High-Flux Solar-Driven Thermochemical Dissociation of CO2 and H2O Using Nonstoichiometric Ceria

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Because solar energy is available in large excess relative to current rates of energy consumption, effective conversion of this renewable yet intermittent resource into a transportable and dispatchable chemical fuel may ensure the goal of a sustainable energy future. However, low conversion efficiencies, particularly with CO2 reduction, as well as utilization of precious materials have limited the practical generation of solar fuels. By using a solar cavity-receiver reactor, we combined the oxygen uptake and release capacity of cerium oxide and facile catalysis of sintering, and losses because of uncontrolled volatilization, whereas ZnO, SnO2, and analoguous volatile oxides that sublime during decomposition require rapid quenching of gaseous products to avoid recombination (10–18). Cerium oxide (ceria) has emerged as a highly potential for a transition away from fossil energy (7).
Thermochemical H₂O-CO₂-splitting cycles over a nonstoichiometric oxide are described by the following pairs of reactions:

Higher temperature, $T_H$

$$\frac{1}{\delta}\text{MO}_2 \rightarrow \frac{1}{\delta}\text{MO}_{2-\delta} + \frac{1}{2}\text{O}_2(g) \quad (1)$$

Lower temperature, $T_L$

$$\text{H}_2\text{O}(g) + \frac{1}{\delta}\text{MO}_{2-\delta} \rightarrow \frac{1}{\delta}\text{MO}_2 + \text{H}_2(g) \quad (2a)$$

Net H₂O dissociation

$$\text{H}_2\text{O}(g) \rightarrow \frac{1}{2}\text{O}_2(g) + \text{H}_2(g) \quad (3a)$$

Lower temperature, $T_L$

$$\text{CO}_2(g) + \frac{1}{\delta}\text{MO}_{2-\delta} \rightarrow \frac{1}{\delta}\text{MO}_2 + \text{CO}(g) \quad (2b)$$

Net CO₂ dissociation

$$\text{CO}_2(g) \rightarrow \frac{1}{2}\text{O}_2(g) + \text{CO}(g) \quad (3b)$$

where M in the present case is Ce or a combination of Ce and a dopant element. At the relatively high temperatures of the present study (>800°C), equilibria of reaction (2b) involving carbonaceous species can be neglected (21).

The solar reactor constructed for the purposes of demonstrating these cycles is schematically shown in Fig. 1. It consists of a cavity receiver containing a porous monolithic ceria cylinder. Concentrated solar radiation enters through a windowed aperture and impinges on the ceria inner walls. Reacting gases flow radially across the porous ceria toward the cavity inside, whereas product gases exit the cavity through an axial outlet port at the bottom. (Inset) The scanning electron micrograph of the porous ceria tube after 23 cycles. Blue arrows indicate ceria reduction (Eq. 1); red arrows indicate oxidation (Eqs. 2a and 2b).

**Fig. 1.** Schematic of the solar reactor for the two-step, solar-driven thermochemical production of fuels. It consists of a thermally insulated cavity receiver containing a porous monolithic ceria cylinder. Concentrated solar radiation enters through a windowed aperture and impinges on the ceria inner walls. Reacting gases flow radially across the porous ceria toward the cavity inside, whereas product gases exit the cavity through an axial outlet port at the bottom. (Inset) The scanning electron micrograph of the porous ceria tube after 23 cycles. Blue arrows indicate ceria reduction (Eq. 1); red arrows indicate oxidation (Eqs. 2a and 2b).

**Fig. 2.** Thermochemical cycling of ceria (325 g) using the solar reactor with (A) CO₂ and (B) H₂O as oxidant. The oxygen and fuel evolution rates as well as the total volume of gas evolved are shown. Temperatures were measured at three positions along the height of the ceria tube. Maximum temperatures ($T_{max}$) attained in the reactor are shown. Conditions for (A) were as follows: Ar sweep gas at a flow rate of 0.0062 liter min⁻¹ g⁻¹ of ceria during the ceria reduction half-cycle, and CO₂/Ar at $p_{CO_2} = 0.78$ atm and a flow rate of 0.035 liter min⁻¹ g⁻¹ of ceria during the ceria oxidation half-cycle. Conditions for (B) were as follows: Ar sweep gas at a flow rate of 0.023 liter min⁻¹ g⁻¹ of ceria during the ceria reduction half-cycle, and H₂O/Ar at $p_{H_2O} = 0.78$ atm and a flow rate of 0.035 liter min⁻¹ g⁻¹ of ceria during the ceria oxidation half-cycle.
With this arrangement, the porous ceria cylinder is directly exposed to concentrated solar radiation impinging on its inner walls. An annular gap between the ceria cylinder and the alumina insulation tiles suppresses undesired reactions between the two components. Reacting gases are injected into this annular gap and directed to flow radially across the porous ceria cylinder toward the cavity inside, whereas product gases exit the cavity through an axial outlet port at the bottom. Complete experimental details, including procedures for estimating uncertainty, are given in (25). Post situ x-ray diffraction showed that, with the exception of the portion in direct contact with the insulation material, the ceria remained phase-pure and free of detectable alumina incorporation (fig. S1).

To drive oxygen evolution (Eq. 1), we purged the solar reactor with flowing argon [partial pressure of O$_2$ (p$_{O2}$) = 10$^{-5}$ atm] and ramped the incident radiation power to about 1.9 kW at a mean solar flux intensity over the aperture of 1500 suns (1 sun = 1 kW m$^{-2}$), typical of a commercial solar dish or a tower concentration system. The temperature of the ceria tube rose to values between 1420$^\circ$C and 1640$^\circ$C, with the exact temperature dependent on the position within the reactor and on the cycle (Fig. 2A). The rise in temperature was rapid below 1250$^\circ$C, averaging 140$^\circ$C min$^{-1}$, but slowed to about 8$^\circ$C min$^{-1}$ as the temperature approached a steady-state value because of increasing heat dissipation by re-radiation through the aperture and conduction heat transfer through the insulation. Oxygen evolution from ceria was observed at an onset temperature of about 900°C, consistent with equilibrium thermogravimetry measurements (fig. S2). The rate of evolution increased with temperature, reaching a peak value of 34 ± 2 ml min$^{-1}$ (STP, standard temperature and pressure) and an average value of 16 ± 1 ml min$^{-1}$ (averaged over the time required to reach 90% of the extent of reaction) on the first cycle (Fig. 2A). When the rate dropped to 20% of the peak value, the evolution reaction was terminated by decreasing the intensity of the incident radiation flux. Upon cooling to ~900°C, CO$_2$ was injected into the solar reactor. Production of CO was immediately observed, reaching a remarkable peak rate of 1.5 × 10$^3$ ± 0.1 × 10$^3$ ml min$^{-1}$ (STP) and an average rate of 5.9 × 10$^2$ ± 0.4 × 10$^2$ ml min$^{-1}$ (STP) (Fig. 2A).

Consistent with the fact that there was no water present in the reactant stream, no gas-phase C$_1$, C$_2$, or C$_3$ hydrocarbons were detected by the gas chromatograph. Carbon-neutral balance (~3% C unaccounted for, well within error) was achieved by summing the flow rates of CO in the reactant stream and CO$_2$ and CO in the product steam. As verification, temperature-programmed oxidation was performed on the ceria after the CO$_2$ dissociation reaction by flowing oxygen into the solar reactor while ramping the temperature to 1000°C (26). Both CO and CO$_2$ levels were below the detection limit, confirming that no appreciable amount of carbonaceous species was deposited onto ceria during CO$_2$ dissociation and that a 100% selectivity toward CO production was achieved. Upon the termination of CO production, the radiation flux was increased and the entire cycle repeated. A slight decline over the four cycles in the nominal reactor temperature attained during the O$_2$ release step (from 1624°C to 1581°C) is responsible for the observed slight decline in O$_2$ release and CO yield. An analogous set of experiments was also performed for H$_2$O dissociation, with H$_2$ production rate reaching a peak value of 7.6 × 10$^2$ ± 0.8 × 10$^2$ ml min$^{-1}$ (STP) and a maximum average value of 3.1 × 10$^2$ ± 0.3 × 10$^2$ ml min$^{-1}$ (STP) (Fig. 2B). A total of 23 cycles were performed. An experimental run performed without the ceria confirmed the absence of O$_2$, CO, or H$_2$ evolution under corresponding reaction conditions.

The characteristics of solar-thermochemical fuel production from ceria reveal several important features of the cycling process. Although the behavior is generally reproducible between cycles, some run-to-run variations are evident. The oxygen evolution reaches a peak value between 17 and 34 ml min$^{-1}$, whereas the total amount evolved ranges from 0.54 to 0.94 liter for 325 g of ceria. As noted, these differences are correlated with the peak reactor temperature obtained (Fig. 2), variations in which are attributed to unstable heat transfer. Taking this temperature variability into account, the total oxygen evolution is found to be generally consistent with thermodynamic expectations (fig. S2). Mass balance considerations further dictate a 2-to-1 molar (and hence volumetric) ratio of fuel produced to oxygen released for full utilization of the ceria nonstoichiometry. For CO$_2$ dissociation, the CO$_2$:O$_2$ ratio ranged from 1.6 ± 0.2:1 to 2.0 ± 0.2:1, whereas for H$_2$O dissociation, the H$_2$:O$_2$ ratio was 1.6 ± 0.2:1. The slight deviation from the ideal value is attributed to small leaks in the system and to the accuracies of the electronic mass flow controller and measured gas composition.

Perhaps the most obvious feature of the cycling behavior in Fig. 2 is the much faster rate of fuel production than that of O$_2$ release. It was observed that lowering the purge gas flow rate during ceria reduction by a factor of 4 had negligible impact on the oxygen evolution rate (Fig. 2), indicating that the convective transport of oxygen gas in the reactor is not likely the rate-limiting step. Furthermore, the substantial difference in the O$_2$ evolution and CO$_2$ dissociation rate suggests that gas-phase transport through the pores of ceria is probably not rate-limiting. We considered, as an alternative, that the oxygen evolution kinetics in the solar reactor are
limited by the heating rate, a factor that does not affect fuel production because this step occurs isothermally. If the heating rate is slow relative to the surface reaction and solid-state diffusion steps involved in oxygen release, we can express the oxygen evolution rate as \( \dot{\partial}/\dot{t} = (\dot{\partial}/\dot{t})_{-3} (\dot{t}/\dot{t}) \), where \( \partial \) is ceria oxygen nonstoichiometry (Eq. 3), \( T \) is temperature, and \( t \) is time. By using the spatially averaged temperature profile in the first cycle in Fig. 2A, we compute a maximum oxygen evolution rate of 65 ml min\(^{-1} \), which, given the approximate nature of the calculation, is comparable to the observed rate.

To eliminate the effect of gas-phase mass and heat transfer, we carried out thermochemical cycling of ceria by using identically prepared monolithic porous samples (annealed for 50 hours to simulate cycling conditions) in a smaller-scale infrared imaging furnace that uses only a 0.4-g sample. Such an experimental setup permitted thermochemical cycling under high-flow, differential reactor conditions, in which the sample temperature could be changed rapidly (average ramp rate of 1700°C min\(^{-1} \)) and the gas composition approached uniformity. Under these ideal conditions in which only surface chemical reactions and solid-state oxygen diffusion in ceria limit the overall reaction rate, oxygen evolution (Fig. 3) attained a peak instantaneous rate ~80 times faster than in the solar reactor and an associated average rate of 2.2 ± 0.2 ml min\(^{-1} \)
\( g \)^\(-1\) of ceria; \( CO_2 \) and \( H_2O \) dissociation reactions were about two and four times faster (although the reactant partial pressures, temperatures, and initial extents of reduction differ slightly between the differential and solar reactor), with rates of 5.1 ± 0.4 and 5.3 ± 0.4 ml min\(^{-1} \)
\( g \)^\(-1\) of ceria, respectively. These rates support the proposition that oxygen evolution kinetics in the solar reactor are limited predominantly by the heating rate.

The solar-to-fuel energy conversion efficiency is defined as

\[
\eta = \frac{r_{\text{fuel}} \Delta H_{\text{fuel}}}{P_{\text{solar}} + r_{\text{inert}} E_{\text{inert}}} \tag{4}
\]

where \( r_{\text{fuel}} \) is the molar fuel production rate, \( \Delta H_{\text{fuel}} \) is the higher heating value of the fuel, \( P_{\text{solar}} \) is the incident solar radiation power, \( r_{\text{inert}} \) is the flow rate of the inert gas during oxygen evolution, and \( E_{\text{inert}} \) is the energy required to separate the inert sweep gas from air (usually \( N_2 \); \( Ar \) was used in this work entirely for reasons of experimental convenience). Based on the experimental data, the peak instantaneous efficiencies for \( CO_2 \) and \( H_2O \) dissociations reached 0.8% and 0.7%, respectively [for detailed calculation procedures, see (25)]. No heat recuperation strategy was used. Upon averaging the efficiencies over the time required to produce 80% of the fuel, the efficiencies become 0.4% (for both \( CO_2 \) and \( H_2O \) dissociations). These experimentally measured efficiencies reflect the cycle irreversibilities resulting from intrinsic material properties as well as solar reactor design and operation. An energy-balance analysis (25) reveals that 50% of the energy loss resulted from heat conduction through the reactor wall and 41% resulted from reradiation through the aperture. The former energy penalty can be dramatically reduced by improving thermal insulation and by scaling up to increase the volume-to-area ratio. The latter can be minimized by augmenting the solar flux such that the aperture size can be reduced. Decreasing heat loss also has the added benefit of increasing the temperature ramp rate. As shown in the earlier comparison of the oxygen evolution kinetics under slow and rapid heating rates, the oxygen evolution kinetics and conversion efficiency are closely coupled to the rates at which the active ceria materials can be heated and cooled.

Beyond efficiency, material stability is an essential criterion for a viable thermochemical process. With use of the differential reactor system, which enables rapid access to multiple cycles, 500 cycles of water dissociation were performed without interruption. The results (Fig. 4), reported in part in an earlier work (21), indicate that, after an initial stabilization period of ~100 cycles, both the oxygen and hydrogen evolution rates remain essentially constant for a subsequent 400 cycles. Scanning electron microscopy examination of samples of porous ceria that underwent heat treatment under similar conditions (fig. S3) revealed that the decrease in reaction rate is accompanied by an increase in particle size. The morphology stabilized after 24 hours of heat treatment at 1500°C, much as the fuel production rate stabilized after an initial period. That ceria can be cycled between two oxidation states without substantial loss of activity can be attributed to its sufficiently large change in oxygen nonstoichiometry at moderate homologous temperatures (~0.6 × \( T_m \)).

In sum, the feasibility of a solar-driven thermochemical cycle for dissociating \( H_2O \) and \( CO_2 \) using nonstoichiometric ceria has been demonstrated in terms of materials, reaction rates, cyclability, reactor technology, and energy conversion efficiency. Essential to this demonstration is a simple and scalable reactor design using porous ceria directly exposed to concentrated solar radiation that enables high-temperature heat transfer to the reaction sites, as required for performing both steps of the cycle. The solar-to-fuel energy conversion efficiency obtained in this work for \( CO_2 \) dissociation is about two orders of magnitude greater than that observed with state-of-the-art photocatalytic approaches (3, 9). The gravimetric hydrogen production rate exceeds that of other solar-driven thermochemical processes by more than an order of magnitude (27, 28). Both the efficiency and the cycling rates in the reactor were limited largely by thermal losses, resulting from conductive and radiative heat transfer. A thermodynamic analysis of efficiency based solely on the material properties of \( CO_2 \) indicates that values in the range of 16 to 19% are attainable, even in the absence of sensible heat recovery (21). Thus, with reactor optimization and system integration substantial increases in both efficiency and fuel production rates are anticipated. The material stability, showing stable fuel production over 500 thermochemical cycles, is already suitable for realistic applications. Furthermore, the abundance of cerium, which is comparable to that of copper (29), is such that the approach is applicable at scales relevant to global energy consumption (21).

References and Notes
Spin Hall Effect Transistor

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The field of semiconductor spintronics explores spin-related quantum relativistic phenomena in solid-state systems. Spin transistors and spin Hall effects have been two separate leading directions of research in this field. We have combined the two directions by realizing an all-semiconductor spin Hall effect transistor. The device uses diffusive transport and operates without electrical current in the active part of the transistor. We demonstrate a spin AND logic function in a semiconductor channel with two gates. Our study shows the utility of the spin Hall effect in a microelectronic device geometry, realizes the spin transistor with electrical detection directly along the gated semiconductor channel, and provides an experimental tool for exploring spin Hall and spin precession phenomena in an electrically tunable semiconductor layer.

Two major themes in semiconductor spintronics research, the spin transistors and the spin Hall effects, have followed distinct and independent scientific paths (1, 2). In the transistor case, the target device concept of a ferromagnetic spin injector and detector connected by a semiconductor channel was established from the outset by Datta and Das (3). The ensuing research has focused on the fundamental physical problems related to the resistance mismatch between the transistor’s components and to the spin manipulation in the semiconductor via spin-orbit coupling effects (4–7). By contrast, in the spin Hall effect case, much of the related intriguing quantum-relativistic physics (16–19) has been established before the first experimental observations (20, 21), but the field is still striving to turn the phenomenon into a concrete device functionality. We demonstrate the applicability of the spin Hall effect in a new type of spin transistor.

The active semiconductor channel in our devices is a two-dimensional electron gas (2DEG) in which the spin-orbit coupling induced spin precession is controlled by external gate electrodes and detection is provided by transverse spin Hall

**Fig. 1.** (A) Schematics of the measurement setup with optically injected spin-polarized electrical current propagating through the Hall bar and corresponding experimental Hall effect signals at crosses H1 and H2. The Hall resistances, \( R_H = V_H/I_ph \), for the two opposite helicities of the incident light are plotted as a function of the focused (1 μm) light spot position, i.e., of the position of the injection point. Increasing \( x \) corresponds to shifting the spot further away from the Hall detectors. (The focused laser beam is indicated by the yellow cylinder in the schematics.) The optical current \( I_{ph} \) is independent of the helicity of the incident light and varies only weakly with the light spot position. The applied bias voltage \( V_{ph} = -15 \) V, the laser intensity is 1000 W/cm², and the laser wavelength is 870 nm. (B) Same as (A) for measurement geometry in which electrical current is closed before the first detecting Hall cross H1. (C) Schematics of the diffusive transport of injected spin-polarized electrons and Monte-Carlo simulations of the out-of-plane component of the spin of injected electrons averaged over the 1-μm bar cross section assuming Rashba field \( \alpha = 5.5 \) meV Å, Dresselhaus field \( \beta = -24 \) meV Å, and different values of the mean free path \( l \).