

REVIEW

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Challenges and perspectives for solar fuel production from water/carbon dioxide with thermochemical cycles

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Abstract

Solar energy is the most sustainable alternative to fossil fuels. The production of solar thermochemical fuels from water/carbon dioxide not only overcomes the intermittent nature of solar energy, but also allows for flexible transportation and distribution. In this paper, the challenges for solar thermochemical H₂/CO production are reviewed. New perspectives and insights to overcome these challenges are presented. For two-step cycles, the main challenges are high temperatures, low conversions and the intensive oxygen removal work. Theoretically feasible temperature and pressure ranges are needed to develop reactant materials. The fundamental mechanism to reduce the temperature and the potential to improve the efficiency by minimizing the oxygen removal work need be revealed. Various material modification strategies and advanced reactors are proposed to improve the efficiency by reducing the temperature and enhancing heat transfer process. But the oxygen removal work required has not been minimized. For multi-step cycles, the main challenges are the separation of corrosive acid and insufficient reaction kinetics. For the separation of acids, many methods have been proposed. But these methods require extra energy and causes undesired side reactions or byproducts. The reaction kinetics have been enhanced by improving catalysts with noble materials or complex fabrication methods. Developing novel multi-step cycles using metal oxides, hydroxides and carbonates may be promising.

Keywords Solar energy, Thermochemical cycle, Solar fuel, Efficiency

1 Introduction

Renewable energy resources are most promising sustainable alternatives to the fossil fuels and are attracting growing attention globally due to increasing climate change [46, 189]. Among different kinds of renewable energy, e.g., solar, wind, water, tidal, geothermal, biomass, solar energy is most abundant and prevalent [24, 115]. The incident solar energy on the surface of the Earth is over

1.3×10^5 TW, which is roughly four orders of magnitude larger than the predicted global energy consumption rate, i.e., ~16.9 TW in 2013 [163]. Moreover, solar energy is attractive with the market and the political stabilization. However, the intermittent nature of solar energy limits its capability of providing continuous power supply. In order to overcome the limitation of intermittence, solar energy can be stored in the form of fuel and heat [45, 173]. Solar fuel, as a stable chemical form for both short- and long-term storage, can be transported and distributed flexibly (see Fig. 1) [173]. The application of the solar fuel is also flexible. Solar H₂ and CO cannot only be used directly as the fuel of power sources but also as feedstocks for other chemicals including methanol, ammonia and other carbon-based fuels [114, 133, 143].

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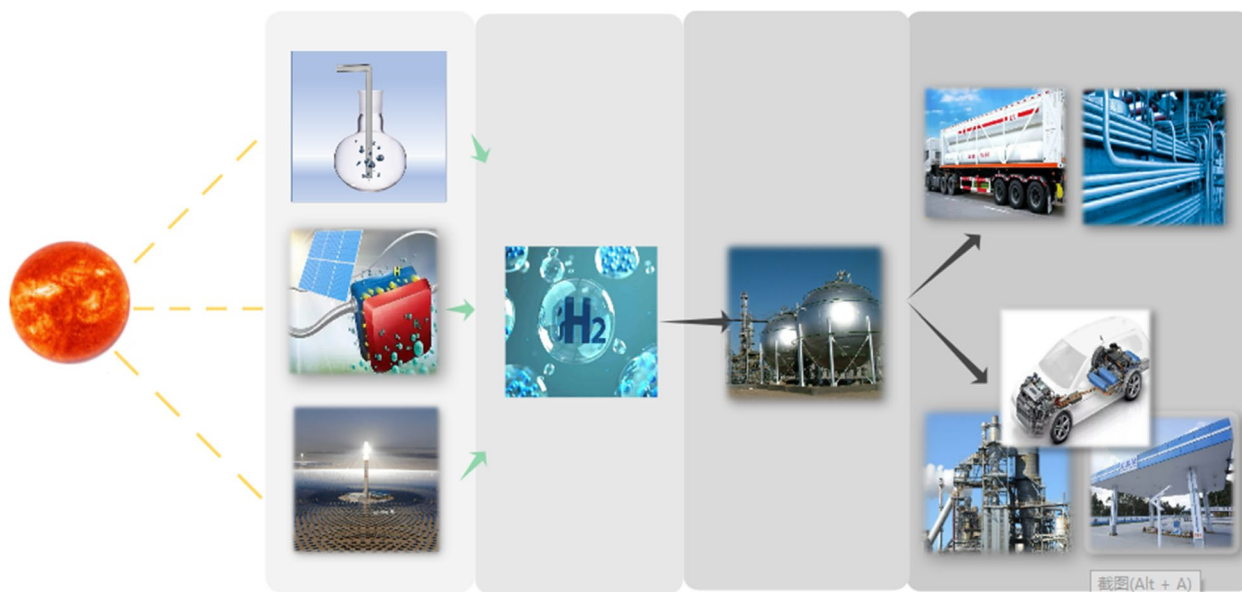


Fig. 1 Flexible paths by introducing solar fuel in the solar energy utilization

The process to produce solar fuel can be viewed as a chemical reaction with reactants of either H₂O or CO₂. Figure 2 shows the reaction process that converts solar energy into solar fuel. Sunlight (photochemical), electricity (photovoltaic), and heat (thermochemical), collected or converted from solar energy, act as the driving force for the reaction [170]. Among the methods, the photovoltaic has been studied extensively and used as an efficiency benchmark for alternative solar-driven

fuel production [132]. While the practical photovoltaic efficiency is impressive, the solar thermochemical pathway using concentrating solar power exhibits a higher theoretical efficiency potential [127, 175, 191]. The higher efficiency potential stems from the fact that more portions of solar resource can be converted to heat an endothermic chemical reaction [175]. Recently, photothermocatalysis is also interesting due to the combination effects on the electronic structure of the catalyst

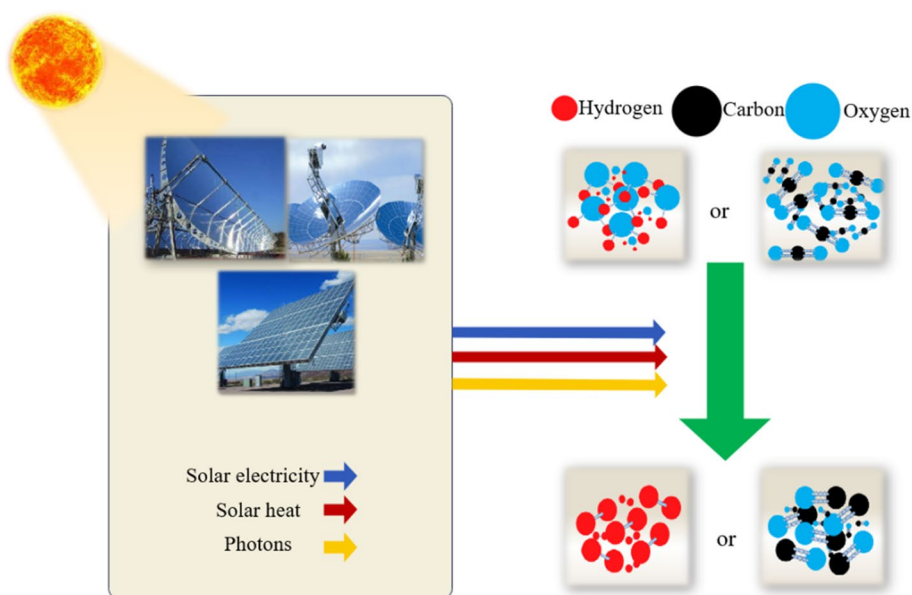


Fig. 2 Reaction process to convert solar energy into solar fuel

and the adsorption state of the reaction species in the catalytic process [119, 203]. However, the operating conditions, i.e., reaction temperature, solar irradiation and wavelengths of different catalytic system, are difficult to be adjusted for a desired performance.

Numerous thermochemical cycles have been investigated to produce H₂ or CO, which can be categorized into two-step and multi-step cycles based on the number of steps. The reaction temperature of the two-step cycle is higher than that of the multi-step cycle. With several decades of research and development, the solar thermochemical fuel production technology still has not been commercially viable. There are two limits, i.e., low efficiency and high cost [54]. Although using full solar spectrum is very promising with a high theoretical conversion efficiency (over 20%) [108], while the state-of-the-art efficiency of the practical solar thermochemical cycle is limited ~5% [129]. The cost of solar fuel production system is associated with feedstocks, the main components of systems, and the balance of system (BoS) expenses, operating costs, and solar energy conversion efficiency. Currently, the estimated leveled cost of hydrogen of the solar thermochemical cycle varies between 3 and 15 \$/kg H₂ [153, 177], while commercial steam methane reforming (SMR) and coal gasification (CG) are much more cost-effective with a LCOH of 1.93–2.26 \$/kg H₂ and 2.24–2.68 \$/kg H₂, respectively [148]. In order to breakthrough these limits, a comprehensive review on solar thermochemical fuel (H₂/CO) production is necessary. In this review, solar thermochemical cycles, including two-step cycle and multi-step cycle, are reviewed from reactions to reactors, as well as the system. The specific technical challenges in solar thermochemical cycles are revealed and discussed, and thermodynamically favorable ways of improving solar thermochemical systems are discussed.

2 Solar concentrators

Solar concentrators are the prerequisite of the solar thermochemical cycle. Categorized by the type, there are four primary configurations, i.e., Parabolic Trough Collector (PTC), Linear Fresnel Reflector (LFR), Parabolic Dish Systems (PDS) and Solar Power Tower (SPT). Figure 3 shows the schematics and corresponding pictures of the four configurations [198, 204].

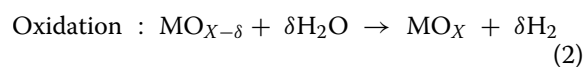
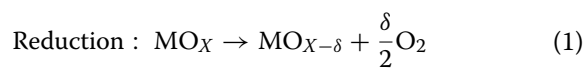
As shown in Fig. 3, the Parabolic Trough Collector (PTC) has parabolic reflector focusing sunlight to the absorber which is mounted in the focal line of the parabola [89]. The Linear Fresnel Reflector (LFR) has long rows of flat or slightly curved mirrors to reflect the sunlight onto a downward facing linear receiver [206]. The Parabolic Dish Collector (PDC) concentrates the sunlight at a focal point mounted above the center of a

parabolic-shaped dish [21]. The PDC including the dish and receiver must track the sun on a two-axis tracking system to maintain light convergence at its focal point [22]. The Solar Power Tower (SPT) has a field of heliostats reflecting and concentrating the sunlight onto a central receiver placed in the top of a fixed tower. Here, heliostats are flat or slightly concave mirrors tracking the sun during the day. Due to the different mechanisms, the four configurations have different operating temperature ranges, concentrations, and costs. Table 1 lists the properties of the four configurations [22].

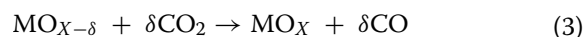
As listed in the Table 1, SPT and PDC have relatively higher concentration ratios. That is because both SPT and PDC are point-focus systems, which can achieve higher concentration ratios with complex and expensive two-axis solar tracking [198]. On the other hand, PTC and LFR are line-focus systems that have lower concentration ratios with simpler, less expensive one-axis solar tracking [206]. Since the operating temperature is determined by the concentration, SPT and PDC can supply the heat required for high-temperature thermochemical cycles (>1000 K). In addition, SPT is anticipated to be feasible for large scale high-temperature solar thermochemical cycles, as SPT is able to achieve an even higher operating temperature with a lower cost.

3 Two-step cycle

The two-step thermochemical cycle mostly operates between the oxidized and reduced state of a metal oxide, which is expressed as:



Or



The endothermic reduction reaction proceeds at a much higher temperature than that for exothermic oxidation. Although there are other two-step cycles involving sulphates, e.g., MnO/MnSO₄, FeO/FeSO₄, and CoO/CoSO₄ [4], the sulphates is not popular due to the demand for the gaseous products separation of SO₂ and O₂. A large number of metal oxides have been proposed for thermochemical cycles. Based on whether the metal oxides remain in the condensed state or not, metal oxides can be categorized as the volatile and the non-volatile [127]. Based on

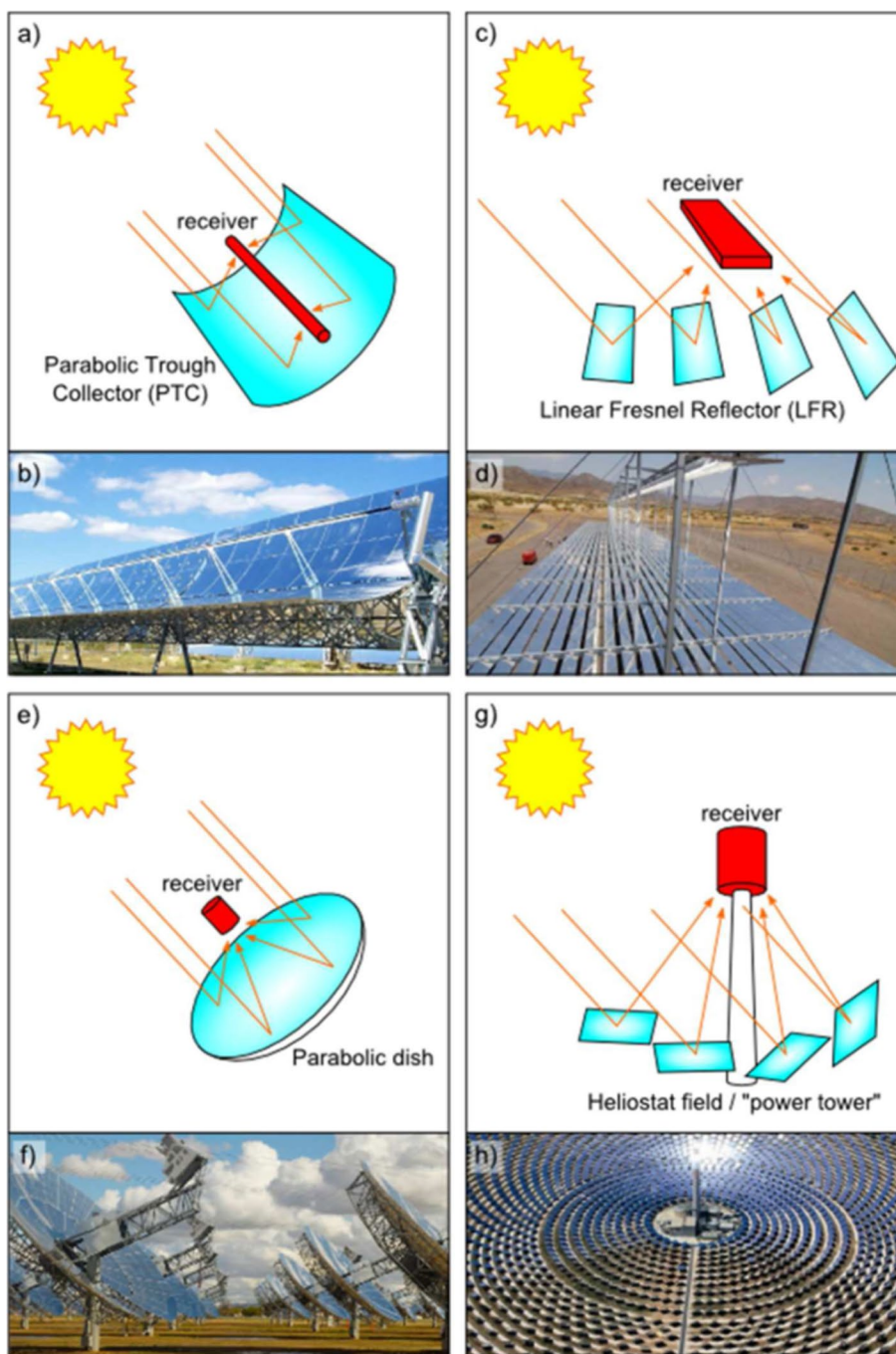


Fig. 3 Four configurations of the CSP technologies [198]

the reduction mechanism, the non-volatile metal oxides can be further classified to be the stoichiometric, and the non-stoichiometric. The stoichiometric metal oxide is reduced to a lower-metal-valence oxide or the respective metal, while the non-stoichiometric metal oxide is reduced partially [131]. The non-stoichiometric metal oxides are non-volatile due to a relatively high structural

and crystalline stability at high temperatures [35, 77, 100, 131]. Figure 4 shows the category.

3.1 Volatile metal oxide

Most volatile metal oxide cycles including ZnO/Zn [27, 101, 107], Loutzenhiser, P. G. et al. 2010; [197], SnO₂/SnO [1, 5] and GeO₂/GeO [96] all operate at temperatures

Table 1 Properties including operating temperature, relative cost, and concentration ratio of the four configurations [22]

| Type | Operating temperature range (°C) | Cost | Concentration ratio |
|------|----------------------------------|-----------|---------------------|
| SPT | 300–2000 | High | 150–1500 |
| PTC | 50–400 | Low | 15–45 |
| LFR | 50–300 | Very low | 10–40 |
| PDC | 150–1500 | Very high | 100–1000 |

higher than 1700 K. However, the volatile cycle requires a high-temperature separation method, e.g., quench [20, 59, 146, 149, 159], to prevent products recombination, which strongly lowers the conversion and efficiency. The majority of the high-grade thermal energy is lost through the separation method.

The reduction of ZnO at 1 atm cannot proceed spontaneously until the temperature reaches ~ 2300 K (corresponding $\Delta G^\circ = 0$) [101]. Although lower pressures and/or a carrier gas can shift the thermodynamic equilibrium to favor the reaction at lower temperatures, the reduction reaction temperature is still above ~ 1700 °C [27], Loutzenhiser, P. G. et al. 2010). SnO₂ has a lower reduction temperature ~ 1600 °C [1, 5, 158]. The conversion rate of SnO₂ reduction is high and less dependent on the quenching rate than that of ZnO because of a narrower gap between reaction temperature and SnO condensation temperature [5]. GeO₂/GeO cycle [195], also referred as KIER 4, has a potential lower reduction temperature 1400–1800 °C. But the research on GeO₂/GeO cycle is not enough to verify its practical feasibility.

For the oxidation, there are some challenges related to the kinetics of the oxidation. The recent researches for volatile metal oxides mainly focus on modifying the morphologies to enhance the reaction kinetics and heat transfer of

the oxidation, e.g., nanoparticles and micro-nanofibers. Table 2 lists the specific reactants and morphologies. For Zn oxidation, the exothermic oxidation reaction proceeds at temperatures lower than 1300 K [107]. The oxidation reaction proceeds faster at a high temperature with molten zinc [197]. Nonetheless, the ZnO layer formed during oxidation limited the conversion. Further, it requires extra work for the system to continuously feed Zn and simultaneously remove ZnO layer in the real system. Wegner et al. [196] proposed a process for the oxidation, i.e., encompasses the formation of Zn nanoparticles followed by their in situ hydrolysis for H₂ generation. The high specific surface area of the nanoparticle enhances the reaction kinetics and heat/mass transfer, which in turn permits operating at short residence times. The continuous operation mode of the oxidation can be realized by following the procedure of Zn-evaporation, H₂O or CO₂ quenching, and oxidation-reaction. Although the process improves kinetics with a promising conversion, there is still more unsolved issues when incorporating the oxidation with the reduction step at such a high temperature. Specifically, extra energy is required to heat the Zn to 1023 K for nanoparticle formation since the Zn from the reduction step is expected to be quenched to a low temperature (298 K). The activation energies for SnO oxidation is higher than that for Zn, which indicates a slower re-oxidation rate for SnO [31]. Abanades et al. [30] investigated and compared the conversion and the reaction rate of Zn and SnO nanoparticles hydrolysis in a fixed-bed. Their result shows that the SnO nanoparticle has much higher conversion whereas the Zn particle has a much faster reaction rate.

3.2 Non-volatile metal oxide

In contrast to volatiles, non-volatile cycles inherently avoid undesired oxidization of gaseous products between the steps. Non-volatile cycles, including Fe₃O₄/FeO [32,

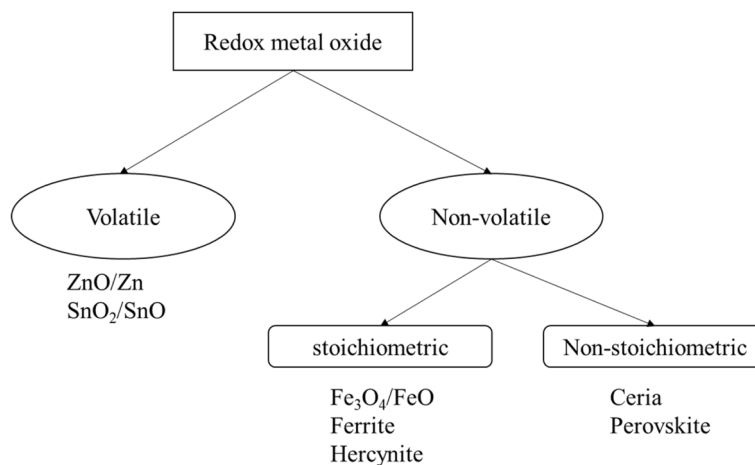
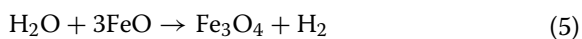
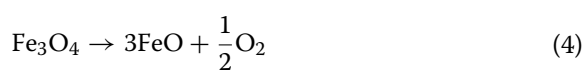
**Fig. 4** Category of the redox metal oxide

Table 2 Specific reactants and corresponding morphologies for the oxidation step of the volatile cycles

| Reactants | Formation | Operating temperature, T (K) |
|-----------|---|--------------------------------|
| Zn | Nanoparticles [196] | 1023 |
| Zn | Nanoparticle-dispersed carbon micro-nanofibers [23] | 873 |
| SnO | Nanoparticles [30, 31] | - |
| SnO | Nanopowders [2] | 1073 |

57], $\text{CeO}_2/\text{Ce}_2\text{O}_3$ [6] and Perovskite (ABO_3), are limited by the high vacuum for lower reduction temperature or higher conversion. The recent improvements in non-volatile cycles with respect to the reactant material are reviewed in this section.

The reactions of $\text{Fe}_3\text{O}_4/\text{FeO}$ pair are:



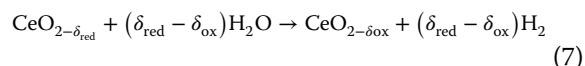
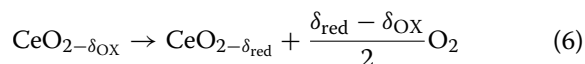
Although the cycle is volatile at 1 bar [179, 188], it becomes non-volatile at 1700 K under an inert atmosphere, e.g., under nitrogen gas flow. However, it requires another large energy input, e.g., pumping power for the inert sweeping gas. The PROMES group experimentally investigated the performance of the cycle under nitrogen gas flow at 0.1 bar with a solar furnace [32]. They found that the conversion of the reduction can reach 100%, while the oxidation kinetics is limited by the coagulation due to alternating fusion and solidification of FeO within the cycle. As a result, a granulation is needed in the continuous process, even though it is hard to be implemented. The mixed solid solutions of $\text{Fe}_3\text{O}_4/\text{FeO}$ and $\text{M}_3\text{O}_4/\text{MO}$ (ferrites) can further reduce the reduction temperature [102]. Lots of ferrites with lower reduction temperatures have been investigated, which are listed in Table 3. Based on the theoretical thermodynamic analysis [15], the stabilities of M-ferrite follows the rank of $\text{Fe}_3\text{O}_4 > \text{CoFe}_2\text{O}_4 \sim \text{NiFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4$. Moreover, Fresno et al. [60, 61] experimentally evaluated the activity of commercially available ferrites with different compositions, NiFe_2O_4 , $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, ZnFe_2O_4 , $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ and CuFe_2O_4 . The net hydrogen production and cyclability after the first reduction-oxidation cycle decreases in the order $\text{NiFe}_2\text{O}_4 > \text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4$. Among the ferrites in Table 3, $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ has the lowest

Table 3 Ferrites investigated for thermochemical cycles

| Ferrites | Reduction temperature (K) |
|--|---------------------------|
| $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ [48, 186] | 1073 |
| ZnFe_2O_4 [90–92, 182, 184, 185, 187] | 1773 |
| MFe_2O_4 (M = Ni or CO) [10, 43] | 1673 |
| $\text{Al}_a\text{Cu}_b\text{Fe}_c\text{O}_4$ ($3a + b + 3c = 8$) [95] | 1673 |
| $\text{Fe}_3\text{O}_4/\text{m-ZrO}_2$ [71] | 1673 |
| $\text{M}_x\text{Fe}_{3-x}\text{O}_4/\text{m-ZrO}_2$ (M = Ni or CO) [102, 104] | 1673 |
| $\text{Fe}_3\text{O}_4/\text{YSZ}$ [70, 86, 101, 103, 105] | 1673 |

reduction temperature, while the cyclability is unfeasible. $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2$ has the highest hydrogen production rate [60, 61, 79]. ZnFe_2O_4 is least desirable because of the high temperature for the reduction.

$\text{CeO}_2/\text{Ce}_2\text{O}_3$ was originally proposed as a stoichiometric redox pair under the conditions of 1 atm and 2300 K. Utilizing the non-stoichiometric reduction via the oxygen-vacancies mechanism, $\text{CeO}_{2-\delta}$ can reach a δ value of 0.10 at 1773 K and p_{O_2} of 10^{-6} atm [37, 147]. The reduced $\text{CeO}_{2-\delta}$ can be oxidized by H_2O or CO_2 to produce H_2 and CO [29, 144, 145]:



The reduction temperature is lower than the melting temperature of CeO_2 , which not only alleviates the high temperature requirement but also avoids the impact of the sublimation. Figure 5 shows the non-stoichiometry of CeO_2 at different temperatures and partial pressures of oxygen by the thermogravimetric analysis [127]. In Fig. 5, the oxygen non-stoichiometry increases with the decrease of P_{O_2} . The high temperature and low non-stoichiometry are main challenges for the CeO_2 cycle. Modifying CeO_2 by adding MO_x (M = Mn, Fe, Ni, Cu) [90], Kaneko, Hiroshi et al. 2007; Kaneko, H. et al. 2007), developing mixed solid solution [164], and morphological modifications [85, 152] have been proposed. The production rate has been increased, while the cyclability has not been verified. Adding transition metal ions including Zr [97] and Sm [36] into ceria is attractive with promising conversions and cyclability.

Perovskite (ABO_3) is attractive due to the high structural and crystalline stability at high temperatures [77]. The reactions can be expressed as:

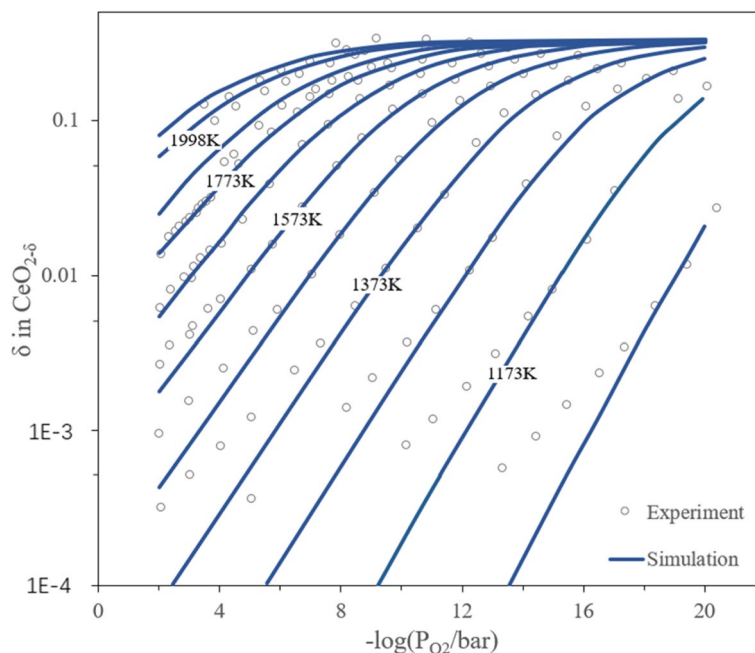
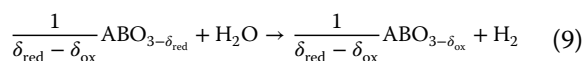
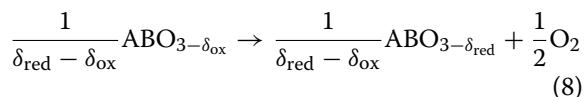


Fig. 5 Non-stoichiometry of CeO_2 at different temperatures and partial pressures of oxygen [127, 207]



ABO_3 is known for a higher reduction extent than other cycles at relatively low temperatures. But it has a poorer oxidation performance [41, 53]. More than 100 perovskites are identified as thermodynamically favorable for the cycle based on the high-throughput density functional theory (HT-DFT) study [49]. Many experimental researches have been performed to investigate different kinds of perovskites, which are summarized and listed in Table 4.

Recently, high entropy oxides (HEOs) have attracted significant interest due to their unique properties and designable structures. HEOs are referred to as a new

group of crystalline solid solution materials formed from five or more ceramic elements with an equimolar ratio [13]. The thermochemical performance of the metal oxides can be improved by the dual actions of oxygen vacancies [13, 122]. The first action of oxygen vacancy is for adsorption and dissociation of $\text{H}_2\text{O}/\text{CO}_2$ molecules. The second action is to anchor the doped ions by creating extra accommodation sites and strong adsorption [192]. In order to overcome the problem of the reduction/oxidation reactions time imbalance, Gao et al. [64] used short-term microwave irradiation to increase the oxygen vacancy of the $(\text{FeMgCoNi})\text{O}_{1.2}@\text{SiC}$. The maximum hydrogen yield of 122 mL/g at 700 W can be obtained. Later, they enlarged the Metal–Oxygen bond length of the spinel phase of FeMgCoNiO_x and produced more oxygen vacancies by introducing Zr^{4+} [65]. A H_2 yield of 4.84 mmol/g can be obtained with $\text{FeMgCoNiO}_x/\text{Zr}_{0.6}$. But the cyclability of most HEOs are still not verified.

Table 4 Perovskites investigated for thermochemical cycles

| Perovskites | Characteristics | Operating temperature, T (K) |
|---|---|------------------------------|
| $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ [40, 52, 134, 201] | Doping Sr enhances conversion but impacts the kinetics of oxidation | 1323 |
| $\text{La}_{1-x}\text{Ca}_x\text{MO}_3$ [42, 193] | Doping Ca is better than doping Sr in enhancing the conversion | 1273–1673 |
| $\text{La}_{0.6}\text{Sr}_{0.4}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ [39, 77, 130, 166] | Doping Mn and Sr enhances the conversion and lowers the reduction temperature | 1323–1673 |

3.3 Reactors

The solar reactor (receiver), proceeds the reaction driven by solar energy, is very important. In this review, solar reactors are classified to be stationary-bed, moving-bed and fluidized-bed reactors based on the method to load the reactant. Figure 6 shows the schematics of these reactors.

3.3.1 Stationary-bed reactors

The stationary-bed reactor simply packs reactants for the reactor bed. In contrast to the other two kinds of reactors, the stationary-bed reactor does not need energy for the movement. But its heat and mass transfer processes are generally insufficient. Moreover, heat recuperation of the high-temperature reduction cannot be applied easily. In this section, some typical stationary-bed reactors including ceramic honeycomb reactor [8, 161], porous monolithic reactor [35] and indirectly irradiated reactor [118, 128] are reviewed.

Ceramic honeycomb reactors have been developed by loading solid reactant powders on the multi-channeled ceramic honeycomb. Agrafiotis and Roeb et al. [66, 161]

developed a volumetric solar reactor equipped with a multi-channeled ceramic honeycomb receiver coated with an active ferrite powder. Figure 7 shows a ceramic honeycomb reactor, which is subjected directly to concentrated solar irradiation. The reactor allows the quasi-continuous removal of the evolved oxygen and hydrogen gases by alternate between steam flow and inert gas flow. However, it is difficult to adjust the appropriate alternating time with different scales and solar radiation. Later, the DLR group [159] developed another honeycomb reactor consisting of two separate chambers, which realized the quasi-continuous operating and continuous supply of hydrogen. Further, the reactor is scaled up to 100 kW and installed at the SSPS solar power plant in Spain for quasi-continuous hydrogen production [28]. Table 5 lists the research progress in improving the honeycomb reactor. For the honeycomb reactor, the degradation of the redox material coated on a support structure is a challenge that has not been overcome.

The porous reactor can solve the problems of undesired products from the metal oxides and ceramic [165],

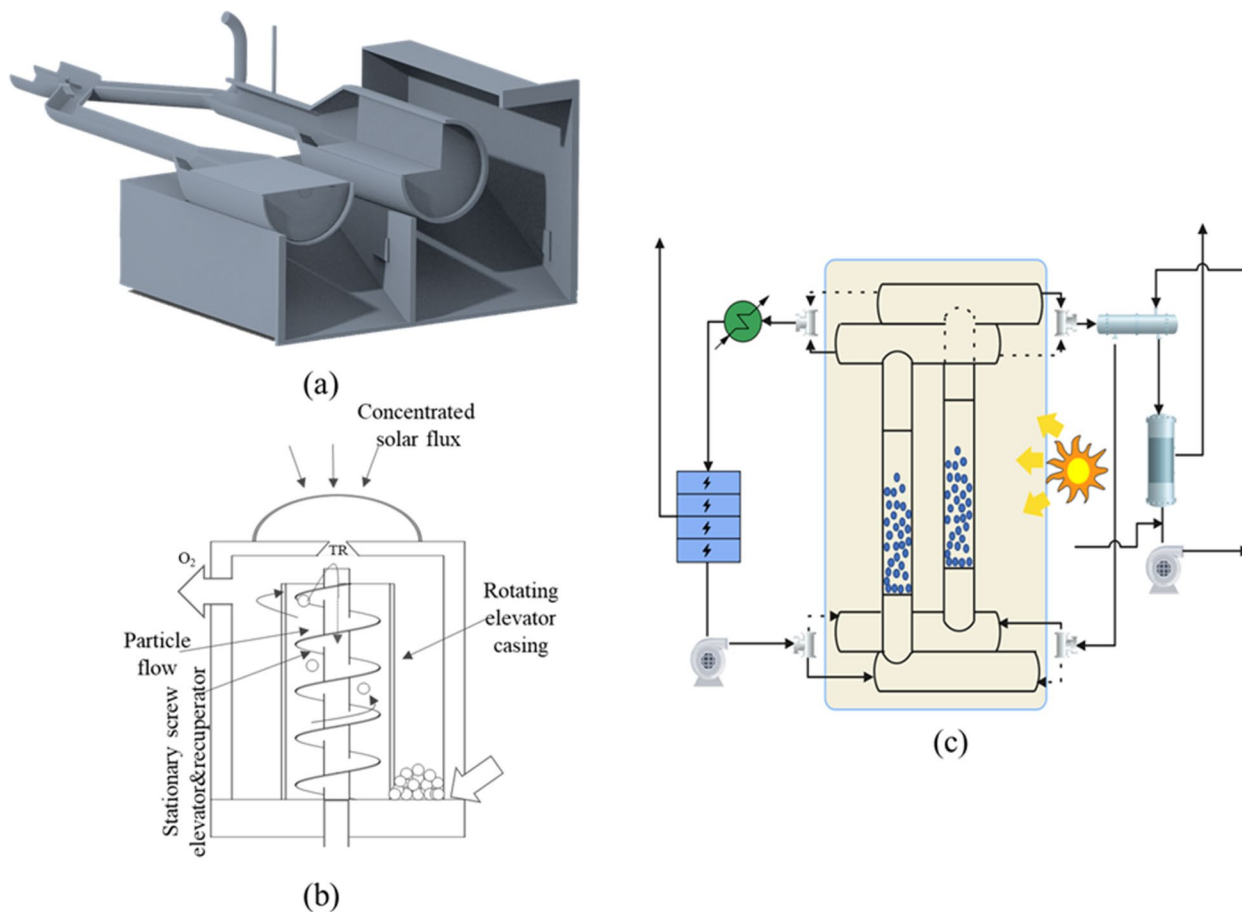


Fig. 6 The general schematics of (a) stationary-bed reactor [159], (b) moving-bed reactor [51] and (c) fluidized-bed reactor [83]

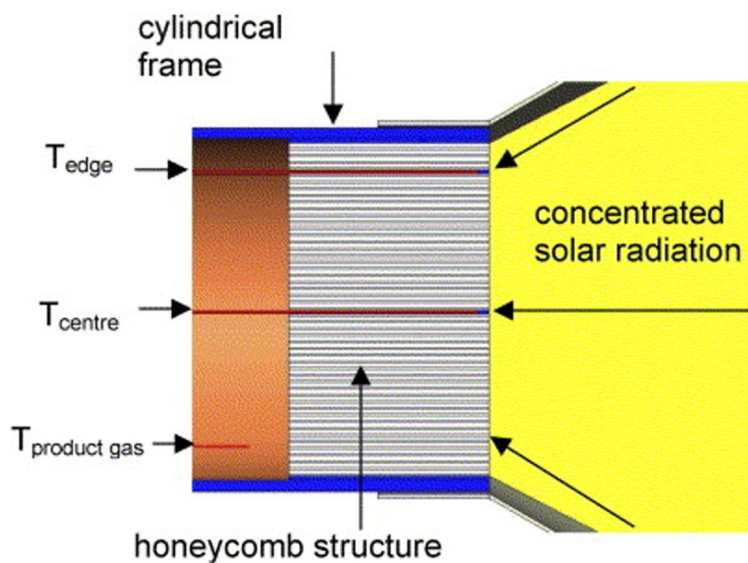


Fig. 7 Schematics of the honeycomb receiver [8]

which packs the reactants as a fixed bed. Figure 8 shows a porous monolithic reactor, which consists of a thermally insulated cavity receiver containing a porous monolithic ceria cylinder [35]. The porous monolithic reactor can be further improved with a reticulated porous ceramic (RPC) foams made of pure solid reactants, e.g., CeO_2 [63]. Compared with the porous monolithic reactor, the RPC foam reactor can be more advanced with volumetric radiative absorption and enhanced reaction rates by optimizing the pore size and mass loading [14, 19, 63].

In contrast to the directly irradiated reactors, indirectly irradiated reactors eliminate a transparent window by enclosing reactants in opaque absorbing tubes or a separate cavity (in Fig. 9 [11]). Inside the cavity, rays bounce around multiple times for a high optical efficiency (a low solar reflection), e.g., rays would not bounce out of the cavity with an ideal design [172]. But a large temperature difference can occur within the indirectly irradiated reactors, affecting reaction rates and limiting the utilization of reactive particles [17, 76].

3.3.2 Moving-bed reactors

Moving-bed reactors are rotational, in which the rotation can be applied to the whole packed bed (Figs. 10 and 11) [80], Kaneko, Hiroshi et al. 2007; [171] and reactive

particles (Fig. 12) [50, 51, 176]. A continuous evolution of the fuel can be achieved by rotating between the reduction and oxidation. In addition, the reactor enables solid–solid heat recovery in an effective opposing arrangement [44, 110, 111]. However, the mass of the reactant mounted on the support is limited and only the reactant coated on a limited surface area can react effectively. It is hard to adjust the kinetics of both reduction and hydrolysis with rotation. The reactant mass, solar radiation and rotation speed have to be adjusted for different scales and locations [34]. Minimizing the power required for the rotation is another challenge that need to be overcome.

3.3.3 Fluidized-bed Reactors

Fluidized-bed reactors, also known as aerosol reactors, are realized by flowing a carrier gas through the reactor to create the internal circulation. In the reactor, reaction particles did not sinter or coagulate throughout successive reactions. Fluidized-bed reactors commonly have better heat and mass transfer process and smaller risk of severe thermal shocks [141, 150]. However, large inert gas usage consumes lots of pumping power, which lowers the overall efficiency. In this study, fluidized reactors are classified as the upward-fed reactor, gravity-fed reactor, and rotational aerosol reactor.

Table 5 Research progress in improving honeycomb reactors

| Improvements | Methods |
|---------------------------------|---|
| Continuous operation [159, 160] | Using two separate chambers with fixed honeycomb absorbers in both chambers built |
| Reducing thermal loss [84, 98] | Using a hemispherical absorber shape and a secondary concentrator |

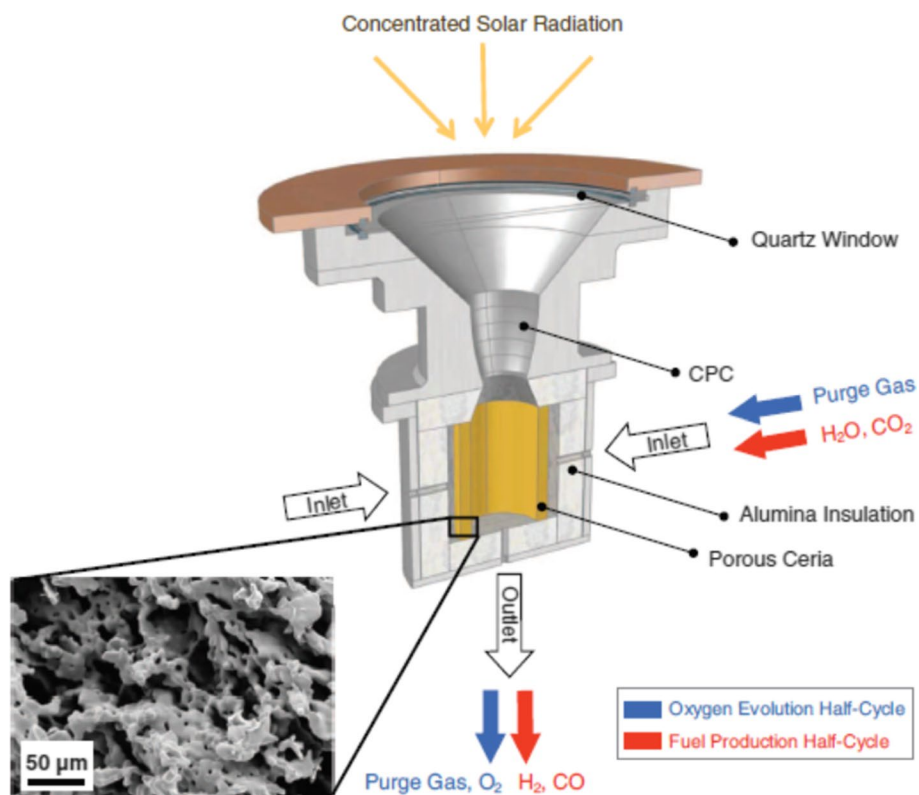


Fig. 8 Solar porous monolithic reactor [35]

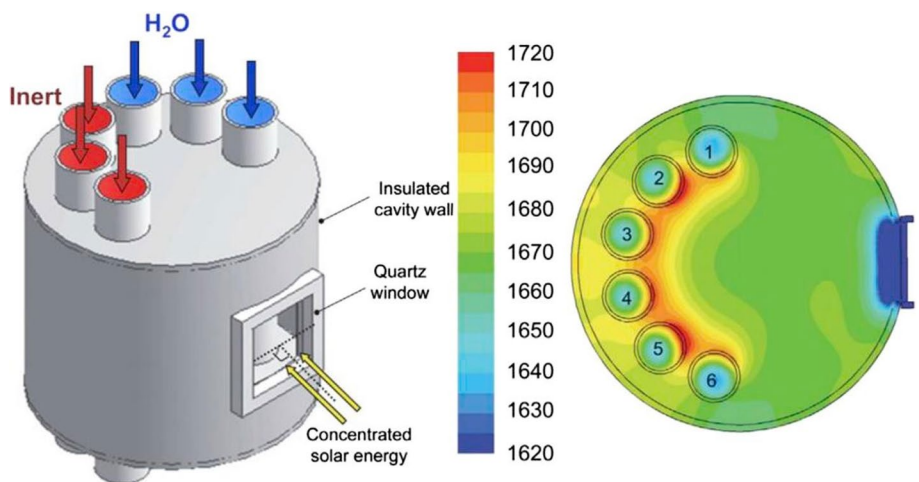


Fig. 9 Packed-bed solar reactor [11]

The upward-fed reactor absorbs solar radiation through the top of the bed (In Fig. 13) [69, 72, 73]. The inert gas and the oxidation reactant gas including H₂O [169] and CO₂ [123] are fed consecutively. The recent researches on the upward-fed single bed reactor focus on enhancing the conversion by optimizing

the reactant particle size and gas flow rate [199]. Using the dual-reactor configuration in Fig. 14 [83], the heat of the inert gas can be recuperated at some extent. Still, the overall energy efficiency is low even with the heat recuperation. Minimizing the pumping power is a big challenge.

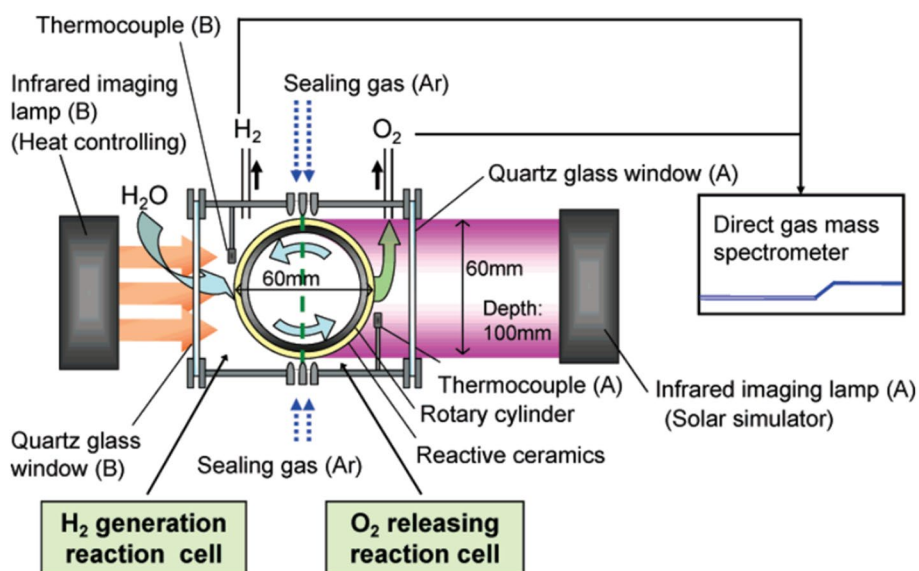


Fig. 10 A rotary-type solar reactor using CeO₂-MO_x for solar hydrogen production [93]

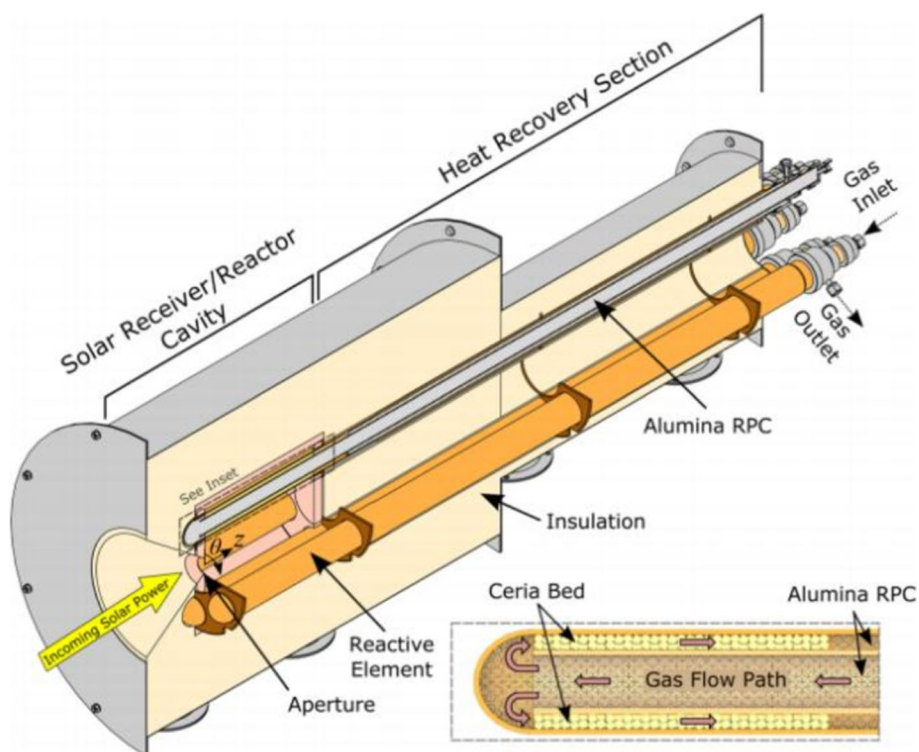


Fig. 11 A 4.4 kW solar reactor capable of continuous CO production and gas-phase heat recuperation [80]

The gravity-fed reactor can significantly decrease the pumping power by using gravity. In a gravity-fed solar-thermochemical reactor (GRAFSTR) [106] shown in Fig. 15, gravity-driven reactive flows on a sloped surface by feeding reactants continuously from the top with an aerosolized

vortex flow. However, agglomerated particles may block the outlet and affect the conversion. To resolve the issue, proper operation methods are needed to prevent outlet blockages. Nevertheless, the economic viability and practical applicability of the reactor have not been validated.

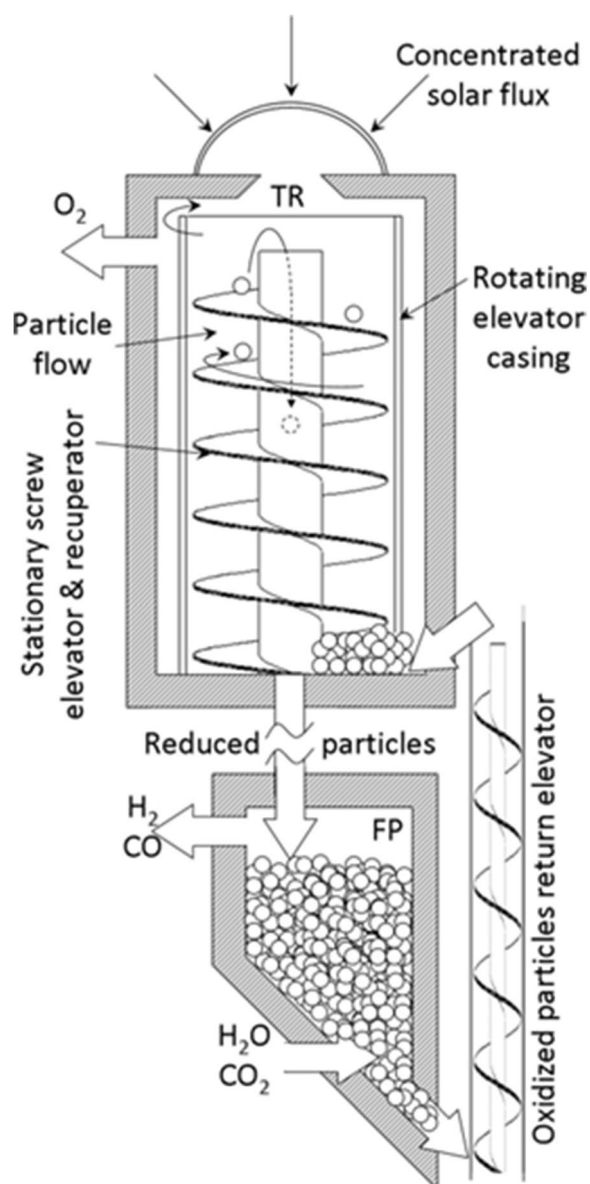


Fig. 12 Moving packed particle bed reactor [51]

Rotational aerosol reactors require the high-temperature resistant rotational assembly. Figure 16 shows a typical rotational aerosol reactor, which uses a crew feeder for the rotation [3]. The reactant powder can be fed continuously in the reactor, while the reduced gaseous products are swept out of the reactor. The reactor with a rotating chamber receiver and an open window is more promising as it has been scaled up from 10 kW [81] to 100 kW [107]. The reactor in Fig. 17 has a dynamic feeder that extends and contracts within the cavity, enabling even spreading of solid reactants along the entire cavity wall. The efficiency of the reactor is unfeasible due to the energy consumption from the rotational assembly and the carrier gas.

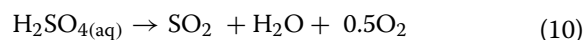
4 Multi-step cycle

The maximum operating temperature of thermochemical cycles decreases with reaction steps increasing. The multi-step cycle has lower operating temperatures at the expenses of more complex reactions and separation processes. The majority of multi-step cycles involve acids, which require the system to be high temperature corrosion resistant [162, 183]. Electro-chemical methods are also used in some multi-step cycles to simplify process and enhance conversion. There are different kinds of multi-step cycles with the operating temperature below 1100 K, among which the sulphur-iodine (S-I) cycle, the Westinghouse cycle and the copper-chlorine (Cu-Cl) cycle are relatively mature. The comparisons of these multi-step thermochemical cycles are listed in Table 6.

4.1 Sulphur-iodine cycle

The S-I cycle [47, 202] consists of three reactions:

Sulfuric acid decomposition:



Bunsen reaction:



Hydroiodic acid decomposition:



4.1.1 Sulfuric acid decomposition

The endothermic sulfuric acid decomposition proceeds at a temperature over 1050 K. There are three sub-steps for the sulfuric acid decomposition:

- 1) H_2SO_4 solution is vaporized to concentrated sulfuric acid;
- 2) Concentrated sulfuric acid decomposes into SO_3 and H_2O ;
- 3) The unstable SO_3 decomposes into SO_2 and O_2 .

For the sulfuric acid decomposition process, the challenges are the poor catalyst activity, inefficient reactor, and insufficient product separation. The poor catalyst activity affects the production rate of SO_3 decomposition. Many studies try to improve the catalyst, including Pt-based catalysts [68, 142], complex metal oxides [180] and transition metal oxides [99, 205]. Compared to the other two kinds, complex metal oxides have better activities [180]. However, the techno-economic feasibility of

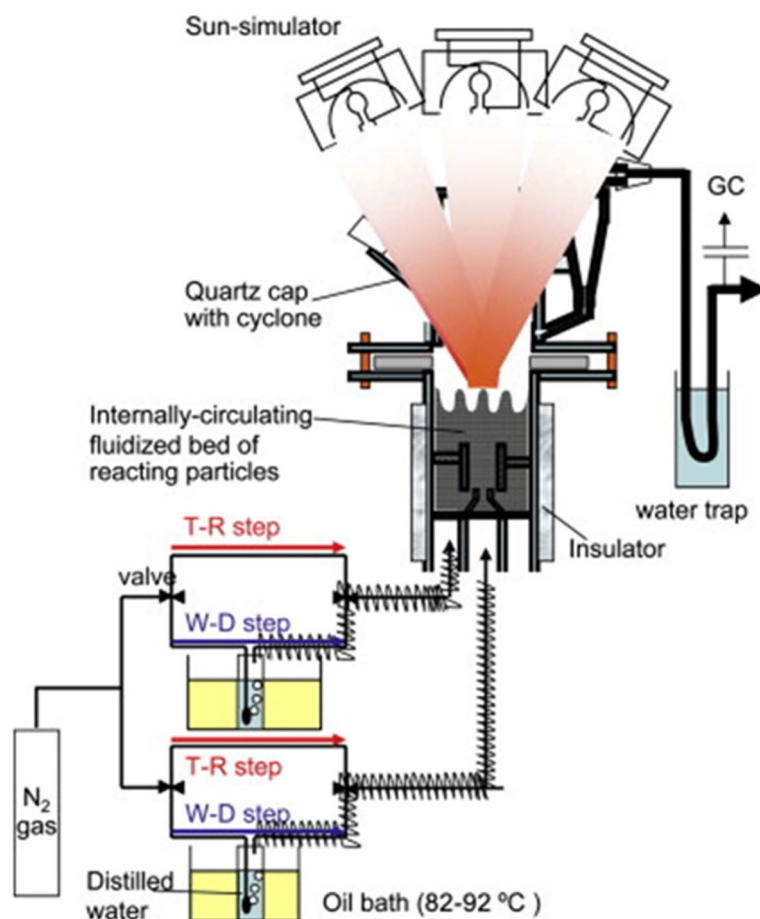


Fig. 13 Solar thermochemical reactor with fluidized beds [69]

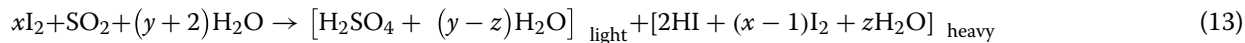
using complex metal oxides in large scale systems has not been verified considering the complexity and expenses in manufacturing. Besides catalysts, the reactor is also critical for SO_3 decomposition. The reactor using moving catalyst particles as the solar energy absorption media has been developed (Fig. 18) [9] to improve the heat transfer process. The extra heat, after the reaction, can be used to evaporate sulfuric acid into SO_3 and steam. Such catalytic systems exhibited excellent high temperature mechanical properties [74]. Nonetheless, moving catalyst particles require extra work.

The separation of SO_2 and O_2 is another challenge. For the separation, yttria-stabilized zirconia (YSZ) membrane has been proposed, which increases the decomposition yield from 62.3% to 90.1% [18]. But the energy required to make the partial pressure difference between the membrane has not been investigated. Ionic liquids as absorbents for SO_2 , e.g., 1-Butyl-3-methylimidazolium

chloride ([BMIm][Cl]) and 1-Butyl-3-methylimidazolium acetate ([BMIm][OAc]), have also been proposed [112]. Hydroxyl ammonium ionic liquids [154] and Caprolactam tetrabutyl ammonium bromide ([CPL][TBAB]) [121] exhibited better potential for the separation process. Nonetheless, the entire system become more complex and energy consuming.

4.1.2 Bunsen reaction

The Bunsen reaction is an exothermic reaction that conventionally operates at 400 K. Excessive H_2O is added practically to make the reaction thermodynamically feasible. It is difficult to separate HI and H_2SO_4 mixed solution since the distillation causes reverse Bunsen reaction. HI concentration of HI- H_2O solution is close to HI and H_2O azeotrope, which requires excess heat to vaporize H_2O from HI. Commonly, extra I_2 is added to make a spontaneous separation of the reaction products by gravity [67]:



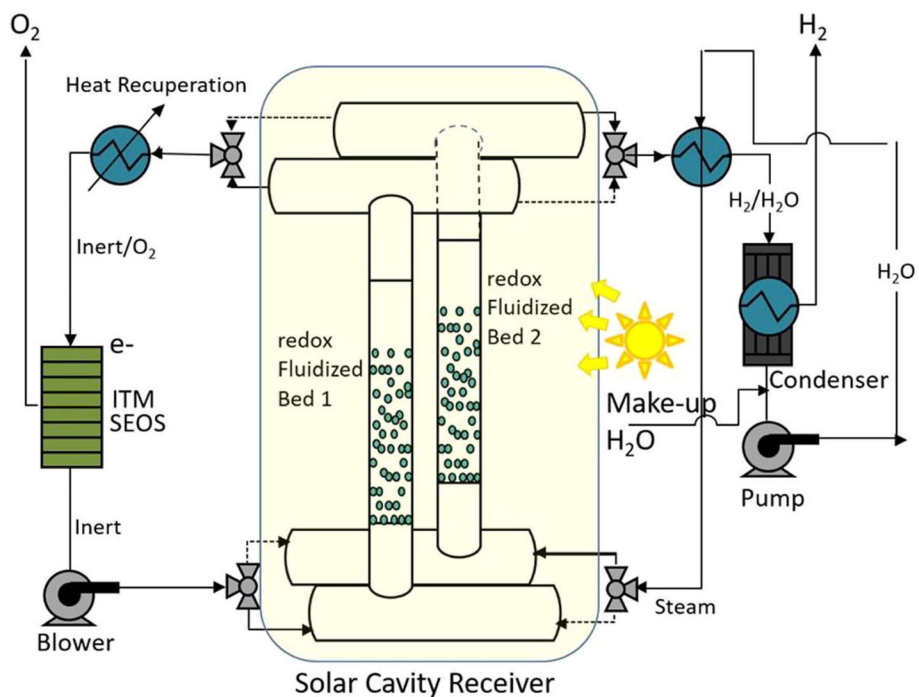


Fig. 14 Solar cavity receiver consisting of dual fluidized bed reactors [83]

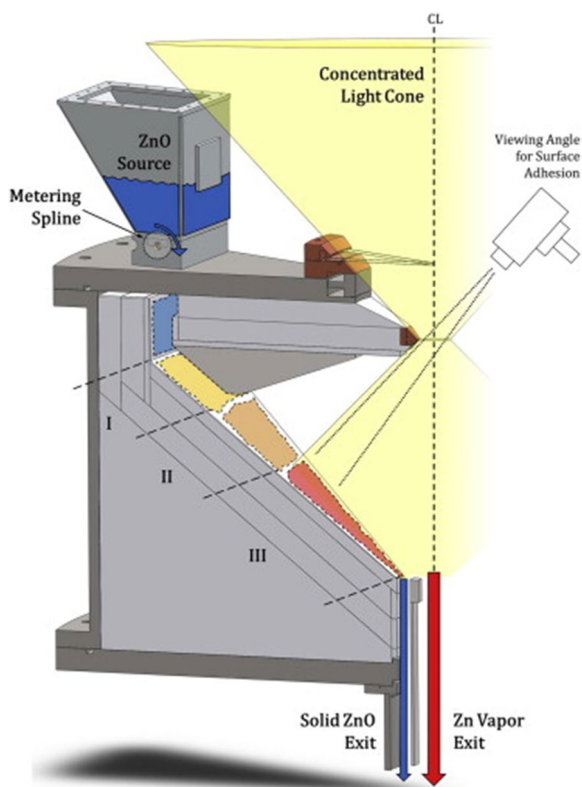
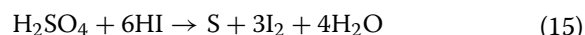
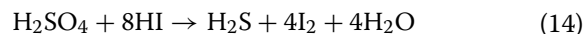


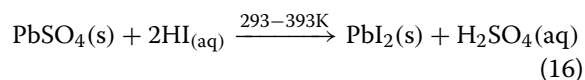
Fig. 15 Gravity-fed solar-thermochemical reactor (GRAFSTR) [106]

The mixture of HI/I₂/H₂O solution and H₂SO₄/H₂O solution can be separated by a liquid–liquid phase separator. The pure concentrated HI vapor can be obtained through distilling HI/I₂/H₂O solution and H₂SO₄/H₂O solution is concentrated for the next cycle. This method introduces several new problems:

- 1) The assistant distillation and purification for pure HI vapor and concentrated H₂SO₄ significantly reduce the efficiency and increase the cost.
- 2) Purification of HI from HI_x solution needs a great amount of energy to overcome HI–H₂O azeotrope.
- 3) Some undesired side reactions may occur:



In order to overcome the above challenges, PbSO₄ has been added in the mixture of H₂SO₄ and HI solution to trigger the nature phase separation [167]. The corresponding chemical reaction steps are given as follows:



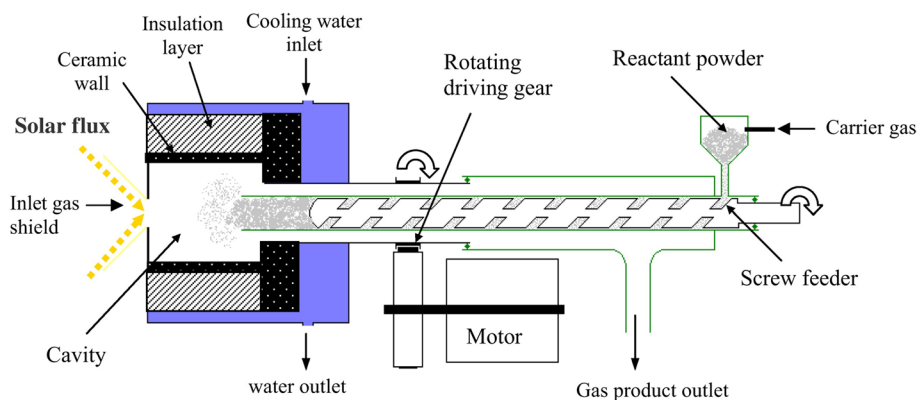


Fig. 16 Aerosol reactor with rotation [3]

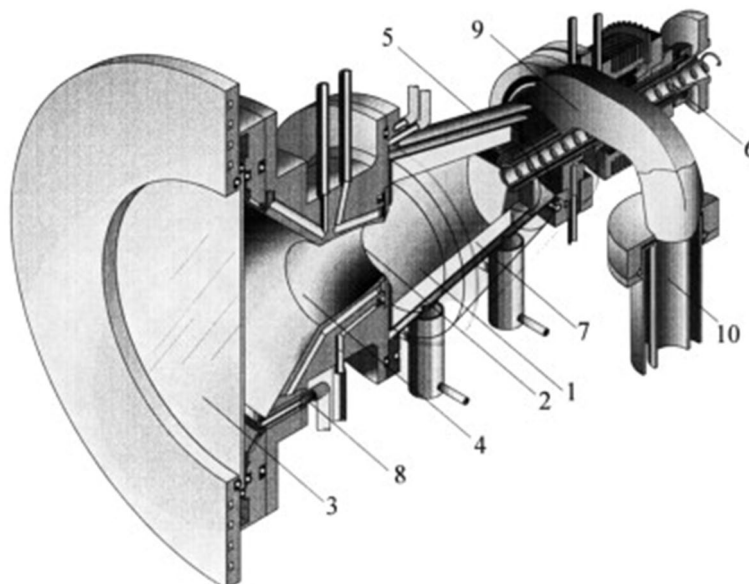
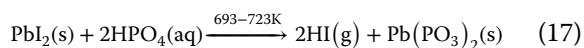


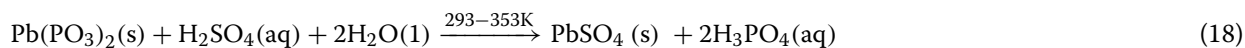
Fig. 17 Aerosol reactor with rotating assembly [81]

Table 6 Comparison of different multi-step thermochemical cycles

| Cycles | Advantages | Disadvantages |
|-------------------------------|-------------------------------------|--|
| Sulphur-Iodine (S-I) cycle | High efficiency and production rate | Side reactions and high temperature |
| Westinghouse cycle | Simple reactions | Low electrical efficiency |
| Copper Chlorine (Cu-Cl) cycle | Lower temperature | Side reactions and low electrical efficiency |



H₂SO₄ (aq) and PbI₂ (s) can be separated easily. Similarly, high concentrations of HI(g) can be obtained by allowing HPO₄ to react with PbI₂. The intermediates of PbSO₄ and PbI₂ are recycled. Energy consumption for distilling H₂SO₄ solution and purifying HI is reduced.



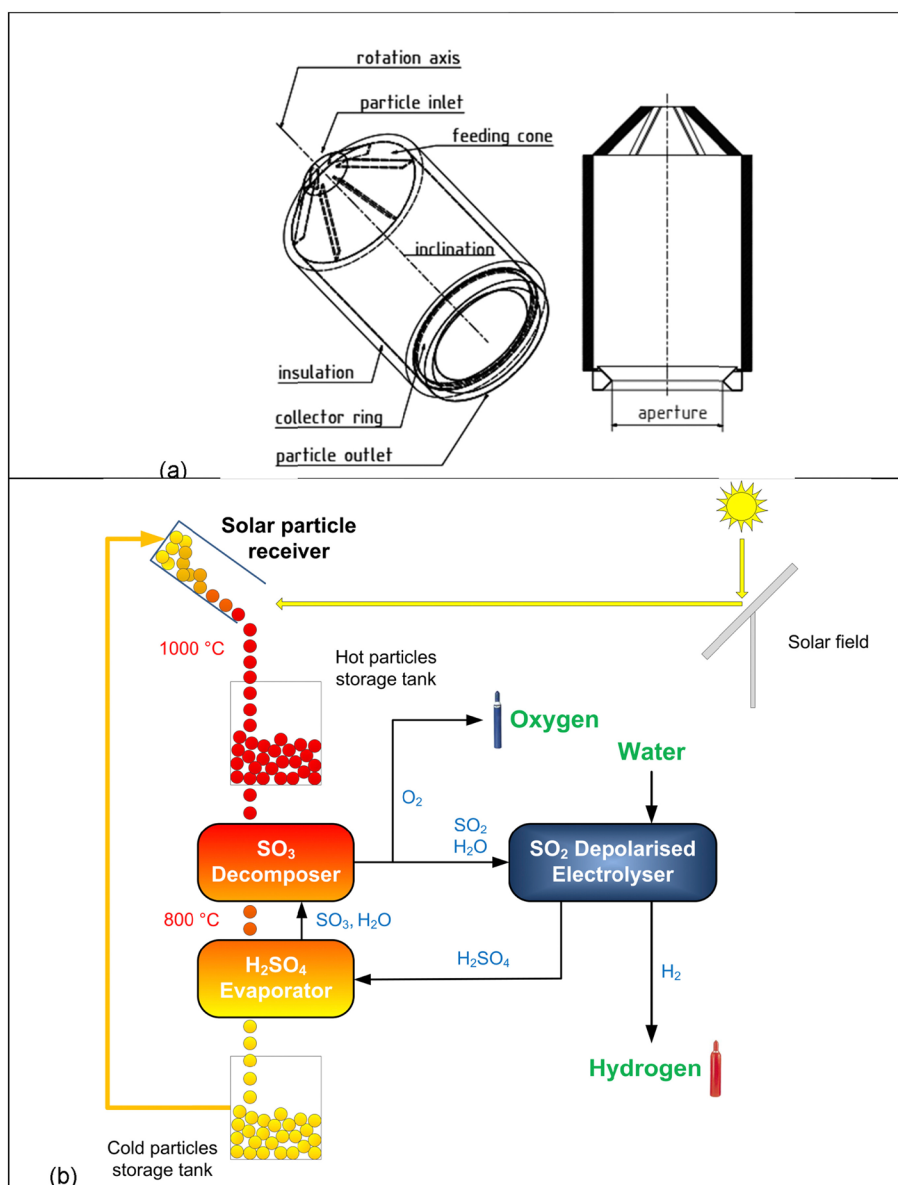


Fig. 18 Centrifugal particle receiver using particles with catalytic function [9]

4.1.3 Hydroiodic acid decomposition

The endothermic hydroiodic acid decomposition can be ideally driven by the heat recuperated from sulfuric acid decomposition. As the mixture (HI_x) of HI, I₂ and H₂O are due to the excessive H₂O and I₂ in the Bunsen reaction, the actual hydroiodic acid decomposition step becomes:



Hydroiodic acid decomposition reaction requires catalysts. There are much research progress made in the

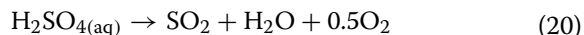
catalyst to improve the reaction kinetics, including Pt based catalyst [78, 109, 194], active carbon [117, 151] and metal oxides supported by Pt and Ni [33]. It was reported that Pt-25%Ir/ C is a promising candidate for high activity and stability [78].

4.2 Westinghouse cycle

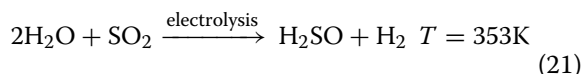
The Westinghouse cycle [25], namely the hybrid sulfur cycle [116, 190], avoids the Bunsen reaction and hydroiodic acid decomposition by introducing an electrochemical reaction. The process become much simpler.

However, it brings many challenges for the electrolysis. The cycle consists of the following reactions:

Sulfuric acid decomposition:



Aqueous sulfur dioxide electrolysis:



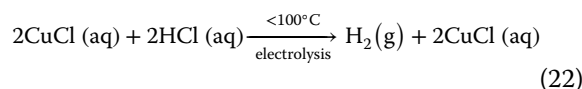
High temperatures contribute to enhancing reaction kinetics and decreasing the concentration of SO₂ [125], while high pressures increase the sulfur dioxide solubility [126]. The electrolysis step can be driven by solar PV power (see Fig. 19) [82] or solar thermal power cycle (see Fig. 20) [74]. For the electrolysis, the practical electrical power, due to the high cell potential, can be larger than that of the water electrolysis [75, 87, 178], which makes the cycle less efficient than the direct water electrolysis. The cell potential increases due to the complex and irreversible mechanisms for SO₂ oxidation and the increased membrane resistance in the presence of concentrated sulfuric acid [88, 156]. Consequently, developing more active catalysts and more conductive membranes are meaningful. For the catalyst, the catalyzed carbon is

considered as the best support [16]. Platinum (Pt) and Palladium (Pd) are found to have the high activity. Compared with the Pd/C, Pt/C had better catalytic activity [38]. In addition, gold is more active than Pt [155].

4.3 Copper chlorine cycle

Copper chlorine cycle does not only operate at a much lower temperature (maximum 530 °C [56]) but demands a low voltage for the electrochemical step [12, 66, 136, 158, 174, 195]. Based on the theoretical analysis [168], the solar copper chlorine cycle with the heat recover achieved the thermal efficiency of 49.84% and the exergy efficiency of 58.23%. In addition, the manufacturing materials are not required to be high-temperature corrosion-resistant [140]. There are four steps within the cycle [113, 139, 157, 200].

Hydrogen production step:



Evaporation step:

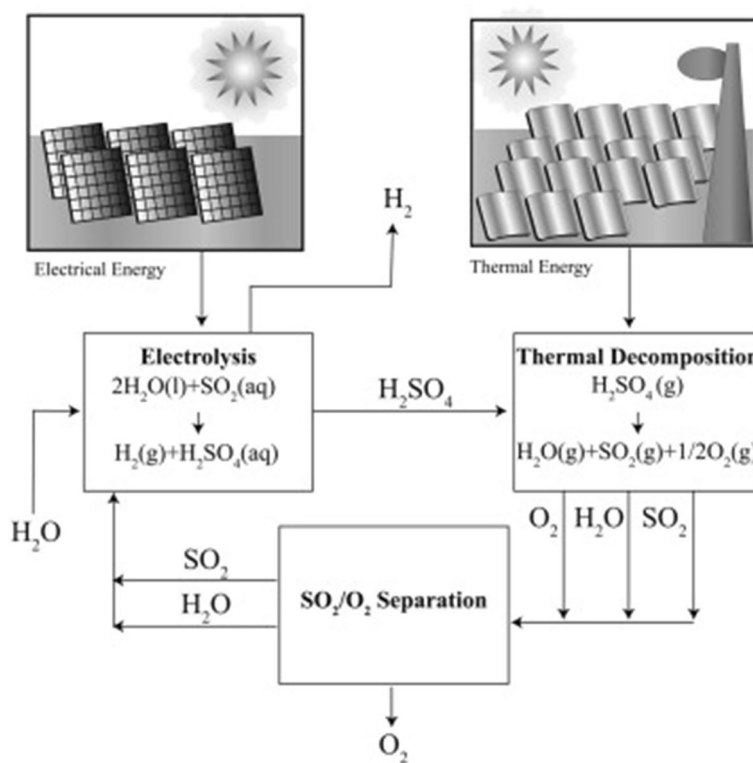
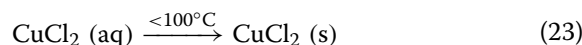


Fig. 19 Schematic of solar HyS cycle [82]

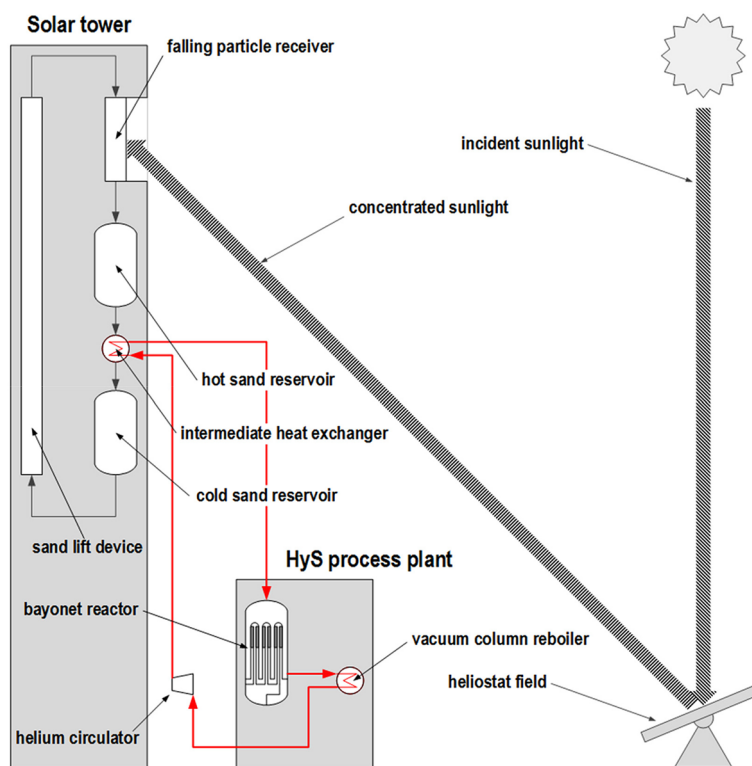
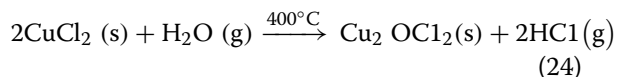
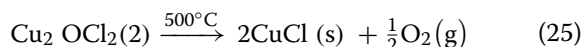


Fig. 20 Solar plant with thermal energy storage coupled to a HyS cycle [74]

Endothermic hydrolysis step:



Oxygen production/ Thermolysis step:



The main challenges for the copper chlorine cycle are the membrane of the electrolyzer [136, 139], the evaporation rate [136], and the side reaction [138]. For the membrane, the crossover of copper ion cannot be prevented by Nafion [181]. The physically modified Nafion, polymer matrix with inter-winding Nafion chains, the polysulfone membranes based on Radel NT5500, and the porous polyethylene membrane have been proved to be with higher copper diffusion and lower permeability [137, 140]. For the evaporation, spray drying and crystallization are two commonly-used methods for the evaporation. Spray drying is with a high evaporative drying rate [135] while the crystallization can be scaled up easily [140]. For undesired side reactions, i.e., $\text{CuCl}_2(\text{s})$ dissociates into $\text{CuCl}(\text{s})$ and $\text{Cl}_2(\text{g})$, excess steam is used to enhance conversion of

$\text{CuCl}_2(\text{s})$ [58]. But the excessive reactants require extra energy, which significantly decreases the efficiency [55].

5 Challenges of solar thermochemical cycles

As discussed above, there have been many research achievements for solar fuel production with thermochemical cycles. There are several challenges need to be addressed.

For reactants of two-step cycles, the material modification is attractive to improve the redox performance e.g., lower reduction temperature and higher conversion. With the development of the computational implements on the first-principle theory and high-throughput density functional theory, more material screening processes are provided. However, there are not much convincing guidance for modification strategies. Although the research on experimentally testing and improving the existing perovskites is ongoing, it takes much more efforts and time than the theoretical method to reach a conclusion. For the volatile metal oxides, there have been theoretical feasible reduction temperature boundaries [7, 62]. But the theoretical feasible temperature boundary of the attractive non-volatile metal oxides is rarely defined. For non-volatile metal oxides, the low oxygen partial pressure maintained by inert gas sweeping and vacuum pumping

can effectively decrease the reduction temperature. But the extra pumping power and sweeping gas preheating are significant, which largely impacts the overall efficiency. Therefore, the fundamental mechanism to reduce the temperature and the potential to improve the efficiency by minimizing the oxygen removal work have not been revealed clearly.

For the reactor of two-step cycles, the stationary bed, moving bed, and fluidized bed all have pros and cons. The stationary bed did not require parts and energy for the movement. However, heat recuperation and the heat/mass transfer process are insufficient. Although porous foam has been used to enhance the heat/mass transfer, the scaling up capacity and techno-economic feasibility have not been verified. For the moving bed, the heat recovery can be employed. However, the reactant mass, solar radiation and movements need be adjusted for different scales. Moreover, the power required for the rotation impacts the efficiency. For the fluidized bed (aerosol), the heat and mass transfer processes are enhanced. The 100-kW aerosol reactor has been developed and demonstrated. But the preheating and pumping power required for the inert carrier gas lowers the efficiency. Considering the scale-up capability, the stationary bed and fluidized bed are promising. The stationary bed need improve the heat/mass transfer processes and heat recuperation. The fluidized bed need minimize the extra energy consumption for the inert carrier gas.

For multi-step cycles, the separation of liquid acids is technically difficult. Introducing intermediate reactants and adding reactants have been proposed. But these methods may cause extra energy losses and undesired side reactions. In addition, reactions kinetics need be improved. Many advanced catalysts have been proposed. Their techno-economical feasibilities have rarely been validated. Using electro-chemical reactions can simplify the process and avoid the complicated acid separation. However, the electro-chemical reactions may require noble material for the membrane and catalyst. In addition, there is a gap between the theoretical and practical cell efficiency, which needs to be further minimized for

a high overall efficiency of the cycle. The comparison of major challenges for different cycles are summarized and listed in Table 7.

6 Outlook

Thermochemical cycles offer valuable options for fuel production with solar energy. The challenges of both two-step and multi-step cycles have been discussed in sections above. Here, new perspectives concerning from reactions to reactors and accessory separation processes are provided, in order to address the challenges and improve the efficiency.

For reactant candidates of two-step cycles, theoretical method is necessary to further select the existing metal oxides and develop novel metal oxides. Assuming that the reduction and oxidation are at equilibrium ($\Delta G_{\text{red}} = \Delta G_{\text{ox}} = 0$), the relations of reaction temperatures, reaction enthalpy and reaction entropy can be quantified for existed metal oxides. As a result, theoretical temperature limit (the lowest reduction temperature) can be evaluated. Thermodynamically favorable temperature and pressure ranges can be obtained. With the DFT calculations, the relationships between the thermodynamic parameters (enthalpy and entropy) and the microscopic electronic structure of metal oxides can be analyzed. The relationships can provide guidance to develop novel metal oxides. Considering the practical reaction conditions, i.e., reactions are not in chemical equilibrium, the fundamental mechanism to reduce the temperature and the potential to improve the efficiency by minimizing the oxygen removal work need be revealed. As the pump efficiency is low in practice, the corresponding exergy loss should never be ignored, which strongly affect the efficiency. Although the sensible heat of the sweeping gas between the reduction and oxidation steps can be theoretically recovered, the exergy loss of the pump cannot be recovered. Developing novel efficient methods to keep a high vacuum is very attractive. Even though other methods including electron-conducting (MIEC) membranes [52] and thermochemical oxygen pump [26, 120] have been proposed, significant energy requirement is not avoided.

Table 7 Comparison of challenges for different thermochemical cycles

| Aspects | Two-step | Multi-step |
|----------------------|--|--|
| Reaction temperature | High (> 1200 K) | Moderate (< 1000 K) |
| Reactants | Unsatisfied reaction yield, kinetics and cyclability | Corrosive |
| Endothermic reactor | Large re-radiation loss, poor heat and mass transfer limits, and expensive high-concentration solar receiver | High-temperature corrosion resistant |
| Products separation | / | Separation of acids and gaseous products |
| System operation | Difficult to achieve continuous operation | Complex with multiple chemical processes |

Further, the temperature, conversion and vacuum should be simultaneously optimized, e.g., the lowest temperature or highest conversion may not be optimal. The cycles with both moderate temperature and oxygen removal work may have the potential to reach a high efficiency.

For two-step cycle reactors, the gap between the experimental and theoretical efficiency is large, which is mainly caused by the insufficient heat recovery and heat/mass transfer processes. For the heat recovery, the theoretically feasible heat recuperation methods, e.g., solid–solid heat recuperation for solid reactants and gas–gas heat recuperation for sweeping gas, can hardly be achieved in practice. The heat recuperation become more difficult in the case of scaling up reactors. Absorbing solar energy with a heat transfer fluid and releasing heat for the reduction away from the solar receiver has the potential to improve the heat recovery. In order to enhance the heat/mass transfer, porous foam stationary bed has been used, which in turn increases the pressure drop of the sweeping gas. As a result, the pumping power required become larger, which lowers the efficiency. To improve heat transfer and reduce pressure drop in the stationary-bed reactor, microchannel reactors can be tried. The reactants can be packed as structured micro channel and the pressure drop can be kept relatively low.

In terms of multi-step cycles, the separation of acids is difficult. Adding extra reactants for the separation and reaction spontaneity cause extra energy loss. The issue of energy loss has not been systematically analyzed or addressed. Introducing electrochemical reaction to multi-step cycles helps simplify reactions. But it sacrifices high grade electricity. The low practical efficiency of the electrical cell limits the overall efficiency of the system. Designing novel multi-step cycles is welcome. Ideal cycles, with both advantages of low-temperature and simpler reactions, are anticipated. The use of automatic separation of products and introducing non-corrosive solid–gas reactions are feasible to avoid halide mixtures and the corresponding separations. Developing multi-step reactions by replacing the stoichiometric reduction of metal oxides seems to be feasible. Hydroxides and carbonates can be involved in such solid–gas reactions, e.g., replacing water with a better oxidizing compound, such as potassium hydroxide, to enhance the oxidation of the reduced metal oxide.

7 Conclusions

In this work, the advances of both two-step and multi-step thermochemical cycles for solar fuels production have been reviewed comprehensively. The challenges and perspectives concerning fundamental thermodynamics of reactants, mechanisms of reactors and performance

of accessory separation processes are discussed and provided.

For two-step cycle reactants, non-volatile metal oxides including cerium-based oxides and the perovskite-based oxides are more promising. High temperature and low conversion at ambient pressure challenge the applications of non-volatile metal oxides. Theoretically feasible temperature and pressure ranges are needed to develop reactant materials. Various material modification strategies including doping and mixed solid solutions have been proved to be effective for reducing reaction temperature or increasing conversion. But the extra pumping power and sweeping gas preheating are significant, which significantly impacts the overall efficiency. The fundamental mechanism to reduce the temperature and the potential to improve the efficiency by minimizing the oxygen removal work need be revealed. The temperature, conversion and vacuum should be simultaneously optimized based on the overall efficiency.

With respect to two-step cycle reactors, the stationary bed, moving bed and fluidized bed are reviewed. The stationary bed did not require energy for the movement. But the heat recuperation and heat/mass transfer are insufficient. For moving bed reactors, the heat recovery can be realized. But the power required for the movement impacts the efficiency. For fluidized bed reactors, the heat and mass transfer processes are enhanced. But the preheating and pumping power required for the inert carrier gas lowers the efficiency. To address the issues mentioned, reactors with secondary heat transfer fluid and microchannel reactors can be tried.

In terms of the multi-step cycle, the operating temperature in multi-step cycles is much lower than two-step cycles. Currently, the main challenges for multi-step cycles are the separation of corrosive acid and insufficient reaction kinetics. For the separation of acids, many methods have been proposed, including electrochemical reactions. These methods require extra energy and causes undesired side reactions or byproducts. The reaction kinetics have been enhanced by improving catalysts with noble materials, e.g., Pt, or complex fabrication methods. But more research is needed to verify the techno-economic feasibility for a large-scale system. In addition, developing novel multi-step cycles may be promising. The stoichiometric reduction of metal oxides can be used for reduction, while hydroxides and carbonates can be involved in the oxidation.

Abbreviations

| | |
|-------------|---|
| [BMIm][Cl] | 1-Butyl-3-methylimidazolium chloride |
| [BMIm][OAc] | 1-Butyl-3-methylimidazolium acetate |
| [CPL][TBAB] | Caprolactam tetrabutyl ammonium bromide |

| | |
|---------|---|
| MIEC | Electron-conducting |
| GRAFSTR | Gravity-fed solar-thermochemical reactor |
| HT-DFT | High-throughput density functional theory |
| RPC | Reticulated porous ceramic |
| YSZ | Yttria-stabilized zirconia |

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Authors' contributions

CC and FJ were major contributors in writing the manuscript. BC L and TX L analyzed the data. QB L and HG J reviewed and edited the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analysed during this study are included in this published article.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing financial interest.

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