1 Sample preparation and characterisation

To prepare the powders of CeO$_2$ and Ce$_{0.85}$Zr$_{0.15}$O$_2$, Ce(NO$_3$)$_3$·6H$_2$O and ZrO(Cl)$_2$·8H$_2$O were dissolved in the required ratios in deionized water. In addition citric acid and ethylene glycol were added in a molar ratio of 1 : 2 : 3 (cations : citric acid : ethylene glycol). The obtained mixture was stirred at 373 K for 1 h and then heated stepwise to 473 K. After water evaporation a viscous yellow gel was formed by polyesterification. This gel was further heated to 723 K to induce pyrolysis. Finally the produced yellow powder was calcined in an electrical furnace at 1023 K in air for 2 h to remove any remaining carbonaceous species.

Figure 1: The xrd scan for Ce$_{0.85}$Zr$_{0.15}$O$_2$, with the peak positions for pure CeO$_2$ also shown.

To confirm the composition of the samples both XRD patterns and EDX spectra were analysed. Figure 1 and 2 show these spectra for Ce$_{0.85}$Zr$_{0.15}$O$_2$. 
Figure 2: An EDX spectrum of the Ce$_{0.85}$Zr$_{0.15}$O$_2$ porous granules. A quantitative analysis of this scan gave the Ce to Zr ratio as 85.36 : 14.64.

Figure 3: An SEM image of the Ce$_{0.15}$Zr$_{0.15}$O$_2$ porous granules.

Figure 3 shows an SEM of one of the Ce$_{0.15}$Zr$_{0.15}$O$_2$ porous granules. Five such large granules weighing a total of approximately 1.2 g were used in the TGA. This is illustrated in figure 1 of the manuscript.
2 TGA

Figure 4: A schematic of the system used showing the TGA, the samples and the gas flows. Note the input Ar stream comes from the oxygen pump, and the outflow stream goes through the oxygen sensor.
2.1 Determining $\Delta h_\delta$

The partial molar enthalpy can be obtained using the equation

$$\frac{1}{2} \ln \left(\frac{p_{O_2}}{p^\circ}\right) = -\frac{\Delta h_\delta}{RT} + \frac{\Delta s_\delta}{R} \bigg|_{\delta=\text{const}}.$$  (1)

Plots of $\frac{1}{2} \ln(p_{O_2})$ vs. $\frac{1}{RT}$ for a given value of $\delta$ should give $\Delta h_\delta$ as the slope. This method of extracting $\Delta h_\delta$ is illustrated in figure 6. Note that none of the points were obtained by extrapolating, and each individual data set was interpolated separately.
Figure 6: **Above:** The experimental data from the literature, [1, 2] and this work plotted along with interpolations and the constant $\delta$ value vertical lines. Where each vertical line cuts an interpolation line is taken as a data point for that value of $\delta$. **Below:** Plots of $\frac{1}{2}\ln(P_{O_2})$ vs. $-\frac{10^3}{RT}$ and linear fits for each value of $-\log(\delta)$ for which the slope gives $\Delta h^\circ_\delta$ and the intercept is $\frac{\Delta s^\circ_\delta}{R}$.

### 3 Fitting Ce$_{0.95}$Zr$_{0.05}$O$_2$ literature data

The fit of literature data for Ce$_{0.95}$Zr$_{0.05}$O$_2$ seen in figure 7 shows deviations for very small $\delta$. This could be due to large errors in the acquisition of this data.
or indeed in extracting it. There is also the possibility that the partial molar enthalpy does have a $\delta$ dependence for very small $\delta$.

Figure 7: The literature data for Ce$_{0.95}$Zr$_{0.05}$O$_2$ as well as a fit of the simple model to the data.
4 Alternative Model

Figure 8 shows the fit of the alternative model, in which the maximum vacancy concentration $\delta_m$ was fixed, and an additional parameter $a$ was added.

$$\Delta s_{\text{vac}} = \delta \Delta s_{\text{th}} + a R (x \ln(x) + (1 - x) \ln(1 - x))$$ (2)

where

$$\Delta s_{\text{th}} = \frac{1}{2} s_{\text{O}_2} + \Delta s_v + \frac{1}{\delta_m} R \ln(\omega_{\text{defects}})$$ (3)

$$1 \leq a \leq 3.$$ (4)

The value of $a$ is then a measure of the type of defect associations which are dominant in the lattice, where $a = 3$ implies no defect clusters are present and $a = 1$ corresponds to all defects forming $(\text{Ce}^{\prime}_{\text{Ce}} \text{V}^{\bullet\bullet}_{\text{O}} \text{Ce}^{\prime}_{\text{Ce}})^{\times}$ clusters.
Figure 8: Fits of the alternative $\omega$-model given in the manuscript plotted along with the literature, [1, 2] and experimental CeO$_2$ data obtained in this work. It can be seen that this model does not fit the smaller $\delta$ values very well.

References
