Supporting Information

Incorporation of Square-Planar Pd^{2+} in Fluorite CeO_2: Hydrothermal Preparation, Local Structure, Redox Properties and Stability

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Lattice Parameter

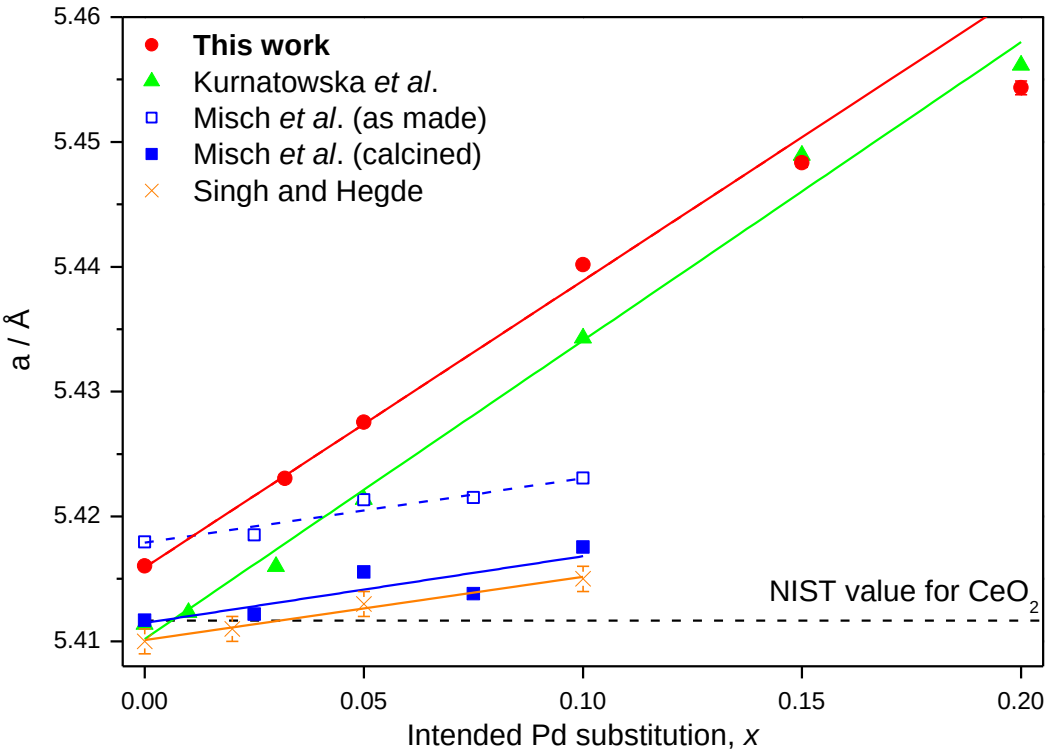

Figure S1. Refined lattice parameter, a, *as a function of* x *in* $Ce_{1-x}Pd_xO_{2-\delta}$. *Linear fit to* $0 \leq x \leq 0.15$ *has been extrapolated up to* $x = 0.20$ *with lattice parameters for* $Ce_{1-x}Pd_xO_{2-\delta}$ *reported by Kurnatowska* et al.,[1] *Misch* et al.,[2] *and Singh and Hedge*[3] *included for comparison. When not shown, error bars are smaller than data points.*

Rietveld Refinement

Values for the Ce and O U_{iso} (0.00766(5) Å^2 and 0.0174(5) Å^2, respectively) were taken from a refinement of highly crystalline CeO_2 (NIST) where the site occupancies were fixed at 1. Although the Pd and Ce were refined on separate sites, the Pd U_{iso} was taken to be the same as that of Ce. Pd coordinates were fixed on the square planar 24*e* site, and the Pd and Ce occupancies were fixed to give the correct Pd:Ce ratio.

Table S1: Structural parameters determined by Rietveld refinement for Pd-CeO2 materials

x	24*e* site Pd occupancy	Refined O occupancy	R_{wp}	R_p	χ^2
0	0	1.009(5)	4.54%*	3.50%*	1.036*
0.05	0.0083	0.988(5)	3.59%	2.78%	1.152
0.10	0.0167	0.943(5)	3.72%	2.88%	1.218
0.15	0.025	0.925(6)	4.20%	3.29%	1.491
0.20**	0.0333	0.855(6)	5.51%	4.40%	1.680

* Different scan parameters to other powder patterns. **not phase pure.

The O occupancy shows a decrease with increasing *x*, in line with the chemical formula $Ce_{1-x}Pd_xO_{2-x}$

General Characterisation

Table S2. ICP-OES measured metal content by mass of $Ce_{1-x}Pd_xO_{2-\delta}$ with calculated formula, assuming remaining mass is oxide.

Intended *x*	Ce / %	Pd / %	Na / %	Calculated Formula
0.05	72.5(3)	2.85(30)	0.18(30)	$Ce_{0.94(3)}Pd_{0.049(6)}Na_{0.01(2)}O_{2.8(1)}$
0.20	65.4(3)	12.6(3)	0.09(30)	$Ce_{0.79(3)}Pd_{0.200(8)}Na_{0.01(2)}O_{2.3(1)}$

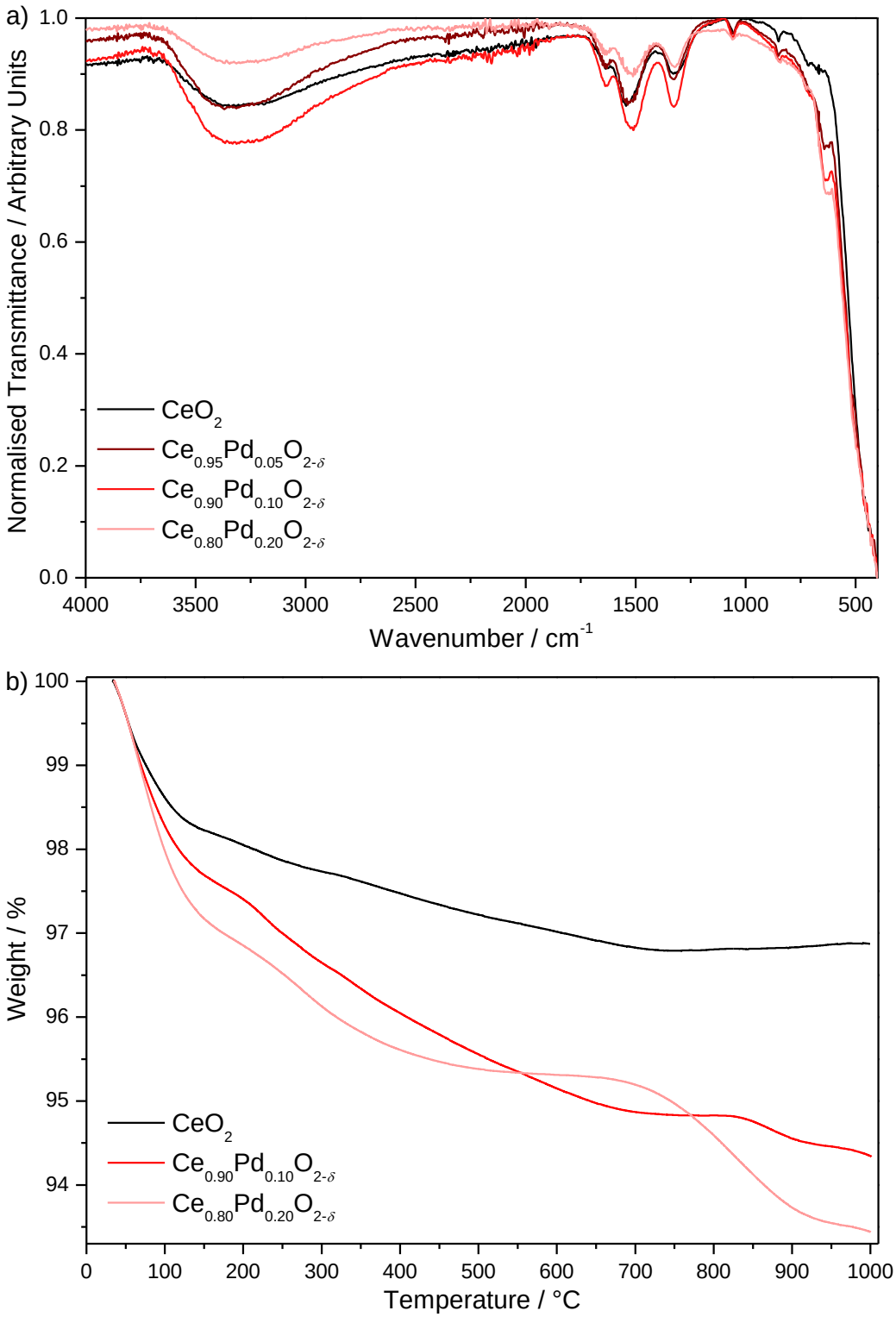

Figure S2 a) FTIR spectra and b) TGA of $Ce_{1-x}Pd_xO_{2-\delta}$ ($0 \leq x \leq 0.20$) prepared hydrothermally.

Table S3. Measured values of x *from EDX elemental analysis (from high resolution TEM) of four different areas of* $Ce_{0.90}Pd_{0.10}O_{2-\delta}$ *and* $Ce_{0.80}Pd_{0.20}O_{2-\delta}$.

Intended *x*	Area 1 *x*	Area 2 *x*	Area 3 *x*	Area 4 *x*	Average *x*	Standard Deviation
0.10	0.116	0.121	0.107	0.097	0.110	0.011
0.20	0.190	0.166	0.183	0.185	0.181	0.011

X-ray Absorption Spectroscopy

Ce L_{III}-Edge XANES

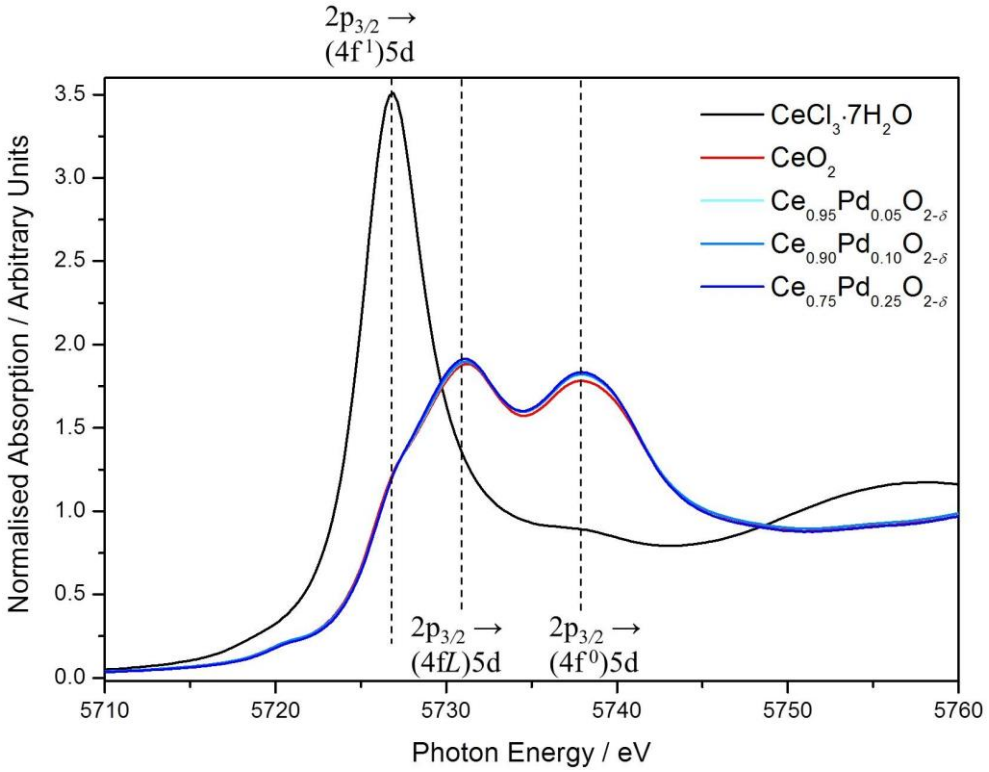

Figure S3. Ce L_{III}*-edge XANES spectra of* $Ce_{1-x}Pd_xO_{2-\delta}$ *(x = 0.05, 0.10, 0.25) compared to* Ce^{3+} *(*$CeCl_3 \cdot 7H_2O$*, Sigma-Aldrich) and* Ce^{4+} *(*CeO_2*, Sigma-Aldrich) references.*

The labelling of the spectral features is according to the literature (see Takhashi et al.,[4] and references therein), which highlights the fact that the Ce in the Pd-containing samples is virtually unchanged from the highly crystalline CeO_2 reference material.

Pd K-edge XANES

Pd K-edge XANES spectra of $Ce_{1-x}Pd_xO_{2-\delta}$ show a slight shift (~1.2 eV) in edge position compared to that of PdO. This could be attributed to differences in local structure and not an increased oxidation state since previous Pd K-edge XANES experiments[5] show that Pd in the +4 oxidation state is expected to have a larger edge shift of approximately 3.2 eV. Indeed, Kim *et al.* found that the K-edge of Pd was very sensitive to local environment as well as oxidation state.[5] However, the change in intensity of the white line, suggesting an increase of the unoccupied state density, would also be consistent with charge being extracted from Pd^{2+} ions to give a net charge slightly higher than 2+. The oxygen vacancies needed to compensate lattice Ce-substitution by Pd, could be stabilised around Pd ions removing charge from the cations, which is consistent with the EXAFS analysis where an an average coordination number of 7 instead of 8 for the second Pd-O shell is obtained.

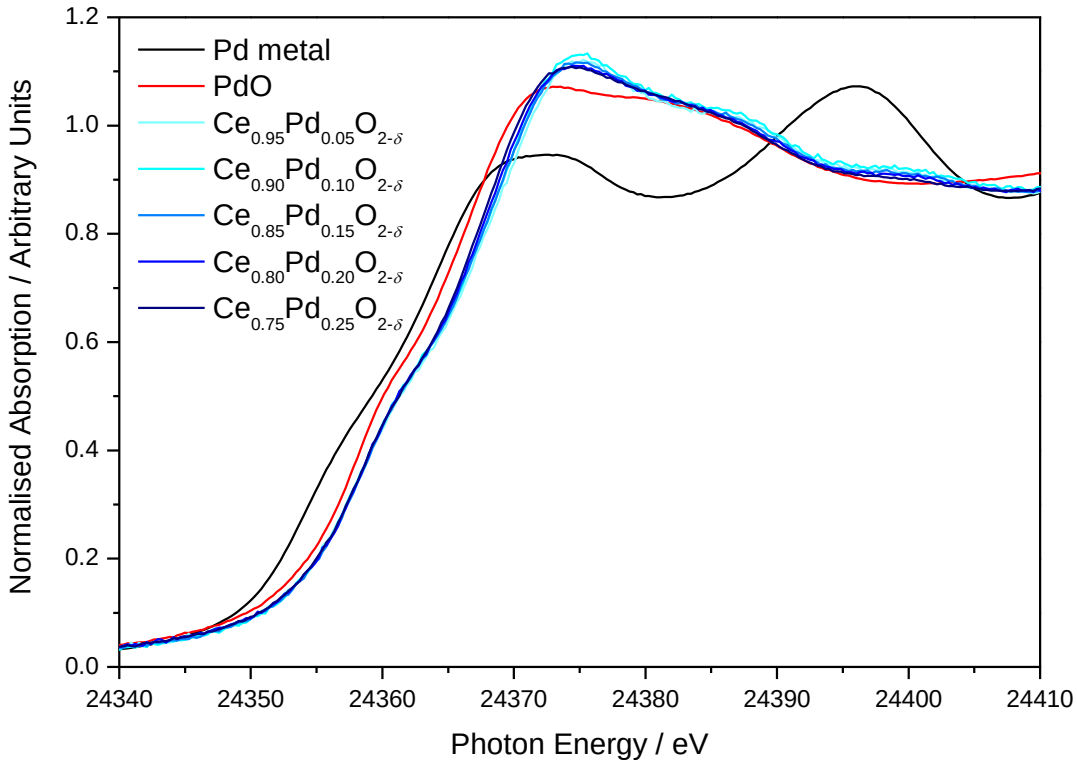

Figure S4. Pd K-edge XANES spectra of $Ce_{1-x}Pd_xO_{2-\delta}$ (x = 0.05, 0.10, 0.15, 0.20, 0.25) compared to Pd metal foil (B18 reference) and Pd^{2+} (PdO, Sigma-Aldrich) references.

Temperature Programmed Reduction

Table S4. Analysis of TPR results shown in Figure 6. The % Ce^{4+} reduced is calculated assuming all Pd^{2+} is reduced to Pd^{0}.

Intended *x*	T_{max} / °C	H oxidised / mmol g^{-1}	Ce^{4+} reduced / %
0.05	140	1.36	13.8
0.10	120	2.23	19.2
0.15	96	3.13	25.3
0.20	73	4.08	32.7
0.25	65	4.37	26.3

TEM EELS elemental mapping

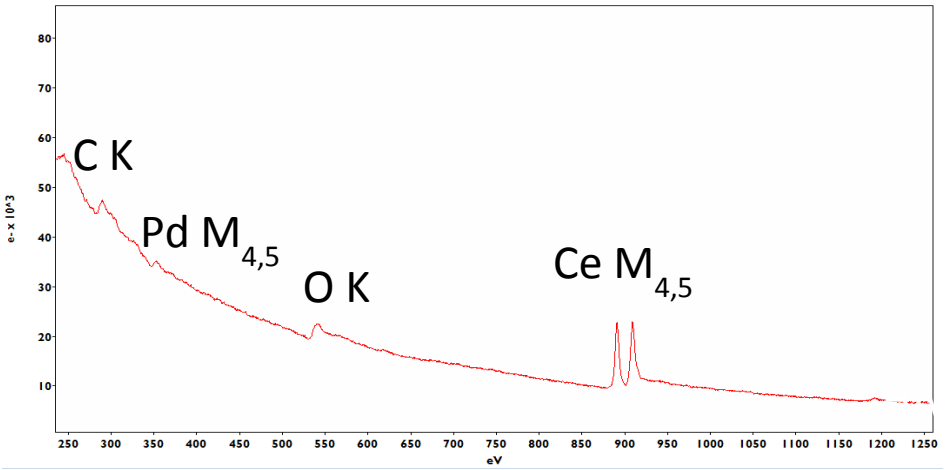

Figure S5: Typical EELS data recorded from Pd-CeO_2 using TEM

References

[1] M. Kurnatowska, L. Kepinski and W. Mista, *Appl. Catal. B*, 2012, **117–118**, 135.
[2] L. M. Misch, J. A. Kurzman, A. R. Derk, Y.-I. Kim, R. Seshadri, H. Metiu, E. W. McFarland and G. D. Stucky, *Chem. Mater.*, 2011, **23**, 5432.
[3] P. Singh and M. S. Hegde, *Crystal Growth & Design*, 2010, **10**, 2995.
[4] Y. Takahashi, H. Sakami, M. Nomura, *Anal. Chim. Acta*, 2002, **468**, 345.
[5] Kim, S.-J.; Lemaux, S.; Demazeau, G.; Kim, J.-Y.; Choy, J.-H. *J. Mater. Chem.* **2002**, *12*, 995.