

Supporting Information: Perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ Solid Solutions for Solar-Thermochemical Fuel Production: Strategies to Lower Operation Temperature

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S1: Energy dispersive X-ray spectroscopy analysis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{1-x}\text{Co}_x\text{O}_{3-\delta}$

In Figure S1 energy dispersive X-ray spectroscopy (EDX) images of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$ are displayed. From these images it is observed that the metal ions are homogeneously distributed in the grains. The differences one can observe for the metal cations are related to morphological differences, refer to the scanning electron microscopy image in the top left corner.

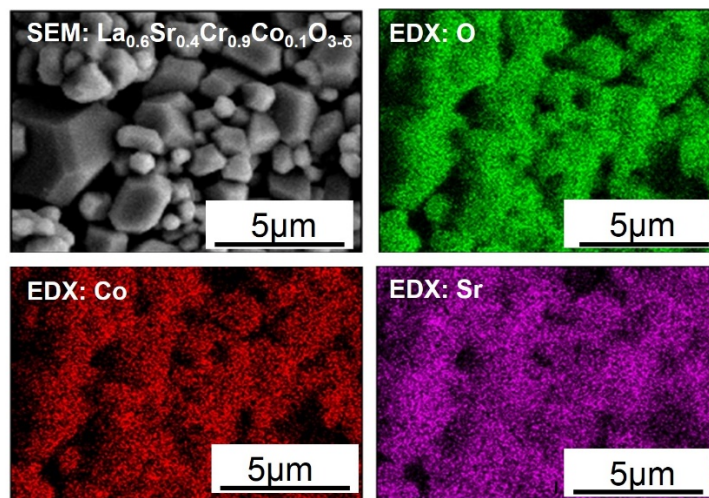


Figure S1. Energy dispersive X-ray spectroscopy analysis of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_{3-\delta}$. Top left is a scanning electron microscopy image of the area used to analyse the distribution of the chemical elements, here it is shown for Co, Sr, and O.

S2: Calculation of the Weight of one atomic layer of CO₂ Covering the Surface of a Perovskite Sample.

Surface area of the perovskite powder can be estimated by a simple calculation from approximation of the radius of the grains. Afterwards, we estimate the mass of one atomic layer of CO₂ covering an area equivalent to this surface area and compare it to the mass changes we observe in the thermogravimetric experiments. The total surface area of the grains, TA_{grains} , can be estimated by

$$TA_{grains} = A_{grain} N_{grains}$$

$$TA_{grains} = A_{grain} \frac{m_{sample}}{V_{grain} \hat{\rho}_p}$$

$$TA_{grains} = \frac{3 \hat{r}_{grain}^2 m_{sample}}{r_{grain} \hat{\rho}_p}$$

Here m_{sample} is the weight of the sample, r_{grain} is the radius of the grains, and ρ_p is the density of the perovskite powder. In the intermediate steps, we used A_{grain} , V_{grain} and N_{grain} to assign for area of one grain, volume of a single grain and number of grains for the latter. For density we use the theoretical density $\rho_p = 6.34 \text{ g/cm}^3$ for the perovskite composition $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ which is determined from the molar mass of the metal ions plus oxygen with the stoichiometry of a rhombohedral unit cell (6 A-site atoms, 6 B-site atoms, and 18 oxygen atoms) and the volume parameter, $V_{unit,R3c}$, determined by Rietveld refinement, ie. $V_{unit,R3c} = 345 \text{ \AA}^3$. Lastly, the radius is estimated from the SEM pictures and here we used $r_{grain} = 2 \text{ \mu m}$. The mass of the sample is $m_{sample} = 200 \text{ mg}$. Using these parameters we arrive at a surface area of the grains of 0.047 m^2 .

The mass of one atomic layer of CO₂, m_{CO_2} , covering the surface of every single grain in the perovskite solution $\text{La}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ sample can be estimated via a simple calculation:

$$m_{CO_2} = N_{CO_2} \hat{M}_{CO_2}$$

$$m_{CO_2} = \frac{TA_{grains}}{A_{CO_2}} M_{CO_2}$$

Here, N_{CO_2} is the number of CO_2 molecules needed to cover the entire surface of the grains in a 200mg sample of $La_{0.6}Sr_{0.4}Cr_{0.8}Co_{0.2}O_{3-\delta}$, M_{CO_2} is the molar mass of CO_2 , TA_{grains} is the total surface area of all grains and A_{CO_2} is the cross section of an adsorped CO_2 molecule. For the parameters $TA_{grains} = 0.047m^3$, $A_{CO_2}(g) = 17\text{\AA}^2$, and $M_{CO_2} = 44\text{g/mol}$, the mass of one atomic layer of CO_2 is equal to $m_{CO_2} = 0.0012\text{mg}$. In the thermogravimetric measurements the mass changes are 0.6mg for a 200mg sample. Hence the actual weight changes are 500x times larger than the weight of one atomic layer of CO_2 . Thus, adsorption of CO_2 can not be used to describe the large mass changes observed in the thermogravimetric measurements.