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Perovskite Oxides: A Multifunctional Material Class for Solar-to-Fuel Energy Conversion

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Abstract

Harnessing concentrated solar energy for thermochemical water and carbon dioxide splitting presents a promising pathway to produce liquid hydrocarbon fuels as a sustainable alternative to fossil fuels. This process relies on advanced redox materials to facilitate efficient chemical reactions within thermochemical cycles. Traditionally, research has focused on binary oxides, particularly ceria, due to its redox capabilities. However, ceria's high reduction temperature and limited tunability via extrinsic doping hinder its optimization for enhanced fuel production. In contrast, perovskite oxides have emerged as a highly adaptable material class, offering broader compositional flexibility to fine-tune reduction temperatures, oxygen exchange characteristics, and fuel yields. This review explores the fundamental structural and defect thermodynamics of perovskites, emphasizing the role of oxygen vacancies in catalytic reactions. Additionally, we discuss advanced strategies for discovering and optimizing new perovskite compositions for improved solar-driven fuel synthesis. Recent investigations highlight Fe, Mn, Co, and Cr-based perovskites, achieving fuel yields of several hundred mmol per gram per cycle. Ultimately, this review provides an in-depth analysis of the principles, progress, and future prospects of perovskite oxides in next-generation solar-to-fuel technology.

Keywords: Perovskite oxides, thermochemical cycle, solar-to-fuel conversion, oxygen vacancies, redox materials

INTRODUCTION

In the 21st century, meeting global energy demands while reducing greenhouse gas emissions and environmental pollution is crucial. Nuclear energy, though a potential solution, raises safety concerns and is limited by geographical dependencies and uneven resource distribution. A promising approach is to enhance energy independence by reducing reliance on politically sensitive materials and increasing the share of solar energy, thereby contributing to global stability and sustainability. Solar energy is abundant, with the Earth receiving approximately 120,000 TW per year—far exceeding the global energy consumption of around 15 TW. However, its intermittent nature and relatively low power density, which varies by geographic location, pose challenges. Beyond natural photosynthesis, various technologies exist to harness solar energy, with photovoltaics being the most prominent. While solar electricity can be used immediately or fed into power grids, energy storage remains a major hurdle, particularly for managing daily and seasonal fluctuations. Batteries, a common solution, depend on materials that are either scarce or economically critical, such as cobalt and rare earth elements, making large-scale deployment challenging despite advancements in recycling. To transition towards a more sustainable and geographically independent energy future, novel storage solutions are necessary. Three key sectors—industrial, residential, and transportation—stand to benefit significantly from

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renewable energy storage in the form of fuels. Liquid fuels are especially vital for transportation and industrial processes, where fossil fuels currently dominate. Thus, efficient solar-to-fuel conversion technologies are essential for providing renewable alternatives. Solar-to-fuel processes mimic natural photosynthesis, utilizing H_2O and CO_2 as starting materials that are converted into H_2, CO, or syngas using solar energy. These gas mixtures can then be synthesized into liquid fuels such as methanol, gasoline, or kerosene via Fischer-Tropsch synthesis, increasing energy density for storage and distribution. Various methods exist for these conversions, with thermochemical cycles being particularly promising. These cycles use concentrated solar heat to drive high-temperature endothermic reactions, followed by lower-temperature exothermic reactions to produce fuel efficiently.

A key advantage of thermochemical cycles is their ability to utilize the full solar spectrum while temporally separating O_2 and H_2 production. Their high theoretical efficiency makes them a compelling solar-to-fuel technology, with reported annual conversion efficiencies exceeding 20%. Studies on materials such as iron, zinc, and manganese oxides, coupled with solar collector technologies like dish and tower plants, confirm that thermochemical cycles offer superior efficiency compared to photovoltaics combined with conventional electrolysis.

WORKING PRINCIPLE OF SOLAR-TO-FUEL CONVERSION

The Thermochemical Cycle

One of the simplest approaches to solar-to-fuel conversion is the direct splitting of H_2O or CO_2 into H_2 and O_2 (or CO and O_2) under highly concentrated sunlight at temperatures exceeding 2000 K. At such extreme conditions, these splitting reactions become thermodynamically favorable, allowing the gases to be separated and subsequently utilized for fuel production at lower temperatures. The feasibility of this direct approach has been demonstrated in solar-driven prototype plants for CO_2 splitting.

However, due to excessive heat losses and the demanding material constraints at such high temperatures, alternative methods are preferred. Metal oxides are commonly used to facilitate these splitting reactions at more manageable temperatures. Unlike conventional chemical catalysts that require only trace amounts, the fuel yield in thermochemical cycles is directly proportional to the amount of metal oxide present in the reactor.

Table 1. Comparison of Solar Thermochemical Hydrogen Production Efficiencies Across Different Reaction Cycles Using Tower and Dish Solar Concentrators.

Table 1. Efficiencies of solar thermochemical hydrogen production in different reaction cycles from Sandia National Laboratories for tower or dish solar concentrators[22]						
Cycle name	Highest operation temperature	Solar plant type	Thermo-chemical efficiency Optical efficiency	Optical efficiency	Receiver efficiency	Annual efficiency for H_2 production
Conventional electrolysis		Tower	30%	57%	83%	14%
Zinc oxide	1800 °C	Tower	45%	51%	72%	16.5%
Manganese oxide	1550 °C	Tower	50%	55%	78%	21%
Cadmium carbonate	1450 °C	Tower	50-70%	50%	67%	20%
Conventional electrolysis		Dish	26%	85%	86%	19%
Iron oxide	2100 °C	Dish	50%	74%	62%	23%
Zinc ferrite	1800 °C	Dish	52%	77%	62%	25%

In metal oxide-based thermochemical cycles, the endothermic reaction involves the release of oxygen from the metal oxide at high temperatures. Table 1. In the subsequent low-temperature step, oxygen from H_2O or CO_2 is incorporated back into the metal oxide, generating H_2 or CO. The efficiency of this process depends on the thermodynamics, kinetics, and chemical and mechanical stability of the metal oxides used. For commercial viability, thermochemical cycles must achieve competitive efficiency compared to other renewable energy technologies such as photovoltaics coupled with electrolysis [1-7].

The thermochemical production of syngas follows a series of endothermic and exothermic reaction steps:

1. **Endothermic Reduction:** The metal oxide undergoes thermal reduction using concentrated solar energy:
2. **Exothermic Oxidation:** The reduced metal oxide reacts with either H_2O or CO_2

$$ABO_3 \leftrightarrow ABO_{3-\delta} + \frac{\delta}{2} O_2(g) \tag{1}$$

$$ABO_{3-\delta} + \delta H_2O \leftrightarrow ABO_3 + \delta H_2(g) \tag{2a}$$

$$ABO_{3-\delta} + \delta CO_2 \leftrightarrow ABO_3 + \delta CO(g) \tag{2b}$$

The spontaneity of these reactions depends on the Gibbs free energy change (ΔG\Delta GΔG), which is influenced by the perovskite composition, temperature, and pressure conditions. The reduction step occurs at high temperatures and low oxygen partial pressures, while the oxidation step proceeds at a lower temperature.

To ensure efficient solar-to-fuel conversion, the catalyst materials must meet key thermodynamic criteria:

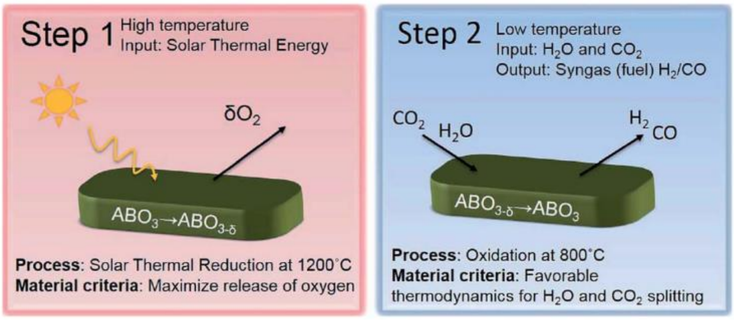

Figure 1. Schematic of the 2-step water-splitting or CO2-splitting reaction using a non-stoichiometric perovskite oxide.24 In high-temperature step

- The reduction reaction (ΔG_{red}) must be thermodynamically favorable under high-temperature, low-oxygen conditions.
- The oxidation reaction must proceed efficiently, with the Gibbs free energy change for H_2O or CO_2 splitting (ΔG_{gs}) being sufficiently low.

Research into metal oxide-based thermochemical cycles dates back to the 1970s when iron oxide was first explored for this purpose. Since then, various metal oxides have been investigated, with promising results reported for iron, zinc, and cerium-based materials. Fig. 1 These materials demonstrate significant potential for improving the efficiency and scalability of solar-driven fuel production.

SOLAR CONCENTRATORS AND REACTORS

Solar reactors and concentrators are essential components of Concentrated Solar Power (CSP) or Concentrated Solar Thermal (CST) technology. These systems are not limited to solar-to-fuel thermochemical cycles but can also drive various endothermic reactions using concentrated solar energy. This section provides a brief overview of the basic technical aspects of CST as applied to perovskite-based solar-to-fuel conversion [8-10].

A typical solar thermochemical cycle setup consists of two key components:

SOLAR CONCENTRATOR

- This component concentrates sunlight into a reaction chamber where the metal oxide is exposed to reaction gases, facilitating solar-driven redox reactions.
- Various solar concentrator designs exist, including parabolic troughs, linear Fresnel reflectors, dish/engine systems, and central receivers (solar towers).
- Among these, 3D concentrators (dish/engine and central receiver setups) achieve higher solar concentration ratios (CC), allowing for increased operating temperatures and making them more suitable for thermochemical fuel production. Existing 3D concentrators operate within a C range of 200–3000.

Reactor Mechanism

- The reactor must efficiently **switch between high and low temperature regimes** to accommodate the thermochemical cycle requirements.
- It must also manage the gas feed supply for oxidation and reduction steps.

Types of Solar Concentrators

- **2D Concentrators:** Include parabolic troughs and linear Fresnel reflectors. These offer moderate solar concentration and are primarily used in commercial solar thermal power plants.
- **3D Concentrators:** Include solar dishes and central receiver systems (solar towers). These systems enable much higher concentration ratios and temperatures, making them well-suited for solar-driven thermochemical fuel production.

Challenges in Reactor Design

The efficiency of a solar reactor depends on several factors:

- **Efficient Solar Energy Absorption:** Maximizing light capture for thermal energy conversion.
- **Uniform Heat Distribution:** Preventing localized overheating and ensuring even reaction rates.
- **Optimized Gas Interaction:** Enabling rapid and efficient chemical reactions.
- **Minimized Thermal Losses:** Reducing heat dissipation to improve overall efficiency.

An efficient solar reactor should also enable continuous or quasi-continuous operation with heat recuperation to improve energy efficiency. This can be achieved by:

1. **Batch-type Temporal Cycle Reactors:** Multiple reactor chambers cycle between oxidation and reduction states.
2. **Continuous Reactors:** A moving oxidized and reduced metal oxide cycle enables uninterrupted thermochemical fuel production.

Solar Reactor Designs

Various reactor concepts have been explored for solar-driven fuel production:

- Multi-tubular reactors
- Fixed-bed reactors
- Fluidized-bed reactors
- Moving packed-bed reactors
- Counter-rotating ring reactors
- Solar vortex reactors
- Liquid metal reactors for efficient heat transfer

Recent advancements in reactor design and process optimization have improved solar-to-fuel conversion efficiencies to **above 5%.**

Laboratory-Scale Testing

For research and development, laboratory-scale setups are used to test new materials and evaluate thermodynamic properties. Common lab-scale reactors include:

- Thermogravimetric analysis (TGA) setups
- Small irradiation furnaces
- Lab-size fluidized-bed reactors

These experimental setups enable the characterization of new materials and the optimization of thermochemical cycle parameters before scaling up for industrial applications [11–14].

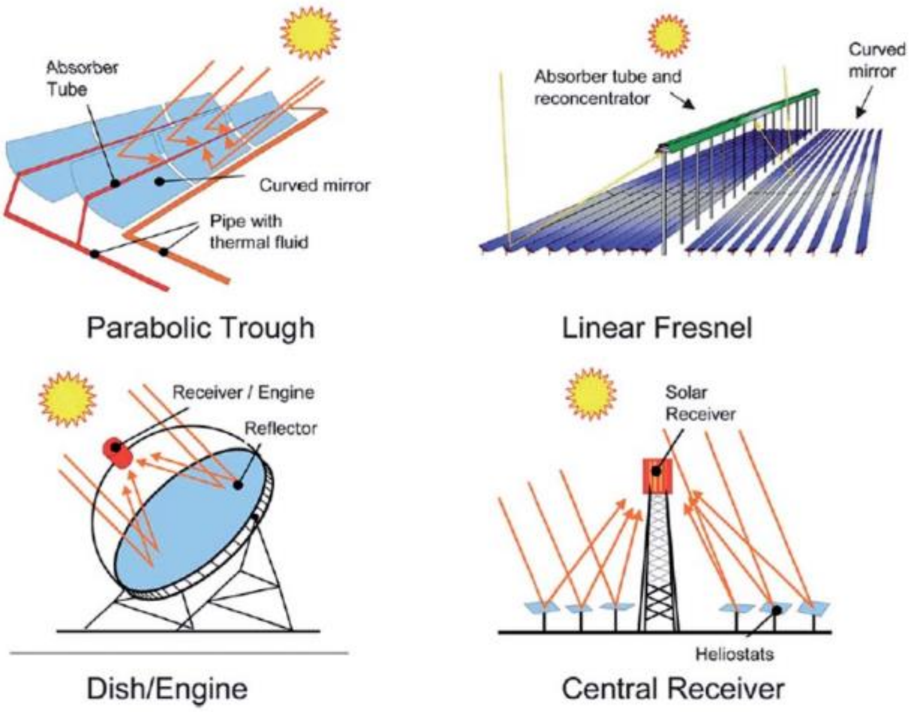

Figure 2. Schematic of the four solar concentrating technologies currently applied at commercial plants: parabolic trough collectors, linear Fresnel reflector systems, dish-engine systems and power towers also known as central receiver systems. Reproduced from fig. 2 with permission from The Royal Society of Chemistry.

Mechanism of Oxygen Exchange and Defect Chemistry in Perovskites

Perovskites, unlike materials that decompose or change phase during thermochemical cycles (such as zinc oxide), are designed to maintain a single phase under both reducing and oxidizing conditions, ensuring long-term durability in solar-to-fuel conversion processes. The key factors influencing the fuel yield and the reaction kinetics in perovskite-based materials are the oxygen incorporation and release, which are governed by the defect chemistry of the material.

Types of Defects in Perovskites

In perovskite oxides (ABO_3), **point defects** play a significant role in driving thermochemical reactions during solar-to-fuel conversion. There are three primary types of point defects:[14-15]

Electronic Defects:

1. These defects include electrons (e^-) or electron holes (h_s) within the lattice structure.
2. They are present at certain concentrations in undoped perovskites at room temperature or can be intentionally introduced through doping (n-type or p-type).
3. In solar-to-fuel conversion, these electronic charge carriers are critical for enabling charge transfer during the surface reactions (oxygen incorporation/release) and for ambipolar diffusion, which helps to distribute oxygen vacancies across the material.

Oxygen Ionic Defects

1. The most common oxygen defect in perovskites is the oxygen vacancy (V_O). Oxygen vacancies are p-type defects with a double charge.
2. Oxygen interstitials (extra oxygen ions in the lattice) are less common due to the dense packing of the perovskite structure, which makes creating space for interstitials energetically unfavorable.
3. Oxygen vacancies play a central role in enabling the oxidation and reduction processes that occur during the thermochemical cycles. Their concentration directly impacts fuel yield and the rate of oxygen exchange during the cycles.

Cationic Defects

- Like oxygen vacancies, cationic defects typically manifest as cation vacancies rather than interstitials.
- In certain compositions, A-site cation vacancies are more common and energetically favorable than B-site vacancies. However, cationic defects are generally less influential than oxygen vacancies in solar-to-fuel processes.

Role of Oxygen Vacancies in Solar-to-Fuel Conversion

Oxygen vacancies are by far the most critical defect type for solar-to-fuel applications. They are essential for oxygen incorporation and release, which drives the thermochemical redox reactions. The oxygen vacancy concentration fluctuates between oxidizing and reducing conditions, dictating the amount of oxygen that can be stored or released during each cycle.

- Oxidizing Conditions: The material is typically in its highest oxidized state (e.g., ABO_3). At these conditions, oxygen vacancies are minimized.
- Reducing Conditions: The perovskite reaches its most reduced state, commonly at d ≈ 0.5 (e.g., $ABO_{2.5}$), where phase transitions can occur, and the material may undergo decomposition into $A_2B_2O_5$ phases (e.g., brownmillerite).

The stability of the crystal structure under different oxygen non-stoichiometries is crucial for maintaining the material's functionality. Phase transformations, such as the breakdown into $A_2B_2O_5$ phases (e.g., $LaSrCo_2O_5$), may occur, but some perovskites, such as $Ba_{1-x}Sr_xCo_{1-\gamma}Fe_\gamma O_{3-\delta}$ (BSCF), have shown high oxygen vacancy concentrations even beyond typical non-stoichiometric limits. However, maintaining phase stability at high oxygen vacancy levels can be a challenge for some perovskites, as observed in BSCF, where chemical instability and phase instability are noted at higher oxygen vacancies.

Potential of Perovskites for Solar-to-Fuel Applications

- In typical perovskite structures (ABO_3), non-stoichiometries up to d ≈ 0.5 (where 16.7% of oxygen sites are vacant) represent a promising upper limit for solar-to-fuel applications. This range of vacancy concentration is significantly higher than that achievable in other materials like ceria, where only around 2% of oxygen sites are actively involved in reactions like H_2O or CO_2 splitting.
- The oxygen vacancy concentration and the associated non-stoichiometry can be optimized to achieve higher fuel yields in each thermochemical cycle, making perovskites an attractive material for solar-to-fuel technologies.

In summary, oxygen vacancies are the linchpin in determining the effectiveness of perovskites for solar-to-fuel conversion, and understanding their role and behavior under various conditions is essential for improving the performance and efficiency of these materials in energy applications [16-18].

Mechanisms of Oxygen Exchange in Perovskites for Solar-to-Fuel Conversion

Oxygen exchange is central to the operation of perovskites in solar-to-fuel conversion processes, fig 3 as it directly impacts the efficiency of thermochemical redox cycles. The mechanisms of oxygen exchange in perovskites are influenced by their ability to incorporate and release oxygen through lattice defects, particularly oxygen vacancies [19].

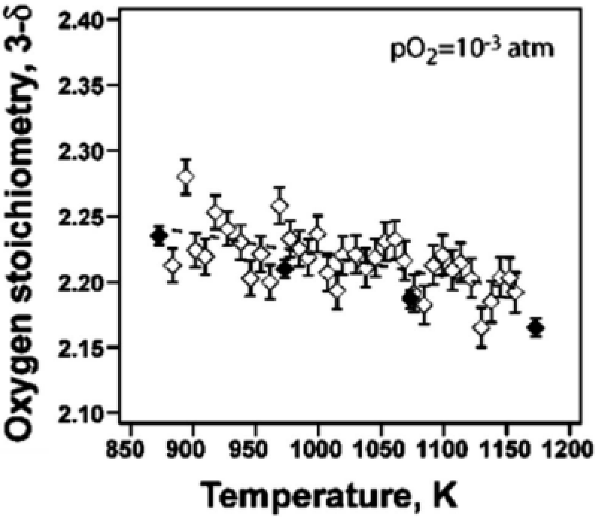

Figure 3. Extremely high oxygen non-stoichiometry d found in the Ba0.5Sr 0.5Co0.8Fe0.2O3d perovskite. Adapted with permission from S. McIntosh, J. F. Vente, W. G. Haije, D. H. A. Blank and H. J. M. Bouwmeester, Chem. Mater., 2006, 18, 2187–2193. Copyright 2006 American Chemical Society.

OXYGEN VACANCY MECHANISMS

Thermodynamic Equilibrium and Oxygen Non-Stoichiometry

- At high temperatures, such as around 1500°C, perovskites may reach thermodynamic equilibrium, where only a small fraction of the oxygen sites are unoccupied. For example, at $p(O_2) = 10^5$ mbar, only about 3% of oxygen sites in ceria (CeO_2) are unoccupied.
- The ability of a perovskite to hold or release oxygen is closely tied to its oxygen vacancy concentration and the partial oxygen pressure ($p(O_2)$) in the environment.

Doped Perovskites for Oxygen Exchange

- Highly p-doped perovskites are commonly used in solar-to-fuel conversion processes. These perovskites are doped with elements like manganese (Mn), chromium (Cr), cobalt (Co), or iron (Fe) on the B-site of the perovskite lattice.
- p-type doping is achieved by introducing positively charged defects, primarily electron holes and oxygen vacancies. These defects allow the perovskite to exhibit redox properties, enabling it to absorb and release oxygen under different conditions.

Extrinsic vs. Intrinsic Behavior

- In these materials, the p-type defect level is largely determined by the level of doping, which remains relatively constant across the operating temperature range of the solar-thermochemical cycle.
- This behavior is referred to as extrinsic doping, as the total defect level does not fluctuate significantly with temperature changes. The oxygen vacancies in these materials shift in concentration as the perovskite is oxidized or reduced, thereby facilitating H_2O or CO_2 splitting reactions.

Role of Oxygen Vacancies in Redox Reactions[20-21]

The oxygen vacancies in p-doped perovskites play a crucial role in the oxidation and reduction reactions. During oxidation, the material captures oxygen (by filling vacancies), and during reduction, the material releases oxygen (by creating vacancies). This cycling between oxidation and reduction enables the thermochemical splitting of H_2O and CO_2, driving the fuel production process.

Yield and Thermochemical Efficiency of Solar-to-Fuel Thermochemical Cycles Based on Perovskite Materials

The performance of perovskite materials in solar-to-fuel thermochemical cycles has been extensively studied, with a focus on their fuel yields and thermochemical efficiencies. These studies highlight the potential of perovskites in producing fuels like H_2 and CO through solar-driven redox cycles.

Fuel Yield

- Fuel yield (typically measured in mmol of fuel per gram of oxide) is one of the most commonly used parameters to evaluate the performance of perovskites in thermochemical cycles.
- A wide range of fuel yields have been reported for different perovskite compositions. For example, undoped ceria (CeO_2) has a fuel yield of about 169 mmol/g per cycle when reduced at 1500°C and oxidized at 1000°C. Some perovskite-based materials report fuel yields as high as 757 mmol/g per cycle, demonstrating significant promise for these materials in solar-to-fuel applications.
- Most studies focus on perovskites containing manganese (Mn), often mixed with elements like lanthanum (La), strontium (Sr), barium (Ba), and calcium (Ca), which show promising performance in the thermochemical cycles.
- The reduction temperatures for these materials typically fall in the range of 1000–1400°C, and oxidation temperatures are around 800–1100°C.
- Perovskites offer a key advantage: they enable lower reduction temperatures compared to traditional materials like ceria, which generally requires higher reduction temperatures (around 1500°C). This makes perovskites attractive for improving the thermal efficiency of solar-to-fuel processes.

Thermochemical Efficiency [22-24]

Thermochemical efficiency is a critical factor for assessing the commercial viability of perovskites in solar-to-fuel conversion. It is typically calculated as the ratio of the enthalpy of the produced fuel (ΔHfuel\Delta H_{\text{fuel}}) to the heat input (QinputQ_{\text{input}}):

ηconv=ΔHfuelQinput\eta_{\text{conv}} = \frac{\Delta H_{\text{fuel}}}{Q_{\text{input}}}

- The solar-to-fuel efficiency is another important parameter, which is typically calculated on an annual average basis. For successful commercial implementation, a target efficiency of around 20% is often considered competitive.
- The chemical efficiency and thermal efficiency of a material also play a significant role. Materials that can efficiently exchange oxygen during redox cycles, and those that can perform the cycles with small temperature differences between oxidation and reduction steps, are preferred.
- For example, $La_{1-x}Sr_xMnO_{3-\delta}$, a strontium-doped lanthanum perovskite, has been shown to have a larger fuel yield compared to ceria but lower thermochemical efficiency under certain conditions. This suggests that ceria remains a strong competitor in terms of efficiency, although perovskites hold potential for higher fuel yields under optimized conditions.

CHALLENGES AND CONSIDERATIONS

- While fuel yields are a useful measure of material performance, they cannot predict the overall competitiveness of a thermochemical cycle. The full performance of a cycle depends on factors like the reaction times, gas partial pressures, and temperature profiles.
- Additionally, discrepancies may arise when extrapolating experimental data, as many studies focus on limited temperature ranges and thermogravimetric data. Therefore, it is important to account for full cycle conditions and materials' behavior at both high and low temperatures.
- CALPHAD (Calculation of Phase Diagrams) and other advanced modeling techniques are often used to predict the behavior of materials across wider temperature ranges, providing more comprehensive insights into their performance in solar-to-fuel cycles [25-29].

CONCLUSION

Perovskites, particularly those doped with elements like **manganese**, **lanthanum**, and **strontium**, show great potential for **solar-to-fuel conversion**. While **fuel yields** are high, **thermochemical efficiency** is a more decisive factor for commercial applications. Although **ceria** currently leads in efficiency, **perovskites** offer the potential for improvements in **fuel yield** and **lower operating temperatures**, making them promising candidates for future solar-driven fuel production technologies.

Conclusion

In early studies, the thermodynamic properties of various materials were tuned to meet the specific needs of thermochemical cycles. Among the materials tested, several acceptor-doped perovskite compositions have been studied, including manganites, ferrites, cobaltates, chromates, and aluminates. Compared to ceria, perovskites offer the advantage of requiring lower reactor temperatures for reduction and a larger potential change in nonstoichiometry. However, two areas that often still need improvement in perovskites are their chemical stability and lower enthalpies, which can limit thermal efficiency and necessitate larger temperature swings. Significant progress can be anticipated in the coming years, driven by material screening studies and computational methods aimed at predicting new, promising compositions.In addition to favorable thermodynamic properties, other essential characteristics such as mechanical and thermal stability, chemical reactivity, and reaction kinetics need to be optimized. These complex requirements present challenges for both material development and reactor design, especially for achieving efficiencies greater than 20%, which could surpass current solar fuel technologies, like coupled photovoltaics and electrolysis. While acceptor-doped cubic perovskites are the focus of most current research, there remains considerable potential in perovskite-related materials, particularly in structures that have yet to be systematically explored, such as layered materials or those that accommodate oxygen interstitials. These unexplored structures may lead to the discovery of highly efficient solar-to-fuel reactor materials.

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