Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Thermodynamics of paired charge-compensating doped ceria with superior redox performance for solar thermochemical splitting of H_2O and CO_2

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Supplementary Information

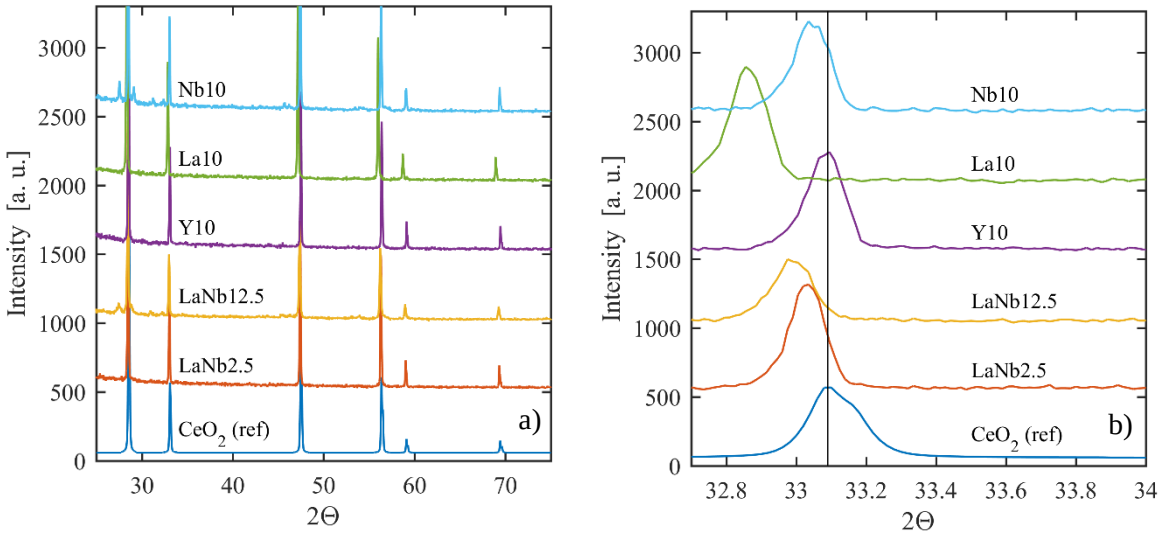


Fig. S1a) XRD patterns of LaNb2.5, LaNb12.5, Y10, La10 and Nb10 after TG analysis. A reference pattern of undoped ceria is included for comparison. b) Close up of peaks around 33.1°.

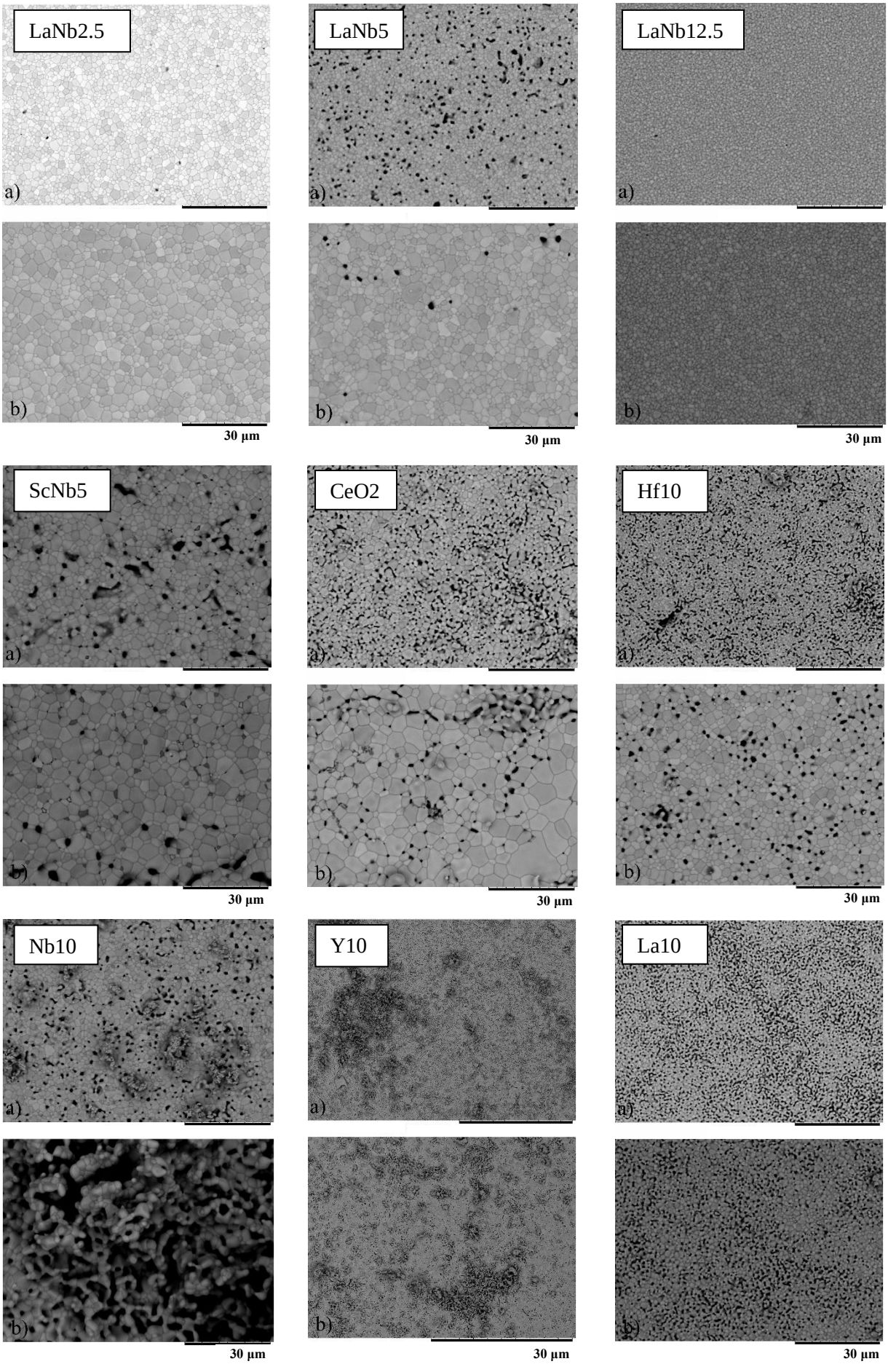
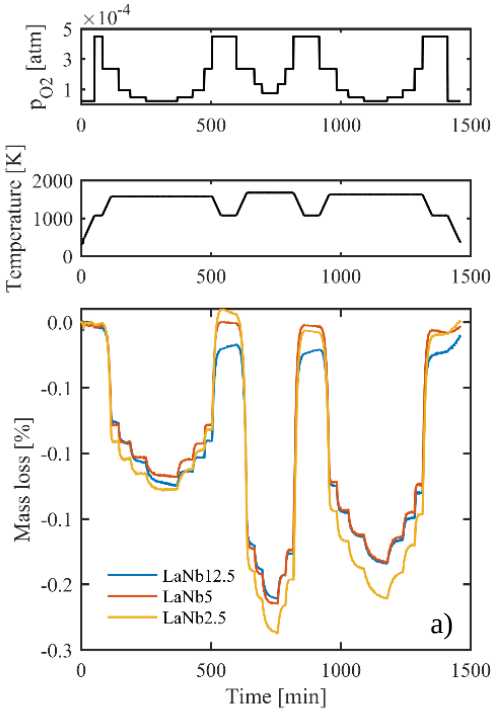
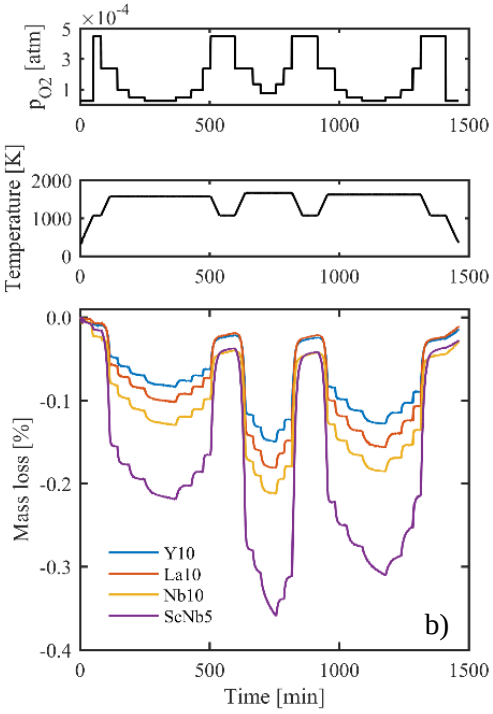
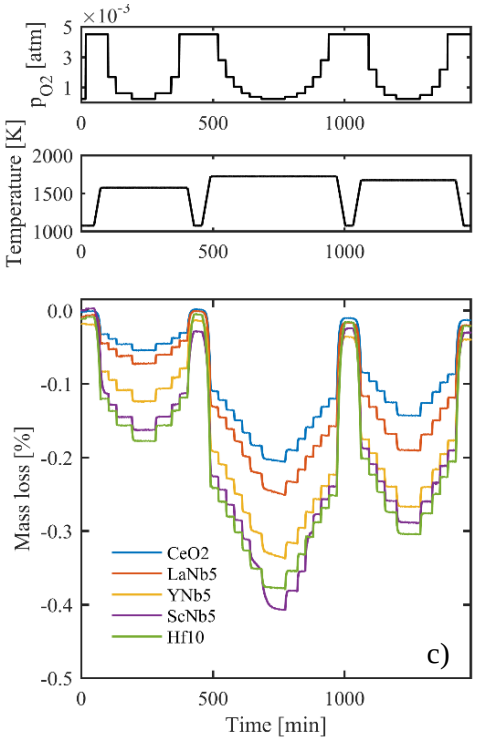
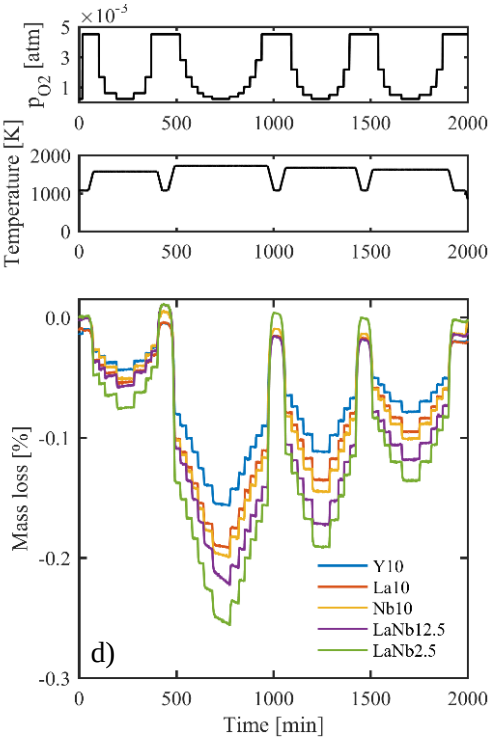

LaNb2.5
a)
b)
30 µm
LaNb5
a)
b)
30 µm
LaNb12.5
a)
b)
30 µm
ScNb5
a)
b)
30 µm
CeO2
a)
b)
30 µm
Hf10
a)
b)
30 µm
Nb10
a)
b)
30 µm
Y10
a)
b)
30 µm
La10
a)
b)
30 µm

Fig. S2 SEM images of pellet surfaces (a) before and (b) after TG analysis.


×10^-4
p_O2 [atm]
Temperature [K]
Mass loss [%]
Time [min]
LaNb12.5
LaNb5
LaNb2.5
a)


×10^-4
p_O2 [atm]
Temperature [K]
Mass loss [%]
Time [min]
Y10
La10
Nb10
ScNb5
b)


×10^-3
p_O2 [atm]
Temperature [K]
Mass loss [%]
Time [min]
CeO2
LaNb5
YNb5
ScNb5
Hf10
c)


×10^-5
p_O2 [atm]
Temperature [K]
Mass loss [%]
Time [min]
Y10
La10
Nb10
LaNb12.5
LaNb2.5
d)

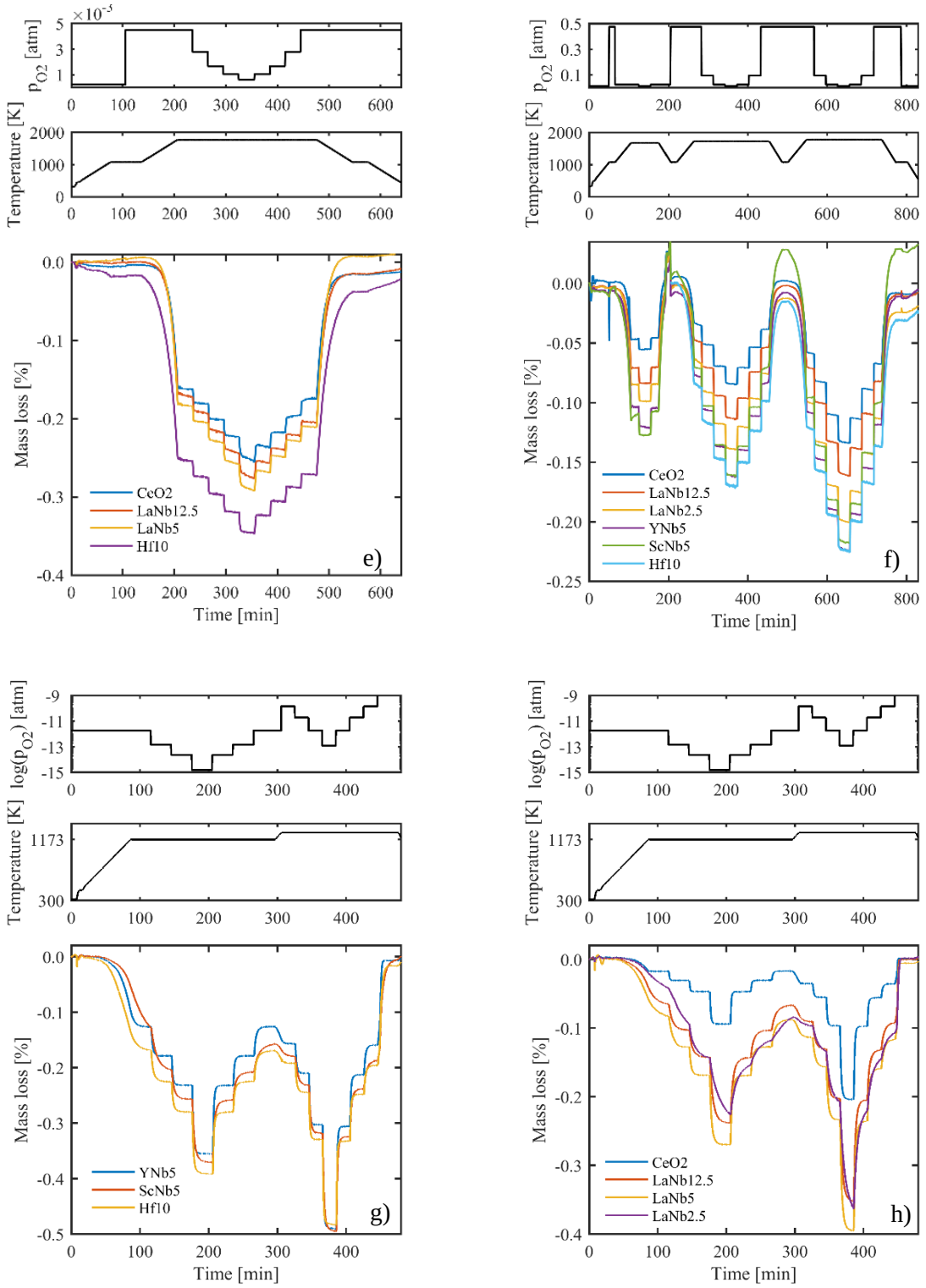
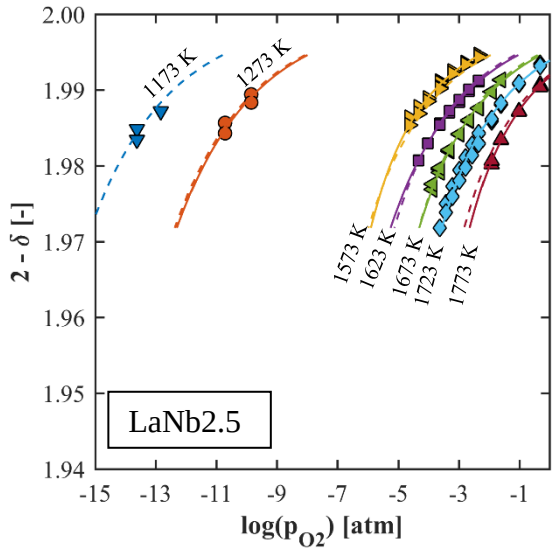
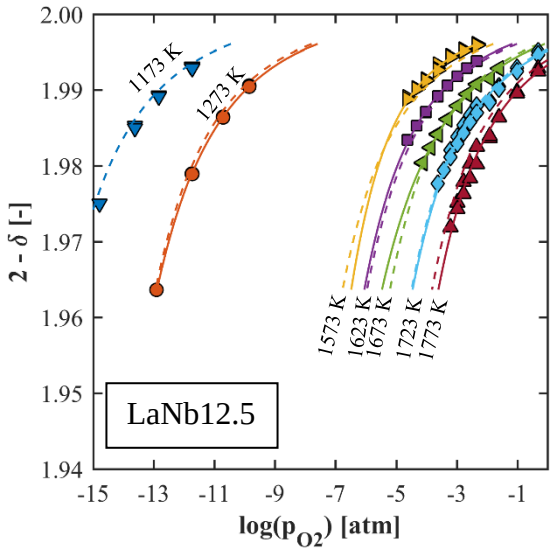
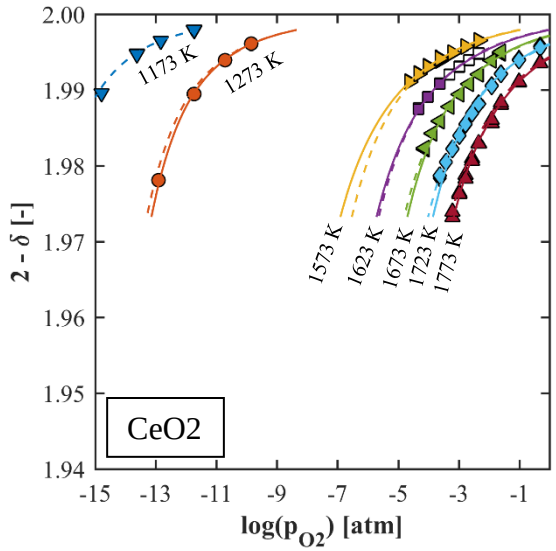
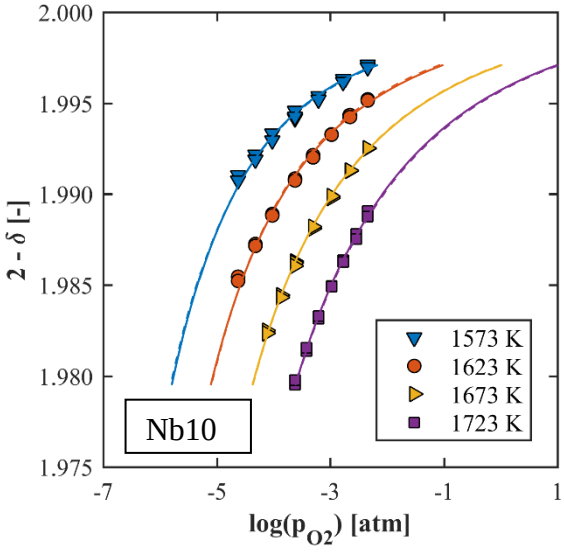


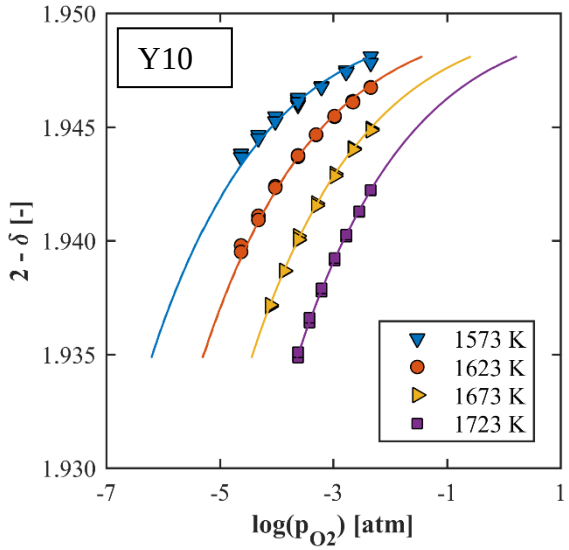
Fig. S3 TG experiments in the range (a) and (b) 1573 – 1673 K and 2.5 x 10^{-5} – 4.8 x 10^{-4} atm, (c) and (d) 1573 - 1773 K and 2.5 x 10^{-4} – 4.8 x 10^{-3} atm, (e) 1773 K and 6.5 x 10^{-4} – 4.8 x 10^{-3} atm, (f) 1673 – 1773 K and 4.8 x 10^{-3} – 5.0 x 10^{-1} atm (g) and (h) 1173 – 1273 K and 1.6 x 10^{-15} – 1.4 x 10^{-10} atm


2.00
1.99
1.98
1.97
1.96
1.95
1.94
2 - δ [-]
1173 K
1273 K
1573 K
1623 K
1673 K
1723 K
1773 K
LaNb2.5
-15 -13 -11 -9 -7 -5 -3 -1
log(p_O2) [atm]


2.00
1.99
1.98
1.97
1.96
1.95
1.94
2 - δ [-]
1173 K
1273 K
1573 K
1623 K
1673 K
1723 K
1773 K
LaNb12.5
-15 -13 -11 -9 -7 -5 -3 -1
log(p_O2) [atm]


2.00
1.99
1.98
1.97
1.96
1.95
1.94
2 - δ [-]
1173 K
1273 K
1573 K
1623 K
1673 K
1723 K
1773 K
CeO2
-15 -13 -11 -9 -7 -5 -3 -1
log(p_O2) [atm]


2.000
1.995
1.990
1.985
1.980
1.975
2 - δ [-]
1573 K
1623 K
1673 K
1723 K
Nb10
-7 -5 -3 -1 1
log(p_O2) [atm]


1.950
1.945
1.940
1.935
1.930
2 - δ [-]
Y10
1573 K
1623 K
1673 K
1723 K
-7 -5 -3 -1 1
log(p_O2) [atm]

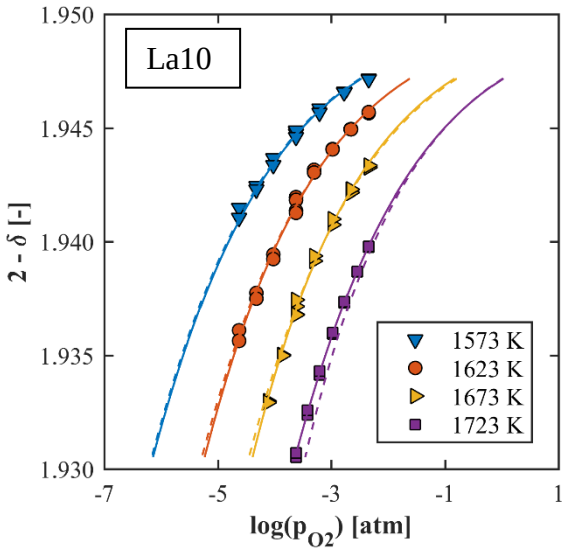
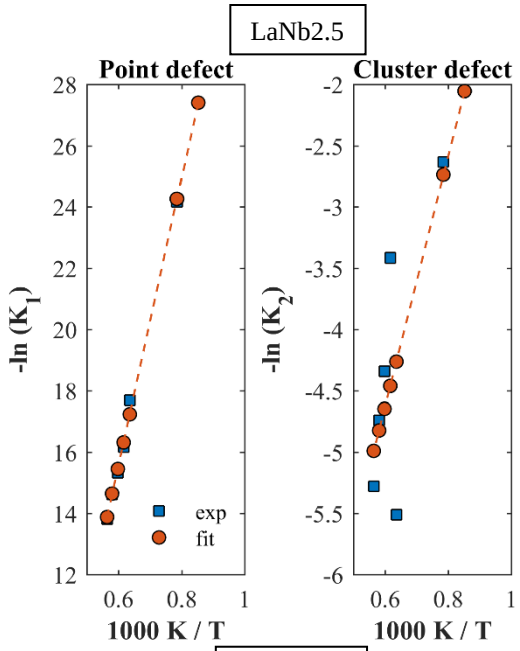
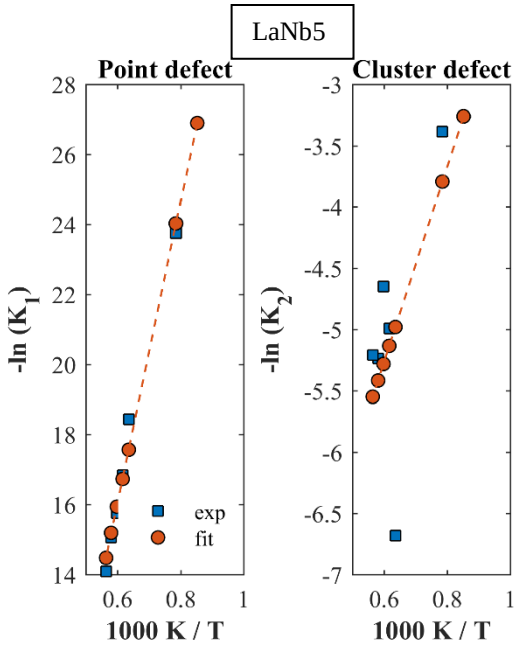
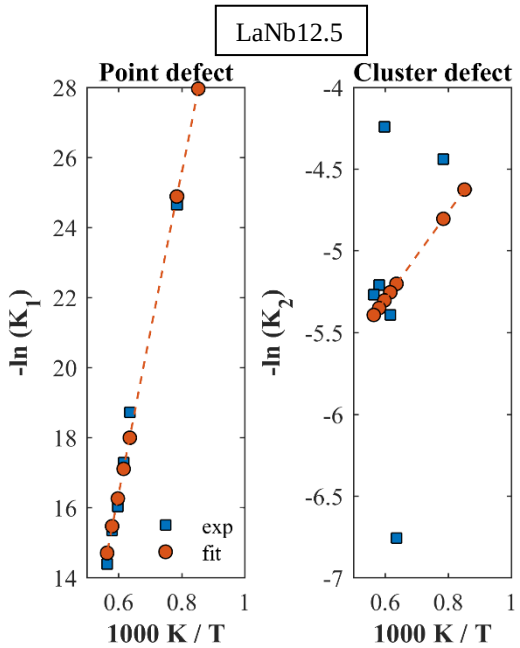
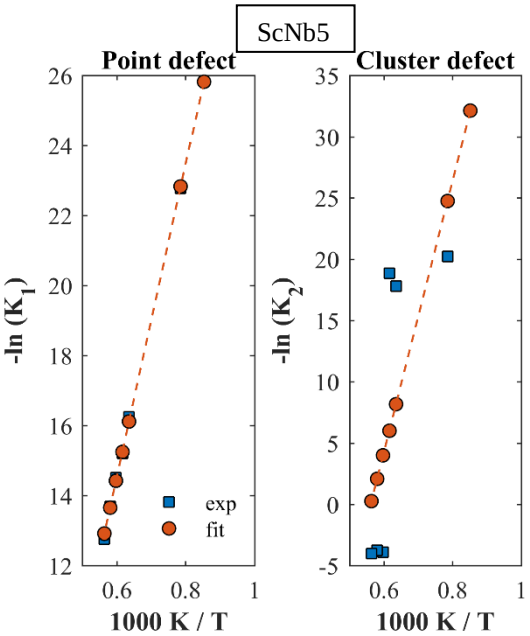

1.950
1.945
1.940
1.935
1.930
2 - δ [-]
La10
1573 K
1623 K
1673 K
1723 K
-7 -5 -3 -1 1
log(p_O2) [atm]

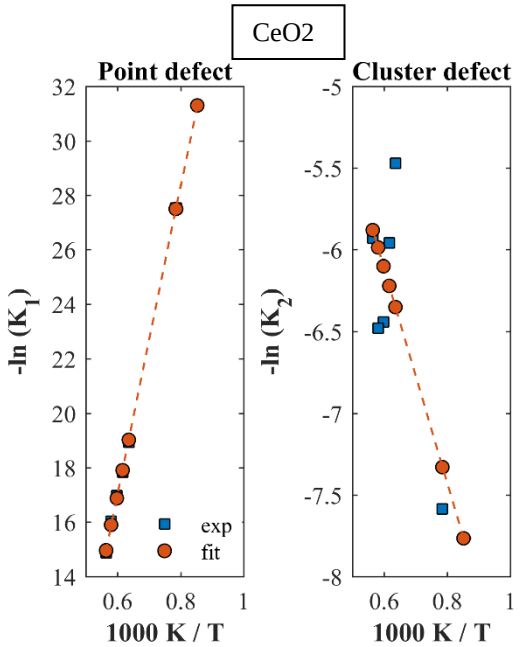
Fig. S4 Measured nonstoichiometries (symbols) of investigated materials. Solid lines show the predicted nonstoichiometry based on isothermally derived equilibrium constants; the dashed lines are based on the inversed temperature dependence of ln(K1) and ln(K2).

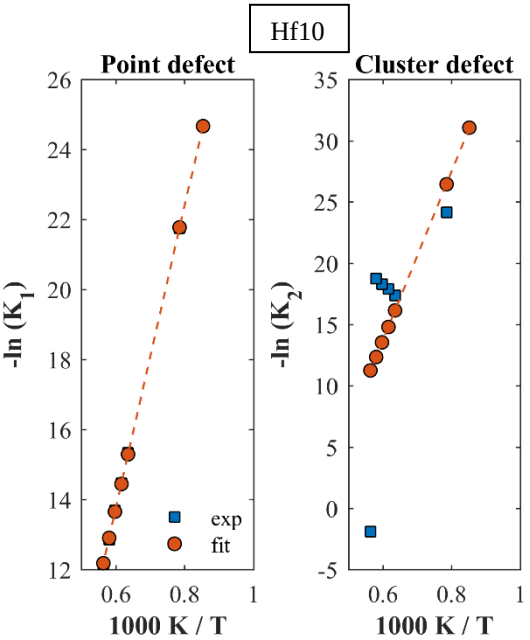

LaNb2.5
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T


LaNb5
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T


LaNb12.5
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T


ScNb5
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T


CeO2
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T


Hf10
Point defect
Cluster defect
-ln (K1)
-ln (K2)
exp
fit
1000 K / T

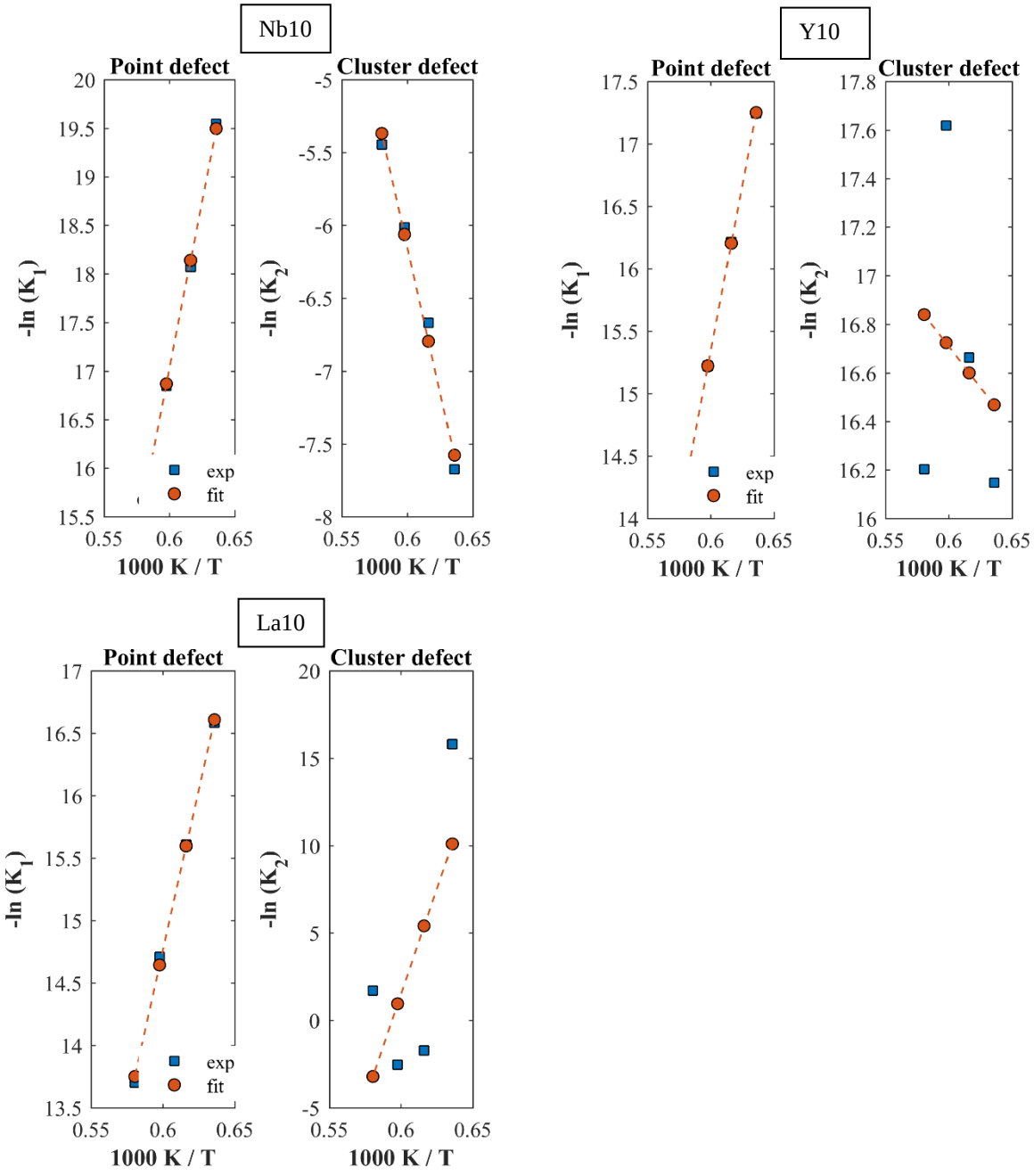


Fig. S5 Equilibrium constants K1 and K2. The squares are isothermally derived values, the dots are based on a linear fit in the Van't Hoff plot.

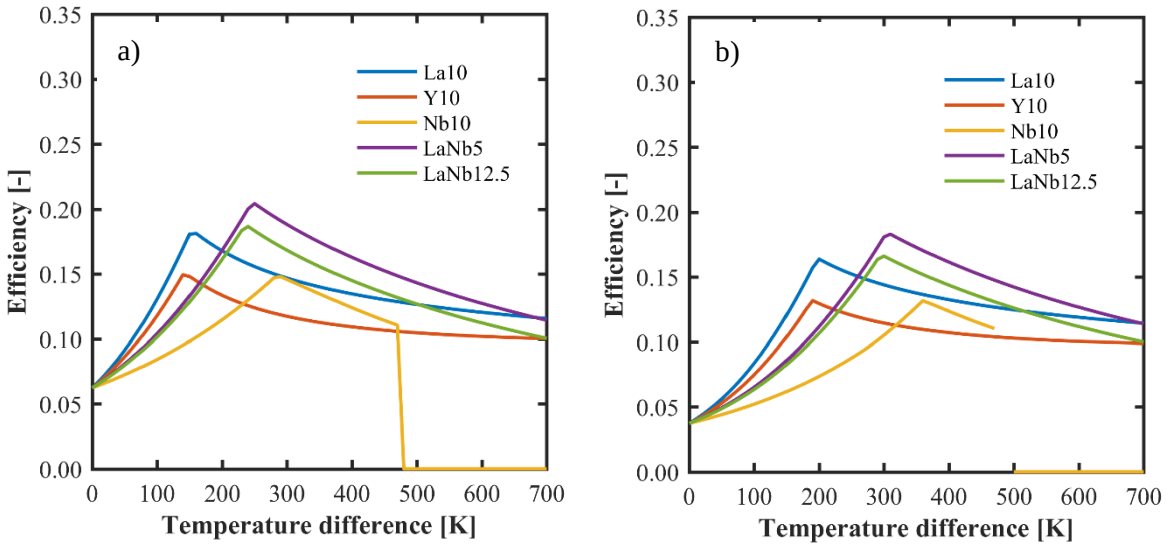


Fig. S6 Solar-to-fuel energy conversion efficiency as a function of the temperature swing between reduction and oxidation for the production of H_2 from H_2O (a) and CO from CO_2 (b).