Perspectives of Perovskites for Solar Thermochemical Splitting of CO₂ or H₂O Molecules

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Solar thermochemical splitting cycles (TSCs) are a promising technology for producing renewable hydrogen, or hydrocarbon fuels, from a feedstock of H₂O, or H₂O and CO₂, and solar energy. At present, perovskite materials have been only investigated in isolation for potential use in high-temperature two-step TSC. Their ability in isolation to gain or lose oxygen at different temperatures and their heating duties for CO₂ or H₂O are not satisfactory arguments in favor of or against the specific use. The design, prototyping, and testing of a specific solar receiver/reactor for the production of CO or H₂ are necessary to prove the technology.

1. Introduction

Perovskite compounds are materials with a crystal structure similar to that of natural perovskite. The general chemical formula is ABX₃, with A and B being cations and X an anion bonding the cations. Perovskite compounds have a wide range of properties and applications. Since the invention of perovskite solar cells, there has been considerable interest in perovskites for energy applications. One of them is the solar thermochemical splitting of the CO₂ (or H₂O) molecule, to produce CO (or H₂) and O₂. Most fundamental works have been performed so far, with only very few demonstration plants described in the literature. Two-step thermochemical splitting cycles (TSCs) based on metal oxide redox reactions include an endothermic reduction of the metal oxide into a reduced-valence metal oxide plus oxygen using energy. This is followed by exothermic oxidation of the reduced metal oxide with CO₂, which yields CO together with oxygen and the initial metal oxide. The metal oxide is then recycled. In two-step cycles, the metal oxide is first reduced according to

\[ 1/\Delta \delta \times M_x O_y - \delta_{\text{ox}} \rightarrow (1/\Delta \delta) \times M_x O_y - \delta_{\text{red}} + 1/2 O_2 \]  

\[ (1/\Delta \delta) \times M_x O_y - \delta_{\text{red}} + CO_2 \rightarrow (1/\Delta \delta) \times M_x O_y - \delta_{\text{ox}} + CO \]  

\[ 2CO_2 \rightarrow CO + 3/2O_2 \]  

where \( \Delta \delta = \delta_{\text{red}} - \delta_{\text{ox}} > 0 \) is the change in the oxygen nonstoichiometry in the metal oxide, where \( \delta_{\text{red}} \) is the nonstoichiometry in the reduced state and \( \delta_{\text{ox}} \) is that in the oxidized state. In the second step, the reduced metal oxide is oxidized with CO₂

2. Results and Discussions

Various volatile and nonvolatile metal oxides, such as ZnO, SnO₂, Fe₂O₃, NiO, CeO₂, doped ceria (such as CZH materials), samarium and erbium oxide, and finally perovskites, have been proposed for the solar TSC.

Volatile metal oxides (MOs) are highly speculative solutions. Nonvolatile MOs are more likely to result in a product. Only in a very few cases attempts have been made to demonstrate the techniques with a solar concentrator plus reactor integrating the chemical reactor. In most cases, only basic activities have been performed on the material. The most valuable demonstrations have been attempted with nonvolatile MOs.

Solar reactors for effecting this cycle include cavity receivers with rotating or stationary structures, glass dome reactors, aerosol flow reactors, particle reactors, and moving and fluidized bed reactors.

The most promising receiver/reactor designed to date is the cavity receiver containing a reticulated porous ceramic (RPC) foam made of pure CeO₂. A schematic of the receiver/reactor is proposed in Figure 1. The RPC was directly exposed to concentrated thermal radiation at mean solar flux concentration ratios of up to 3015 suns. During the endothermic reduction step, solar radiative power inputs were in the range of 2.8–3.8 kW. The reactor temperatures were 1400–1600 °C. This produced CeO₂₋₋ δ with oxygen deficiency δ ranging between 0.016 and 0.042. During the subsequent exothermic oxidation step, reactor temperatures below 1000 °C, CeO₂₋₋ δ stoichiometrically reoxidized with CO₂. This oxidation resulted in the generation of CO. The design was preliminary. The solar-to-fuel energy conversion efficiency is defined as the ratio of 1) the product of the higher heating value (HHV) of the CO produced by the CO mass flow rate, to 2) the sum of the solar
During oxidation.

The activity was followed only and lack of performance and durability.

This is only one production was possible over a small number of hours because of the decay of the characteristics and properties of the RPC.

Current solar receiver/reactors have a low technology readiness level (TRL), and lack of performance and durability. Thus, although perovskites should not be judged only based on their ability in isolation to gain or lose oxygen at different temperatures, but based on their use in a device, it must be noted that the device in Figure 1, even if a giant step forward in the demonstration of the technology, is not yet a satisfactory design for the benchmark of different materials.

Regarding perovskites, no receiver/reactor has been designed, prototyped, and tested so far featuring this material. Thus, all the information available is based on computations or experimental material properties in isolation.

From a purely theoretical point of view, perovskites have the advantage of high CO (or H₂) production capacities under large CO₂ (or H₂O) flow rates. Although this could be exploited in the material of a solar receiver/reactor, it is not the only property of the material of relevance for the specific application. Only a few of the many options to build perovskites for the solar thermochemical splitting of the CO₂ molecule have been explored, and the field is still untapped.

The high CO production capacities under large CO₂ flow rates have been highlighted, for example. This is only one example of the many supporting the view of a higher than CeO₂ production of CO performing the two-step cycle with a sample of perovskite oxide material. For unsupported perovskite oxides Laₓ₂₋ₓFeₓ₂₋ₓO₁₉ (A = Sr, Ce; B = Co, Mn), the release of O₂ started at 800 °C and the largest O₂ production was 11.8 mL/g perovskite at 1300 °C. Despite the promising O₂ production at a low reduction temperature, the CO production was less than the reference CO production of 4.5 mL/g for CeO₂ with reduction at 1400 °C.

Jiang et al. claimed improvements obtained by using ZrO₂, Al₂O₃, and SiO₂ supports, with the best results with the SiO₂ supports. LaFe₀.₃Co₀.₇O₃ (25 wt%)/SiO₂ exhibited the highest reaction activity among the investigated perovskite oxides. The CO production was 7.6 mL/g material⁻¹ (30.4 mL/g perovskite⁻¹) with a reduction of the sample at 1300 °C. The activity was followed only over ten cycles of the reaction, which is not enough to prove stability. The authors did not fully explain the reasons for the observed differences.

Thus, perovskites in theory may have higher production capacities than other materials (such as ceria oxides). However, their superior performance in terms of oxygen capture from the splitting of the CO₂ (or the H₂O) molecule gathered from basic material analyses is difficult to translate into a better receiver/reactor. According to Muhich et al., perovskite heating duties for CO₂ (or H₂O) outweigh their higher production capacities. This work is a simple thermodynamic analysis for a solar thermochemical plant for syngas generation via H₂O/CO₂ splitting redox cycles. Of all the materials considered in Muhich et al., the solar-to-fuel energy conversion efficiency was higher in relative order Zr-doped CeO₂ > undoped CeO₂ > La₀.₆Ca₀.₄MnO₃ > La₀.₆Ca₀.₄Mn₀.₆Al₀.₄O₁ > La₀.₆Sr₀.₄MnO₃ > La₀.₆Sr₀.₄Mn₀.₆Al₀.₄O₁.

The ordering is a result of the relative reducibility and oxidizability. Doped and undoped ceria favor oxidation. Conversely, perovskites favor reduction. Thus, perovskites require high flow rates of excess H₂O and CO₂ during oxidation.

Solid–solid heat recuperation during the swing of temperature between the redox steps is critical for ceria because of its low specific oxygen exchange capacity per mole and cycle. Gas–gas heat recuperation is conversely more critical for the perovskites due to the considerable excess of H₂O/CO₂.

The thermochemical two-step splitting process for the CO₂/H₂O molecule uses a first higher temperature endothermic step in an inert gas and a second lower temperature exothermic step with CO₂/H₂O. The ability to capture and release oxygen is crucial, same as rapidity to reach the optimum operating temperatures.

The result of Muhich et al. is basic redox material thermodynamics and not the performance of a receiver/reactor.
specifically developed to take advantage of the different properties of one material or the other. According to previous studies,[16–47] perovskites are a promising redox material for the thermochemical splitting of the CO2 (or H2O) molecule, potentially better than competitor materials. According to others, such as Muhich et al,[25] Zr–CeO2 is the most promising redox material, better than perovskites, as perovskites only “seem promising” due to high H2/CO production capacities under large H2O/CO2 flow rates, but then they perform poorly from an efficiency perspective due to the high heating duties, especially for steam. Although this conclusion could be changed by changing the particular perovskite or changing the modeling assumptions, it must be stressed once more as the best material for the application here considered should not be defined in isolation.

Details of the specific receiver/reactor design are fundamentals to assess the performance of one material versus that of others, as the ability to gain or lose oxygen at different temperatures is not the only property of concern of one material, same as the heating duties for CO2 (or H2O). Thus, what is needed is to develop a receiver/reactor for a two-step perovskite cycle to capitalize on the advantages perovskites have over competitor materials while minimizing the downsides.

Receiver/reactor designs in general are only preliminary, and specifically for perovskites practically never attempted so far. Thus, the problem now is to design a solar thermochemical device that may produce CO (or H2) and O2 with only feedstock CO2 (or H2O) plus sun energy with a two-step TWS based on specific perovskites. If this device could show not only advantages versus devices based on competitor materials, but also advantages versus other alternatives such as lower temperature three-step TWS with other materials with continuous concentrated solar energy input downstream of a conventional receiver and thermal energy storage,[66] or even electrolysis from photovoltaic electricity, which is ultimately the reference technology for green hydrogen,[67] then the technology will be of value in the transition to the hydrogen economy.[68–70]

3. Conclusions

Regarding the techno-economic expectations, there are estimations for hydrogen more than CO. The levelized cost of hydrogen (LCOH) predicted in Moser et al.[71] for ceria oxide two-step cycles is 6.68 $/kg H2 (8.05$/kg H2) in the best-case scenario. As a benchmark comparison with PV-electrolysis cost,[72] high-efficiency solar cells connected to electrolyzers are predicted to permit the production of hydrogen at 5.9$/kg H2, while the cost of hydrogen from conventional silicon photovoltaic solar farms and electrolyzers is rated at 4.9$/kg H2.

Future costs of green hydrogen from solar photovoltaic electricity and electrolyzers are now estimated at 1.5–2$/kg H2 by 2025/2030,[73,74] slightly above the cost of hydrogen from steam reforming of methane at 1.25$/kg H2 in the hypothesis of cost of natural gas of 3$ per thousand cubic feet. Similar prices by 2030 are predicted for solar hydrogen from the thermochemical splitting of the water molecule using lower temperature three-step schemes,[73] albeit at the price of more intense further research and development.

Conflict of Interest

The author declares no conflict of interest.

Keywords

CO production, H2 production, perovskites, thermochemical splitting cycles

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