{0.35}O_{6-\delta}$ single cell operated under a constant voltage of 0.714 V at 750 °C. The flow of H_2 was 60 cm^3 min^{-1}.

Tab. S2. Calculated ASR values for the $Y_{1-x}Ca_xBaCo_2O_{5+\delta}$ cathodes.

temperature / °C	ASR / Ω cm^2		
	x = 0	x = 0.1	x = 0.2
650	0.298	0.203	0.142
700	0.125	0.087	0.068
750	0.058	0.044	0.032
800	0.031	0.021	0.018
850	0.014	0.012	0.010

Tab. S3. Comparison of peak power density for LSGM electrolyte-supported cells between $Y_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$ and selected double perovskite cathodes.

Cathode	anode	Electrolyte thickness / μm	Temperature / °C	Power density / mW cm^{-2}	reference
$NdBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$	Ni–GDC	300	850	904	[1]
$Pr_{1.1}Ba_{0.9}Co_2O_{5+\delta}$	Ni-SDC	300	800	732	[2]
$PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$	Ni-GDC	300	800	1021	[3]
$PrBaC_2O_{5+\delta}$-SDC	Ni-SDC	300	800	758	[4]
$NdBaC_2O_{5+\delta}$-SDC				707	
$SmBaC_2O_{5+\delta}$-SDC				685	
$GdBaC_2O_{5+\delta}$-SDC				608	
$YBaCo_{1.4}Cu_{0.6}O_{5+\delta}$	Ni–GDC	300	850	815	[5]
$YBa_{0.5}Sr_{0.5}Co_{1.4}Cu_{0.6}O_{5+\delta}$	Ni–GDC	300	850	398	[6]
$SmBa_{0.5}Sr_{0.5}CoCuO_{5+\delta}$	NiCu–GDC	300	850	857	[7]
$NdBaCoFeO_{5+\delta}$-30SDC	Ni-SDC	300	800	892	[8]
$PrBa_{0.8}Ca_{0.2}Co_2O_{5+\delta}$	$PrBaMn_2O_{5+\delta}$	250	700	460	[9]
$Y_{0.8}Ca_{0.2}BaCo_2O_{5+\delta}$-GDC	$Sr_2FeMo_{0.65}Ni_{0.35}O_{6-\delta}$	300	850	1066	This work
			800	841	
			750	634	
			700	430	

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