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Supplementary information

Optimizing Dense Particles for Efficient Thermochemical Fuel

Generation through A Unified Particle-Level Model

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1. Detail description of surface kinetic parameters fitting strategy

The simplification from eqs. 12 and 23 to eqs. 33 and 34 was based on the following two assumptions:

(i) the total number of oxygen vacancies in the bulk is much greater than on the surface (hence

the time variation is much larger in the bulk resulting in negligible $\rho_{Ce,s} \frac{\partial [V_O]_s}{\partial t}$ term in eq. 12). Note that we only neglect the surface oxygen vacancies when calculate the bulk species concentrations. The vacancies on the surface can be replenished by migration from the bulk with the surface concentration calculated with eqs. 9, 10, 19 and 20 (site balance), eqs. 11 and 21 (Electroneutrality), eq. 22 (OH⁻ evolution), and eq. 24 (equilibrium of species transport between the bulk and the surface). For example, from Figure 17 in literature ¹, the vacancy concentration ratio between the surface and the bulk, ranges from 1.5 to 15, with a larger ratio at lower temperatures. At 1000°C, the ratio of surface to bulk vacancy concentration ranges from 1.5 to 4. Assuming a reference particle size of 1 μ m, with δ value of 0.2 for the surface and 0.05 for the bulk (concentration ration of 4), the calculated number of oxygen vacancies on

the surface is $\tilde{\rho}_{Ce,s}S_R[V_O^{\bullet}]_{s=2.27\times10^{-5}}$ mol/m²×1.26×10⁻¹¹ m²=5.7×10⁻¹⁷ mol ($S_R = aV_R$, where a=0.54112 nm is the lattice constant of CeO₂), while the number of oxygen vacancies in the bulk is $\tilde{\rho}_{Ce}V_R[V_O^{\bullet}]_{b=4.14\times10^4}$ mol/m³×4.19×10⁻¹⁸ m³ = 8.8×10⁻¹⁵ mol, which is 154 times larger than that of the surface.

(ii) the size of particle for the kinetic parameters' fitting was smaller enough that the

concentration distribution within the bulk solid is uniform. Hence $V_0^{\bullet} = -\tilde{\rho}_{Ce} \frac{\partial [V_0^{\bullet}]_b}{\partial t}$. The experimental data with a particle size of 5 μ m reported by R. J. Carrillo et al. in literature and the fitting method a particle size of 400 nm described by Zhao et al. were used for parameter fitting ^{1, 2}. In their method, the authors demonstrated that at a sphere radius of 200 nm, due to the rapid bipolar diffusion coefficient of ceria, the concentration difference of vacancies between the surface and bulk of the particles decreased from less than 4% to less than 0.001% from 600 °C to 1000 °C (from Figure 19 in literature ¹). For 5 μ m particle at higher temperature, as Table 1 shows, the relative difference of the oxygen vacancy concentration between the center and the surface is even smaller. Therefore, it was assumed that vacancies in the bulk are uniformly distributed to reduce computational complexity during the surface kinetic parameters fitting and the oxygen vacancies are uniformly distributed and the consumption in the bulk can

be written as
$$J_{V_{O}^{\bullet}} = -\tilde{\rho}_{Ce} \frac{\partial [V_{O}^{\bullet}]_{b}}{\partial t}$$
 in eqs. 12 and 23.

Table S1 Relative difference of the oxygen vacancy concentration between the center

and the surface for 5 μ m particle size

Temperature (K)	Relative difference		
1473	1.92×10 ⁻¹³		
1573	4.15×10 ⁻⁹		
1673	2.83×10 ⁻¹⁰		
1773	9.052.83×10-7		

2. Derivation of Resistance

The resistance can be partitioned into three parts attributed to gas-solid mass transfer (r_g), surface reaction (r_s) and bulk diffusion (r_b). For r_b , on the assumption that all oxygen vacancies are fully ionized, the ionic conductivity can be calculated using the Nernst-Einstein relation³,

$$\sigma_{\mathrm{O}^{2-}} = \frac{4F^2(2-\delta)D}{RTV_{\mathrm{m}}} \qquad \qquad \wedge * \text{ MERGEFORMAT (S1)}$$

where $V_{\rm m}$ is the molar volume of the ceria (cm³/mol).

The current density due to oxygen for a one-dimensional case is given by

$$I_{\rm O^{2-}} = \frac{\sigma_{\rm O^{2-}}}{2F} \nabla \mu_{\rm O^{2-}} = \frac{\sigma_{\rm O^{2-}}}{2F} \frac{d\mu_{\rm O^{2-}}}{dr} \qquad \forall \text{MERGEFORMAT (S2)}$$

Further, the expression of bulk diffusion chemical potential difference can be derived,

$$\Delta \mu_{\rm b} = RT \ln \frac{(2 - \delta_{\rm sb})}{(2 - \delta_{\rm b})} = 2Fr_{\rm b} |I_{\rm O^{2-}}| \quad \forall \text{MERGEFORMAT (S3)}$$

To determine the other two types of resistance: r_s and r_b , here we unifed the species passing through gas-solid mass transfer and cerium oxide. We defined the $\delta_{surface}$ and δ_{inlet} to be the equilibrium non-stoichiometry of the actual p_{O_2} around the surface and at the inlet. The thicknesses of gas-solid mass transfer and surface reaction interface are difficult to determine and not very well defined either. In the oxygen permeation model, Virkar assumed that the "interfacial zones" are of a certain thickness and used the assumption to describe transport properties through both interfacial zones in terms of conductivity and thickness ⁴. $\sigma_{O^{2-}}^{i}$ and $\sigma_{O^{2-}}^{ii}$ are the oxygen ionic conductivities for gas-solid mass transfer interface and surface reaction interface, respectively. l^i and l^{ii} are the thickness of gas-solid mass transfer interface and surface reaction interface, respectively. The specific conductance (S/cm²) and specific resistance ($\Omega \cdot cm^2$) are introduced,

$$\kappa_{O^{2-}}^{i} = \frac{\sigma_{O^{2-}}^{i-}}{l'} = \frac{1}{r_g} \qquad \qquad \wedge * \text{ MERGEFORMAT (S4)}$$
$$\kappa_{O^{2-}}^{ii} = \frac{\sigma_{O^{2-}}^{ii}}{l'^{ii}} = \frac{1}{r_s} \qquad \qquad \wedge * \text{ MERGEFORMAT (S5)}$$

With the above terminology, ionic current densities across gas-solid mass transfer interface and

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surface reaction interface are given by

$$I_{O^{2-}}^{i} = \frac{\kappa_{O^{2-}}^{i}}{2} \Delta \mu_{g} \qquad \qquad \wedge * \text{ MERGEFORMAT (S6)}$$
$$I_{O^{2-}}^{ii} = \frac{\kappa_{O^{2-}}^{ii}}{2} \Delta \mu_{s} \qquad \qquad \wedge * \text{ MERGEFORMAT (S7)}$$

The current densities from the bulk to the gas inlet are assumed to be equal during the redox process,

$$I_{O^{2-}} = I_{O^{2-}}^i = I_{O^{2-}}^{ii}$$
 * MERGEFORMAT (S8)

The oxygen chemical potentials of gas-solid mass transfer and surface reaction

$$\Delta \mu_{\rm s} = RT \ln \frac{(2 - \delta_{\rm surface})}{(2 - \delta_{\rm sb})} = 2Fr_{\rm s} |I_{\rm O^{2-}}| \land \text{MERGEFORMAT} (S9)$$
$$\Delta \mu_{\rm g} = RT \ln \frac{(2 - \delta_{\rm inlet})}{(2 - \delta_{\rm surface})} = 2Fr_{\rm g} |I_{\rm O^{2-}}| \land \text{MERGEFORMAT} (S10)$$

Eqs S3, S9, and S10 provide the calculation expressions for determining the resistance $r_{\rm g}, r_{\rm s}$ and $r_{\rm b}$.

3. Numerical solutions Validation

The coupled equations are solved using the COMSOL Multiphysics 6.1. The multifrontal massively parallel sparse direct solver (MUMPS) is utilized with a relative tolerance of 10⁻⁵. The mesh independent study is conducted by evaluating the relative errors of simulation results for 4 different element numbers (denoted as N_{element} , 1, 10, 100 and 10000, respectively, and the reference value is 100). The relative error $\sigma_{\delta} = |\delta - \delta_{\text{ref}}|/\delta_{\text{ref}}$ in the average δ at the end of reduction is calculated in Table S2. The differences in the simulation results of different element numbers are negligible and N_{element} =100 is considered to be independent of the number of elements.

Table S2

Results of the mesh independent study

N _{element}	1	10	100	10000
σ_δ	1.50×10^{-7}	9.56×10 ⁻⁸	7.79×10 ⁻⁸	5.06×10 ⁻⁷

Supplementary Figures



Fig. S1 Comparison between the model predicted (solid line) and measured (dash line) reaction rate and δ for (a) the reduction process and (b) the oxidation process under various

temperatures and partial pressures.

In Fig. S2a, taking a particle size of 5 μ m as an example, under the same reaction temperature and oxygen partial pressure conditions, the model's predicted results are highly consistent with the experimental results ² in terms of reaction rate and δ value. In Fig. S2b, a further comparison was made between the CeO₂ material doped with 10% Hf and having a particle size of about 100 μ m (pentagram symbol) ⁵, and the predicted results of our kinetic model were compared under the same oxygen partial pressure of 10⁻⁴ atm. The data for CeO₂ doped with 10% Hf was obtained from the mass change between 60 and 90 minutes about 1773 K, and further derived the variation of δ values from the mass change using the calculation formula shown in equation R1. The kinetic behavior of CeO₂ material doped with 10% Hf is similar to the model prediction, with a slightly lower initial reaction rate than the model prediction but reaching a larger δ value. This can be attributed to two factors. Firstly, doping usually leads to a small loss in reduction kinetics. Secondly, the heating process in the experiment may also contribute to the observed differences. These data further demonstrate the accuracy of our kinetic model predictions.



Fig. S2 Comparison between model predictions and experimental results reported in the literature: **a.** $d_p = 0.2 \ \mu \text{m}$, **b.** $d_p = 100 \ \mu \text{m}$.



Fig. S3 δ as a function of time under T_{red} =1723 K (black line) and T_{red} =1923 K (red line).



Fig. S4 Time required for redox extent to 75% under different r_p and \tilde{D} . (a) Reduction process at T_{red} =1673 K and p_{O_2} =10⁻⁵ atm. (b) Oxidation process at T_{ox} =1173 K and p_{H_2O} =0.5 atm.



Fig. S5 δ (left) and $r_{\rm g}$, $r_{\rm s}$ and $r_{\rm b}$ (right) values as a function of time under different D values during reduction process at $T_{\rm red}$ =1673 K and $P_{\rm O_2,s}$ =10⁻⁵: (a) $r_{\rm p}$ =100 μ m, (b) $r_{\rm p}$ =1000 μ m and (c) $r_{\rm p}$ =100 cm.

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