**SUPPLEMENTARY INFORMATION**

**Beyond Ceria: Theoretical Investigation of Isothermal and Near-Isothermal Redox Cycling of Perovskites for Solar Thermochemical Fuel Production**

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![Graph](image_url)

**Figure S1.** Partial molar enthalpy change per mole of monoatomic oxygen versus nonstoichiometry for each of the materials considered.
Figure S2. Equilibrium oxygen content of LSMA6464 versus $pO_2$ at 1473-1773 K. The markers indicate measured data extracted from Takacs et al. The solid lines represent defect model fits considering (1) production of doubly ionized oxygen vacancies and reduction of Mn$^{4+}$ to Mn$^{3+}$ and (2) disproportionation of Mn$^{3+}$ to Mn$^{4+}$ and Mn$^{2+}$. 
Figure S3. Logarithm of the equilibrium constants of oxygen vacancy formation ($K_1$) and disproportionation ($K_2$) versus inverse temperature for LSMA6464. Markers represent the extracted value at a single temperature and the solid lines represent linear fits.
Figure S4. Equilibrium oxygen content of LCM40 versus $pO_2$ at 1473-1773 K. The markers indicate measured data extracted from Takacs et al. The solid lines represent defect model fits considering (1) production of doubly ionized oxygen vacancies and reduction of Mn$^{4+}$ to Mn$^{3+}$ and (2) disproportionation of Mn$^{3+}$ to Mn$^{4+}$ and Mn$^{2+}$. 
Figure S5. Logarithm of the equilibrium constants of oxygen vacancy formation ($K_1$) and disproportionation ($K_2$) versus inverse temperature for LCM40. Markers represent the extracted value at a single temperature and the solid lines represent linear fits.
Figure S6. Equilibrium oxygen content of LCMA6464 versus $pO_2$ at 1473-1773 K. The markers indicate measured data extracted from Takacs et al. The solid lines represent defect model fits considering (1) production of doubly ionized oxygen vacancies and reduction of Mn$^{4+}$ to Mn$^{3+}$ and (2) disproportionation of Mn$^{3+}$ to Mn$^{4+}$ and Mn$^{2+}$.
Figure S7. Logarithm of the equilibrium constants of oxygen vacancy formation ($K_1$) and disproportionation ($K_2$) versus inverse temperature for LCMA6464. Markers represent the extracted value at a single temperature and the solid lines represent linear fits.
Figure S8. Solar-to-fuel energy conversion efficiencies for H₂O splitting versus operating temperature for isothermal redox cycles using ceria. The reduction \( pO_2 \) was \( 10^{-6} \) atm and the geometric concentration ratio was 3000. The gas-to-gas heat recovery effectiveness was varied from 0.80 to 0.95. The reduction \( pO_2 \) was controlled via (a) inert gas sweeping, (b) a mechanical vacuum pump, (c) an electrochemical oxygen pump, or (d) a thermochemical oxygen pump.
Figure S9. Solar-to-fuel energy conversion efficiencies for H₂O splitting versus temperature swing for nonisothermal redox cycles using ceria. The reduction \( pO_2 \) was \( 10^{-6} \) atm, zero solid-to-solid heat recovery was considered, and the geometric concentration ratio was 3000. The gas-to-gas heat recovery effectiveness was varied from 0.80 to 0.95. The reduction \( pO_2 \) was controlled via (a) inert gas sweeping, (b) a mechanical vacuum pump, (c) an electrochemical oxygen pump, or (d) a thermochemical oxygen pump.
Figure S10. Sensitivity analysis showing $\eta_{\text{solar-to-fuel}}$ versus an assumed percent decrease in $\delta_{\text{red}}$ for TSRC with LCM40 and LSMA6464.