Supplemental Information

Thermodynamic Properties, Defect Equilibria, and Water Splitting Behavior of Ga- doped LSM Perovskite

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Thermogravimetric Analysis Conditions and Results

Input *n*CO2/*n*CO and Corresponding Calculated pO_2 (atm)									
Temperature = 1250 °C									
*n*CO2/*n*CO	65.71	266.67							
Log(pO_2)	-6.66	-5.43							
Temperature = 1300 °C									
*n*CO2/*n*CO	31.89	50.38	90.63	139.09	266.67				
Log(pO_2)	-6.69	-6.29	-5.77	-5.4	-4.92				
Temperature = 1350 °C									
*n*CO2/*n*CO	15.76	21.88	31.89	50.38	90.63	266.67			
Log(pO_2)	-6.74	-6.45	-6.12	-5.72	-5.22	-4.52			
Temperature = 1400 °C									
*n*CO2/*n*CO	7.50	8.43	10.40	12.50	13.03	16.21	20.60	21.88	
Log(pO_2)	-5.52	-5.45	-5.23	-4.98	-4.93	-4.47	-4.58	-4.22	
*n*CO2/*n*CO	26.05	34.57	37.27	48.15	65.71	70.00	115.38	139.09	266.67
Log(pO_2)	-6.84	-6.74	-6.56	-6.4	-6.36	-6.17	-5.96	-5.91	-5.76

Table SI.1. Input ratios of CO_2 and CO molar flowrates during thermogravimetric experiments for equilibrium mapping and their corresponding pO_2 calculated using the Cantera Python suite.

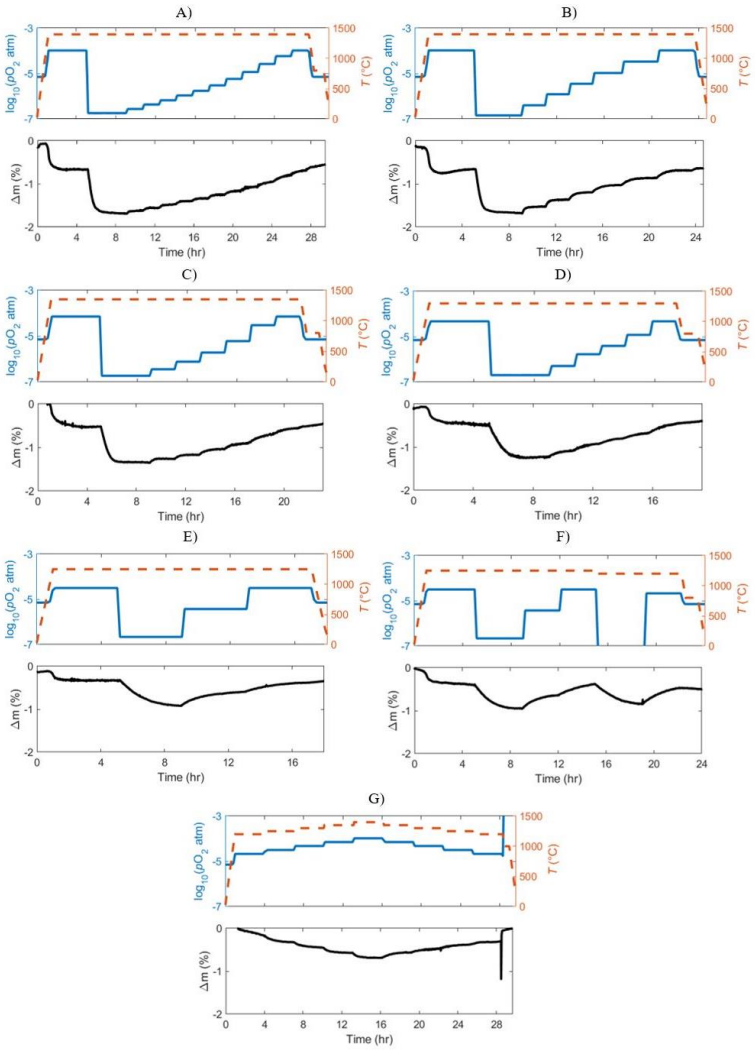

Figure SI.1: TGA curves for each LSMG6482 CO_2/CO experiment.

Figure SI.1: Experimental conditions (pO_2, blue and temperature, red) and Δm during each TGA experiment: A-F) Isothermal experiments at 1250 to 1400 °C, and G) an experiment with stepwise changes in both pO_2 and temperature. Δm curves during experiments A-F were determined by referencing the mass at the final isothermal measurement before cooling to the mass at the final measurement in experiment G with equivalent pO_2 and temperature.

Validation of Thermogravimetric Methodology

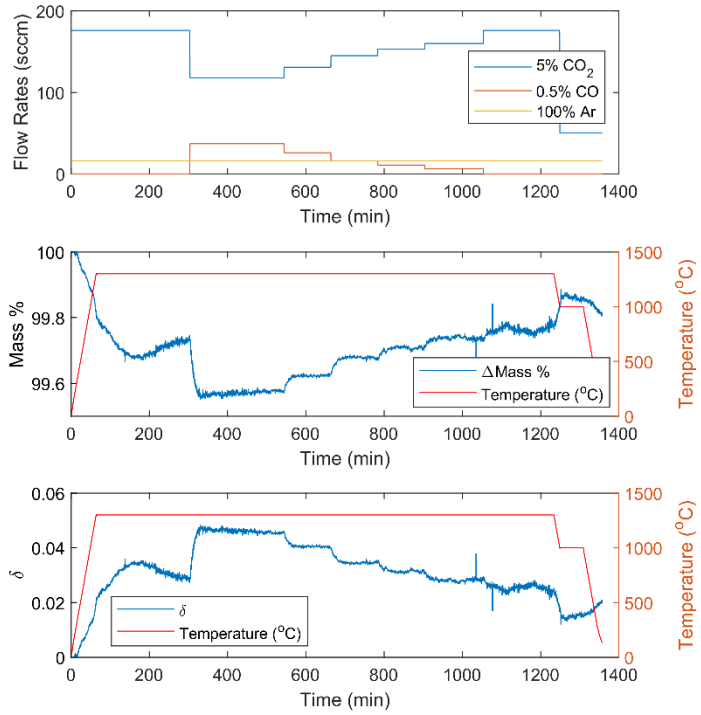

Figure SI.2. Top: Input flowrates for 1300°C thermogravimetric experiment. Middle: Relative mass of ceria sample as a function of time. Bottom: δ in $CeO_{2-\delta}$ as a function of time.

Figure SI.2: The validity of the calculated pO_2 given a set of input nCO_2/nCO was tested using a ceria powder (69mg) at the 1300C experimental conditions described in Table SI.1. The measured equilibrium δ was recorded at each condition and used alongside thermodynamic data from Panlener et al. to determine the pO_2 of the atmosphere [1]. The measured pO2 was compared to the estimated pO2, resulting in excellent agreement, with the best agreement at the lower pO2 and all error ≤5%. The results are summarized in Table SI.2.

nCO_2/nCO input	31.89	50.38	90.63	139.09	266.67
δ Measured	0.030	0.025	0.019	0.016	0.013
Log(pO_2) Measured	-6.78	-6.42	-5.93	-5.60	-5.16
Log(pO_2) Calculated	-6.69	-6.29	-5.77	-5.4	-4.92
Log(pO_2) % difference	1%	2%	3%	4%	5%

Table SI.2. Thermogravimetric results for δ in $CeO_{2-\delta}$ at 1300C. pO_2 Measured is the pO_2 estimated based on measured delta using thermodynamic data from Panlener et al. pO_2 Calculated is based on Cantera predictions of equilibrium for the input ratio of nCO_2/nCO.

Defect Model Fitting Parameter Convergence

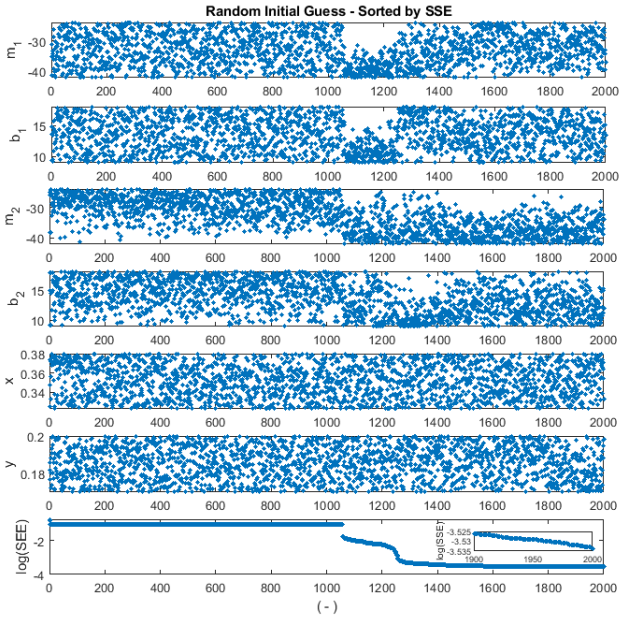

Figure SI.3: 2000 Random initial guesses used in the defect model fitting MATLAB code, sorted by the resulting SSE.

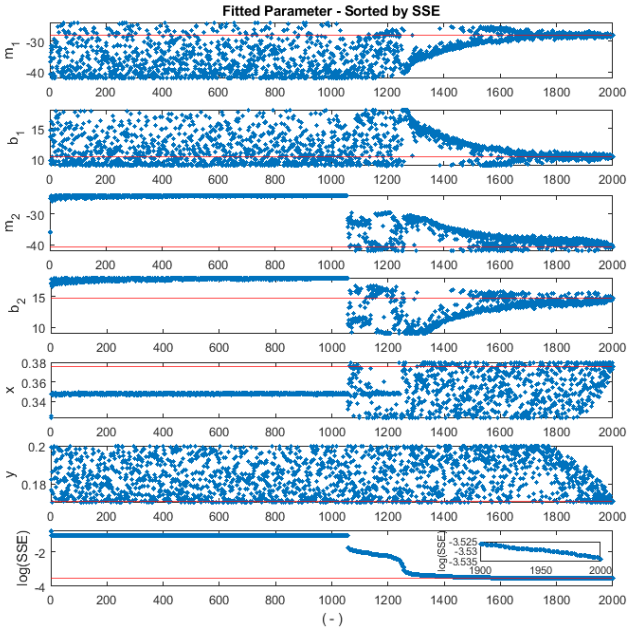

Figure SI.4: Fitted parameters after each random initial guess in the defect model fitting MATLAB code, sorted by the resulting SSE. Red lines indicate the final fitted value.

Figure SI.3 and SI.4: To ensure a global minimum was achieved when minimizing the difference between measured values of δ and those predicted by the defect model, a large bin of randomized initial guesses for each fitting parameter was generated and the minimization was performed 2000 times. The initial guesses are plotted in Figure SI.3 followed by the corresponding fitted parameter in Figure SI.4. Each set of plots have been sorted by the resulting SSE, plotted on a log scale in the bottom subplot of each figure. Here, it is apparent that there were 3 local minimums, highly sensitive to the initial guess of the parameter set, indicated by 3 separate plateaus. A satisfactory convergence of SSE $\leq 10^{-5}$ over 100 guesses.

Limited Data Fitting Results

Parameters	*Limited Data*	*Full range*	*% Difference*
m_1	-30.058	-29.560	1.68%
b_1	11.738	11.507	2.01%
m_2	-39.713	-40.011	0.75%
b_2	14.240	14.474	1.62%
x	0.364	0.360	1.16%
y	0.171	0.174	2.11%
SSE	0.0022	0.0026	15.49%

Table SI.3: Comparison of fitting parameters when using either the trace oxygen limited data set or the full range of data.

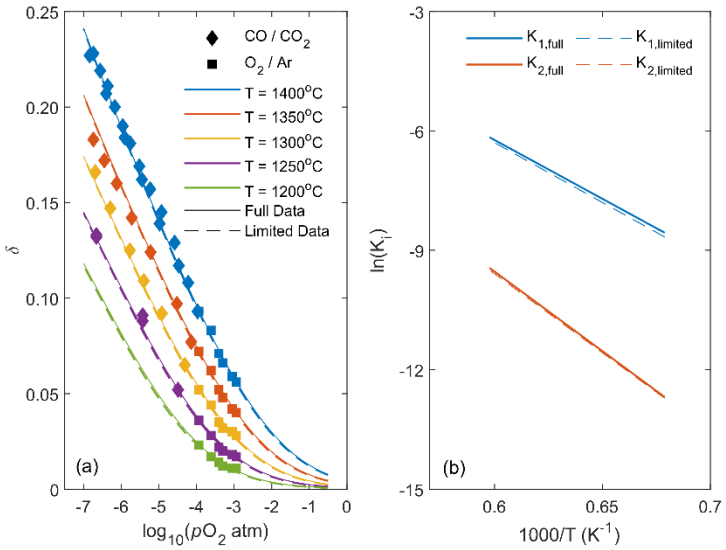

Figure SI.5: Comparison of (a) defect models using the full data set (solid lines) vs limiting data collection in the TGA to just data obtainable through trace oxygen mixing (dashed lines) and (b) the resulting defect equilibrium constants as a function of temperature.

References

[1] R. J. Panlener, R. N. Blumenthal, and J. E. Garnier, “THERMODYNAMIC STUDY OF NONSTOICHIOMETRIC CERIUM DIOXIDE,” *Journal of Physics and Chemistry of Solids*, vol. 36, no. 11. pp. 1213–1222, 1975. doi: 10.1016/0022-3697(75)90192-4.