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3. References

1. Computational details
   a. Structure optimizations

Both, ASE and GPAW are open-source codes available from the Department of Physics at the Technical University of Denmark and are available at https://wiki.fysik.dtu.dk/ase/ and https://wiki.fysik.dtu.dk/gpaw/.

Table S1: Minimum and maximum values of calculated lattice constants (a) and magnetic moments of the transition metals (M) at the B sites of cubic (space group 221) ABO$_3$, AA’BO$_3$, ABB’O$_3$ and AA’BB’O$_3$ perovskites.

| Type of perovskite | a (Å)            | M(B) (μ$_B$)    | M(B’) (μ$_B$)   |
|-------------------|------------------|----------------|----------------|
| ABO$_3$           | 3.7357 – 4.2914  | 0.2453 – 3.8368|                 |
| AA’BO$_3$         | 3.7953 – 4.2000  | 0.2757 – 3.7985| 0.2760 – 3.8000 |
| ABB’O$_3$         | 3.6000 – 4.1419  | 0.0040 – 4.2172| -3.1064 – 3.8337|
| AA’BB’O$_3$       | 3.7998 – 4.1274  | -2.2340 – 3.880 | -2.3856 – 3.5935|

The DFT-computed lattice constants compare well, within the uncertainty of DFT calculations$^1$–$^2$, with the experimental values for cubic perovskites of similar composition. For example, the relative error is 1.06% when comparing DFT-computed 3.9566 Å (La$_{0.5}$Sr$_{0.5}$MnO$_3$) to an experimental value of 3.915 Å (La$_{0.67}$Sr$_{0.33}$MnO$_3$)$^3$ or 0.07-1.38% when comparing DFT-computed 3.9276 Å (La$_{0.5}$Sr$_{0.5}$Fe$_{0.5}$Co$_{0.5}$O$_3$) to experimental values of about 3.925 Å (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$)$^4$ and 3.874 Å (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$)$^5$ or 2.17% when comparing 3.9183 Å (SrCoO$_3$) to an experimental value of 3.835 Å (SrCoO$_3$)$^6$.

b. Free energy computations

Free energies of the chemical species $i$ ($G_i$) were calculated via:

$$G_i(T,P) = N_i \mu_i (T,P) = E_i + U_{ZPE,i} - S_i (T,P)$$

where $T$ and $P$ are the absolute temperature (298.15 K) and pressure (1.013 bar), $N_i$ is the number of atoms, $\mu_i$ is the chemical potential, $E_i$ is the total electronic energy determined from DFT-based structure optimization, $U_{ZPE,i}$ is the zero-point vibrational energy, and $S_i$ is the entropy. Gases are assumed to be ideal, while liberated lattice oxygen is treated using the harmonic approximation where all degrees of freedom are treated as frustrated harmonic vibrations and pressure-volume contributions are neglected. Thermodynamic properties were calculated from vibrational frequencies and standard statistical mechanical equations evaluated through ASE. Free energy corrections of the solids are neglected.$^7$
Analogously, the enthalpy of forming oxygen vacancies ($\Delta H_v[O]$) at the surface is defined as:

$$\Delta H_v[O] = \Delta G_v[O] + T\Delta S_v[O]$$

where $\Delta S_v[O]$ is the entropy of forming oxygen vacancies.

Free energies and enthalpies are relative to the chemical potential of stable H$_2$O and H$_2$ gas, that is, $E^r$ is given with:

$$E^r_o = E[H_2O] - E[H_2]$$

where $E[H_2O]$ and $E[H_2]$ are the total electronic energy of reference H$_2$O and H$_2$ molecules in the gas phase.

### c. Scaling relations

Eq. (5) in the main text is based on data for TiO$_2$ (rutile), Ti$_2$O$_3$, Cu$_2$O, ZnO (wurtzite), MoO$_3$, Ag$_2$O, Ba$_2$Sr$_2$Co$_3$O$_{16.5}$ (cubic), and La$_{0.67}$Sr$_{0.33}$FeO$_{2.5}$ (cubic). Data for cubic ZrO$_2$, cubic Y$_2$Zr$_3$O$_{15}$, Y$_2$O$_3$-stabilized ZrO$_2$, CeO$_2$, and La$_{0.67}$Sr$_{0.33}$MnO$_3$ was disregarded due to a large deviation of oxygen nonstoichiometry ($\delta$) between the thermochemical data for bulk metal oxides and the DFT data for metal oxide surfaces. Differences of factor 16-32 for the nonstoichiometry of ZrO$_2$ ($\delta = 2$ for the ZrO$_2$/Zr bulk couple vs. $\delta = 0.0625$ for the Zr$_3$O$_{12}$/Zr$_3$O$_{15}$ surface model couple), Y$_2$Zr$_3$O$_{15}$ ($\delta = 2$ for the ZrO$_2$/Zr bulk couple vs. $\delta = 0.0625$ for the Y$_2$Zr$_3$O$_{15}$/Y$_2$Zr$_3$O$_{29}$ surface model couple), CeO$_2$ ($\delta = 1$ for the CeO$_2$/Ce bulk couple vs. $\delta = 0.0625$ for the Ce$_3$O$_7$/Ce$_3$O$_{15}$ surface model couple), and of factor 3, which is relatively high when compared to the other computed perovskite models, for La$_{0.67}$Sr$_{0.33}$MnO$_3$ ($\delta = 1$ for the Mn$_2$O$_3$/MnO bulk couple vs. $\delta = 0.33$ for the La$_{0.67}$Sr$_{0.33}$MnO$_3$ surface model couple).

Calculations of $\Delta G_v^{\infty}$ at 1200 K to 1800 K and $-\Delta G_v^{\infty}$ at 800 K to 1400 K for metal oxides where the underpinning thermochemical data is not available, namely the perovskites evaluated in this work, were based on the scaling of these two bulk quantities with $\Delta G_v^{\infty}$ at 298 K and 1 bar across 27 solid metal oxide and six metal/metal oxide pairs. Thermodynamic properties obtained through scaling relations are defined per mole of monoatomic oxygen. The data for the derived linear scaling relations ($R^2 > 0.83$) are shown with Table S2 and Table S3, where a and b represent the following factors in Eq. (4):

$$-\Delta G_v^{\infty} = a \frac{kJ \text{ mol}^{-1}}{kJ \text{ mol}^{-1}} \Delta G_v^{\infty} + b \text{ kJ mol}^{-1}$$

Table S2. DFT-derived linear scaling factors a and b, based on the scaling of $-\Delta G_v^{\infty}$ with a stoichiometric amount of CO$_2$ in the inlet gas and $\Delta G_v^{\infty}$ at 298 K and 1 bar across 27 solid metal oxide and six metal/metal oxide pairs.

| $T$ (K) | a       | b       |
|---------|---------|---------|
| 800     | -0.9622 | 552.73  |
| 900     | -0.9633 | 555.07  |
| 1000    | -0.9647 | 557.63  |
| 1100    | -0.9654 | 559.59  |
| 1200    | -0.9652 | 561.04  |
| 1300    | -0.9625 | 561.90  |
| 1400    | -0.9594 | 562.50  |

Table S3. DFT-derived linear scaling factors a and b, based on the scaling of $-\Delta G_v^{\infty}$ with 1% CO in CO$_2$ in the inlet gas and $\Delta G_v^{\infty}$ at 298 K and 1 bar across 27 solid metal oxide and six metal/metal oxide pairs.

| $T$ (K) | a       | b       |
|---------|---------|---------|
| 800     | -0.9622 | 583.36  |
| 900     | -0.9633 | 589.53  |
| 1000    | -0.9647 | 595.91  |
| 1100    | -0.9654 | 601.71  |
| 1200    | -0.9652 | 606.99  |
| 1300    | -0.9625 | 611.67  |
| 1400    | -0.9594 | 616.10  |

Table S4. DFT-derived linear scaling factors a and b, based on the scaling of $\Delta G_v^{\infty}$ at $p_{O_2} = 10^{-4}$ bar with $\Delta G_v^{\infty}$ at 298 K and 1 bar across 27 solid metal oxide and six metal/metal oxide pairs.

| $T$ (K) | a       | b       |
|---------|---------|---------|
| 1200    | 0.9652  | -296.51 |
| 1300    | 0.9625  | -322.25 |
| 1400    | 0.9594  | -347.67 |
| 1500    | 0.9551  | -372.30 |
| 1600    | 0.9514  | -396.93 |
| 1700    | 0.9452  | -419.97 |
The data for the derived linear scaling relations is given with Tables S5-S8. The free energies of the oxide oxidation and reduction of the computed perovskites are not shown here, but can be provided on demand.

d. Stability computations

Eq. 5 displays the schematic reaction between an ABO$_3$ perovskite and CO$_2$, forming a carbonate and a metal oxide with the B cation. Eq. 6 illustrates the dissociation of an ABO$_3$ perovskite into A and B metal oxides.

\[
\begin{align*}
\frac{1}{144} \cdot E(\text{ABO}_3) + x \cdot E(\text{CO}_2) & \rightarrow x \cdot E(\text{ACO}_3) + E(\text{B}_2\text{O}_3) + \frac{2x - y}{14} \cdot E(\text{O}_2) \\
\frac{1}{144} \cdot E(\text{ABO}_3) & \rightarrow \frac{\frac{14 \cdot x \cdot E(\text{A}_2\text{O}_3)}{14} + \frac{14 \cdot x \cdot E(\text{B}_2\text{O}_3)}{14} + 3 \cdot \frac{x \cdot \frac{14 \cdot x}{14} - \frac{14 \cdot x}{14} - \frac{14 \cdot x}{14}}{14}}{144} \cdot E(\text{O}_2)
\end{align*}
\]

where $E(\text{ABO}_3)$, $E(\text{CO}_2)$, $E(\text{ACO}_3)$, $E(\text{A}_2\text{O}_3)$ and $E(\text{B}_2\text{O}_3)$ are the DFT total energies of the ABO$_3$, CO$_2$, ACO$_3$, O$_2$, A$_2$O$_3$ and B$_2$O$_3$ compound, respectively. $E(\text{O}_2)$ was taken as the energy reference of stable H$_2$O and H$_2$ in the gas phase, due to the difficulty of DFT to describe the triplet state of O$_2$ correctly.

2. Supporting data

a. Experimental data

i. XRD of CeCoO$_3$

![Figure S1: XRD spectrum of as-prepared CeCoO$_3$ (peak labels from Wolcyrz et al. and Smith et al.)](image_url)

ii. XRD of as-prepared perovskites to be tested via TGA

* Orthorhombic perovskite (Pnma) * Orthorhombic perovskite (Pnma) * Hexagonal perovskite (P6_3cm) * Rhombohedral perovskite (R-3cH)
iii. Oxygen nonstoichiometry

Figure S2: RT-XRDs of as-prepared YFeO$_3$, YMnO$_3$, YCo$_{0.3}$Fe$_{0.7}$O$_3$, YCo$_{0.1}$Fe$_{0.9}$O$_3$, LaFeO$_3$, LaCo$_{0.5}$Fe$_{0.5}$O$_3$ and LaCo$_{0.5}$Ni$_{0.5}$O$_3$. Peak labels for YFeO$_3$, YCo$_{0.3}$Fe$_{0.7}$O$_3$, YCo$_{0.1}$Fe$_{0.9}$O$_3$ from du Boulay et al.$^{12}$, for YMnO$_3$ from Gibbs et al.$^{13}$, for LaFeO$_3$ from Maregio et al.$^{14}$, for LaCo$_{0.5}$Fe$_{0.5}$O$_3$ from McCready et al.$^{15}$ and for LaCo$_{0.5}$Ni$_{0.5}$O$_3$ from Vyshatko et al.$^{16}$.

Figure S3: Percent mass change as a function of time subjected to 873, 1073 and 1273 K in 1% CO in CO$_2$ ($p_{O_2} = 1.88\times10^{-21}$, $3.79\times10^{-15}$ and $7.75\times10^{-11}$ bar O$_2$, respectively) for oxidation experiments of LaCo$_{0.5}$Fe$_{0.5}$O$_3$, LaFe$_{0.5}$Ni$_{0.5}$O$_3$, LaCo$_{0.5}$Ni$_{0.5}$O$_3$, LaFeO$_3$, YMnO$_3$, YFeO$_3$ and YCo$_{0.5}$Fe$_{0.5}$O$_3$.

Figure S4: Percent mass change as a function of time subjected to 1573 K in $1\times10^{-4}$, $3.04\times10^{-4}$ and $5.07\times10^{-4}$ bar O$_2$ for reduction experiments of LaCo$_{0.5}$Fe$_{0.5}$O$_3$, LaFe$_{0.5}$Ni$_{0.5}$O$_3$, LaCo$_{0.5}$Ni$_{0.5}$O$_3$, LaFeO$_3$, YMnO$_3$, YFeO$_3$ and YCo$_{0.5}$Fe$_{0.5}$O$_3$. 
Figure S5: $\delta_{\text{red}}$ and $\delta_{\text{ox}}$ for YCo$_{0.5}$Fe$_{0.5}$O$_3$, LaFe$_{0.5}$Ni$_{0.5}$O$_3$, LaCo$_{0.5}$Ni$_{0.5}$O$_3$, YMnO$_3$, YFeO$_3$, and LaCo$_{0.5}$Fe$_{0.5}$O$_3$. $\delta_{\text{red}}$ results from reduction at 1573 K and 5.07$\times$$10^{-4}$, 3.04$\times$$10^{-4}$ and 1$\times$$10^{-4}$ bar O$_2$ (beige bars, from left to right). $\delta_{\text{ox}}$ results from oxidation at 873, 1073 and 1273 K and 1% CO in CO$_2$ ($p_{O_2} = 1.88\times10^{-21}$, $3.79\times10^{-15}$ and $7.75\times10^{-11}$ bar O$_2$, respectively, blue bars).

Figure S6: Percent mass change as a function of time at 873, 1073 and 1273 K in 1% CO in CO$_2$ ($p_{O_2} = 1.88\times10^{-21}$, $3.79\times10^{-15}$ and $7.75\times10^{-11}$ bar O$_2$, respectively) and 100% CO$_2$ ($p_{O_2} = 3.67\times10^{-9}$, $4.63\times10^{-7}$ and $1.27\times10^{-5}$ bar O$_2$, respectively) for oxidation experiments of LaFe$_{0.5}$Ni$_{0.5}$O$_3$, LaCo$_{0.5}$Ni$_{0.5}$O$_3$ and YCo$_{0.5}$Fe$_{0.5}$O$_3$. 
Figure S7: Percent mass change as a function of time at 873, 1073 and 1273 K in 1% CO in CO\(_2\) (\(p_{O_2} = 1.88\times10^{-21}, 3.79\times10^{-15}\) and 7.75\(\times10^{-11}\) bar O\(_2\), respectively) for oxidation experiments of YFeO\(_3\), YCo\(_{0.1}\)Fe\(_{0.9}\)O\(_3\), YCo\(_{0.3}\)Fe\(_{0.7}\)O\(_3\) and YCo\(_{0.5}\)Fe\(_{0.5}\)O\(_3\).

Figure S8: Percent mass change as a function of time at 1573 K in 1\(\times10^{-4}\), 3.04\(\times10^{-4}\) and 5.07\(\times10^{-4}\) bar O\(_2\) for reduction experiments of YFeO\(_3\), YCo\(_{0.1}\)Fe\(_{0.9}\)O\(_3\), YCo\(_{0.3}\)Fe\(_{0.7}\)O\(_3\) and YCo\(_{0.5}\)Fe\(_{0.5}\)O\(_3\).

iv. TGA

Figure S9: Percent mass change as a function of time for BaCoO\(_3\), SrCoO\(_3\), BaMnO\(_3\), SrMnO\(_3\) and SrTiO\(_3\).
v. HT-XRD for material stability

Figure S10: HT-XRD spectra in CO₂ between 310 and 1275 K of a) SrTiO₃ (peak labels from Howard et al.¹⁷) and b) SrCoO₃ (peak labels from Wang et al.¹⁸, Zeng et al.¹⁹, Saito et al.²⁰, Hanawalt et al.²¹ and Stromme et al.²²), c) SrMnO₃ (peak labels from Kuroda et al.²³), d) BaCoO₃ (peak labels from Jacobson et al.²⁴, Liu et al.²⁵, Stromme et al.²², Bell et al.²⁶ and Saito et al.²⁰) and e) BaMnO₃ (peak labels from Negas et al.²⁷, Liu et al.²⁸ and McMurdie et al.²⁹and f) ratio between ΣE_p, carb and ΣE_i, carb for 36 ABO₃-type perovskites with divalent A-cations (round symbols), with SrTiO₃, SrCoO₃, SrMnO₃, BaCoO₃ and BaMnO₃ highlighted in orange, red, light green, dark green and light blue, respectively.
Figure S11: HT-XRD spectra in 0.2 bar $O_2$ between 310 and 1275 K of a) SrTiO$_3$ (peak labels from Howard et al.$^{17}$) and b) SrCoO$_3$ (peak labels from Wang et al.$^{18}$, Zeng et al.$^{19}$, Davey et al.$^{20}$, Hanawalt et al.$^{21}$, Saito et al.$^{20}$, Takeda et al.$^{31}$ and Liu et al.$^{35}$), c) SrMnO$_3$ (peak labels from Kuroda et al.$^{23}$), d) LaAlO$_3$ (peak labels from Lehnert et al.$^{32}$), e) BaCoO$_3$ (peak labels from Jacobson et al.$^{24}$ and Spitsbergen et al.$^{13}$), f) BaMnO$_3$ (peak labels from Negus et al.$^{27}$ and McMurdie et al.$^{29}$) and g) ratio between $\Sigma E_p$,$_{\text{phase}}$ and $\Sigma E_r$,$_{\text{phase}}$ for 63 ABO$_3$-type perovskites with divalent A-cations (round symbols) and trivalent and tetravalent A-cations (square symbols), with SrCoO$_3$, SrTiO$_3$, SrMnO$_3$, BaCoO$_3$, BaMnO$_3$ and LaAlO$_3$ highlighted in orange, red, light blue, light green, dark green and dark blue, respectively.
vi. RT-XRD

Figure S12: RT-XRD spectra before and after TGA with CO\textsubscript{2} of a) SrTiO\textsubscript{3} (peak labels from Howard \textit{et al.}\textsuperscript{12}), b) SrMnO\textsubscript{3} (peak labels from Kuroda \textit{et al.}\textsuperscript{23}), c) SrCoO\textsubscript{3} (peak labels from Takeda \textit{et al.}\textsuperscript{31}, Grenier \textit{et al.}\textsuperscript{34} and Stromme \textit{et al.}\textsuperscript{22}), d) BaMnO\textsubscript{3} (peak labels from Negas \textit{et al.}\textsuperscript{27} and Bell \textit{et al.}\textsuperscript{26}) and e) BaCoO\textsubscript{3} (peak labels from Jacobson \textit{et al.}\textsuperscript{24} and Hanawalt \textit{et al.}\textsuperscript{21}).
Figure S13: HAADF STEM images of BaCoO₃: a) material flakes (bright areas) suspended over the vacuum window in the amorphous carbon support foil (the dark grey left part of the micrograph), and b-h) the drift corrected, elemental maps and their overlays.
Figure S14: HAADF STEM images of SrTiO₃: a) material flakes (bright areas) suspended over the vacuum window in the amorphous carbon support foil (the dark grey left part of the micrograph), and b-i) the drift corrected, elemental maps and their overlays.
Figure S15: HAADF STEM images of SrCoO$_3$: a) material flakes (bright areas) suspended over the vacuum window in the amorphous carbon support foil (the dark grey left part of the micrograph), and b-i) the drift corrected, elemental maps and their overlays.
Figure S16: HAADF STEM images of SrMnO$_3$: a) material flakes (bright areas) suspended over the vacuum window in the amorphous carbon support foil (the dark grey left part of the micrograph), and b-f) the drift corrected, elemental maps and their overlays.

b. Thermochemical equilibrium analysis

Thermochemical data\textsuperscript{35} was extrapolated for CeO$_2$ $\geq$ 1300 K, Co$_3$O$_4$ $\geq$ 1300 K, CuO $\geq$ 1400 K, Fe$_2$O$_3$ $\geq$ 1800 K, Mn$_3$O$_4$ $\geq$ 1900 K, Mn$_2$O$_3$ $\geq$ 1500 K, MoO$_3$ $\geq$ 1500 K, Na$_2$O$_2$ $\geq$ 1000 K, RhO $\geq$ 1200 K, Rh$_2$O$_3$ $\geq$ 1400 K, RuO$_2$ $\geq$ 1400 K, Sb$_2$O$_3$ $\geq$ 1800 K, SbO$_2$ $\geq$ 1300 K, SnO $\geq$ 1400 K, SnO$_2$ $\geq$ 1600 K, Tl$_2$O $\geq$ 1100 K, and Tl$_2$O$_3$ $\geq$ 1200 K using second-order polynomial regressions with R$^2$ between 0.99932 and 0.99998.

Table S5. Enthalpies of reduction at 298 K ($\Delta h_{0}^\circ$) and Gibbs free energies of the oxide reduction at 298 K ($\Delta g_{0}^\circ$) and oxide oxidation at 298 K ($-\Delta g_{0}^{\circ}$) of 27 solid metal oxide and six metal/metal oxide pairs at 1 bar, calculated from experiment-derived tabulated thermochemical data.\textsuperscript{35}

| Product of the oxide oxidation | Reactant of the oxide oxidation | $\Delta h_{0}^\circ$ (kJ mol$^{-1}$) | $\Delta g_{0}^\circ$ (kJ mol$^{-1}$) | $-\Delta g_{0}^{\circ}$ (kJ mol$^{-1}$) |
|-------------------------------|---------------------------------|-----------------------------------|---------------------------------|-----------------------------------|
| Ag$_2$O                       | Ag                              | 62.20                             | 21.63                           | 492.74                            |
| Au$_2$O$_3$                   | Au                              | -53.84                            | -51.86                          | 566.22                            |
| CeO$_2$                      | Ce$_2$O$_3$                    | 762.33                            | 685.67                          | -171.30                           |
| Co$_3$O$_4$                  | CoO                             | 392.38                            | 304.62                          | 209.75                            |
| Compound | Metal | Value 1 | Value 2 | Value 3 |
|----------|-------|---------|---------|---------|
| Cu₂O     | Cu    | 237.77  | 217.06  | 297.31  |
| CuO      | Cu₂O  | 351.62  | 295.25  | 219.12  |
| Fe₂₃₇.₇₇O | FeO   | 604.50  | 521.81  | -7.44   |
| Fe₂O₃    | Fe₂O₄ | 471.96  | 392.85  | 121.52  |
| Fe₂O₄    | FeO   | 464.27  | 389.07  | 125.29  |
| Mn₂O₄    | MnO   | 202.82  | 153.75  | 360.61  |
| Mn₂O₃    | Mn₃O₄ | 312.29  | 269.89  | 244.48  |
| MoO₃     | MoO₂  | 190.45  | 141.08  | 373.29  |
| Na₂O     | Na₂O  | 750.61  | 694.51  | -180.14 |
| NbO₂     | NbO   | 619.23  | 574.94  | -60.57  |
| Nb₂O₅    | NbO₂  | 345.02  | 331.81  | 182.55  |
| Rh₂O₃    | RhO   | 305.01  | 253.02  | 261.35  |
| RuO₂     | Ru    | 338.09  | 319.70  | 194.67  |
| Sb₂O₃    | Sb₂O₃ | 590.11  | 526.30  | -11.93  |
| SnO₂     | SnO   | 871.11  | 814.54  | -300.17 |
| Ti₂O₃    | TiO   | 711.28  | 666.23  | -151.86 |
| Ti₃O₅    | Ti₃O₃ | 753.96  | 739.75  | -225.38 |
| Ti₄O₇    | Ti₄O₅ | 748.93  | 689.21  | -174.85 |
| Ti₅O₇    | Ti₅O₇ | 185.40  | 162.72  | 351.65  |
| Tl₂O₃    | Tl₂O  | 710.44  | 661.25  | -146.89 |
| V₂O₃     | VO    | 416.73  | 358.81  | 155.56  |
| V₂O₄     | V₂O₃  | 246.86  | 201.81  | 312.56  |
| V₂O₅     | V₂O₄  | 531.83  | 485.47  | 28.90   |
| WO₂₋₇₂   | WO₂   | 432.34  | 387.67  | 126.70  |
| WO₂₋₉₂   | WO₂₋₇₂| 496.50  | 450.34  | 64.03   |
| WO₂₋₉₆   | WO₂₋₉₂| 397.50  | 351.29  | 163.08  |
| WO₃      | WO₂₋₉₆| 341.41  | 295.35  | 219.01  |
| ZnO      | Zn    | 700.92  | 640.95  | -126.59 |
| ZrO₂     | Zr    | 1097.46 | 1039.72 | -525.36 |
Table S6. Gibbs free energies of the oxide oxidation between 800 K and 1400 K (\(-\Delta_{\text{G}}^\circ\)) of 27 solid metal oxide and six metal/metal oxide pairs in 100% CO₂, calculated from experiment-derived tabulated thermochemical data.\(^{35}\)

| Product of oxide oxidation | Reactant of oxide oxidation | 800 K | 900 K | 1000 K | 1100 K | 1200 K | 1300 K | 1400 K |
|---------------------------|-----------------------------|-------|-------|--------|--------|--------|--------|--------|
| Ag₂O                     | Ag                          | 490.92| 497.25| 505.33 | 515.03 | 526.23 | 541.29 | 558.97 |
| Au₂O₃                    | Au                          | 577.56| 583.08| 589.47 | 596.67 | 604.61 | 613.27 | 623.40 |
| CeO₂                     | Ce₂O₃                       | -125.80| -115.85| -105.63| -95.13 | -84.38 | -76.34 | -50.44 |
| Co₃O₄                    | Co                           | 287.61| 304.33| 320.80 | 336.84 | 352.36 | 362.51 | 372.32 |
| CuO                      | Cu₂O                        | 313.71| 315.71| 317.43 | 318.88 | 320.09 | 321.09 | 317.25 |
| Cu₂O₃                    | Cu                           | 219.73| 219.26| 218.81 | 218.43 | 218.086| 217.79 | 217.55 |
| Fe₉₉₅₆O₆                 | FeO                         | 38.34 | 43.88 | 48.67 | 53.27 | 57.90 | 62.69 | 67.67  |
| Fe₂O₃                   | Fe₂O₄                        | 171.16| 183.63| 195.69 | 207.27 | 218.82 | 230.22 | 241.41 |
| Fe₃O₄                   | FeO                          | 164.25| 171.68| 178.94 | 186.01 | 192.88 | 199.51 | 205.91 |
| Mn₉₉₅₆O₆                 | MnO                         | 353.08| 351.20| 349.24 | 347.21 | 345.09 | 342.90 | 340.62 |
| Mn₂O₃                   | Mn₂O₄                        | 224.972| 220.67| 216.29 | 209.54 | 195.68 | 181.52 | 167.12 |
| MoO₃                    | MoO₂                         | 364.20| 360.41| 354.82 | 348.06 | 339.60 | 330.28 | 319.71 |
| Na₂O₂                   | Na₂O₃                        | -176.95| -177.13| -177.58| -178.40| -180.10| -182.01| -184.02|
| Nb₂O₃                   | NbO                          | -75.57| -78.40| -80.91 | -82.88 | -83.22 | -83.24 | -83.12 |
| Nb₂O₅                   | Nb₂O₃                        | 216.17| 223.26| 230.46 | 237.71 | 248.63 | 259.70 | 267.07 |
| Rh₂O₃                   | RhO                          | 256.95| 255.48| 253.91 | 252.25 | 250.52 | 248.72 | 245.13 |
| Ru₂O₃                   | Ru                           | 221.49| 228.92| 245.83 | 266.49 | 287.28 | 303.34 | 319.66 |
| Sb₂O₃                   | Sb₂O₄                        | 4.34  | 6.15  | 7.79  | 9.30  | 10.72  | 12.06  | 15.62  |
| Sn₂O₅                   | SnO                          | -301.94| -303.98| -306.25| -308.65| -311.13| -313.17| -314.30|
| Ti₉₉₅₆O₆                 | TiO                         | -192.09| -199.22| -205.31| -210.56| -215.16| -219.27| -223.04|
| Ti₂O₃                  | Ti₂O₅                        | -206.79| -198.92| -191.82| -185.26| -178.99| -172.79| -166.46|
| Ti₃O₆                  | Ti₃O₉                        | -160.04| -156.27| -152.17| -147.73| -142.97| -137.82| -132.49|
| TiO₂                    | TiO₃                         | 360.56| 363.52| 368.37| 372.11| 374.96| 378.71| 382.62 |
| Ti₂O₆                  | Ti₂O₉                        | -154.02| -155.66| -157.25| -158.75| -160.16| -161.474| -162.69|
| Product of the oxide oxidation | Reactant of the oxide oxidation | -\(\Delta G_{0}^{\circ}\) (kJ mol\(^{-1}\)) |
|-------------------------------|---------------------------------|-------------------------------|
|                              |                                 | 800 K | 900 K | 1000 K | 1100 K | 1200 K | 1300 K | 1400 K |
| Ag\(_2\)O | Ag | 521.55 | 531.71 | 543.62 | 557.15 | 572.17 | 591.07 | 612.58 |
| Au\(_2\)O | Au | 608.19 | 617.54 | 627.76 | 638.79 | 650.56 | 663.05 | 677.00 |
| CeO\(_2\) | CeO\(_2\) | -95.17 | -81.39 | -67.34 | -53.01 | -38.44 | -17.57 | 3.17 |
| Co\(_3\)O \(_4\) | CoO | 318.24 | 338.79 | 359.09 | 378.96 | 398.28 | 412.28 | 425.92 |
| CuO | CuO | 344.34 | 350.17 | 355.72 | 361.00 | 366.04 | 370.86 | 370.86 |
| Cu\(_2\)O | Cu | 250.36 | 253.72 | 257.10 | 260.55 | 264.03 | 267.57 | 271.16 |
| Fe\(_{1.97}\)O | FeO | 68.97 | 78.34 | 86.96 | 95.39 | 103.85 | 112.46 | 121.28 |
| Fe\(_3\)O \(_4\) | FeO | 201.79 | 218.09 | 233.98 | 249.39 | 264.77 | 280.00 | 295.02 |
| Fe\(_2\)O | FeO | 194.89 | 206.14 | 217.23 | 228.13 | 238.83 | 249.29 | 259.51 |
| Mn\(_3\)O | MnO | 383.719 | 385.66 | 387.53 | 389.33 | 391.04 | 392.68 | 394.22 |
| Mn\(_2\)O \(_3\) | MnO | 255.68 | 255.13 | 254.58 | 251.66 | 241.63 | 231.30 | 220.72 |
| MoO | MoO \(_2\) | 394.83 | 394.87 | 393.11 | 390.18 | 385.54 | 380.05 | 373.32 |
| Na\(_2\)O | Na\(_2\)O | -146.32 | -142.67 | -139.29 | -136.28 | -134.15 | -132.24 | -130.42 |

Table S7. Gibbs free energies of the oxide oxidation between 800 K and 1400 K (\(-\Delta G_{0}^{\circ}\)) of 27 solid metal oxide and six metal/metal oxide pairs at 1% CO in CO\(_2\), calculated from experiment-derived tabulated thermochemical data.\(^{15}\)
| Product of the oxide reduction | Reactant of the oxide reduction | Δ\(\Phi_{O_2}^{\circ}\) (kJ mol\(^{-1}\)) |
|-------------------------------|--------------------------------|----------------------------------|
|                               |                                | 1200 K                           |
|                               |                                | 1300 K                           |
|                               |                                | 1400 K                           |
|                               |                                | 1500 K                           |
|                               |                                | 1600 K                           |
|                               |                                | 1700 K                           |
|                               |                                | 1800 K                           |
| Ag\(_2\)O                    | Ag                             | -261.70                          |
|                               |                                | -340.09                          |
|                               |                                | 348.92                           |
|                               |                                | -87.81                           |
|                               |                                | -55.562                          |
|                               |                                | 46.44                            |
|                               |                                | 206.62                           |
| Au\(_2\)O                    | Au                             | -301.65                          |
|                               |                                | -373.63                          |
|                               |                                | 306.99                           |
|                               |                                | -122.86                          |
|                               |                                | -81.44                           |
|                               |                                | 21.85                            |
|                               |                                | 176.96                           |

Table S8. Gibbs free energies of the oxide reduction between 1200 K and 1800 K (\(\Delta\Phi_{O_2}^{\circ}\)) of 27 solid metal oxide and six metal/metal oxide pairs at \(pO_2 = 10^{-4}\) bar, calculated from experiment-derived tabulated thermochemical data.\(^{35}\)
| Compound | Oxidation State | Energy (kJ/mol) |
|----------|----------------|----------------|
| CeO₂     | 0              | -344.15        |
| Co₃O₄    | 2              | -387.87        |
| CuO      | 1              | -432.71        |
| Cu₂O     | 1              | -478.63        |
| Fe₂O₃    | 3              | -525.54        |
| Fe₃O₄    | 4              | -261.70        |
| FeO      | 0              | -481.00        |
| MnO₃     | 3              | -344.15        |
| Mn₂O₅    | 3              | -387.87        |
| MoO₃     | 4              | -432.71        |
| Na₂O₂    | 2              | -344.15        |
| NbO₂     | 3              | -525.54        |
| Nb₂O₃    | 4              | -261.70        |
| Rh₂O₃    | 2              | -301.65        |
| RuO₂     | 4              | -344.15        |
| Sb₂O₃    | 5              | -387.87        |
| SnO₂     | 4              | -432.71        |
| Ti₂O₃    | 3              | -478.63        |
| Ti₃O₅    | 4              | -525.54        |
| Ti₄O₇    | 5              | -261.70        |
| TiO₂     | 0              | -481.00        |
| TiO₃     | 3              | -301.65        |
| TiO₅     | 4              | -344.15        |
| V₂O₅     | 2              | -432.71        |
| V₂O₃     | 3              | -478.63        |
| WO₂      | 6              | -525.54        |
| WO₂₉     | 7              | -261.70        |
| WO₃₉₆    | 8              | -301.65        |
| ZnO      | 0              | -387.87        |
| ZrO₂     | 0              | -432.71        |
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