Redox Kinetics Study of Fuel Reduced Ceria for Chemical-Looping Water Splitting

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ABSTRACT: Chemical-looping water splitting is a novel and promising technology for hydrogen production with CO2 separation. Its efficiency and performance depend critically on the reduction and oxidation (redox) properties of the oxygen carriers (OC). Ceria is recognized as one of the most promising OC candidates, because of its fast chemistry, high ionic diffusivity, and large oxygen storage capacity. The fundamental surface redox pathways, including the complex interactions of mobile ions and electrons between the bulk and the surface, along with the adsorbates and electrostatic fields, remain yet unresolved. This work presents a detailed redox kinetics study with emphasis on the surface ion-incorporation kinetics pathway, using time-resolved and systematic measurements in the temperature range 600–1000 °C. By using fine ceria nanopowder, we observe an order-of-magnitude higher hydrogen production rate compared to the state-of-the-art thermochemical or reactive chemical-looping water splitting studies. We show that the reduction is the rate-limiting step, and it determines the total amount of hydrogen produced in the following oxidation step. The redox kinetics is modeled using a two-step surface chemistry (an H2O adsorption/dissociation step and a charge-transfer step), coupled with the bulk-to-surface transport equilibrium. Kinetics and equilibrium parameters are extracted with excellent agreement with measurements. The model reveals that the surface defects are abundant during redox conditions, and charge transfer is the rate-determining step for H2 production. The results establish a baseline for developing new materials and provide guidance for the design and the practical application of water splitting technology (e.g., the design of OC characteristics, the choice of the operating temperatures, and periods for redox steps, etc.). The method, combining well-controlled experiment and detailed kinetics modeling, enables a new and thorough approach for examining the defect thermodynamics in the bulk and at the surface, as well as redox reaction kinetics for alternative materials for water splitting.

1. INTRODUCTION

Hydrogen is an important environmentally friendly energy carrier because of its high gravimetric energy density and zero emission. Moreover, hydrogen finds wide applications in a variety of industries, including crude oil refining, chemical production, aerospace, metal refining, food processing, and electronics manufacturing. Currently, steam methane reforming (SMR) is the major hydrogen production method. However, SMR leads to significant greenhouse gas emission, and it has already reached its maximum efficiency (70–85%).1 The growing demand for clean and cost-efficient hydrogen sources has led to significant efforts to develop alternative technologies.2,3

Among a variety of options, thermochemical water splitting (TCWS) has recently attracted significant attention, because of its potential for high conversion efficiencies with limited emissions.4,5 This approach is based on a two-step mechanism using a metal oxide (such as ceria-based materials) to dissociate H2O into H2 and heat to reduce the metal oxide:

\[
\text{Me}_x\text{O}_y \rightarrow \text{Me}_x\text{O}_{y-1} + \frac{1}{2}\text{O}_2 \tag{1}
\]

endothermic reduction step:

\[
\text{H}_2\text{O} + \text{Me}_x\text{O}_{y-1} \rightarrow \text{H}_2 + \text{Me}_x\text{O}_y
\tag{2}
\]

exothermic oxidation step:

The reduction step proceeds at higher temperature (above 1400 °C) to form oxygen vacancies and release O2, while the oxidation step takes place at lower temperature (below 1000 °C) to dissociate H2O and generate H2. During this process, the metal oxide transports oxygen between the two steps, remaining intact at the end of the cycle. As such, it is commonly referred to as the "oxygen carrier (OC)". Various studies have examined different material options for TCWS, and a brief summary is presented in Table 1. Although exhibiting remarkable potentials, major challenges are related to the need for expensive high quality heat and large temperature swing which can render the process less efficient. An immediate extension of TCWS is reactive chemical-looping water splitting (RCLWS), in which, the reduction step...
64 is replaced by a fuel reduction reaction:

\[ \text{MeO} + \text{CH}_4 \rightarrow \text{Me}_2\text{O}_{y-1} + \text{CO} + 2\text{H}_2 \]  

(3)

The utilization of fuel ensures an enhanced catalytic reaction at lower temperature with significantly improved extent of OC reduction and, hence, larger oxygen carrying capacity. The required high quality heat and large temperature swing could be replaced by an isothermal redox operation, hence leading to a much reduced cost, enhanced stability, and improved system efficiency. In contrast to TCWS, the net reaction, combining eqs 2 and 3, is a fuel reforming reaction, where a fuel is selectively oxidized to form hydrogen and syngas. In the case of natural gas, the syngas stream has a H2:CO close to 2:1, ideal for the production of H2 (after shift), methanol, or liquid fuel via Fischer–Tropsch process with CO2 separation. With the abundance and low price of natural gas, RCLWS offers a simple and promising solution for co-producing hydrogen and syngas.

Several studies have examined various metal oxide candidates for RCLWS, including ceria, copper, ferrites, tungsten, and perovskites, etc. The reported H2 production rates and total production using RCLWS are summarized in Table 2. It is generally observed that the use of ceria as an OC leads to higher H2 production because of its fast surface kinetics, high oxygen ionic diffusivity, large oxygen carrying capacity, and robust structural stability. The ability of ceria to accommodate high surface active site concentrations facilitates a relatively quick surface ion-incorporation process.44,45 The large nonstoichiometry capacity allows it to effectively adsorb and release oxygen as it responds to the operating conditions. This property has been exploited in a large number of applications, including three-way catalyst, solid oxide fuel cells, and electrolyzers. For the same reason, CeO2 has been suggested as a promising OC candidate for RCLWS.

| temp (°C; red/ox) | tot H2 prodn (μmol/g) | peak H2 rate (μmol/g/s) | feed H2O (%) | oxygen carrier | reducer | ref |
|-------------------|------------------------|--------------------------|--------------|----------------|----------|-----|
| 1500/800          | 278                    | 6.8                      | 44–52        | CeO2 (with Rh) | this study | 6   |
| 1500/1500         | 126                    | 1.0                      | 15           | CeO2           | this study | 7   |
| 1350/1000         | 32                     | 0.15                     | 40           | CeO2           |          | 8   |
| 1500/1150         | 414                    | 4.2                      | 50, 84       | CeO2           |          | 9   |
| 1500/1000         | 28                     | 81                       | 83           | CeO2           |          | 10  |
| 1500/750          | 161                    | 83                       | 83           | CeO2 (10% Pr)  |          | 11  |
| 1400/1050         | 338                    | 5.8                      | 83           | CeO2 (25%Zr 1%Gd)|          | 12  |
| 1300/800          | 109                    | 3.8                      | 83           | CeO2(50%Zr)    |          | 13  |
| 1400/1050         | 467.7                  | 38.3                     | 83           | CeO2           |          | 14, 15 |
| 1500/500          | 210                    | 84                       | 84           | CeO2           |          | 16  |
| 1500/1000         | 153                    | 83                       | 83           | CeO2 (10% Mn)  |          | 17  |
| 1290/1000         | 62                     | 16.4                     | 21           | CeO2 (20% Zn)  |          | 18  |
| 1200/900          | 57                     | 81                       | 81           | Ni3Mn3Fe5O14   |          | 19  |
| 1190/900          | 2120                   | 9.4                      | 56           | Zn–Fe–O       |          | 21  |
| 1700/575          | 4270                   | 9.1                      | 56           | FeO           |          | 20  |
| 1400/1000         | 195                    | 5.8                      | 40           | La2O3 (with Sr, Mn) |          | 8   |
| 1350/1000         | 307                    | 1.3                      | 40           | La2O3 (with Sr, Mn) |          | 21  |
| 1400/1000         | 407                    | 5.6                      | 40           | La2O3 (with Sr, Mn) |          | 22  |

Note some studies tested various material compositions for repeated cycles. The highest values are chosen and listed here for comparison. The conversion of the H2 production unit from mL/g to μmol/g utilizes the ideal gas law at standard temperature and pressure (25 °C, 1 atm).
The bulk-phase properties of ceria-based materials have been widely studied. The physical, chemical, and electrochemical properties of pure and doped ceria at equilibrium have been examined and documented. Recently, there is an increasing effort toward a better understanding of the surface-oriented defect chemistry of ceria, owing to the growing interests in fuel cells, electrolyzers, and water splitting. Density functional studies examined surface defect formation and the energy landscape of the redox process. In situ techniques, such as in situ X-ray photoelectron spectroscopy (XPS), have emerged recently and have been successfully applied to ceria.

The majorit of the work concentrated on the surface and intermediate species at equilibrium. Despite the recent efforts in developing analytical models for reaction kinetics, the fundamental surface redox pathway of ceria is not well understood. The complexities involved in the interactions of mobile ions, and electrons between the bulk and the surface, along with the adsorbates and electrostatic fields remain yet unresolved.

Applying ceria in RCLWS requires a good knowledge of the time-resolved reactivity under conditions relevant for its application (temperature and gaseous composition), which is still missing.

In this work, we investigate the ceria redox mechanism with an emphasis on the surface ion-incorporation kinetics pathway, using a detailed time-resolved measurement under conditions relevant for RCLWS. Isotermal redox cycles of CeO$_2$ nanoparticles are carried out in a button cell reactor in the temperature range 600–1000 °C. H$_2$ is used as a surrogate fuel in this study in order to explore the fundamentals of redox reactions on ceria. The reaction kinetics is determined by quantifying the flue stream composition using an online quadrupole mass spectrometer (QMS). H$_2$ is produced by water splitting during the oxidation cycle as a mixture of H$_2$O vapor and Ar is flown over CeO$_2$ samples. An order-of-magnitude higher hydrogen production rate is observed as compared to the state-of-the-art TCWS (Table 1) and RCLWS (Table 2) methods, resulting from the utilization of fine ceria nanopowder, which also ensures a surface-reaction-limited process. Kinetic models are subsequently developed to characterize the oxygen-ion-incorporation dynamics during the redox process. The model consists of a series of intermediate steps: adsorption/dissociation of gaseous reactant, charge transfer on the surface, and the bulk-to-surface transport. The model reveals the importance of the surface defect and its connection to the bulk phase. Driven by the difference of the defect formation energy, the surface is enriched with the key defects (oxygen vacancy and polarons), consistent with the in situ observations reported in the literature. With the proposed kinetics, the rate-limiting step is identified, and suggestions are obtained for the development of better materials in the future.

2. EXPERIMENT

The experimental setup consists of a gas delivery system, a control unit, a central quartz reactor tube, and a real time flue gas analysis system with an online mass spectrometer. The system layout and the details of the reactor are shown in Figure 1. Four Brooks GF40 MultiFlo digital thermal mass flow controllers (MFCs) are used for the gas flow control. The reactor is made of a quartz tube positioned inside an ATS 3210 split tube furnace that provides an isothermal environment up to 1100 °C. As shown in Figure 1b, the reactor consists of an outer tube (305 mm length, 25.4 mm outer diameter (o.d.), and 21.6 mm inner diameter (i.d.)), and an inner concentric 6.4 mm o.d. quartz tube with an expanding section of 19.1 mm o.d., 38.1 mm length. Gases flow through the central tube, impinge on the bottom of the outer tube, and exit reversely through the exhaust. Capillary probes made of quartz (0.53 mm i.d., 0.80 mm o.d.) are used to sample minute amounts of gases, before and after reactions. The probe sampling the exhaust flow is located close to the outer tube, around 1–2 mm above the top of the expansion section of the inner tube. A quadrupole mass spectrometer (HPR20 from Hiden Analytical Inc.) is used to analyze the flue gas composition. The QMS has a response time of less than 300 ms and a wide bandwidth of species detection capability.

Ceria powder from Sigma-Aldrich (99.95% purity) is used for the reaction study. Table 3 lists the properties of the sample. The BET surface area is 15.4 m$^2$/g, and the average size of the particle is 50 nm. A 100 mg amount of ceria powder is embedded in quartz wool and placed at the bottom of the outer quartz tube.
Table 3. Some Physical Properties of the CeO$_2$

| property            | value (unit) |
|---------------------|--------------|
| density, $\rho$     | 7.22 g cm$^{-3}$ |
| molar density, $\rho_{\text{m}}$ | $4.19 \times 10^{3}$ mol m$^{-3}$ |
| lattice constant, $a$ | 0.54112 nm |
| surface molar density, $\rho_{\text{surf}}$ | $2.27 \times 10^{-5}$ mol m$^{-2}$ |
| melting point       | 2750 K       |
| relative dielectric constant (0.5–500 MHz) | 11 |
| fresh sample        |              |
| bulk density        | 0.53 g cm$^{-3}$ |
| purity              | 99.95%       |
| specific surface area, $s_0$ | 15.4 m$^2$ g$^{-1}$ |
| particle size       | 50 nm        |
| cycled sample       |              |
| specific surface area, $s_1$ | 3.99 m$^2$ g$^{-1}$ |
| particle size       | ~200 nm      |

A lesser amount of sample is also tested (50 and 25 mg), and negligible difference is found in the obtained redox kinetics. The sample undergoes redox cycles, with argon as purging gas flowing in between. Oxidation is performed using a gas mixture of water vapor and argon. Ar is slowly bubbled through a 1 gallon bottle filled with deionized water maintained at 80 ± 0.5 °C in an insulated heat bath to prepare the oxidizing mixture. The steam mixture is further diluted with Ar to achieve the desirable H$_2$O concentration. The total flow rate into the reactor during the oxidation step is maintained constant at 337 cm$^3$(STP)/min, and the H$_2$O mole fraction is varied between 5% and 26%. H$_2$–Ar mixture is used for the reduction, with the total flow fixed at 350 cm$^3$(STP)/min and the H$_2$ mole fraction from 5% to 20%. While the ultimate technology objective is to use methane for oxidation, H$_2$ is used as a surrogate to examine the process which is further oxidized with Ar to be removed from the system. The steam mixture is further diluted with Ar to achieve the desirable H$_2$O concentration. The total flow rate into the reactor during the oxidation step is maintained constant at 337 cm$^3$(STP)/min, and the H$_2$O mole fraction is varied between 5% and 26%. H$_2$–Ar mixture is used for the reduction, with the total flow fixed at 350 cm$^3$(STP)/min and the H$_2$ mole fraction from 5% to 20%. While the ultimate technology objective is to use methane for oxidation, H$_2$ is used as a surrogate to examine the process which is further oxidized with Ar to be removed from the system.

3. THEORY

To model the reaction kinetics, ceria particles at cyclic stationary state are treated as identical spheres with diameter $r_p = 100$ nm (Table 3). The particle size is assumed to remain unchanged during the redox cycle, as CeO$_2$ is known to maintain its fluorite structure even under large nonstoichiometry at elevated temperatures.

The overall reaction between the bulk ceria and the external gas-phase reactants may be written as

$$\text{H}_2\text{O}(g) + 2\text{Ce}^{4+} + V_{O^\bullet\bullet} = \text{H}_2(g) + O_{O^\bullet}^\bullet + 2\text{Ce}^{3+}$$

where $V_{O^\bullet\bullet}$ is a doubly charged oxygen vacancy, $O_{O^\bullet}^\bullet$ is an oxygen ion on a normal site. Ce$^{4+}$ denotes a polaron (a localized electron, Ce$^{3+}$), and Ce$^{3+}$ is a regular Ce$^{4+}$ cation. Ce$^{4+}$ and $V_{O^\bullet\bullet}$ are believed to be the major defects in the bulk as well as on the surface.

Equation 8 merely describes the overall equilibrium between the defects in the bulk ceria and oxygen from the H$_2$O/H$_2$ environment. The electrochemical process, however, involves 248 serial steps of important heterogeneous surface reactions, i.e., adsorption/dissociation of gaseous reactant forming adsorbates, ion/electron transfer on the surface, and association and desorption of products. The surface chemistry is further connected with the bulk phase via bulk-to-surface transport driven by the electrochemical potential gradient. Bulk-phase diffusion continues to adjust the spatial defect distribution and eventually equilibrates the sample with the environment. Figure 2 schematically highlights the key steps in the oxidation direction.

In the following two subsections, we will present the submodels for the surface chemistry and diffusion process, respectively.

Surface Chemistry. The surface water splitting and oxygen incorporation reactions are modeled using a two-step mechanism (Figure 2a):
R2:

$$2\text{OH}_2^+(s) + 2\text{Ce}^{4+}(s) \xrightarrow{k_{1a}} 2\text{O}_2^+(s) + 2\text{Ce}^{3+}(s) + \text{H}_2(g)$$  

(10)

297 0H2 is a hydroxyl ion group on an oxygen anion site. The
298 surface reactions are assumed to occur only within the first unit
299 cell layer on the surface, and s in the parentheses emphasizes
300 this assumption. R1 describes the adsorption and dissociation
301 process: a H2O molecule is adsorbed onto an oxygen vacancy
302 site and dissociates into a hydroxyl ion and an extra proton,
303 which then bonds to an adjacent oxygen to form a second OH2
304 group. R2 describes the charge-transfer process, followed by the
305 association and desorption of H2.
306
307 Using the law of mass action, we express the species reaction
308 rates for R1 and R2 as
309
310 $$r_1 = k_{1a}P_{\text{H}_2\text{O}}[\text{V}^{{\ast}\ast}\text{O}_2^+]_s - k_{1b}[\text{OH}_2^+]_s^2$$  

(11)

311 $$r_2 = k_{2a}[\text{OH}_2^+]_s^2[\text{Ce}^{4+}_s]_s^2 - k_{2b}P_{\text{H}_2}[\text{O}_2^+]_s^2[\text{Ce}^{3+}_s]_s^2$$  

(12)

312 In eqs 11 and 12, the brackets denote the mole of species
313 per mole of CeO2. The subscript, s, again, emphasizes that the
314 concentrations of the reactant are taken on the surface. k1a and
315 k1b denote the rate coefficients (unit, s⁻¹) of the aforementioned
316 reactions and are assumed to follow the Arrhenius
317 expression. Partial pressure of H2 or H2O in the gas phase is
318 defined with respect to the reference value (i.e., 1 atm). Because
319 the high flow rates used in this study, the gas residence
320 time through the control volume (Figure 1b) is much shorter
321 (<300 ms) as compared to chemistry, and thus the reactant
322 partial pressure on the surface is essentially identical to that in
323 the gas phase as measured in the QMS. Therefore, the measured
324 P_{\text{H}_2\text{O}} and P_{\text{H}_2} accurately represent the redox environment to
325 which the ceria sample is exposed. At equilibrium, r1 and r2
326 are zero. This leads to the definition of the corresponding
327 equilibrium constants K1 and K2.
328
329 A similar pathway has been discussed in the literature. 45,50−53
330 Feng et al. 45 emphasized the importance of the charge-
331 transfer process, by further breaking R2 into OH2 + Ce4+ +
332 OH2 + Ce3+, following by the dissociation 2OH2 = 2O2 +
333 H2(g). Similar steps were calculated in a theoretical study by
334 Marrocchelli and Yildiz. 51 Hansen and Wolverton 52 calculated
335 the minimum energy pathway during R2 and concluded that
336 the process may happen asymmetrically: Ce4+ hops close to
337 OH2 and weakens the O–H bond; the weakly bonded proton
338 then moves toward the adjacent OH2 and forms H2 as the last
339 Ce3+ is oxidized. Identifying the detailed elementary steps
340 during R2 is beyond the scope of this study. Here we couple
341 the charge transfer with the H2 formation process and model it
342 as a single step.
343
344 The governing equations for the surface species are written as
345
346 $$\frac{\partial \tilde{C}_i}{\partial t} = \tilde{R}_i + \tilde{J}_i \quad i = \text{O}_2^+, \text{V}_2^{{\ast}\ast}\text{O}_2^+$$  

(13)

347 where \(\tilde{C}_i\) is the species concentration on the surface, \(\tilde{R}_i\) is the
348 production/consumption rate of species i, and \(\tilde{J}_i\) is the diffusion
349 flux from the bulk phase. We proceed by coupling these species
350 equations with the O- and Ce-site conservation equations and
351 the electroneutrality condition:
352
353 O-site:
354
355 $$[\text{V}_2^{{\ast}\ast}\text{O}_2^+]_s + [\text{OH}_2^+]_s + [\text{O}_2^+]_s = 2$$  

(14)

356 Ce-site:
357
358 $$[\text{Ce}^{4+}_s]_s + [\text{Ce}^{3+}_s]_s = 1$$  

(15)

359 electroneutrality:
360
361 $$2[\text{V}_2^{{\ast}\ast}\text{O}_2^+]_s + [\text{OH}_2^+]_s = [\text{Ce}^{3+}_s]_s$$  

(16)

362 It is worth noting that the electroneutrality condition may
363 break down in the space-charge region (SC) on the surface. 324
364 The doubly charged oxygen vacancies along with the polarons
365 form a double layer (i.e., positive charge from V2+ on one
366 layer and negative charge from Ce3+ on the other), creating a 327
367 large disturbance of the spatial electrostatic potential gradient
368 near the surface. This may lead to charge enrichment and
369 simultaneous countercharge depletion in this region. However,
370 Chueh and co-workers reported surface enrichment for both
371 V2+ and Ce3+ in SC for Sm-doped CeO2. Feng et al. 53
372 further quantified the contribution of the electrostatic potential
373 gradient near the surface under redox conditions and concluded
374 that the charge neutrality is preserved near the surface. As such,
375 we adopt the electroneutrality assumption in this study for the
376

Figure 2. (a) Schematics of the water splitting pathway. The ion-incorporation surface process comprises the adsorption and dissociation of H2O forming OH− (R1) and charge transfer, association, and desorption of H2 (R2). The heterogeneous chemistry is linked to bulk phase via the bulk-to-

surface transport of the electron defect, e, and the oxygen vacancy defect, V2+. (b) Schematics of the surface enrichment of Ce3+ relative to the bulk.
We proceed by describing the surface kinetics. Since the proton conductivity is less pronounced compared to the major defects (vacancies and polarons) in the bulk, we assume that all hydroxyl ions are confined to the surface layer and hence neglect its diffusion. Thus, we express the species conservation equations for the surface hydroxyl group and the surface oxygen vacancy as

\[
\frac{\partial \rho_{\text{Ce},s}}{\partial t} = \rho_{\text{Ce},s}(2r_1 - 2r_2) (17)
\]

\[
\frac{\partial \rho_{\text{V},s}}{\partial t} = -\rho_{\text{Ce},s}r_1 + \dot{J}_{\text{V},s} (18)
\]

where \(\rho_{\text{Ce},s}\) is the surface molar density of the ceria unit cell (unit, mol m\(^{-2}\)). With the knowledge of \(J_{\text{VO}}\), eqs 17 and 18 complete the description of the surface species evolution under the redox conditions.

**Bulk-to-Surface Transport.** The conservation of a defect species \(i\) can be expressed as

\[
\frac{\partial C_i}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r}(r^2J_i) = 0 \quad i = \text{V}^\bullet^\bullet, \text{Ce}^\bullet^\bullet (19)
\]

where \(C_i\) is the molar concentration and \(J_i\) the flux of the defect species \(i\). In eq 19, we assume a 1D spherically symmetric diffusion. The flux density is expressed using the Nernst–Planck equation:

\[
J_i = -D_i \frac{\partial \mu_i^*}{\partial r} \quad (20)
\]

where \(D_i\) is the diffusion coefficient, \(R\) the universal gas constant, and \(T\) the temperature. \(\mu_i^*\) is the electrochemical potential.

The diffusion process involves the exchange of defects between two points, \(x_1\) and \(x_2\):\(^\ddagger\)

\[
\text{V}^\bullet^\bullet(x_1) + \text{O}_0^\bullet(x_2) \rightleftharpoons \text{V}^\bullet^\bullet(x_2) + \text{O}_0^\bullet(x_1) (21)
\]

\[
\text{Ce}^\bullet^\bullet(x_1) + \text{Ce}^\bullet^\bullet(x_2) \rightleftharpoons \text{Ce}^\bullet^\bullet(x_2) + \text{Ce}^\bullet^\bullet(x_1) (22)
\]

By rearranging the above equations, we obtain equivalently

\[
\text{V}^\bullet^\bullet(x_1) - \text{O}_0^\bullet(x_2) \rightleftharpoons \text{V}^\bullet^\bullet(x_2) - \text{O}_0^\bullet(x_1) (23)
\]

\[
\text{Ce}^\bullet^\bullet(x_1) - \text{Ce}^\bullet^\bullet(x_2) \rightleftharpoons \text{Ce}^\bullet^\bullet(x_2) - \text{Ce}^\bullet^\bullet(x_1) (24)
\]

**Equations 23 and 24 restate the diffusion process in terms of the "defect elements", i.e., the structural defect minus the original normal site.\(^\ddagger\)** Thus, \(\mu_i^*\) for the oxygen vacancy and polaron can be expressed as

\[
\mu_i^* = \mu_i^0 + RT \ln a_i + \frac{z_i e F \phi}{a_i} \quad j = \text{V}^\bullet^\bullet, \text{O}_0^\bullet, \text{Ce}^\bullet^\bullet, \text{Ce}^\bullet^\bullet (27)
\]

where \(\mu_i^0\) is the chemical potential at the reference condition and \(z_i\) the effective charge. \(\phi\) is the internal electrostatic potential. \(F\) is the Faraday constant. \(a_i\) is the activity, defined as

\[
a_i = \rho_{\text{Ce},s} \rho_{\text{V},s} \quad (28)
\]

where \(\chi\) is the activity coefficient and \(C_{\text{Ce},s}\) is a reference molar concentration. Assuming that \(\chi\) is independent of concentration, we express the spatial derivatives of \(\mu_i\) as

\[
\frac{\partial \mu_i}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \text{J}_i \right) = \frac{\partial \mu_i^0}{\partial r} + \frac{z_i e F}{RT} \frac{\partial \phi}{\partial r} (29)
\]

Substituting eqs 25–29 into eq 19 yields

\[
\frac{\partial [\text{V}^\bullet^\bullet]}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 [\text{V}^\bullet^\bullet] \text{J}_{\text{V},s} \right) \left[ \frac{\partial (\mu_{\text{V}^\bullet^\bullet}^0 - \mu_{\text{O}_0^\bullet}^0)}{\partial r} ight]
\]

\[
\quad + RT \frac{\partial}{\partial r} \ln \left[ \frac{[\text{V}^\bullet^\bullet]}{[\text{O}_0^\bullet]} \right] + 2F \frac{\partial \phi}{\partial r} \quad (30)
\]

\[
\frac{\partial [\text{Ce}^\bullet^\bullet]}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 [\text{Ce}^\bullet^\bullet] \text{J}_{\text{Ce},s} \right) \left[ \frac{\partial (\mu_{\text{Ce}^\bullet^\bullet}^0 - \mu_{\text{Ce}^\bullet^\bullet}^0)}{\partial r} ight]
\]

\[
\quad + RT \frac{\partial}{\partial r} \ln \left[ \frac{[\text{Ce}^\bullet^\bullet]}{[\text{Ce}^\bullet^\bullet]} \right] - F \frac{\partial \phi}{\partial r} \quad (31)
\]

Coupling with the Ce- and O-site conservation equations and the electroneutrality condition:

O-site:

\[
[V^\bullet^\bullet] + [O_0^\bullet] = 2 \quad (32)
\]

Ce-site:

\[
[\text{Ce}^\bullet^\bullet] + [\text{Ce}^\bullet^\bullet] = 1 \quad (33)
\]

**Equations 30–34 formulate a complete description of the bulk diffusion process.**

The characteristics and the properties of the ceria sample allows us to significant simplify these equations. The electronic and ionic diffusivities \((D_{\text{Ce}^\bullet^\bullet} D_{\text{V}^\bullet^\bullet})\) of ceria are very high and bring the bulk defects to dynamic equilibrium during the redox process. Using the diffusivity data reported in ref 63, the characteristic time, \(t\), for a diffusion-limited process from the expression \(t \sim R^2/4D\), is estimated to be less than 200 ms, which is significantly faster compared to the surface chemistry. A more rigorous calculation that takes into account the temporal and spatial variation of the defect concentration is included in Appendix A, which shows that the concentration variation caused by the mass-transfer resistance is less than 4%. This estimation indicates that the bulk diffusion within the ceria macroparticle is fast enough that any spatial variations of \(\mu_{\text{V}^\bullet^\bullet}^*\) and \(\mu_{\text{Ce}^\bullet^\bullet}^*\) can be readily removed via diffusion. As such, the conversion process is essentially surface-reaction-limited. Thus, \(\mu_{\text{V}^\bullet^\bullet}^*\) and \(\mu_{\text{Ce}^\bullet^\bullet}^*\) remain uniform throughout the particle while responding dynamically.
The surface via diffusion. Equations 30 and 31 can be simplified as

\[
\mu^{*}_{\text{O}} = \text{constant}:
\]

\[
\frac{\partial}{\partial r} \left( \mu^{0}_{\text{O}} - \mu^{0}_{\text{O}} \right) + RT \frac{\partial}{\partial r} \ln \left( \frac{[V^{*}_{\text{O}}]}{[O^{\text{X}}]} \right) + 2F \frac{\partial \phi}{\partial r} = 0
\] (35)

where

\[
\mu^{*}_{\text{Ce}} = \text{constant}:
\]

\[
\frac{\partial}{\partial r} \left( \mu^{0}_{\text{Ce}} - \mu^{0}_{\text{Ce}} \right) + RT \frac{\partial}{\partial r} \ln \left( \frac{[C^{*}_{\text{Ce}}]}{[C^{\text{Ce}}]} \right) - F \frac{\partial \phi}{\partial r} = 0
\] (36)

However, the uniformity of the \( \mu^{*}_{\text{O}} \) and \( \mu^{*}_{\text{Ce}} \) does not necessarily mean the same value of the defect concentration, \( V^{*}_{\text{O}} \) and \( C^{*}_{\text{Ce}} \) in the bulk and at the surface. In fact, owing to the difference of the standard chemical potentials \( \mu^{0}_{\text{O}} - \mu^{0}_{\text{O}} \) and \( \mu^{0}_{\text{Ce}} - \mu^{0}_{\text{Ce}} \) between the bulk and the surface, a pronounced surface defect segregation phenomenon (see schematics in Figure 2b) has been observed in several studies. Chueh et al. reported a two-order-of-magnitude surface-to-bulk \( C^{*}_{\text{Ce}} \) enrichment for Sm-doped ceria at 466 °C. Similar results were observed for the oxygen vacancies by Feng et al. To model the surface effect, we assume that \( \mu^{0}_{\text{O}} \) varies from the bulk \( (r < r_{p}) \) to the surface \( (r = r_{p}) \) according to a step function, as depicted in Figure 3. Thus, the defect concentration in the bulk phase is

\[
\Delta \mu^{0}_{T} = \Delta \mu^{0}_{T} - T \Delta \mu^{0}_{T}
\] (42)

Creation of one defect involves breaking up four Ce–O bonds in the bulk, but fewer on the surface. Thus, defects are more energetically favored on the surface. On the other hand, the defect formation causes the relaxation of the adjacent atoms with reduced vibrational frequency and increased amplitude, leading to increased entropy. The entropy increase is higher in the bulk, because more adjacent atoms are relaxed, and the relaxation from its dense-packed crystal is more dramatic. Thus, both \( \Delta \mu^{0}_{T} \) and \( \Delta \mu^{0}_{T} \) are negative. Based on the measurements by Chueh et al., we obtain \( \Delta \mu^{0}_{T} = -113.7 \text{ kJ mol}^{-1} \), and \( \Delta \mu^{0}_{T} = -50.2 \text{ kJ mol}^{-1} \). Sm-doped ceria (see Appendix B for calculation).

**Numerical Simulation.** With the assumption of a uniform bulk defect concentration, and eq 37 to connect bulk to surface, we can simplify eq 18 by considering the conservation of the overall oxygen vacancy within the particle:

\[
\frac{\partial}{\partial t} (\rho^{*}_{\text{Ce}} V_{R} [V^{*}_{\text{O}}]) = -S_{\rho} \rho^{*}_{\text{Ce}} r_{f}
\] (43)

where \( V_{R} \) and \( S_{\rho} \) are the volume and the surface area of the particle, and \( \rho^{*}_{\text{Ce}} \) is the molar density of the unit cell in the bulk. Equation 43 describes the fact that the surface splitting reaction leads to the consumption of oxygen vacancy. We note here that the moles of the oxygen vacancy on the surface is negligible compared to the bulk, and thus is neglected from the left-hand side of eq 43.

Equations 17, 37, and 43 form the complete description of the redox process. The unknown (not kinetic) parameters are \( k_{R} K_{i} \) (\( i = 1, 2 \)), \( \Delta \mu^{0}_{T} \) and \( \Delta \mu^{0}_{T} \). With the time-resolved profiles of \([\text{H}_{2}O]\) and \([\text{H}_{2}]\) measured using the QMS, the entire conversion process can be predicted. These equations are integrated numerically, and the predicted reactivity is compared to the experimental measurement. The unknown parameters are then varied to minimize the difference:

\[
f = \sum_{\text{all tests}} \left( \sum_{0 \leq t < t^{*}} \left( \hat{\omega}^{\text{predicted}} - \hat{\omega}^{\text{measured}} \right) \right)^{2}
\] (44)

Here the reaction rates \( \hat{\omega}^{\text{predicted}} \) or \( \hat{\omega}^{\text{measured}} \) are normalized by the maximum rate in each test. The minimization is performed numerically in MATLAB using fminsearch solver. The redox measurements at 600, 700, 800, 900, and 1000 °C are used to extract the unknown parameters. \( \Delta \mu^{0}_{T} \) and \( \Delta \mu^{0}_{T} \) for Sm-doped ceria calculated in Appendix B are taken as the initial guess, but 499...
500 variations are allowed to account for the difference between Sm-doped and undoped ceria. To ensure a global minimum, the initial guess is randomly sampled over a wide range of values (ln $k_0$ from $-20$ to $20$, $E$ from $0$ to $200$) for 200 tests, and the results with minimum $f$ are chosen.

4. RESULTS

CeO$_2$ Morphology Evolution and Cyclic Repeatability. Figure 4 shows the SEM images of the fresh (panel a) and aged (panel b) ceria powder. It is found that the fresh sample contains particles of size $\sim 50$ nm, clumping together into a mushroom-like structure. During pretreatment, the surface area is reduced and the particles sinter into an interconnected structure with a size $\sim 200$ nm (based on the BET measurement). This structural relaxation is caused by sintering during the initial redox treatment (first 100 cycles). Samples after additional 20 redox cycles are also examined, and the same microstructure and redox rates are obtained, indicating that a periodic and reversible stationary equilibrium is reached.

Figure 5 shows the profiles of $H_2$ and $H_2O$ for three redox cycles at 1000 °C. Reduction proceeds for 2 min with 14% $H_2$ at 350 cm$^3$(STP)/min, while oxidation with 26% $H_2O$ for 2 min. Two min Ar purging is used in between to remove residuals. $H_2$ spikes with the rise of $H_2O$, with the peak $H_2$ over 7%, roughly a quarter of the feed $H_2O$. After the peak, $H_2$ drops quickly, and diminishes after 0.5 min. The $H_2$ near the end of the oxidation phase is essentially zero. After oxidation, the ceria sample is also tested with 1% O$_2$ (Ar balance), and no further consumption of O$_2$ is observed. This indicates a complete reoxidation of ceria with $H_2O$. Similarly, the produced $H_2O$ during reduction spikes at the beginning of each reduction cycle. The peak $H_2O$ reaches around 3%, approximately one-fifth of the feed $H_2O$ during reduction. $H_2O$ decays slower as compared to $H_2$ during oxidation, and approaches zero after 2 min, indicating a slower reactivity compared to oxidation. The cycles are repeatable with no noticeable difference.

Figure 6 compares the total cumulative $H_2$ and $H_2O$ production during the oxidation and reduction steps, respectively, for eight cycles measured at 1000 °C. The total $H_2$ production closely matches with the $H_2O$ production, indicating cyclic regenerability. The total produced $H_2$ is about 1250 $\mu$mol g$^{-1}$ ceria, corresponding to a $\Delta\delta$ of 0.215.

Effect of Temperature. Figure 7 compares $\omega_{H_2}$ and $\omega_{H_2O}$ as a function of temperature from 500 to 1000 °C. In each plot, the reaction rate exhibits a fast initial stage, followed by a quick decrease. During oxidation, the fast initial rise of $H_2$ corresponds to the rapid ion-incorporation process with the enriched surface oxygen vacancies, as shown in section 5. The reactant concentration on the surface plays a significant role in determining the maximum rate. For temperatures lower than 700 °C, $H_2$ production is limited, owing to the slow oxygen removal kinetics and hence limited oxygen vacancy created in the previous reduction step. Increasing the temperature until...
551 850 °C leads to a significant jump, and the peak rate doubles almost every 50 °C. Further increase in the temperature, however, only mildly improves \( \text{H}_2 \) production rates during the initial stage. As will be discussed in section 5, the nonlinear temperature dependence is caused by the surface defect segregation. Following the peak, \( \text{H}_2 \) production sharply decays and approaches zero after 0.5 min, exhibiting linear dependence on temperature, as it is mainly controlled by the available oxygen vacancy in the bulk phase.

Compared with oxidation, the reduction step is slower and more sensitive to temperature. A fast initial spike is again observed, followed by a slower decay. The peak occurs around

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**Figure 6.** Total \( \text{H}_2 \) and \( \text{H}_2\text{O} \) production during the oxidation and reduction, respectively, for eight cycles at 1000 °C.

**Figure 7.** (a) \( \text{H}_2 \) production rate (\( \mu \text{mol g}^{-1} \text{s}^{-1} \)) during the oxidation step and (b) \( \text{H}_2\text{O} \) production rate (\( \mu \text{mol g}^{-1} \text{s}^{-1} \)) during the reduction step. Temperature is varied from 1000 to 500 °C. 26% \( \text{H}_2\text{O} \) at 337 cm\(^3\) (STP)/min is used for oxidation, and 14.3% \( \text{H}_2 \) at 350 cm\(^3\) (STP)/min is used for reduction. The uncertainties of the rate measurements are ±0.5 \( \mu \text{mol g}^{-1} \text{s}^{-1} \) for \( \text{H}_2 \) production, and ±0.75 \( \mu \text{mol g}^{-1} \text{s}^{-1} \) for \( \text{H}_2\text{O} \) production.
0.08 min similar to that shown in Figure 7a, while the decay continues even after 1 min (see Figure 8). During the initial stage, the rise of $\omega_{H_2O}$ depends almost linearly on the temperature throughout the entire range, indicating a large activation energy barrier. However, $\omega_{H_2O}$ profiles start to overlap during the decay stage for temperature above 850 °C, as the removal of oxygen essentially brings the surface closer to the beginning of the oxidation phase, where the segregation effect reduces the difference among different temperatures.

Figure 8 emphasizes the observed behavior of the peak rates at varying temperature. The peak $H_2$ rate exhibits a sigmoidal profile with a rapid increase around a threshold temperature of 700 °C, while the peak $H_2O$ rate continuously increases with temperature. The total $H_2/H_2O$ production during the 2 min oxidation/reduction process is illustrated in Figure 9. In all the cases, a close match is found between the $H_2$ and $H_2O$ production. Governed by the temperature sensitive reduction step, the overall $H_2$ production rises continuously with temperature. Figure 10 compares
The difference in the profiles of the nonstoichiometry $\Delta\delta$, as calculated in eq 7, during oxidation and reduction. The initial stage of oxidation ends within 15 s, but accounts for more than 80% of the overall change, and the residual oxidation only leads to a minor increase. Raising the temperature enlarges the overall oxygen carrying capacity, but the conversion follows a similar pattern. In comparison, reduction proceeds more gradually, and it is more temperature sensitive. The transition between the initial and residual stages is less obvious, and both stages equally contribute to the overall nonstoichiometry change. The reduction continues after 2 min although the rate is too slow to be of practical interest.

Table 4. Fitted Kinetic Parameters for Both the Forward and Backward Reactions

| Reaction   | $k$ ($s^{-1}$)                                      |
|------------|-----------------------------------------------------|
| Forward    | $1.3 \times 10^2 \exp((-7.0 \pm 7 \text{ kJ mol}^{-1})/RT)$ |
| Backward   | $8.2 \times 10^{14} \exp((-210 \pm 50 \text{ kJ mol}^{-1})/RT)$ |
| Equilibrium| $1.6 \times 10^{-13} \exp((203 \pm 50 \text{ kJ mol}^{-1})/RT)$ |
| Backward   | $1.5 \times 10^{14} \exp((-190 \pm 50 \text{ kJ mol}^{-1})/RT)$ |
| Overall    | $4.4 \times 10^9 \exp((-97 \pm 5 \text{ kJ mol}^{-1})/RT)$ |

Table 5. Parameters for the Transport and Bulk Defect Equilibria

| $\Delta h_T$ (kJ mol$^{-1}$) | $\Delta s_T$ (J mol$^{-1}$ K$^{-1}$) | $\Delta h_b$ (kJ mol$^{-1}$ K$^{-1}$) | $\Delta s_b$ (J mol$^{-1}$ K$^{-1}$) |
|-------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| $\text{CeO}_2$                | ref 48                                | ref 49                                | ref 44†                               |
|                               | $-107.6 \pm 16.8$                     | $-54.0 \pm 11.9$                      | $445.2$                               |
|                               | $467.4 \pm 8.9$                       | $172.9 \pm 6.4$                       | $131.8$                               |
| $\text{Sm}_0.2\text{Ce}_0.8\text{O}_1.9$ | $-95.7$                              | $-26.5$                               | $373.2$                               |
|                               | $373.2$                               | $101.5$                               |                                       |

Note that ref 48 reports varying enthalpy and entropy with $\delta$; the values are averaged for $\delta = 0-0.05$. The values are calculated based on the chemical potential of atom oxygen as reported in ref 44. See Appendix B for calculations.
The measured peak H₂ rate is \( \sim 160 \, \mu\text{mol g}^{-1}\text{s}^{-1} \) at 1000 °C and 60 \( \mu\text{mol g}^{-1}\text{s}^{-1} \) at 700 °C (also included in Table 2 for comparison). The fast H₂ production rate is because of the fine particles, and hence large surface area, used in the measurements. Comparing to TCWS, the utilization of fuel in the reduction step creates many oxygen vacancies and hence leads to an enhanced H₂ production. The oxygen removal in reduction is the limiting step and is more temperature sensitive. 700 °C is the threshold temperature to achieve a large oxygen nonstoichiometry and hence enables a transition to a fast H₂ production rate in the following oxidation step. Therefore, 700 °C (or above) along with a longer residence time in reduction is beneficial.

**Effect of H₂O/H₂ Concentration.** Figure 11 and Figure 12 show the effect of H₂O and H₂ concentration, respectively. The measured rates are plotted in panel a, while the peak rate and the total production are highlighted in panel b. \( \omega_{\text{H}_2} \) becomes taller and narrower at higher H₂O concentration. The peak rate linearly depends on the H₂O concentration, while the total production remains the same. In contrast, a stronger reducing environment shifts the entire \( \omega_{\text{H}_2} \) curve outwardly and hence enlarges the overall oxygen carrying capacity. The peak rate also linearly depends on the H₂ concentration.

**5. DISCUSSION**

The kinetics and the defect equilibrium parameters derived in this study for undoped ceria are summarized in Table 4 and Table 5. The values of \( \Delta h_0^0 \) and \( \Delta s_0^0 \) are close to those obtained for Sm-doped ceria (see Appendix B). The bulk equilibrium for reaction 40 is also calculated by combining eqs 9, 10, and 39 along with the water splitting reaction, \( \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g}) \), as

\[
K_b = \exp \left( -\frac{\Delta h_0^0 - T\Delta s_0^0}{RT} \right) = \frac{P_{\text{O}_2}^{1/2} [V^*]_{\text{b}} [\text{Ce}^2_0]^2}{[\text{O}^2_0]_{\text{b}} [\text{Ce}^{\text{x}}_0]^2} \left( K_1 K_2 K_T K_W \right)^{-1}
\]

Here \( K_1, K_2, K_T, \) and \( K_W \) are the equilibrium constants for the surface reactions R1 and R2, the bulk-to-surface transport, and the water splitting reaction, respectively. The calculated bulk phase equilibrium \( \left( \Delta h_0^0 \right) \) is in a close match with the literature,\(^{38,49}\) as shown in Table 5. Figure 13 depicts the isothermal bulk oxygen vacancy concentration as a function of \( P_{\text{O}_2} \), compared with the measurements reported by Panlener et al.\(^{48}\) and Tuller and Nowick.\(^{49}\) Quantitative agreement is found at large nonstoichiometry, although discrepancy

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**Figure 13.** Isothermal oxygen nonstoichiometry as a function of \( P_{\text{O}_2} \) for CeO₂ from 800 to 1000 °C (solid lines). Dashed lines are based on the conductivity measurements by Tuller and Nowick.\(^{49}\) Symbols are from Panlener et al.\(^{48}\) Gray lines are for guiding the eyes.

**Figure 14.** Comparison between the model predictions (lines) and the measurements (circles) for both oxidation (upper panels) and reduction (lower panels). The scales in the y-axis are different at lower temperature for clarity.
632 is seen when $p_{O_2}$ is high, resulting from a slightly larger $\Delta h_0^s$. Both ref 49 and the current study report a dependence of $-1/6$ near stoichiometry, while Panlener et al.46 reported a dependence close to $-1/S$, possibly due to the existence of impurities.47

Figure 14 shows a comparison between the measured reactivity and model predictions for both oxidation and reduction.

An excellent match is found for all cases. The predictions well-characterize the spike–decay behaviors of both redox steps. The temperature dependence is precisely represented; the subtle difference between the reduction and oxidation steps is also adequately captured.

Figure 15 shows the calculated energy landscape (black lines) for the surface chemistry (see Table 4). The energy levels for the intermediate species on the surface as well as the transition states are plotted in reference to the perfect crystal as the ground state. R1 is highly exothermic with a minor barrier. The second step is highly endothermic, and requires a significant energy to break up the O–H bond. The intermediate species, $OH^-$, lies in a deep valley, and hence one may expect high surface coverage at low temperature. The overall $H_2$ production process (eq 8) is exothermic with the enthalpy of reaction around $-120 \text{ kJ mol}^{-1}$. The theoretical calculations by Hansen and Wolverton52 (red lines) and Marrocchelli and Yildiz51 (blue lines) are also included in this plot for comparison. Both obtained similar reaction energy for the first step, although they split it and simulated the adsorption and the dissociation processes separately. Similarly, no substantial activation barriers were found for R1 in either work. Marrocchelli and Yildiz51 modeled the breaking of the O–H bond as a symmetric process and reported a significant barrier around 400 kJ mol$^{-1}$ for $H_2$ formation. In contrast, Hansen and Wolverton52 identified an asymmetric pathway with a much lower barrier (281 kJ mol$^{-1}$). The current study reported a barrier around 200 kJ mol$^{-1}$. The lower barrier may result from alternative fast desorption.

![Figure 15. Energy landscape for the reaction pathway (black), and comparison with the theoretical calculations by Hansen and Wolverton52 (red) and Marrocchelli and Yildiz51 (blue). The dashed black line on the left side denotes the bulk-phase defect. $\Delta h_0^b$ and $\Delta h_0^s$ denote the defect formation energy for bulk (eq 40) and surface (eq 41), respectively, and $\Delta h_T^0$ denotes the difference. Unit is kJ mol$^{-1}$.](image)

![Figure 16. Concentrations of the bulk and surface species for oxidation (a, b) and reduction (c, d) at 1000 and 700 °C.](image)
pathways, especially at large nonstoichiometry when the surface defect vacancy concentrations are high. Marrocchelli and Yildiz reported a similar overall energy of reaction (Δh0°) for eq 41 as in this study, while Hansen and Wolverton reported a slightly lower value. The bulk-phase defect formation energy, Δh0°, is also included in Figure 15, and the difference between the bulk and the surface is Δh0°.

Figure 16 plots the species concentration in the bulk and on the surface. The reduction reaction starts from stoichiometry (complete oxidation from the previous step), while oxidation begins with the defects determined from the previous reduction step. During the oxidation step, all species undergo a quick decay, leading to a rapid H2 production during the initial stage as observed in Figure 7. The initial stage is followed by a much slower decay as the conversion transits to the second stage where the species concentrations are mainly affected by the equilibrium with the H2O/H2 environment. Hydroxyl quickly formed as the reaction starts and remains in a quasi-steady state during the rest of the process. Low temperature favors the formation of hydroxyl ions, owing to the large energy barriers as seen in Figure 15. The bulk defect concentrations are highly sensitive to temperature, as evident from the large Δh0° shown in Table S, leading to a significant difference between the high and low temperature cases. On the other hand, the surface defect is less dependent on the temperature. In all cases, the concentrations on the surface are observed to be much higher than the bulk. The surface segregation effect is more significant at low temperature, causing an order-of-magnitude improvement compared to the bulk phase. Similar behavior is observed during the reduction step, where the segregation effect is more pronounced near the end of conversion.

To further examine the surface segregation effect, Figure 17a shows the calculated equilibrium concentration of CeCe′ in the bulk and on the surface as a function of the effective pO2. Each line corresponds to the same range of H2O:H2 ratio, from 10−3 (reducing) to 103 (oxidizing). Under all conditions, the surface [CeCe′] value is significantly greater than the bulk, indicating that the surface is more reduced. The ratio between surface and bulk, as shown in Figure 17b, ranges from 1.5 to 15, favoring the low temperature. Apart from the difference in the absolute values, the temperature and oxygen dependence also differs remarkably between bulk and surface. [CeCe′] on the surface is only weakly sensitive to temperature and becomes almost the same above 800 °C (with H2O:H2), causing the overlap of the measured reaction rates during the first stage of oxidation (Figure 7a) and the second stage of reduction (Figure 7b). [CeCe′] in the bulk generally exhibits −1/6 dependence on the pO2 as expected from eq 45. On the other hand, the pO2 dependence for surface [CeCe′] flattens from −1/6 with decreasing pO2 and eventually goes to zero as the surface becomes fully reduced. This nonlinearity results from the reduced concentration of the normal sites (O2°, CeCe′ in eq 45) on the surface.

As a result, the ratio in panel b exhibits a nonlinear pattern with pO2. Figure 18 shows the forward and the backward reaction rates for the redox processes. At all temperatures, the H2O adsorption and dissociation step (R1) during oxidation is much faster; equilibrium is quickly established and maintained throughout the rest of the conversion. In contrast, the ion/electron-transfer process (R2) is slower and its backward reaction rate is close to zero. This indicates that the reaction is limited by the charge-transfer process (R2), as also observed by Feng et al.

Compared to oxidation, the reduction rate is much slower. The forward and backward rates for both steps are at similar magnitude, and equilibria are established during most of the conversion process. The low rates for R1 are mainly attributed to the low H2O produced during reduction. A more reducing environment (e.g., higher H2 concentration) effectively shifts the equilibrium backward, leading to more reduced ceria, as observed in Figure 12.

The surface segregation effect along with the plausible rate-limited step observed in this study suggests directions for improving the water splitting activity of ceria and potentially other oxygen-incorporation materials. The reduction step is in general much slower, and it limits the redox capability at low temperature (≤700 °C). Therefore, promoting the reduction step is essential to the low temperature water splitting process. On the other hand, the surface is nearly enriched with the defects at high temperature (>700 °C), and the overall H2 production is constrained by the charge-transfer step. Thus, efforts should concentrate on accelerating the charge-transfer step at high temperature.

6. CONCLUSIONS

This work presents a detailed redox study with emphasis on identifying the surface ion-incorporation kinetics pathway. Time-resolved kinetics is measured for ceria nanopowder in a button cell reactor for 600−1000 °C at atmospheric pressure. The ceria sample is alternatively exposed to water vapor in the oxidation cycle to produce H2 and H2/Ar mixture in the reduction cycle to remove the lattice oxygen. The ceria sample undergoes structural and morphological changes during the initial redox treatment before reaching cyclic equilibrium.
We find an order-of-magnitude higher H₂ production rate compared to the state-of-art thermochemical water splitting and reactive chemical-looping water splitting studies. The high redox rates are attributed to the fine particles and hence large surface areas used in the study, which ensure a surface-limited-process. The peak rates measured are 160 μmol g⁻¹s⁻¹ at 1000 °C and 60 μmol g⁻¹s⁻¹ at 700 °C. The maximum nonstoichiometry change (Δδ) achieved is 0.215 at 1000 °C. It is found that the H₂ production rate depends weakly on temperature in the range 800–1000 °C, while the reduction process critically depends on the reaction temperature. Overall, reduction is the limiting step especially at low temperature, and it determines the total amount of the hydrogen produced in the following oxidation step.

The redox kinetics is modeled using a two-step surface chemistry while considering bulk-to-surface transport equilibrium. The proposed surface chemistry comprises an H₂O adsorption/dissociation step and a charge-transfer step. Kinetics and equilibrium parameters are extracted and excellent agreement is achieved between the model predictions and the measurements. Driven by the difference in the free energy of formation, the surface defect concentration is found to be an order-of-magnitude higher than the bulk. The model reveals that the surface defects are abundant during the redox conditions, and the charge-transfer process is the rate-determining step for H₂ production.

The kinetic model along with the surface-controlled experiments provides a new approach to examine the redox pathways and defect equilibrium for alternative materials. The kinetics study also provides guidance for the design and the practical application of the chemical-looping water splitting technology: (1) finer particles are preferred to enable faster kinetics; (2) the operating temperature is recommended to be higher than the threshold 700 °C to ensure fast redox conversion; (3) an oxidation period less than 30 s suffices to regenerate the oxygen vacancy while a slightly longer residence time in reduction is beneficial.

### APPENDIX A

The diffusion flux for Vₐ̅° and CeCe can be expressed as

\[ -\frac{J_{V_{\bar{\alpha}}}^{\bar{\alpha}}}{\rho_{Ce} [V_{\bar{\alpha}}^{\star}] D_{V_{\bar{\alpha}}}} = \frac{\partial [V_{\bar{\alpha}}^{\star}]}{\partial r} \left( \frac{1}{[V_{\bar{\alpha}}]} + \frac{l}{2 - [V_{\bar{\alpha}}^{\star}]} \right) + \frac{2F \partial \phi}{RT} \frac{\partial \rho_{\bar{\alpha}}}{} \frac{\partial r}{(A1)} \]

\[ -\frac{J_{CeCe}}{\rho_{Ce} [CeCe] D_{CeCe}} = \frac{\partial [CeCe]}{\partial r} \left( \frac{1}{[CeCe]} + \frac{l}{1 - [CeCe]} \right) - \frac{F \partial \phi}{RT} \frac{\partial \rho_{Ce}}{} \frac{\partial r}{(A2)} \]

Here we consider the region sufficiently away from the surface, such that the defect segregation effect is not important (i.e., μ° is constant).
Eliminating the electrostatic potential, we have

\[
\frac{\partial J_{V^\bullet}}{\partial r} = -\frac{2J_{CtCt}}{\rho_{Ct}[V_{O^\bullet}]D_{V_{O^\bullet}}} - \frac{\partial J_{CtCt}}{\partial r} + \rho_{Ct}[CtCt]D_{CtCt}
\]

\[
\frac{\partial J_{V^\bullet}}{\partial r} = \frac{\partial J_{CtCt}}{\partial r} = \rho_{Ct}[CtCt]D_{CtCt}
\]

\[
\frac{\partial J_{V^\bullet}}{\partial r} = \frac{\partial J_{CtCt}}{\partial r} = \rho_{Ct}[CtCt]D_{CtCt}
\]

where

\[
D = \frac{3D_{V_{O^\bullet}}D_{CtCt}}{D_{CtCt} + 2D_{V_{O^\bullet}}} \left(1 + \frac{[V_{O^\bullet}]}{6 - 3[O^\bullet]} + \frac{4[O^\bullet]}{3 - 6[O^\bullet]}\right)
\]

\(D\) is the chemical (or ambipolar) diffusion coefficient, which critically depends on the operating condition, as well as the dopant/impurity concentrations. A range of values have been reported in the literature. To evaluate the contribution of the solid-phase diffusion to the overall redox process, we use the chemical diffusivity reported by Stan et al., which is in the lower range of the available data in the literature (see ref 57 for comparison) and, hence, leads to an estimation of the upper bound for the diffusional resistance.

The governing equations for \(V_{O^\bullet}\) in the bulk phase can be expressed as

\[
\frac{\partial C_{V^\bullet}}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{V^\bullet}}{\partial r}\right) = 0
\]

With substitution of eq A6 into eq A7, we have

\[
\frac{\partial C_{V^\bullet}}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{V^\bullet}}{\partial r}\right) = 0
\]

with initial condition

\[
C_{V^\bullet}(t = 0) = C_{V^\bullet,0}
\]

and the following boundary conditions:

\[
sD \frac{\partial C_{V^\bullet}}{\partial r} \bigg|_{r=R} = \omega
\]

\[
\frac{\partial C_{V^\bullet}}{\partial r} \bigg|_{r=0} = 0
\]

In eq A9, \(s\) is the surface area, as listed in Table 3. \(\omega\) is the surface \(H_2\) (or \(H_2O\)) production rate (unit, mol s\(^{-1}\)). Equations A8–A11 are solved for the oxidation reaction of the particle with \(R = 100\) nm. The peak \(H_2\) production rate at each temperature is used to represent \(\omega\), and \(\Delta\delta\) is used as the initial condition. Calculation shows an upper bound for the diffusional contribution. Figure 19 plots the normalized difference of \(V_{O^\bullet}\) between the center and the surface:

\[
\Delta = \frac{C_{V^\bullet}(r = 0) - C_{V^\bullet}(r = R)}{C_{V^\bullet}(r = R)}
\]

when \(C_{V^\bullet}(r = R) = \frac{1}{2}C_{V^\bullet,0}\)

From Figure 19, the maximum difference is found to be less than 4% at 600 °C and reduces to less than 0.001% at 1000 °C. Calculation here indicates that the bulk diffusion is unlikely to be rate-limiting in the redox process.

**APPENDIX B**

Chueh et al. measured both the bulk and the surface concentration Ce\(^{3+}\) (or Ce\(^{4+}\)) for Sm\(_{0.2}\)Ce\(_{0.8}\)O\(_{1.9}\) under equilibrium for the temperatures at 466, 521, 586, and 650 °C. The authors compared the chemical potential of atomic oxygen for the surface and bulk and attributed the higher concentration of Ce\(^{3+}\) to the higher entropy of the surface oxygen. Here, we take into account the difference of the defect formation energy as well as the entropy and present a detailed analysis following an approach similar to that detailed in section 3 (see Figure 3).

The site conservation and electroneutrality conditions are

\[
[V_{O^\bullet}^\bullet] + [O^\bullet] = 1.9
\]

\[
[Ce_{Ct}] + [Ce_{Ct}] + [Sm_{Ct}] = 1
\]

\[
2[V_{O^\bullet}^\bullet] = [Sm_{Ct}] + [Ce_{Ct}]
\]

In the bulk phase, \([Sm_{Ct}] = 0.2\). By substituting eqs B1–B3 into eq 45, and fitting with respect to the measurements of the bulk \([Ce_{Ct}]\) and \([V_{O^\bullet}^\bullet]\), we obtain the equilibrium constant for the bulk-phase defects, \(K_b\):

\[
K_b = \exp \left(-\frac{379.5 \text{ kcal mol}^{-1} - (97.1 \text{ kcal mol}^{-1}) T}{RT}\right)
\]

The bulk-to-surface transport equilibrium is described by eq 37. The dopant concentration on the surface, \([Sm_{Ct}]\), is in the range between 0.26 and 0.35, slightly greater than the bulk.
For simplicity, we use $[\text{Sm}_{3+}] = 0.3$. Note here the right-hand side of eq B1 becomes 1.85 for the surface $(\text{Sm}_{3+} \text{Ce}_{0.7} \text{O}_{1.85})$.

By substituting eqs B1–B3 into eq 37, and comparing with the measurements of the surface $[\text{Ce}^{3+}]_{\text{surf}}$ at given temperature and oxygen partial pressure, we obtain the equilibrium constant for the transport, $\Delta \mu^0_T$:

$$
\Delta \mu^0_T = \left( -113.7 \frac{\text{kJ}}{\text{mol}} \right) - \left( -50.2 \frac{1}{\text{mol K}} \right) T
$$

The model predictions are plotted in Figure 20 along with the measurements, and an excellent agreement is found for both the surface and the bulk defect concentrations.

![Figure 20. (a) Comparison of the surface (closed) and bulk $\text{Ce}^{3+}$ (open) concentrations between the measurements (symbols) by Chueh et al. and the model predictions (lines). (b) Ratio of the surface to bulk $\text{Ce}^{3+}$ concentrations. Symbols are from ref 44, and lines are from the modeling.](image)

It is interesting to note that compared to the bulk, the surface has 30% less defect formation enthalpy and over 50% less defect formation entropy. The ratio of the surface-to-bulk $\text{Ce}^{3+}$ is highest at low temperature and drops dramatically as the temperature is raised. Crossover, $\Delta \mu^0_T = 0$, is reached when $T = 2265 \text{ K}$, approaching the melting point.

Chueh et al. reported the chemical potential of atomic oxygen for the surface and bulk, defined as

$$
\mu_O = \frac{1}{2} \mu_{O_2} = \frac{1}{2} (\mu_{O_2}^0 + RT \ln p_{O_2})
$$

where $\mu_{O_2}^0$ is the standard potential at 1 atm. $\mu_O$ can further be related to the partial molar enthalpy ($H_O$) and entropy ($S_O$) from $H_O = H_{O_2} - T S_O$. The reported $H_O$ and $S_O$ are $-373.2 \text{ kJ mol}^{-1}$ and $-86.1 \text{ J mol}^{-1} \text{ K}^{-1}$ for $[\text{Ce}^{3+}]_{\text{bulk}} = 0.0071$, and $-277.5 \pm 28.7 \text{ kJ mol}^{-1}$ and $28.7 \pm 28.7 \text{ J mol}^{-1} \text{ K}^{-1}$ for $[\text{Ce}^{3+}]_{\text{surf}} = 0.36$.

To relate the partial molar free energy of the oxygen atom to the defect formation free energy, we consider the defect formation reaction, eqs 40 and 41, at equilibrium. The Gibbs free energy is zero: $\Delta G = 0 = \mu_{\text{O}_2}^0 + 2 \mu_{\text{Ce}^{3+}} + \frac{1}{2} \mu_{\text{O}_2} - 2 \mu_{\text{Ce}^{3+}}$. With substitution of eqs 27 and B6, we obtain

$$
\mu_O = H_O - T S_O
$$

$$
= -\left( \mu_{\text{O}_2}^0 + RT \ln p_{\text{O}_2} \right) + 2 \mu_{\text{Ce}^{3+}} + 2RT \ln \left[ \text{Ce}_{\text{surf}}^{3+} \right] - \mu_{\text{O}_2}^0

- RT \ln \left[ \text{O}^{2-} \right] - 2 \mu_{\text{Ce}^{3+}} - 2RT \ln \left[ \text{Ce}_{\text{surf}}^{3+} \right] - \Delta \mu^0_T

= \left\{ \left( h_{\text{O}_2}^0 + 2h_{\text{Ce}^{3+}} - h_{\text{O}_2}^0 - 2h_{\text{Ce}^{3+}} \right)

- T \left( s_{\text{O}_2}^0 + 2s_{\text{Ce}^{3+}} - s_{\text{O}_2}^0 - 2s_{\text{Ce}^{3+}} \right) + RT \ln \left[ \text{Ce}_{\text{surf}}^{3+} \right] \right\}

(S7)

Therefore,

$$
H_O = -\left( \Delta h^0 - \frac{1}{2} h_{O_2}^0 \right)
$$

$$
S_O = -\left( \Delta s^0 - R \ln \left[ \text{Ce}_{\text{surf}}^{3+} \right] \right) - 0.5 s_{\text{O}_2}^0
$$

where $\Delta h^0$ and $\Delta s^0$ are the defect formation energy and entropy. Based on the reported values for $H_O$ and $S_O$, we obtain $\Delta h^0 = 899.287.5 \pm 28.7 \text{ kJ mol}^{-1}$ and $\Delta s^0 = 101.5 \text{ J mol}^{-1} \text{ K}^{-1}$ for $[\text{Ce}^{3+}]_{\text{bulk}} = 0.0071$, and $\Delta h^0 = 277.5 \pm 28.7 \text{ kJ mol}^{-1}$ and $\Delta s^0 = 75.0 \pm 95.7 \pm 0.36$. Therefore, the results between the surface and the bulk are $\Delta h^0 = -28.7 \text{ kJ mol}^{-1}$ and $\Delta s^0 = -26.5 \pm 28.7 \text{ J mol}^{-1} \text{ K}^{-1}$.

The results here are in reasonable agreement with the fitted value using the defect model. The difference in $\Delta h^0$ and $\Delta s^0$ may be attributed to the fact that ref 44 used $[\text{Ce}^{3+}]_{\text{bulk}} = 0.0071$ and for $[\text{Ce}^{3+}]_{\text{surf}} = 0.36$ for the calculation, while the results from our model are based on the entire data set. Nevertheless, the difference is within the error bar.

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**Notes**

The authors declare no competing financial interest.

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**NOMENCLATURE**

Symbols

- $a$ lattice constant, m
- $a_i$ activity of species $i$
- $C_i$ species molar concentration, mol m$^{-3}$
- $C_{\text{crit}}$ species molar concentration on the surface, mol m$^{-2}$
- $D_i$ diffusion coefficient, m$^2$ s$^{-1}$
- $E$ activation energy, kJ mol$^{-1}$
- $F$ Faraday constant
- $f$ difference between the measurements and the model predictions
- $h$ molar enthalpy, kJ mol$^{-1}$
- $I_i$ diffusion flux from the bulk phase, mol m$^{-2}$

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