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## Supporting Information

## Reactive stability of promising scalable doped ceria materials for thermochemical two-step CO<sub>2</sub> dissociation

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System	Results	Ref.
Powder and porous ceria (graphene used for sacrificial pore formation); CO <sub>2</sub> splitting; 1450 /1100 °C temperature swings, 2000 cycles	<ul> <li>a) Maximum value of non-stoichiometry (δ) of ceria powder was 0.0383 at 1450 °C and</li> <li>b) Initial fuel production of 86.4 % retained over 2000 cycles and average value of δ was 0.0197.</li> </ul>	1
CeO <sub>2</sub> (isothermal cycling at 1750 K; 45 cycles)	a) During isothermal cycling, $360 \text{ mL min}^{-1}$ of CO produced continuously over 45 redox cycles, and up to 95% of the sensible heat of the process gases recovered.	2
Dual scale porous (mm and µm sized pores) reticulated ceria structure; CO <sub>2</sub> splitting; 1500 °C/ 750 °C temperature swings (500 cycles).	<ul> <li>a) CO<sub>2</sub> splitting with 100% selectivity, 83% molar conversion, and 5.25% solar-to-fuel energy efficiency.</li> <li>b) Dual-scale porosity of ceria structure and lower energy penalty of vacuum pumping as compared to that of inert gas recycling for maintaining a low pO<sub>2</sub> value during the reduction improved the efficiency significantly (stable for 500 consecutive cycles).</li> </ul>	3
Ceria fiberboard (8-µm diameter and over 200 µm in length) and Rh deposited CeO <sub>2</sub> fibers (1512 °C/ 803 °C temp. swing cycles for H <sub>2</sub> O splitting).	<ul> <li>a) The fuel production process transitions from one controlled by surface reaction kinetics at re-oxidation temperatures below ~1000 °C to one controlled by the rate at which the reactant gas is supplied at temperatures above ~1100 °C.</li> <li>b) Application of Rh catalyst particles improves the oxidation rate at low temperatures, but provides no benefit at high temperatures for either oxidation or reduction.</li> </ul>	4
Three types of Ceria nano-structures; flame- made and flower-like agglomerates and sol- gel sub-micro particles. (Isothermal cycling at 1173 K for 10 cycles).	a) Flame-made agglomerates maintained 57 % higher average CO production rates compared to commercial ceria and sol-gel ceria. b) Reported H <sub>2</sub> (480 µmol min <sup>-1</sup> g <sup>-1</sup> ) and CO (230 and 340 µmol min <sup>-1</sup> g <sup>-1</sup> ) production rates and redox capacity ( $\Delta \delta = 0.25$ ) for ceria. Note: methane used as reducing agent	5
Scalable CeO <sub>2</sub> fibers (µm size range), 1000 isothermal cycles followed by 16 swing cycles between 1773K/1073K.	a) Change in non-stoichiometry $(\Delta \delta)$ is 0.04. b) Surface area lost 29% (0.057 m <sup>2</sup> g <sup>-1</sup> ) but retained an open, porous microstructure. c) Proposed that it is beneficial to eliminate the high temperature calcination during manufacture to preserve surface area and then cycle at a lower reduction temperature.	6
Ceria reticulated foam structures with dual- scale porosities (mm and µm sized pores); CO <sub>2</sub> splitting; 1773 K / 873-1273 K, 20 cycles	<ul> <li>a) CO production rates reported are ten times higher for samples with strut porosity than for samples with non-porous struts.</li> <li>b) Shorter cycle time and a mean solar-to-fuel energy conversion efficiency of 1.72%.</li> </ul>	7

**Table S1.** Literature survey of long-term stability tests of ceria based redox materials

S-untaine	Descrife	Def
System	Kesuits	Kel.
1% Rh-CeO <sub>2</sub> co- precipitation synthesis (1500/500 °C temperature swings, 59 cycles)	<ul> <li>a) Direct methane production from CO<sub>2</sub> and H<sub>2</sub>O;</li> <li>b) Catalytic effect of metallic rhodium particles in improving the methane and CO productivities;</li> <li>c) Slight increase in methane signal between with cycle number.</li> <li>d) After 59 cycles the productivities are at about 75% of their initial values (1400/500 °C).</li> </ul>	8
Ce0.85-yZr0.15REyO2-0.5y (RE = Y, La, Sm and Gd); 80 cycles	Ce0.82Zr0.15Sm0.03O1.99 maintains stable yields and improved oxidation kinetics compared to Ce0.85Zr0.15O2. Structural vacancies formed due to Sm <sup>3+</sup> doping enhances oxygen bulk transport, while performances are lower than for non-RE doped ceria-zirconia.	9
Ce <sub>x</sub> Zr <sub>y</sub> Hf <sub>z</sub> O <sub>2</sub> (co-ppt. synthesis), CO <sub>2</sub> splitting (1400 °C/ 1000 °C, 20 cycles)	$Ce_{0.895} Zr_{0.046} Hf_{0.053} O_{1.988}$ (CZH5) produced stable and steady amounts of $O_2$ (114 $\mu$ mol/g) and CO (162 $\mu$ mol/g) in 20 thermochemical cycles.	10
Ce <sub>1-x</sub> Zr <sub>x</sub> O <sub>2</sub> electrospun fibers (0 <x<0.1) 1400<br="" ;="">/800 °C temperature swings; 108 cycles</x<0.1)>	Sintering resistant material with sintering only occurring along the fiber axes, overall CO production and peak production rate stabilize above 3.0 mL g <sup>-1</sup> and 13.0 mL min <sup>-1</sup> g <sup>-1</sup> , respectively.	11
Ce <sub>1-x</sub> Zr <sub>x</sub> O <sub>2</sub> ( $0 < x < 0.4$ ) synthesized using citrate nitrate auto combustion route; 1400/900 °C; 100 cycles	Optimal zirconium content (x = $0.15$ ) Ce <sub>0.85</sub> Zr <sub>0.15</sub> O <sub>2</sub> , improved the specific CO <sub>2</sub> -splitting performance by 50% compared to pure ceria. Declining splitting kinetics were observed over 100 cycles for optimal zirconium composition.	12

Table S1 (continued). Literature survey of long-term stability tests of ceria based redox materials



**Figure S1.** Overview of five TGA cycles with the co-doped ceria samples  $M_{0.05}Hf_{0.05}Ce_{0.9}O_2$  (M = Li, Ca, Mg, Er, and Y) vs.  $Hf_{0.05}Ce_{0.95}O_2$  as a reference.



Figure S2. 50 cycle TGA experiment of pristine ceria.

Label	10Hf before TGA	10Hf after TGA	10Zr before TGA	10Zr after TGA	7Ta before TGA	7Ta after TGA	5Nb before TGA	5Nb after TGA
1	9.58	9.12	10.10	11.50	6.41	7.28	3.45	5.33
2	8.65	8.74	10.82	10.06	6.89	8.50	3.07	5.57
3	9.02	8.58	10.45	10.00	6.87	7.72	5.05	5.18
4	8.98	8.44	9.78	11.45	6.46	7.28	5.49	4.97
5	9.27	9.04	11.21	11.45	6.27	7.43	4.21	5.00
6	7.81	8.78	10.74	9.76	9.79	7.66	3.88	5.00
7	8.91	8.88	10.37	11.04	6.15	7.17	4.29	5.27
8	9.52	8.99	9.60	10.20	6.55	8.36	4.24	5.70
9	9.45	8.44	9.67	10.90	6.20	9.44	4.48	4.90
10	9.48	8.59	8.87	9.46	6.80	8.22	4.94	5.31
Average	9.067	8.760	10.161	10.582	6.839	7.906	4.310	5.223
Standard deviation	0.539	0.245	0.697	0.771	1.071	0.719	0.733	0.266

Table S2. Dopant concentration [mol %] determined from EDX spectra.



**Figure S3.** Peak shift in the region around 28  $^{\circ}$  of PXRD patterns before (a) and after (b) 50 TGA cycles for ceria, 10Hf, 10Zr, 7Ta, and 5Nb.



**Figure S4.** SEM/EDX mapping before (left) and after 50 TGA cycles (right) of 10Zr (a, b), 10Hf (c, d), 7Ta (e, f), and 5Nb (g, h).

Nº c mea rem	of asu- ient	ant	1	2	3	4	5	6	7	8	9	10	x-10
Sample (and label)		Dop											
$Li_{0.05}Hf_{0.05}Ce_{0.9}O_2$	(5Li5Hf)	Li	0	0	0	0	0	0	0	0	0	0	0
		Hf	3.8	3.9	3.0	4.1	5.5	3.0	3.0	3.6	4.0	3.6	3.7 ± 0.7
		Li	-	-	-	-	-	-	-	-	-	-	-
		Hf	-	-	-	-	-	-	-	-	-	-	-
Ca <sub>0.05</sub> Hf <sub>0.05</sub> Ce <sub>0.9</sub> O <sub>2</sub>	(5Ca5Hf)	Ca	5.0	4.9	5.4	5.4	4.9	5.3	5.5	5.2	5.0	5.6	$5.2 \pm 0.3$
		Hf	3.8	3.7	3.3	3.3	4.0	3.9	3.0	3.6	2.8	3.9	3.5 ± 0.4
		Ca	6.2	5.5	5.6	6.1	6.1	6.0	6.0	5.5	5.5	6.1	5.9 ± 0.3
		Hf	4.7	3.7	4.7	3.1	4.5	3.5	4.2	4.1	3.5	4.6	$4.1 \pm 0.6$
0.05Hf0.05Ce0.9O2	(5Mg5Hf)	Mg	5.0	3.9	5.5	4.4	5.8	5.7	3.8	4.0	6.1	4.5	$4.9 \pm 0.9$
		Hf	3.7	3.5	2.9	3.6	3.0	3.6	3.9	3.9	3.6	3.2	3.5 ± 0.3
		Mg	12.5	9.7	9.5	10.1	11.5	11.7	12.9	10.1	9.5	9.1	$10.7 \pm 1.4$
Mg		Hf	3.5	2.8	3.0	2.9	3.3	3.1	3.3	3.1	3.3	3.2	3.1 ± 0.2
${}^{9}O_{2}$	(5Y5Hf)	Y	4.8	5.0	4.8	4.9	4.2	4.6	4.9	5.4	5.7	6.0	$5.0 \pm 0.5$
Y <sub>0.05</sub> Hf <sub>0.05</sub> Ce <sub>0.9</sub>		Hf	4.2	4.0	4.3	3.2	4.1	3.5	4.1	4.1	4.0	4.3	$4.0 \pm 0.3$
		Y	4.1	5.1	4.7	4.8	4.6	5.5	4.6	6.4	5.6	5.6	$5.1 \pm 0.7$
		Hf	3.4	3.2	2.8	3.1	2.9	4.3	5.1	3.5	2.4	4.0	$3.5\pm0.8$
05Ce0.9O2	(5Er5Hf)	Er	4.9	3.7	3.9	4.2	4.2	4.5	4.4	4.5	4.4	4.8	$4.3 \pm 0.4$
		Hf	2.9	4.2	3.6	3.3	3.3	3.5	3.9	3.7	2.8	3.8	3.5 ± 0.4
. <sub>05</sub> Hf <sub>0</sub> .		Er	4.0	4.3	3.8	4.0	4.6	3.7	4.1	6.0	4.4	4.5	$4.3 \pm 0.6$
$\mathrm{Er}_{0.}$		Hf	3.9	3.9	3.7	2.8	2.1	2.9	3.0	2.3	3.6	3.3	$3.1 \pm 0.6$

**Table S3.** Dopant concentration in mol% determined from EDX spectra before TGA cycling experiments (grey) and after TGA cycling experiments (white).



**Figure S5.** PXRD patterns of  $M_{0.05}Hf_{0.05}Ce_{0.9}O_2$  (M = Li, Mg, Ca, Er, and Y) before and after TGA in the region between 28° and 29.5°.

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