Design Principles of Perovskites for Thermochemical Oxygen Separation

Miriam Ezbiri,[a,b] Kyle M. Allen,[a] Maria E. Gálvez,[b] Ronald Michalsky,[b] and Aldo Steinfeld[b]

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 pO₂ gradient with low-grade process heat. Electronic structure calculations show that the activity of O vacancies in metal oxides points the ideal oxygen exchange capacity of perovskites.

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 (pO₂) 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 pO₂ using membranes relies on a stripping gas with even lower pO₂. 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 Cu₃O₂/CuO,[3a,8] Mn₃O₄/Mn₂O₃,[8] and CoO/Co₂O₃,[3a,9] utilizes low-grade process heat and does not require electricity. TSSOS has the potential to separate and concentrate O₂ at low pO₂ via temperature-swing.[3a] The current state-of-the-art TSSOS redox material, Cu₃O₂, has a maximum oxygen exchange capacity (ΔO₂), i.e., the difference in the oxygen non-stoichiometry between reducing and oxidizing conditions) of about 200 mmol O₂ per mol Cu₃O₂ exchanged at approximately 10 μmol O₂ min⁻¹ g⁻¹ when cycled between 1120–1450 K.[3a] We show below that Cu₃O₂ 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.[3a,c,10] The O₂ exchange capacity characterizes the trade-off between high energy conversion ef-
ficiencies 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 $\text{ABO}_3$ 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):

\[
\text{Oxide oxidation: } \text{ABO}_3 + \frac{1}{2} \text{O}_2(g) \rightarrow \text{ABO}_3 \\
\text{Oxide reduction: } \text{ABO}_3 \rightarrow \text{ABO}_3 + \frac{1}{2} \text{O}_2(g)
\]

Conceptually, O$_2$ is stripped from a gas mixture at low p$_{O_2}$ through oxidation of the perovskite at low temperatures. This yields as an output of the oxidation step an inert gas with a lowered p$_{O_2}$ while concentrated O$_2$ is evolved from the solid at an elevated temperature and increased p$_{O_2}$ 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/H or OH/OOH reaction intermediates to the catalyst surface controls the catalytic activity of the electrode surface.[10, 11] The ideal catalytically active 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$_{O_2}$ than the p$_{O_2}$ 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 ($\Delta G$) 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 oxidation 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$_2$O reference—but weakly enough to reduce the oxidized redox material at moderately higher temperatures—softer than the Cu$_2$O/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 in our analysis, this can be achieved with rare materials such as Rh$_2$O$_3$/RhO or toxic materials such as PbO/Pb$_2$O$_3$.[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 ($\Delta G(O)$) using density functional theory (DFT) for twelve perovskites that have attracted attention for solid-oxide fuel cells,[8, 9] air separation,[6c] and solar-thermal applications.[16] Stoichiometric $\text{ABO}_3$(010) and oxygen-deficient $\text{ABO}_3$(010) facets (A = Sr, Ba, or La; and B = 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 $\Delta G(O)$ 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$_2$, respectively.

We validated this descriptor-based design for metal oxide redox materials by means of dynamic O$_2$ exchange experiments using SrCoO$_{3-x}$, BaMnO$_{3-x}$, and BaCoO$_{3-x}$ synthesized via the Pecchini method[19] and commercial Ag$_2$O and Cu$_2$O as
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 O₂ exchange capacity and exchange rates were determined by thermogravimetric analysis (TGA).

Figure 2A and B display dynamic TGA runs for SrCoO₂₋₃, BaCoO₂₋₃, BaMnO₂₋₃, Ag₂O, and Cu₂O (initial stoichiometries) that were cyclically reduced at 900 K and 0.2 bar O₂ (simulating air) and oxidized at 600 K and 0.035 bar O₂ (simulating the composition of the gas phase from reducing ceria for solar-driven splitting of CO₂ and H₂O[19]). As expected, Cu₂O and Ag₂O oxidize and reduce strongly to CuO and Ag, respectively, essentially without exchanging O₂ reversibly. Compared to these reference materials, we find augmented O₂ exchange capacities for the perovskites. SrCoO₂₋₃ reaches a maximum O₂ exchange capacity of 44 ± 0.012 mmol O₂ per mol SrCoO₂₋₃ and a maximum O₂ exchange rate of 12.1 ± 0.003 μmol O₂/min gₚeroxivate⁻¹ whereas BaCoO₂₋₃ and BaMnO₂₋₃ perform at much lower capacities of 3.4 ± 0.015 and 0.5 ± 0.015 mmol O₂ per mol of perovskite and lower exchange rates of 0.8 ± 0.003 and 0.04 ± 0.005 μmol O₂/min gₚeroxivate⁻¹, respectively. As predicted by DFT, the performance of BaCoO₂₋₃ and BaMnO₂₋₃ appears limited by reoxidation and reduction, respectively. This theory-based screening of twelve perovskites identifies a well-known composition, SrCoO₂₋₃ that shows a significantly augmented performance for this novel application compared to the O₂ exchange capacities and rates of the reference materials at the same conditions. Additionally, with an O₂ exchange rate of 12.1 μmol O₂/min gₚeroxivate⁻¹, SrCoO₂₋₃ outperforms the state-of-the-art Cu₂O/CuO cycle, which cannot be used with low-grade process heat at 600–900 K and which has an O₂ exchange rate of only 10 μmol O₂/min gₚeroxivate⁻¹ (for both, oxide reduction and oxidation) at significantly higher—and thereby economically less attractive—temperatures of 1120–1450 K and comparable pO₂[20].

To support that the TGA data is indicative of reversible O₂ exchange, Figure 2C shows the perovskite lattice constants computed using data from HT-XRD analysis. Although all perovskites exhibit thermal expansion upon heating, only SrCoO₂₋₃ shows a major difference in the lattice expansion at varied pO₂, 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 SrCoO₂₋₃ is particularly suitable as a redox material for TSSOS. To understand how the oxide composition controls the O₂ exchange, Figure 3A plots ΔGv[O] versus the DFT-calculated bond length between the transition metal and the nearest O atom (dₚ₉,0) at ABO₃(010). Generally, we observe stable O vacancies (negative ΔGv[O] values) correlating with large dₚ₉,0 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-
tially due to the metal at the B-site interstices, the absolute value of $d_{O_v}$ is governed by the metal at the A site, as demonstrated by the consistently higher $d_{O_v}$ 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 $\Delta G_{[O]}$ versus the DFT-calculated partial charge $q_{O_v}$ of oxygen. We find that perovskites that form O vacancies easily contain weakly charged oxygen. BaCoO$_3$, for instance, accumulates less charge at the O anion than SrCoO$_3$ and BaMnO$_3$, which correlates with the facile reduction of BaCoO$_3$. Generally, $\Delta G_{[O]}$ scales with $q_{O_v}$ with the slope corresponding approximately to the ionization energy of oxygen, $-13.62$ eV per electron$^{[22]}$ and the intercept reflecting entropic contributions to $\Delta G_{[O]}$ 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 SrCoO$_3$(010) and BaMnO$_3$(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 BaMnO$_3$(010) relative to SrCoO$_3$(010). We note that this analysis describes the width of the 2p–3d gap for 3d transition metals at the B site of ABO$_3$ 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 O$_2$ exchange capacity of SrCoO$_3$ than BaMnO$_3$, 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 O$_2$ exchange capacity of a metal oxide, we have determined the O$_2$ exchange capacity for five metal oxides as the difference of the oxygen non-stoichiometry at equilibrium between O$_2$ evolution at 900 K and 0.2 bar $p_{O_2}$ and O$_2$ fixation at 600 K and 0.035 bar $p_{O_2}$ (Figure 4). The plot shows that the O$_2$ 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$_3$, 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 O$_2$ exchange capacity of metal oxides.

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 O$_2$ separation. The defect chemistry of several perovskite families, including LaNiO$_{1.5}$, with a relatively high mobility of O interstitials, has been investigated previously.$^{[23]}$ In these perovskites excess oxygen is incorporated as interstitial O$^{2-}$ 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$_3$.$^{[24]}$ A low Frenkel energy may yield high O vacancy concentrations, in PrBaCo$_2$O$_5$, 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 O$_2$ exchange capacity of metal oxides and perovskites in particular. The computations were validated through dynamic O$_2$ exchange experiments using Ag$_2$O, Cu$_2$O, 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$_{2.5}$ was identified as an ideal material for solar-driven thermochemical separation of O$_2$. 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, O$_2$, and their reduction products was determined at...
the specified $p_O_2$ and temperatures from tabulated free-energy data, with an absolute accuracy of 1–10 kJ mol$^{-1}$.[11,12] Per convention, negative free energy differences mark exergonic reactions. At the computed conditions, the correlations of $\Delta G$ and $\Delta H_m$ for the metal oxide reduction and oxidation 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.[13] 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 linearized Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was employed to optimize the atomic geometries until the maximum force was less than 0.05 eV Å$^{-1}$. 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 x 4 x 4. Compositions containing Mn, Co, or Ni were modeled using spin-polarized calculations and, to avoid remniscent 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 constant lattice constants within ±0.36–3.89% 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.[29] 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 Å of vacuum perpendicular to the surface. The Brillouin zone of surface models (slabs) was sampled using 4 x 4 x 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$_2$B$_2$O$_6$(010) and A$_2$BO$_5$(010) stoichiometry, marked with the conventional ABO$_3$(010) and ABO$_2$(010) notation, respectively. The free energy of forming O vacancies ($\Delta G_v(\text{O})$) at the surface was computed as follows (Eq. (3)):

$$\Delta G_v(\text{O}) = G_v - (G_v^{\prime} - G_v^{\prime})$$

(3)

where $G_v$, $G_v^{\prime}$, and $G_v^{\prime}$ 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 difference of stable H$_2$O 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$_3$ (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[16] 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$_{2.5}$, BaCoO$_{2.5}$, and BaMnO$_{2.5}$, were synthesized using a modified Pecchini method, employing stoichiometric amounts of Mn(NO$_3$)$_2$·4H$_2$O (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$_2$H$_5$O (Alcosuisse, 96.1%), and C$_6$H$_5$O (Fluka, > 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$_{2.5}$ and BaCoO$_{2.5}$ or in pure O$_2$ at 1273 K for 48 h (BaMnO$_{2.5}$). To achieve the desired oxygen site density, the sintered SrCoO$_{2.5}$ was ground, fully immersed in NaClO (Migros, < 5% in H$_2$O), washed with deionized water, and subsequently dried for at least 2 h at 473 K. Ag$_2$O (Merck, >99%) and Cu$_2$O (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$_\alpha_1$ radiation (20–80° 2θ, 0.06 min$^{-1}$ scan rate, 45 kV/20 mA output, PANalytical/X’Pert MPD/DY636, Philips). The original oxygen content of the perovskites was SrCoO$_{2.5}$, BaCoO$_{2.5}$, and BaMnO$_{2.5}$ before the redox cycling, as determined using TGA (STA 409/C3, 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 P$_{O_2}$ and thereafter oxidized by cooling from 900 to 600 K in 100 K intervals at 0.035 bar P$_{O_2}$. 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$_2$O$_3$ crucible supported with an Al$_2$O$_3$ rod on the microbalance of the TGA (±0.1 μg). 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 P$_{O_2}$, which was adjusted by mixing O$_2$ (99.5%, Messer) and N$_2$ (99.999%, Carbagas) using three electronic mass flow controllers (MFC400, Netzsch; accuracy ± 1%, precision ± 1 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 (±1 K). Heating and cooling was performed at +10 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 ($\delta_{\text{red}}$) and after the oxide oxidation ($\delta_{\text{ox}}$):

$$\Delta \delta = \delta_{\text{red}} - \delta_{\text{ox}} = (m_{\text{ox}} - m_{\text{red}})M_0^{-1}$$

where $m_{\text{ox}}$ and $m_{\text{red}}$ are the metal oxide mass (in g, determined using TGA), after the oxide reduction, and after the oxide oxidation, and $M_0$ 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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