# Demonstration of thermochemical oxygen pumping for atmosphere control in reduction reactions

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## ARTICLE INFO

## ABSTRACT

Solar thermochemical cycles as a means to produce fuels such as hydrogen, carbon monoxide, or syngas using a metal oxide as oxygen carrier offer a promising route to the efficient conversion and storage of solar energy. Even though the theoretical potential of such cycles can be very attractive, many challenges for reaching high process efficiencies remain unsolved. One challenging aspect is the parasitic energy cost for maintaining low partial pressures of oxygen during the reduction step. As previously proposed by the authors, thermochemical oxygen pumps have the theoretical potential to maintain low partial pressures of oxygen at considerably lower energy costs than conventional mechanical pumps. The work presented here demonstrates the proof of concept of thermochemical oxygen pumping. The reduction extents of a metal oxide after temperature swing experiments are analyzed for test runs with and without thermochemical oxygen pumping, clearly showing higher reduction extents for the former cases. The effects of different operational parameters on the reduction of the metal oxide are investigated and options for reduction extent enhancement are depicted.

## 1. Introduction

Conversion of solar energy into chemical energy is an appealing alternative to direct electricity generation due to the possibility of long term storage of the chemical energy carriers and their applicability in the transportation sector (Contreras et al., 1997; Romero and Steinfeld, 2012). Solar-thermochemical routes target the production of hydrogen, carbon monoxide, combinations of both – also called syngas – and further processed products, so-called solar fuels (Nakamura, 1977). These routes convert heat directly into chemical energy and are therefore promising technologies with theoretically high conversion efficiencies (Steinfeld, 2005). Even though considerable progress has been made in the last years, the demonstrated efficiencies are still well below the theoretical potential and several challenging tasks have to be solved before a chemical energy carrier at competitive costs can be produced with these concepts (Agrafiotis et al., 2015; Bulfin et al., 2017; Marxer et al., 2017).

Redox cycles for the production of solar fuels can consist of two or more steps at different temperatures and/or oxygen partial pressure levels. The reduction extent of the redox material, which plays a key role for the yield of solar fuels, can be increased by a raise in temperature or a decrease in oxygen partial pressure during the reduction step.

One redox material widely studied (Abanades and Flamant, 2006; Call et al., 2015; Lapp et al., 2012; Muhich et al., 2013; Panlener et al., 1975) and often considered for two step water or carbon monoxide splitting is ceria ($CeO_{2-\delta}$). In this work, we focus on ceria as a redox material, as there is a high amount of data available to compare our data with. However, the basic underlying principle is applicable to many other non-stoichiometric and stoichiometric multivalent oxides, including perovskites (McDaniel et al., 2013; Orfila et al., 2016; Scheffe et al., 2013).

The high temperatures, typically up to 1500 °C, and/or low oxygen partial pressures required to reach a substantial reduction extent in ceria are challenging with respect to process engineering. The temperature of the reduction step cannot be raised indefinitely due to the onset of evaporation in ceria (Knoblauch et al., 2017), due to construction material challenges and due to increased heat losses. Alternatively, lowering the oxygen partial pressure also increases the driving force for the generation of oxygen vacancies in the ceria lattice. This can be achieved by means of sweep gas purging or by lowering of the total pressure. As studies have shown, both approaches are related to significant energy penalties mainly related to sweep gas purification in the first case and pumping efficiencies at low pressures in the second case (Bader et al., 2013; Brendelberger et al., 2015, 2017; Brendelberger and Sattler, 2015; Ehrhart et al., 2016; Ermanoski et al.,

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2013; Lin and Haussener, 2015). Therefore, partial pressures of oxygen seem to be limited for these technologies to values above 1 mbar. Lately another approach was proposed by the authors: thermochemical oxygen pumping (Brendelberger et al., 2017).

Thermochemical oxygen pumps offer the advantage of potentially low energy costs for the removal of oxygen at low oxygen partial pressures. The working principle of such thermochemical oxygen pumps is also based on a redox material like in two-step thermochemical splitting cycles. A metal oxide is reduced at high temperature and/or low oxygen partial pressure and in second step re-oxidized (Brendelberger et al., 2017). In contrast to materials for splitting cycles, in the re-oxidation step the metal oxide directly absorbs oxygen. In the following, we refer to the material capable of splitting an oxidizer (water or carbon monoxide) as *splitting material* (SM) and to the material used for oxygen absorption as *pumping material* (PM). As the PM does not actually need to split an oxidizer but absorbs oxygen directly, it is possible to use a material with lower $\Delta G^0$ than for the splitting material, allowing reduction at lower temperatures or higher oxygen partial pressures and with lower energy input. Typically, these materials also have a higher oxygen storage capacity than ceria under the same conditions.

The range of redox materials applicable for oxygen pumping is broad. Binary oxides such as cobalt oxide (Agrafiotis et al., 2014) may be used as well as phosphates (Aoki et al., 2017) or other perovskites. Among the perovskites, different transition metals can be used in order to adjust the oxygen affinity of the reduced perovskite during the oxidation step, or the reduction temperature and oxygen partial pressure. It is possible to tune the redox properties of perovskite materials by tuning their composition through solid solution formation. As recently demonstrated by the authors, $A(Mn,Fe)O_{3-\delta}$ perovskites with an alkali earth metal on the A site are excellent air separation materials and show oxygen storage capacities tunable by adjusting the Fe content (Vieten et al., 2016, 2017). Fe-rich alkali earth metal perovskites are easier to reduce and can store more oxygen at lower pressures, but Mn-rich alkali earth metal perovskites show a higher oxygen affinity in the reduced state, thus allowing to reach lower oxygen partial pressures.

For the absorption of oxygen the PM will be operated at a temperature significantly lower than the reduction temperature of the SM. With respect to the process efficiency it will be especially interesting to use a PM that can be reduced in an air atmosphere using waste heat from the low temperature splitting step. The use of thermochemical oxygen pumps might open up a path to reach lower partial pressures during the reduction of the SM at significantly lower energy demand, and by this increase the process efficiency.

In this study the working principle of a thermochemical oxygen pump will be demonstrated by showing an increase of reduction extent of a SM by the use of a PM. Further, the effects of different operational parameters are measured and discussed.

## 2. Experimental setup

The main features of the test rig are the two horizontal tube furnaces with alumina reaction tubes in each of the furnaces. The reactive materials are placed in the middle of the tubes in ceramic crucibles. Both tubes are connected to an arrangement of vacuum tight metallic tube elements and valves. Further components are a vacuum pump, pressure gauges, thermocouples, mass flow controllers and an oxygen sensor. A scheme of the test rig is shown in Fig. 1.

The first tube furnace, model STF 16/180 from CARBOLITE GERO with a 301 PID controller, is used to heat the SM. In the following this furnace will be called splitting furnace (SF). A type S thermocouple is used to monitor the temperature. It is placed in a second alumina tube next to the reaction tube inside the furnace. During the experiments the SF is operated at temperatures between 1000 °C and 1500 °C.

The second furnace, model REST E230/3 from GERO, heats the pumping material and will be called pumping furnace (PF). Also here

an additional thermocouple is used to monitor the temperature during the experiment. Since the temperatures in the PF are kept between 650 °C and 700 °C a type K thermocouple is used in the PF.

The reaction tubes in both furnaces are made out of alumina and have an inner diameter of 25 mm. The metallic tube elements are made out of stainless steel and have KF flanges in the section between the two furnaces with DN25 and in the section of the gas inlet with DN16. The evacuated section has a total volume of 1501 cm$^3$. In the non-evacuated sections Swagelok fittings and valves are used.

The vacuum pump is a rotary vane pump of the model RZ 5 from VACUUBRAND which can reach an ultimate vacuum pressure of about $5 \cdot 10^{-4}$ mbar. For pressure measurement a capacitance manometer CDG020D from INFICON is used. The model allows recording pressures between $5 \cdot 10^{-3}$ mbar and 10 mbar with an accuracy of 1%. In addition, a bourdon tube pressure gauge from LEYBOLD AG is used to optically monitor the evacuation and venting progress.

For the oxygen measurement a lambda sensor with a measuring chamber (L-probe with MK) and a power supply (NTV44P) from MESA GmbH are used. The sensor has a measuring range between 21% and $1e-26\%$[1]. The wide range of concentrations is divided into 4 segments, each of which can make use of the full output signal voltage to allow accurate measurement in the relevant range (5% to $1e-3\%$).

Two flow controllers from MKS INSTRUMENTS are used: one for Argon with a maximum value of 3.378 Pa m$^3$/s (2000 sccm) and one for Oxygen with a maximum value of 0.1689 Pa m$^3$/s (100 sccm). A data acquisition system is used in combination with a LabVIEW program to visualize and store the sensor readings throughout the experiments.

Ceria is used as SM which is supposed to split water or carbon monoxide in the targeted application (see top of Fig. 2). The material is used in form of particles with diameters in a range between 212 μm and 500 μm. Details about the particles can be found in Grobbel et al. (2017). The ceria particles are poured into an alumina crucible which is placed in the reaction tube at the centre of the SF.

The PM consists of the perovskite oxide $SrFeO_3$ in form of granules (see bottom of Fig. 2). $SrFeO_3$ is used as a simple prototype material, as its redox properties are well-studied and it can be prepared relatively easy on a larger scale (Marek et al., 2018; Vieten et al., 2016, 2017). It has a comparatively low reduction temperature and a strong oxygen affinity. Based on the $SrFeO_3$ structure, other redox materials could easily be prepared in the future in order to tune their oxygen affinity and redox enthalpy. For instance, perovskites containing Mn or Ti could be used to obtain lower oxygen partial pressures at the expense of higher redox enthalpies, whereas an increase in Co content can have the opposite effect (Bulfin et al., 2017; Ezbiri et al., 2015; Vieten et al., 2018). As the choice of an ideal redox material depends on the application, this study's objective is to deliver a first proof of concept using $SrFeO_3$ as a well-known prototype material. Further details about the properties of the material can be found in Vieten et al. (2017). The $SrFeO_3$ granules are placed in an alumina crucible in the centre of the PF reaction tube.

## 3. Experimental methods

The main objective of the experimental campaign is to demonstrate an increase in reduction extent of the SM during a temperature swing cycle caused by the use of a PM. As a reference case the reduction extent of the SM is determined applying the same experimental procedure but without the use of a PM. The reduction extent of the SM is deduced from the amount of absorbed oxygen during the re-oxidation of the SM. Thereto a defined stream of oxygen and argon is lead through the SF and the oxygen concentration is monitored at the outlet of the SF. The oxygen concentration signal response of the system at the outlet to a step function in oxygen concentration at the inlet is delayed and

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[1] https://www.mesa-international.de/en/l-probe/.