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Supporting Information

Extreme High Temperature Redox Kinetics in Ceria: Exploration of the Transition from Gas-Phase to Material-Kinetic Limitations

Ho-Il Ji[ac], Timothy C. Davenport[a], Chirranjeevi Balaji Gopal[c], 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] *Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA*

[*]Corresponding author. E-mail address: sossina.haile@northwestern.edu

As shown in Figure S1(a), for the majority of the experimental conditions, the measured oxygen partial pressure coincided with the supplied value. At the lowest flow rates, however, the actual pO_2 in the system deviates somewhat from the nominal value, as shown for two representative values of $(1.59 \pm 0.02) \times 10^{-3}$ and $(7.82 \pm 0.14) \times 10^{-4}$ atm. This is a result of slight leaks becoming important relative to the volume of gas supplied. The greatest deviation of ~ 40% is *smaller*, by about a factor of 2, than the typical step change in pO_2 employed in this study. Thus, the impact of the deviation of the actual pO_2 from the nominal value is negligible.

The influence of slight leaks on the reactor flush time is also greatest at low gas flow rates. Shown in Figure S1(b) are the normalized pO_2 profiles for relatively large step changes between 8.0×10^{-4} and 1.6×10^{-3} atm ($|\Delta\log(pO_2/\text{atm})| = 0.30$). Under these conditions, the reactor response time-constant (τ), established by fitting an arbitrary exponential profile of the form of Eq. (3), reaches a stable value of ~ 10 s for flow rates of 100 sccm and higher. At the lowest flow rate, the time constant rises slightly to ~ 12.5 s. The shortest material response time encountered in this work was ~ 103 s, almost an order of magnitude larger than the longest reactor response time, indicating that the material rather than reactor behavior was captured over the entire range of conditions evaluated.

The results presented in Figures 3 and 4 (main text), showing a relaxation time constant that is dependent on flow rate might, at first glance, be attributed to an artifact of the increasing influence of leaks at low flow rates. For such an explanation to apply, it would require that k_{Chem} decrease with increasing oxygen partial pressure. However, as shown in Figure 6 (main text), the surface reaction rate increases with increasing pO_2, and hence leaks cannot be responsible for the observed behavior.

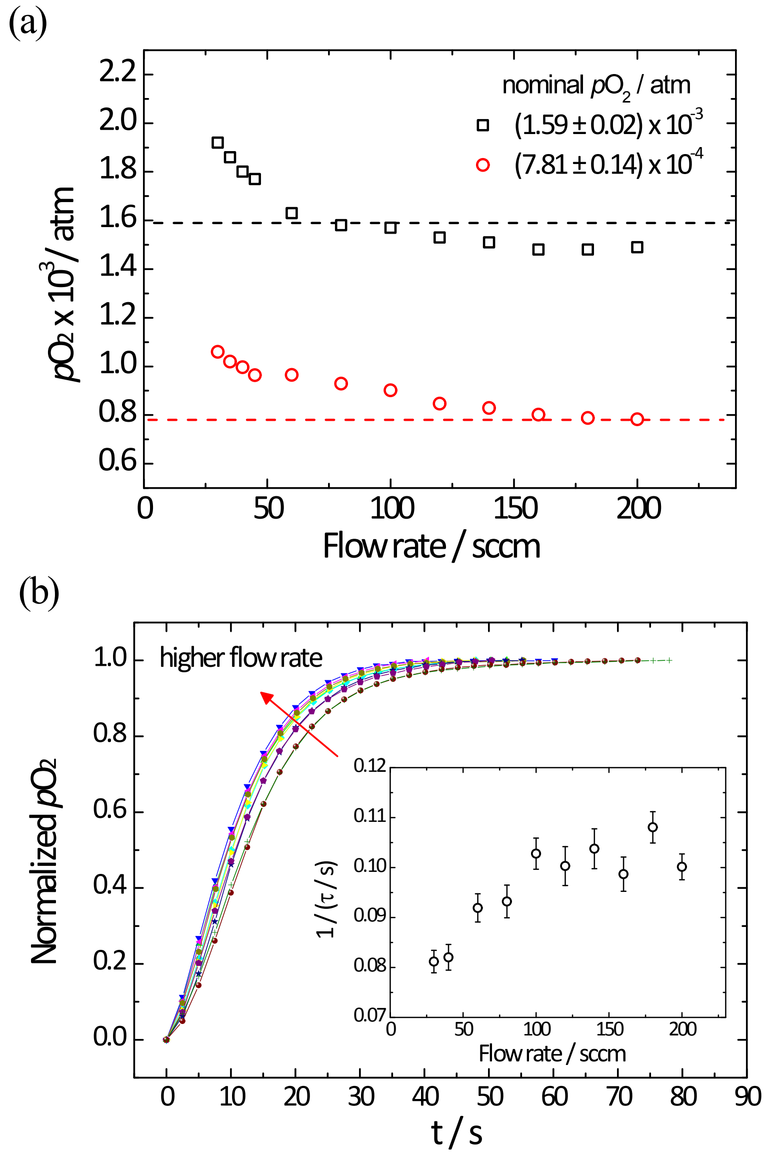

Figure S1. Impact of flow rate on steady state oxygen partial pressure and on the time scale of response of the experimental apparatus to step changes in oxygen partial pressure: (a) Variation in steady state oxygen partial pressure as a function of flow rate (as recorded by the in situ oxygen sensor) for nominal input pO_2 values as specified and also indicated by the horizontal dashed lines; (b) reactor relaxation profiles as a function of flow rate for switching between $(1.59\pm0.02)\times10^{-3}$ and $(7.82\pm0.14)\times10^{-4}$ atm. Inset shows reactor relaxation times. All measurements at T = 1400 °C. The range of flow rates examined, 30 to 200 sccm correspond, for a typical sample mass of 0.38 g, to mass normalized flow rates of 78 to 523 sccm/g.