Supplementary Information

Chemical Surface Exchange of Oxygen on $CeO_{2-\delta}$ in O_2/H_2O atmosphere

Ho-Il Ji [ac], Xin Xu [b], and Sossina M. Haile *[abcd]

[a] *Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA*

[b] *Applied Physics, Northwestern University, Evanston, IL 60208, USA*

[c] *Materials Science, California Institute of Technology, Pasadena, CA 91125, USA*

[d] *Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA*

Calculation of pH_2O at 1400 °C

For converting pH_2O at ~90 °C to that at 1400 °C, the reaction of thermolysis of $H_2O(g)$ is considered as below. Hereafter, subscripts *LT* and *HT* indicate the measured at low and high temperatures, respectively.

	$H_2O(g)$	$\rightarrow$ $H_2(g)$	+ $\frac{1}{2}O_2(g)$	
initial (90 °C)	(pH_2O_{LT}/p_{tot})	~ 0	$(pO_{2,LT}/p_{tot})$	(S1)
change	$-x$	x	$\frac{1}{2}x$	
final (1400 °C)	$(pH_2O_{LT}/p_{tot}) - x$	x	$(pO_{2,LT}/p_{tot}) + \frac{1}{2}x$	

where p_{tot} is total pressure considered as 1 atm here, $pO_{2,\,LT}$ is the oxygen partial pressure at ~90 °C which is unknown, and x is a fractional concentration of H_2O consumed by thermolysis. The pH_2O_{LT} & $pO_{2,\,HT}$ are the experimentally measured values by the *ex-situ* humidity sensor (~ 90 °C) and *in-situ* oxygen sensor (1400 °C), respectively, at total pressure of 1 atm, therefore,

$$\frac{pO_{2,HT}}{p_{tot}} = \frac{pO_{2,LT} + (\frac{1}{2}x \cdot p_{tot})}{p_{tot} + (\frac{1}{2}x \cdot p_{tot})} \tag{S2}$$

$$\frac{pH_2O_{HT}}{p_{tot}} = \frac{pH_2O_{LT} - (x \cdot p_{tot})}{p_{tot} + (\frac{1}{2}x \cdot p_{tot})} \tag{S3}$$

The expression for the thermodynamic equilibrium constant, K_{H_2O}, for reduction reaction at 1400 °C is given

$$K_{H_2O,\,red}(1400\ ^{o}C) = \frac{x \cdot [(pO_{2,LT}/p_{tot}) + \frac{1}{2}x]^{\frac{1}{2}}}{(pH_2O_{LT}/p_{tot}) - x} \tag{S4}$$

By solving simultaneous equations of Equation (S2) and (S4) for $pO_{2,\,LT}$ and x, pH_2O at 1400 °C is simply calculated by Equation (S3). The results for actual experimental conditions are summarized in Table S1.

Table S1. Thermodynamic calculation of pH_2O at 1400 °C

pO_2 at 1400 °C / atm (*in-situ*)	pH_2O at ~ 90 °C / atm (*ex-situ*)	pO_2 at ~ 90 °C / atm (*calculation*)	pH_2O at 1400 °C / atm (*calculation*)
2.258×10^{-4}	0.1640	1.455×10^{-4}	0.1638
3.850×10^{-4}	0.1743	3.195×10^{-4}	0.1742
3.922×10^{-4}	0.0750	3.643×10^{-4}	0.0749
3.783×10^{-4}	0.0232	3.695×10^{-4}	0.0232
7.694×10^{-4}	0.1519	7.291×10^{-4}	0.1518
1.378×10^{-3}	0.1637	1.345×10^{-3}	0.1636

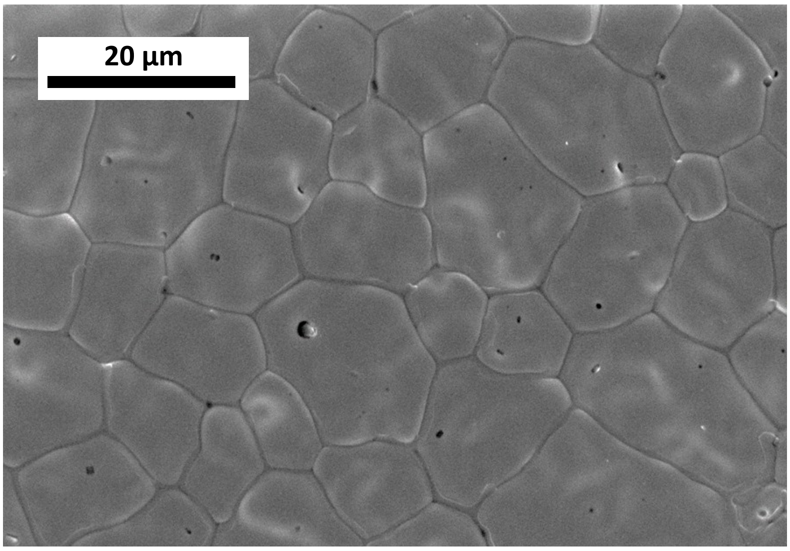

Figure S1. SEM micrograph of surface of dense ceria.

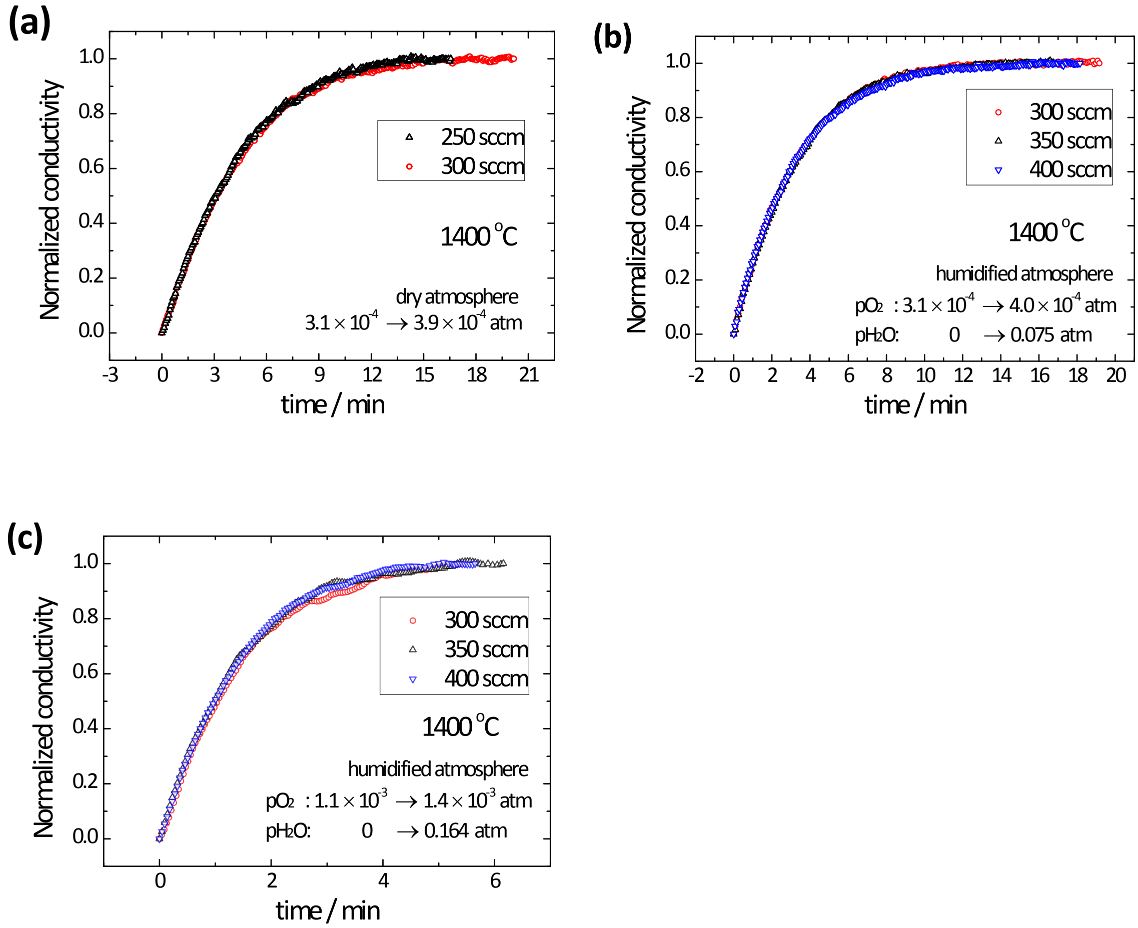

Figure S2. Normalized conductivity relaxation profiles at various flow rates (a) in dry and (b-c) humidified atmosphere at 1400 °C.

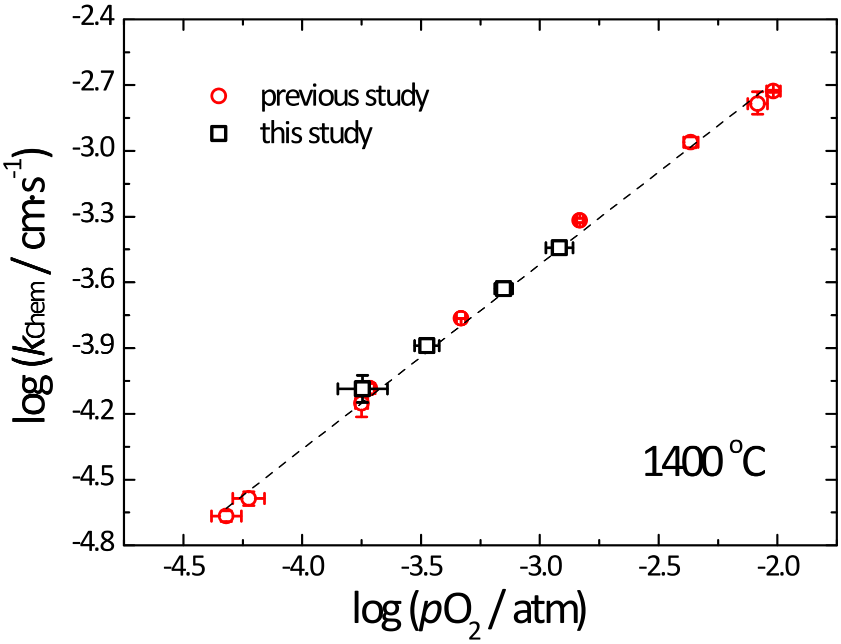

Figure S3. Surface reaction constant of O_2, k_{Chem,O_2}, of ceria as a function of pO_2 at 1400 °C obtained from the best fits to the relaxation profiles in Figure 4 and 5. Shown for comparison is the previous result reported by Ji *et al.*[23]