Electronic supplementary Information

Experimental screening of perovskite oxides as efficient redox materials for solar thermochemical CO$_2$ conversion

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Fig. SI-1 LeBail fits of powder X-ray diffraction data collected on fresh (a) LaMn$_{0.5}$Co$_{0.5}$O$_3$, (b) LaFe$_{0.75}$Co$_{0.25}$O$_3$, (c) LaMn$_{0.5}$Ni$_{0.5}$O$_3$ and (d) LaFe$_{0.75}$Ni$_{0.25}$O$_3$. Experimental (red), calculated (black) and difference (blue) curves are shown.
Fig. SI-2 SEM images of (a), (b) LaMn$_{0.5}$Co$_{0.5}$O$_3$; (c), (d) LaFe$_{0.75}$Co$_{0.25}$O$_3$; (e), (f) La$_{0.5}$Ca$_{0.5}$MnO$_3$ and (g), (h) La$_{0.5}$Sr$_{0.5}$MnO$_3$. (a), (c), (e) and (g) represent as-synthesized materials whereas (b), (d), (f) and (h) represent materials after redox cycling experiments, respectively.
Fig. SI-3 Effect of the temperature on the re-oxidation rate of LaMn$_{0.5}$Co$_{0.5}$O$_3$ during exposure to CO$_2$ after previous reduction at 1400 °C during 45 min in TGA.
Fig. SI-4 LeBail fits of powder X-ray diffraction data collected on (a) Fresh SrFeO$_3$, (b) Fresh Ba$_{0.5}$Sr$_{0.5}$FeO$_3$, (c) Fresh Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.2}$Co$_{0.8}$O$_3$ and (d) SrFeO$_3$ after reduction at 1100 °C. Experimental (red), calculated (black) and difference (blue) curves are shown.
**Fig. SI-5** (a) Comparison of XRD of Ba$_{0.5}$Sr$_{0.5}$FeO$_3$ before and after TGA, confirming the phase stability and the absence of carbonate after exposure to CO$_2$. The peak shift is due to the high reduction extent of the material obtained after TGA. (b) XRD of Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.2}$Co$_{0.8}$O$_3$ after TGA confirming the formation of carbonate phase after exposure to CO$_2$. 
Fig. SI-6 Reduction and re-oxidation profiles as determined by performing TGA for Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.2}$Co$_{0.8}$O$_3$. The high mass increase during exposure to CO$_2$ denotes the formation of carbonates.
Fig. SI-7 Wide angle XRD profiles of freshly prepared La$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Co$_{0.5}$O$_3$, La$_{0.5}$Sr$_{0.5}$Mn$_{0.5}$Fe$_{0.5}$O$_3$ and La$_{0.5}$Sr$_{0.5}$Fe$_{0.8}$Co$_{0.2}$O$_3$. 
Fig. SI-8 TGA of La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ during two cycles with reduction at 1400 °C and oxidation (50% CO$_2$) at 1050 °C, depicting the effect of the initial mixed Mn$^{3+}$/Mn$^{4+}$ valence state on the redox capabilities.
**Fig. SI-9** Wide angle XRD patterns of Ruddlesden-Popper structured mixed oxides synthesized by the solid state method.
Fig. SI-10 LeBail fits of powder X-ray diffraction data collected on (a) fresh La$_{0.5}$Sr$_{1.5}$MnO$_4$ (LSMO-RP1), (b) La$_{0.5}$Sr$_{1.5}$MnO$_4$ after redox cycling, (c) fresh LaSr$_2$Mn$_2$O$_7$ (LSMO-RP2) and (d) LaSr$_2$Mn$_2$O$_7$ after redox cycling. Experimental (red), calculated (black) and difference (blue) curves are shown.
Fig. SI-11 TGA of La$_{0.5}$Sr$_{0.5}$MnO$_3$ (LSMO), La$_{0.5}$Sr$_{1.5}$MnO$_4$ (LSMO-RP1) and LaSr$_2$Mn$_2$O$_7$ (LSMO-RP2) during two redox cycles with thermal reduction at 1400 °C and oxidation (50% CO$_2$) at 1050 °C.
Fig. SI-12 $O_2$ production rate during the first thermal reduction step for SrFeO$_3$ (SFO), La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCFO), La$_{0.6}$Sr$_{0.4}$FeO$_3$ (LSFO), Ba$_{0.5}$Sr$_{0.5}$Fe$_{0.2}$Co$_{0.8}$O$_3$ (BSFCO) and Ba$_{0.5}$Sr$_{0.5}$FeO$_3$ (BSFO).
Fig. SI-13 $O_2$ production rate during the first thermal reduction step for $La_{0.5}Sr_{0.5}MnO_3$ (LSMO), $La_{0.5}Sr_{1.5}MnO_4$ (LSMO-RP1) and $LaSr_2Mn_2O_7$ (LSMO-RP2).