Design Principles of Perovskites for Thermochemical Oxygen Separation

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Separation and concentration of O₂ from gas mixtures is central to several sustainable energy technologies, such as solar-driven synthesis of liquid hydrocarbon fuels from CO₂, H₂O, and concentrated sunlight. We introduce a rationale for designing metal oxide redox materials for oxygen separation through “thermochemical pumping” of O₂ against a *p*O₂ gradient with low-grade process heat. Electronic structure calculations show that the activity of O vacancies in metal oxides pinpoints the ideal oxygen exchange capacity of perovskites.

Thermogravimetric analysis and high-temperature X-ray diffraction for SrCoO_{3-δ}, BaCoO_{3-δ} and BaMnO_{3-δ} perovskites and Ag₂O and Cu₂O references confirm the predicted performance of SrCoO_{3-δ}, which surpasses the performance of state-of-the-art Cu₂O at these conditions with an oxygen exchange capacity of 44 mmol O₂ mol_{SrCoO_{3-δ}}⁻¹ exchanged at 12.1 μmol O₂ min⁻¹ g⁻¹ at 600–900 K. The redox trends are understood due to lattice expansion and electronic charge transfer.

Introduction

Renewable chemical fuels can be synthesized through solar-driven electro-, photo-, and thermochemical splitting of CO₂ and H₂O.^[1] The latter approach utilizes the entire spectrum of concentrated solar radiation as high-temperature process heat for the production of CO and H₂ (syngas) via metal oxide redox cycles.^[1b, 2] A critical drawback of this approach is the inert gas consumed to lower the partial pressure of oxygen (*p*O₂) for shifting the thermodynamic equilibrium of the reduction step to lower temperatures.^[3] This, in turn, requires separation of O₂ from the product gases for recycling the inert carrier gas and closing the material cycle.^[3a, 4] The separation of O₂ has been a requirement in a variety of commercial applications such as oxy-combustion, autothermal gasification of carbonaceous feedstock, and O₂ removal to avoid catalyst passivation

by O₂ in fuel cells and when deoxygenating biofuels to make these more akin to petroleum-derived fuels.^[5] Industrially, O₂ can be separated from air by pressure swing adsorption (PSA) using zeolites and carbon molecular sieves, by ceramic mixed ionic-electronic conducting (MIEC) membranes,^[6] and by cryogenic distillation. PSA and MIEC membranes cannot produce high-purity inert gas,^[6b] and separating O₂ from gas mixtures at low *p*O₂ using membranes relies on a stripping gas with even lower *p*O₂. These separation technologies further require an input of electrical work ranging from 100 to 350 kWh per metric ton O₂,^[6, 7] which penalizes the solar-to-fuel energy conversion efficiencies. Since solar thermochemical cycles inherently suffer from heat losses, it would be beneficial to utilize an oxygen separation technology driven by waste heat.

Thermochemical solid-state O₂ separation (TSSOS) using metal oxide redox materials such as Cu₂O/CuO,^[3a, 8] Mn₃O₄/Mn₂O₃,^[8] and CoO/Co₃O₄,^[8, 9] utilizes low-grade process heat and does not require electricity. TSSOS has the potential to separate and concentrate O₂ at low *p*O₂ via temperature-swing.^[3a] The current state-of-the-art TSSOS redox material, Cu₂O, has a maximum oxygen exchange capacity (Δδ, i.e., the difference in the oxygen non-stoichiometry between reducing and oxidizing conditions) of about 200 mmol O₂ per mol Cu₂O, exchanged at approximately 10 μmol O₂ min⁻¹ g_{Cu₂O}⁻¹ when cycled between 1120–1450 K.^[3a] We show below that Cu₂O cannot be employed with low-grade process heat at 600–900 K. With the aim of augmenting the O₂ exchange capacities and rates of TSSOS redox materials for a more energy-efficient O₂ separation process that utilizes low-grade solar thermal energy at lower temperatures, such as waste heat from solar fuel production processes, we evaluate perovskites that offer high O₂ conductivities and a stable crystal structure over a large range of oxygen non-stoichiometry.^[6a, c, 10] The O₂ exchange capacity characterizes the trade-off between high energy conversion ef-

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iciencies at low temperature during the endothermic reduction and high rates and extend of the oxygen separation process at high oxide reduction temperatures. For a perovskite with $\text{ABO}_{3-\delta}$ stoichiometry—where A and B are metal cations in twelve- and six-coordinated interstices—the TSSOS redox cycle can be represented by Equations (1) and (2):

Conceptually, O_2 is stripped from a gas mixture at low $p\text{O}_2$ through oxidation of the perovskite at low temperatures. This yields as an output of the oxidation step an inert gas with a lowered $p\text{O}_2$ while concentrated O_2 is evolved from the solid at an elevated temperature and increased $p\text{O}_2$ through partial reduction of the metal oxide. In principle, these reactions are analogous to the electrochemical oxygen reduction and evolution reactions (ORR/OER), where the bonding of O/OH or OH/OOH reaction intermediates to the catalyst surface controls the catalytic activity of the electrode surface.^[10,11] The ideal catalytic activity of a surface is determined by an intermediately strong bonding of the key reaction intermediates, which facilitates coverage of the surface with reactants and desorption of products from the surface, as described by the Sabatier principle.^[12] Analogously, we hypothesize that metal oxide redox materials for removal of O_2 from gas mixtures with a lower $p\text{O}_2$ than the $p\text{O}_2$ during the extraction of O_2 from the solid can be characterized with an intermediately strong binding of the lattice oxygen.

Results and Discussion

To test this hypothesis, we screened the redox energetics of binary metal oxides across the periodic table using experiment-based thermochemical data.^[13] Figure 1A shows the free energy (ΔG) of the oxidation and reduction reactions for 32 solid metal oxide and six metal/metal oxide pairs^[14] versus the thermochemical oxide stability.

The analysis utilizes the enthalpy of the oxide reduction at room temperature as a descriptor^[10–12] of the correlated reaction energetics, which is equivalent to the amount of energy required to break metal–oxygen bonds, as shown in Table S2 given in the Supporting Information. Generally, either one of the two reactions is slightly more endergonic, thereby limiting the O_2 exchange capacity. Figure 1B shows the limiting free energy of a redox cycle near the intersection of both correlations. As indicated by the volcano-shaped curve, the ideal redox material binds oxygen strongly enough to oxidize the oxide at relatively low temperatures—stronger than the Ag/ Ag_2O reference—but weakly enough to reduce the oxidized redox material at moderately higher temperatures—weaker than the $\text{Cu}_2\text{O}/\text{CuO}$ reference. The ideal metal oxide compositions are where these effects balance, located near the top of the volcano curve. Ideally, this region corresponds to negative free energies for both reactions. For the temperatures chosen

Figure 1. A) Free energy of the oxide oxidation at 600 K and oxide reduction at 900 K (ΔG_{ox}) versus the enthalpy of the oxide reduction at 298 K (ΔH_{red}). All data are at 1 bar.^[14] Dashed lines are linear regressions. B) The limiting free energy of the redox cycle ($\Delta G_{\text{red,lim}}$) versus ΔH_{red} . The colored compositions were examined experimentally, with blue and red marked materials limited by the oxide reduction and oxidation, respectively, and purple marking materials that facilitate a redox trade-off. C) DFT-models of the oxidized and reduced SrCoO_3 and $\text{SrCoO}_{2.5}$ surface, representatively for strontium cobaltite.

in our analysis, this can be achieved with rare materials such as $\text{Rh}_2\text{O}/\text{RhO}$ or toxic materials such as $\text{PbO}/\text{Pb}_3\text{O}_4$.^[15] Generally, the volcano-like shape of this correlation is due to the fact that the amount of energy absorbed for breaking metal–oxygen bonds during the reduction step correlates with the amount of heat liberated when forming these bonds during the oxidation step. Thus, as shown in Figure S1, the location of the volcano-top can be determined from only computing the reduction enthalpy as the entropy of O_2 gas participating in either reaction is the same for all specific redox couples and as entropic contributions of the solids introduce significant deviation from these correlations only at significantly higher temperatures when approaching melting and boiling points.

To tailor inexpensive and non-toxic metal oxides, we calculated the free energy of oxygen vacancy formation ($\Delta G_{\text{v}}[\text{O}]$) using density functional theory (DFT) for twelve perovskites that have attracted attention for solid-oxide fuel cells,^[6a,10] air separation,^[6c] and solar-thermal applications.^[16] Stoichiometric $\text{ABO}_3(010)$ and oxygen-deficient $\text{ABO}_{2.5}(010)$ facets ($\text{A}=\text{Sr}$, Ba , or La ; and $\text{B}=\text{Mn}$, Co , Ni , or Cu) were modeled (Figure 1C), using the grid-based projector-augmented wave (GPAW) and atomic simulation environment (ASE) electronic-structure code.^[17] Figure 1B shows the thermochemical stability and the reaction energetics as calculated from the scaling of $\Delta G_{\text{v}}[\text{O}]$ and the redox energetics of the bulk oxides (see the Supporting Information).^[18] The analysis predicts an ideal O_2 exchange capacity for SrCoO_3 , relative to too strong and too weak oxygen binding for BaMnO_3 and BaCoO_3 , respectively.

We validated this descriptor-based design for metal oxide redox materials by means of dynamic O_2 exchange experiments using $\text{SrCoO}_{3-\delta}$, $\text{BaMnO}_{3-\delta}$, and $\text{BaCoO}_{3-\delta}$, synthesized via the Pecchini method^[3b] and commercial Ag_2O and Cu_2O as

Figure 2. Dynamic O_2 exchange: TGA runs of A) Ag_2O and Cu_2O and B) $\text{SrCoO}_{3-\delta}$, $\text{BaCoO}_{3-\delta}$, and $\text{BaMnO}_{3-\delta}$. C) Lattice constants of $\text{SrCoO}_{3-\delta}$, $\text{BaCoO}_{3-\delta}$, and $\text{BaMnO}_{3-\delta}$ derived from HT-XRD analyses of oxide reduction at 0.2 bar p_{O_2} (empty circles) and oxide oxidation at 0.035 bar p_{O_2} (filled circles). Error bars are standard deviations within a 68% confidence interval.

reference materials. The composition and surface morphology of all solids were characterized using high-temperature X-ray diffraction (HT-XRD) and scanning electron microscopy (SEM). The O_2 exchange capacity and exchange rates were determined by thermogravimetric analysis (TGA).

Figure 2A and B display dynamic TGA runs for $\text{SrCoO}_{2.95}$, $\text{BaCoO}_{2.58}$, $\text{BaMnO}_{2.94}$, Ag_2O , and Cu_2O (initial stoichiometries) that were cyclically reduced at 900 K and 0.2 bar p_{O_2} (simulating air) and oxidized at 600 K and 0.035 bar p_{O_2} (simulating the composition of the gas phase from reducing ceria for solar-driven splitting of CO_2 and H_2O ^[19]). As expected, Cu_2O and Ag_2O oxidize and reduce strongly to CuO and Ag , respectively, essentially without exchanging O_2 reversibly. Compared to these reference materials, we find augmented O_2 exchange capacities for the perovskites. $\text{SrCoO}_{2.95}$ reaches a maximum O_2 exchange capacity of 44 ± 0.012 mmol O_2 per mol $\text{SrCoO}_{2.95}$ and a maximum O_2 exchange rate of 12.1 ± 0.003 $\mu\text{mol}_{\text{O}_2} \text{min}^{-1} \text{g}_{\text{SrCoO}_{2.95}}^{-1}$ whereas $\text{BaCoO}_{2.58}$ and $\text{BaMnO}_{2.94}$ perform at much lower capacities of 3.4 ± 0.015 and 0.5 ± 0.015 mmol O_2 per mol of perovskite and lower exchange rates of 0.8 ± 0.003 and 0.04 ± 0.005 $\mu\text{mol}_{\text{O}_2} \text{min}^{-1} \text{g}_{\text{perovskite}}^{-1}$, respectively. As predicted by DFT, the performance of $\text{BaCoO}_{3-\delta}$ and $\text{BaMnO}_{3-\delta}$ appears limited by reoxidation and reduction, respectively. This theory-based screening of twelve perovskites identifies a well-known composition, SrCoO_3 , that shows a significantly augmented performance for this novel application compared to the O_2 exchange capacities and rates of the reference materials at the same conditions. Additionally, with an O_2 exchange rate of 12.1 $\mu\text{mol}_{\text{O}_2} \text{min}^{-1} \text{g}_{\text{perovskite}}^{-1}$, $\text{SrCoO}_{3-\delta}$ outperforms the state-of-the-art $\text{Cu}_2\text{O}/\text{CuO}$ cycle, which cannot be used with low-grade process heat at 600–900 K and which has an O_2 exchange rate of only 10 $\mu\text{mol}_{\text{O}_2} \text{min}^{-1} \text{g}_{\text{Cu}_2\text{O}}^{-1}$ (for both, oxide reduction and oxidation) at significantly higher—and thereby economically less attractive—temperatures of 1120–1450 K and comparable p_{O_2} .^[3a]

To support that the TGA data is indicative of reversible O_2 exchange, Figure 2C shows the perovskite lattice constants computed using data from HT-XRD analysis. Although all perovskites exhibit thermal expansion upon heating, only

$\text{SrCoO}_{3-\delta}$ shows a major difference in the lattice expansion at varied p_{O_2} , which can be attributed to the formation and filling of O vacancies.^[20] This, along with the electronic structure trends and the TGA analysis, suggests that $\text{SrCoO}_{3-\delta}$ is particularly suitable as a redox material for TSSOS. To understand how the oxide composition controls the O_2 exchange, Figure 3A plots $\Delta G_v[\text{O}]$ versus the DFT-calculated bond length between the transition metal and the nearest O atom ($d_{\text{B-O}}$) at $\text{ABO}_{2.5}(\text{O}10)$. Generally, we observe stable O vacancies (negative $\Delta G_v[\text{O}]$ values) correlating with large $d_{\text{B-O}}$ values. This is in agreement with the lattice expansion shown in Figure 2C, as the lattice expansion due to a higher chemical potential for oxygen in the gas phase decreases the bonding of oxygen in the solid, which, in turn, increases the length of the metal–oxygen bond. Although the slope of this correlation is essen-

Figure 3. Correlation of $\Delta G_v[\text{O}]$ with A) $d_{\text{B-O}}$ and B) q_{O} (empty, light-gray, and dark-gray symbols mark $\text{SrBO}_{2.5}$, $\text{LaBO}_{2.5}$, and $\text{BaBO}_{2.5}$, whereas circles, squares, diamonds, and triangles mark $\text{ACuO}_{2.5}$, $\text{ANiO}_{2.5}$, $\text{AMnO}_{2.5}$, and $\text{ACoO}_{2.5}$). C) Charge density differences (CDD) of the marked surface after O vacancy formation relative to the stoichiometric surface and the reference gas-phase O_2 (given at the height of the transition metal cation).

tially due to the metal at the B-site interstices, the absolute value of $d_{\text{B-O}}$ is governed by the metal at the A site, as demonstrated by the consistently higher $d_{\text{B-O}}$ values of the Ba versus the Sr compounds. However, the scatter of the correlation shown in Figure 3A suggests that the trends in the free energy of the O vacancy formation and in the metal–oxygen bond length cannot alone be rationalized with geometric arguments.

Figure 3B plots $\Delta G_{\text{v}}[\text{O}]$ versus the DFT-calculated partial charge^[21] of oxygen (q_{O}). We find that perovskites that form O vacancies easily contain weakly charged oxygen. BaCoO₃, for instance, accumulates less charge at the O anion than SrCoO₃ and BaMnO₃, which correlates with the facile reduction of BaCoO₃. Generally, $\Delta G_{\text{v}}[\text{O}]$ scales with q_{O} , with the slope corresponding approximately to the ionization energy of oxygen, -13.62 eV per electron^[22] and the intercept reflecting entropic contributions to $\Delta G_{\text{v}}[\text{O}]$ and the reference chemical potential of oxygen in the gas phase (see the Supporting Information). The quality of this linear correlation suggests that the trend in the free energy of the O vacancy formation is controlled by the enthalpy of breaking metal–oxygen bonds, that is, by the quantity of electric charge transferred from the O atom to the lattice when forming the O vacancy. This is illustrated with Figure 3C, which shows the difference in the charge density distribution due to O vacancy formation at SrCoO₃(010) and BaMnO₃(010). Although the partial charge of the O anion yielding the vacancy is approximately equal at both surfaces (Figure 3B), the charge transfer from the bonding O2p states to the 3d states of the transition metal is significantly higher at BaMnO₃(010) relative to SrCoO₃(010). We note that this analysis describes the width of the 2p–3d gap for 3d transition metals at the B site of ABO₃ perovskites. Incorporating other metal cations into the B interstices, such as lanthanides with f states, may alter these trends due to a different entropy-controlled shape of the states that are accepting electrons when forming O vacancies.

In summary, analogous to the enthalpy difference of bulk oxide reduction, we suggest that the charge transfer from O2p to B-site-metal 3d states explains the higher O₂ exchange capacity of SrCoO_{3- δ} versus BaMnO_{3- δ} at the atomic scale.

In accord with charge transfer controlling the formation of O vacancies at the oxide surface, our Sabatier analysis employs the enthalpy of the bulk oxide reduction as a descriptor of the redox energetics. To demonstrate how this information can be used practically to predict the O₂ exchange capacity of a metal oxide, we have determined the O₂ exchange capacity for five metal oxides as the difference of the oxygen non-stoichiometry at equilibrium between O₂ evolution at 900 K and 0.2 bar p_{O_2} and O₂ fixation at 600 K and 0.035 bar p_{O_2} (Figure 4). The plot shows that the O₂ exchange capacity resembles the volcano-shaped trend of the limiting redox energetics. Relative to this trend across three orders of magnitude are minor deviations, such as for BaCoO_{3- δ} , which are presumably due to differences in surface morphology, crystal structure, and the computational versus experimental non-stoichiometry (see the Supporting Information). This demonstrates how computing the enthalpy of the oxide reduction from first principles allows predicting the O₂ exchange capacity of metal oxides.

Figure 4. Predicting the O₂ exchange capacity and the limiting free energy of solid-state O₂ separation from the enthalpy of the oxide reduction at 298 K and 1 bar.

Although the present article focuses on the thermodynamics of O vacancy formation, the kinetics of conducting these vacancies from and to the surface are of equal importance when designing metal oxides for solid-state O₂ separation. The defect chemistry of several perovskite families, including La₂NiO_{4+ δ} with a relatively high mobility of O interstitials, has been investigated previously.^[23] In these perovskites excess oxygen is incorporated as interstitial O²⁻ or O⁻ anions with anion Frenkel pairs being the predominant intrinsic lattice defects.^[23] Oxygen transport may be anisotropic^[23] or isotropic, such as in Sr_{0.75}Y_{0.25}CoO_{2.625}.^[24] A low Frenkel energy may yield high O vacancy concentrations, in PrBaCo₂O_{5.5} for instance,^[25] with an ordered sublattice of the A cations ensuring high oxygen ion mobility.^[25] Similarly, DFT was used previously to predict and understand oxygen conduction trends in metal oxides.^[18] These and other studies^[23,26] outline the prospects of an advanced understanding of oxygen conduction for designing advanced redox materials.

Conclusions

Based on the Sabatier principle applied to the bonding of lattice oxygen atoms, we implemented a descriptor-based design principle for predicting the O₂ exchange capacity of metal oxides and perovskites in particular. The computations were validated through dynamic O₂ exchange experiments using Ag₂O, Cu₂O, and three perovskites and rationalized based on the composition-dependent bond geometry and charge transfer during the formation of O vacancies at the metal oxide surface. SrCoO_{3- δ} was identified as an ideal material for solar-driven thermochemical separation of O₂. In a broader context, the presented principles may also aid the design of oxygen conductors for related applications, such as solid-oxide fuel cells and air separation using dense ceramic membranes.

Experimental Section

Thermochemical equilibrium calculations—To guide the design of redox materials, the thermochemical equilibrium of binary bulk metal oxides, O₂, and their reduction products was determined at

the specified pO_2 and temperatures from tabulated free-energy data, with an absolute accuracy of $1\text{--}10\text{ kJ mol}^{-1}$.^[13] Per convention, negative free energy differences mark exergonic reactions. At the computed conditions, the correlations of ΔG and ΔH_{red} for the metal oxide oxidation and reduction have average relative errors of 12.4% and 17.6%, respectively. These values increase with increasing temperature due to entropic contributions and indicate that the provided volcano plot could be employed for identifying materials active for thermochemical solid-state O_2 separation.

Electronic structure calculations—Twelve perovskite surfaces were modeled using DFT, performed with the GPAW code.^[17b,c] Exchange-correlation interactions were treated by the revised Perdew–Burke–Ernzerhof (RPBE) functional.^[27] Atomic configurations were handled in ASE.^[17a] A Fermi–Dirac smearing of 0.1 eV was used to achieve convergence, and the structure optimization results were extrapolated to 0 K. The linesearch Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was employed to optimize the atomic geometries until the maximum force was less than $0.05\text{ eV \AA}^{-1}$. The utility of DFT+ U methods for surface calculations is not determined in general and was found unnecessary for many metal oxides.^[18,28] Here, for all DFT calculations the generalized gradient approximation (GGA) was used without a Hubbard U term as we found previously that the Hubbard U correction did not improve the description of surface reactivity with the employed models.^[18] The cubic bulk structures of ABO_3 compositions consisted of one metal atom (Sr, Ba, or La) at the twelve-coordinated A-site interstices, one metal atom (Mn, Co, Ni or Cu) at the six-coordinated B-site interstices, and three oxygen atoms that were allowed to optimize their positions (relax). The bulk structures had periodic boundary conditions in all directions and were modeled using a k -point sampling of $4 \times 4 \times 4$. Compositions containing Mn, Co, or Ni were modeled using spin-polarized calculations and, to avoid reminiscent stress in the calculations, the lattice constants were chosen as the DFT-calculated bulk lattice constants. Table S1 provides a summary of the lattice constants and magnetic moments along with a discussion of the accuracy of the employed DFT methods that predict the lattice constants within $\pm 0.36\text{--}3.89\%$ of experimental values. The AO-terminated $ABO_3(010)$ facet was chosen for modeling the perovskite surfaces as this facet was identified as being the thermodynamically most stable surface of cubic perovskites for various compositions.^[18] The surface models consisted of one upper $ABO_3(010)$ layer that was allowed to relax and one lower $ABO_3(010)$ layer constrained to the bulk geometry. The surfaces were periodically repeated in the directions parallel to the surface and were modeled with $10\text{ \AA}$ of vacuum perpendicular to the surface. The Brillouin zone of surface models (slabs) was sampled using $4 \times 4 \times 1$ k -points. The partial charge density was determined for all atoms contained in the surface models through Bader decomposition.^[21] To model the perovskite surfaces at different O vacancy concentrations, one third of the stoichiometric lattice oxygen in the upper surface layer was removed while the oxygen concentration in the lower surface layer was maintained. This yielded “reduced” and “oxidized” surface models with $A_2B_2O_5(010)$ and $A_2B_2O_6(010)$ stoichiometry, marked with the conventional $ABO_3(010)$ and $ABO_{2.5}(010)$ notation, respectively. The free energy of forming O vacancies ($\Delta G_v[O]$) at the surface was computed as follows [Eq. (3)].^[18]

$$\Delta G_v[O] = G_v - (G_s - G_o^r) \quad (3)$$

where G_v , G_s , and G_o^r are the free energies of the perovskite surface with the O vacancies, the stoichiometric surface and the reference energy of the liberated lattice oxygen [taken as the energy differ-

ence of stable H_2O and H_2 in the gas phase, see Eq. (3) in the Supporting Information], such that negative free energies indicate exergonic reactions. The formation of O vacancies as computed corresponded to formation of one monolayer O vacancies equivalent to an oxygen non-stoichiometry of $\delta = 0.5$ in $ABO_{2.5}$ (Figure 1C). Details on converting the DFT-computed electronic energy to Gibbs free energy at 298.15 K and 1.013 bar, the reference energies, and scaling relations^[18] to estimate the bulk formation energies are provided in the Supporting Information. The error of DFT-computed adsorption energies (employed as a descriptor of surface reactivity, comparable to the energy of forming surface O vacancies in this work) was estimated previously to be 0.08 eV .^[29]

Perovskite synthesis—Three perovskites, namely $SrCoO_{3-\delta}$, $BaCoO_{3-\delta}$, and $BaMnO_{3-\delta}$, were synthesized using a modified Pechini method, employing stoichiometric amounts of $Mn(NO_3)_2 \cdot 4H_2O$ (Alfa Aesar, 98%), $Sr(NO_3)_2$ (Alfa Aesar, 98%), $Co(NO_3)_2$ (Alfa Aesar, 97.7%), $Ba(NO_3)_2$ (Alfa Aesar, 99%), C_2H_6O (Alcosuisse, 96.1%), and $C_6H_8O_7$ (Fluka, $\geq 99.5\%$). The solid products were ground using mortar and pestle, uniaxially pressed into pellets (10 metric tons, 6 and 25 mm in diameter), and sintered in air at 1473 K for 5 h ($SrCoO_{3-\delta}$ and $BaCoO_{3-\delta}$) or in pure O_2 at 1273 K for 48 h ($BaMnO_{3-\delta}$). To achieve the desired oxidation state, the sintered $SrCoO_{3-\delta}$ was ground, fully immersed in NaClO (Migros, $< 5\%$ in H_2O), washed with deionized water, and subsequently dried for at least 2 h at 473 K. Ag_2O (Merck, $\geq 99\%$) and Cu_2O (Johnson Matthey Alfa, 99.5%) were used as reference materials.

Solid-state analysis—XRD and HT-XRD were performed in the Bragg Brentano geometry using CuK_α radiation ($20\text{--}80^\circ$ 2θ , $0.06^\circ\text{ min}^{-1}$ scan rate, 45 kV/20 mA output, PANalytical/X’Pert MPD/DY636, Philips). The original oxygen content of the perovskites was $SrCoO_{2.95}$, $BaCoO_{2.58}$, and $BaMnO_{2.94}$ before the redox cycling, as determined using TGA (STA 409/C/3, Netzsch) of the complete reduction of the metal oxides in 5% H_2 in Ar at 823 K and 1 bar. To estimate changes in the lattice constants, the perovskites were reduced by heating from 600 to 900 K in 100 K steps at 0.2 bar pO_2 and thereafter oxidized by cooling from 900 to 600 K in 100 K intervals at 0.035 bar pO_2 . The morphology of all materials was analyzed using SEM (15 kV accelerating voltage, TM-1000, HITACHI) and is shown in detail in the Supporting Information.

Thermochemical cycling experiments—Starting materials (0.1 g) were placed in an Al_2O_3 crucible supported with an Al_2O_3 rod on the microbalance of the TGA ($\pm 0.1\text{ }\mu\text{g}$). The materials were thereafter exposed to a gas flow (constant flow rate of 200 mL min^{-1} at 273 K and 1 bar) with specified pO_2 , which was adjusted by mixing O_2 (99.5%, Messer) and N_2 (99.999%, Carbogas) using three electronic mass flow controllers (MFC400, Netzsch; accuracy $\pm 1\%$, precision $\pm 1\text{ mL min}^{-1}$). The mass change of the samples was recorded during two consecutive redox cycles with oxide reduction at 900 K and 20 vol% O_2 and oxide oxidation at 600 K and 3.5 vol% O_2 , respectively ($\pm 1\text{ K}$). Heating and cooling was performed at $+10\text{ K min}^{-1}$ and -10 K min^{-1} , respectively. To correct for buoyancy, blank runs were performed using the same measurement conditions employed for the experimental runs.

The oxygen exchange capacity (dimensionless) was defined as the difference in the oxygen non-stoichiometry of the metal oxides after the oxide reduction (δ_{red}) and after the oxide oxidation (δ_{oxi}):

$$\Delta\delta = \delta_{\text{red}} - \delta_{\text{oxi}} = (m_{\text{red}} - m_{\text{oxi}})M_o^{-1} \quad (4)$$

where m_{red} and m_{oxi} are the metal oxide mass (in g, determined using TGA), after the oxide reduction, and after the oxide oxidation, and M_o is the molar mass of oxygen (in g mol^{-1}). The uncer-

tainties of the oxygen exchange capacities and rates were estimated using error propagation from the accuracies of the experimental analysis.

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