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Tailoring the properties of BGLC double perovskites

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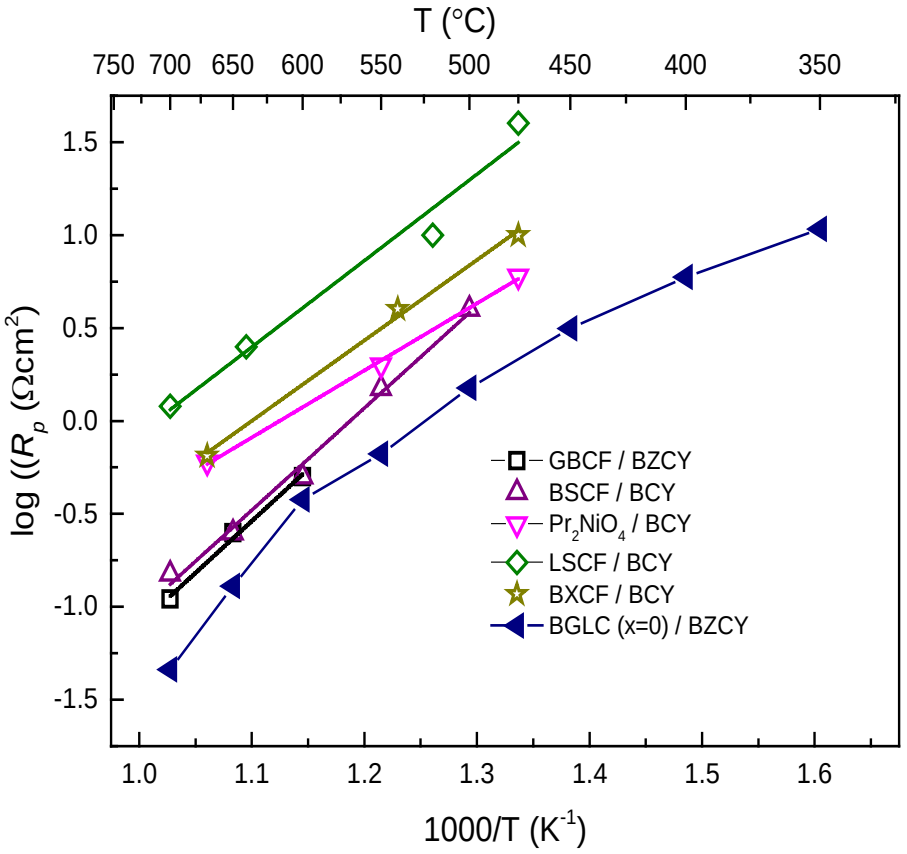
Electra

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

- Primary problems
  - How can we understand the influence of A-site substitution of $Ba_{1-x}La_{0.2+x}Gd_{0.8}Co_2O_{6-\delta}$?
  - Can we derive a general defect chemical model which describes all experimental data?

Double perovskites identified as promising candidate materials as PCEC electrodes

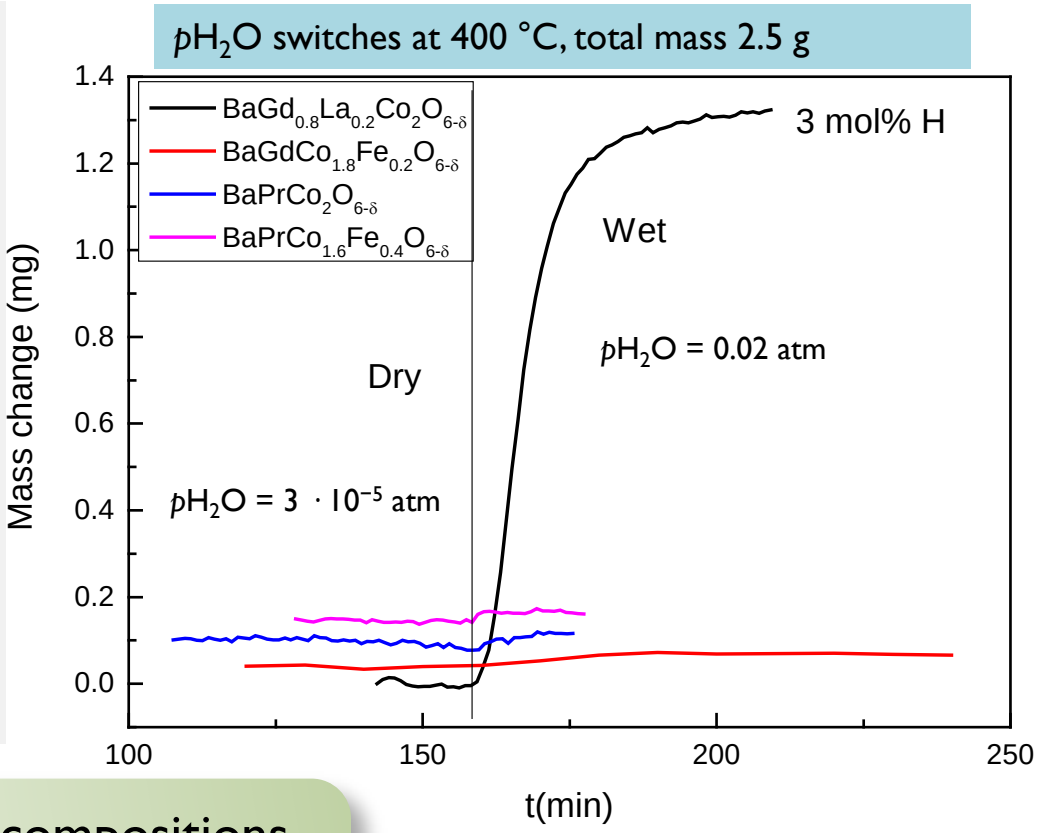
- $BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$ (BGLC):
  - Lowest reported ASR for PCECs
  - 0.04 Ωcm^2 at 700°C



[1] R. Strandbakke et al., *Solid State Ionics* (2015)
[2] J. Dailly et al., *Electrochimica Acta* (2010)
[3] Y. Lin et al., *Journal of Power Sources* (2008)
[4] H. Ding, X. Xue, *Int. Journal of Hydrogen Energy* (2010)

Double perovskites identified as promising candidate materials as PCEC electrodes

- $BaGd_{0.8}La_{0.2}Co_2O_{6-\delta}$ (BGLC):
  - Lowest reported ASR for PCECs
  - 0.04 Ωcm^2 at 700°C
- Proton incorporation suggested to facilitate fast electrode kinetics
- Decomposition of BGLC observed in steam pressures over 0.5 atm



Investigation of various compositions in terms of stability, electrochemical activity and defect chemistry

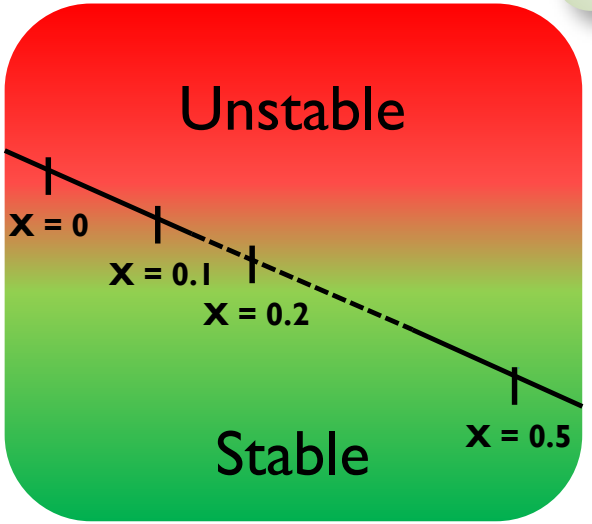
R. Strandbakke et al., *Solid State Ionics* (2015)

Tailoring the composition towards higher stability in high steam pressures

Decomposition in steam related to the A-site basicity?

$$A' \quad A'' \quad B$$
$$Ba_{1-x}La_xGd_{0.8}La_{0.2}Co_2O_{6-\delta}$$

Partial substitution of La on Ba-site to reduce basicity



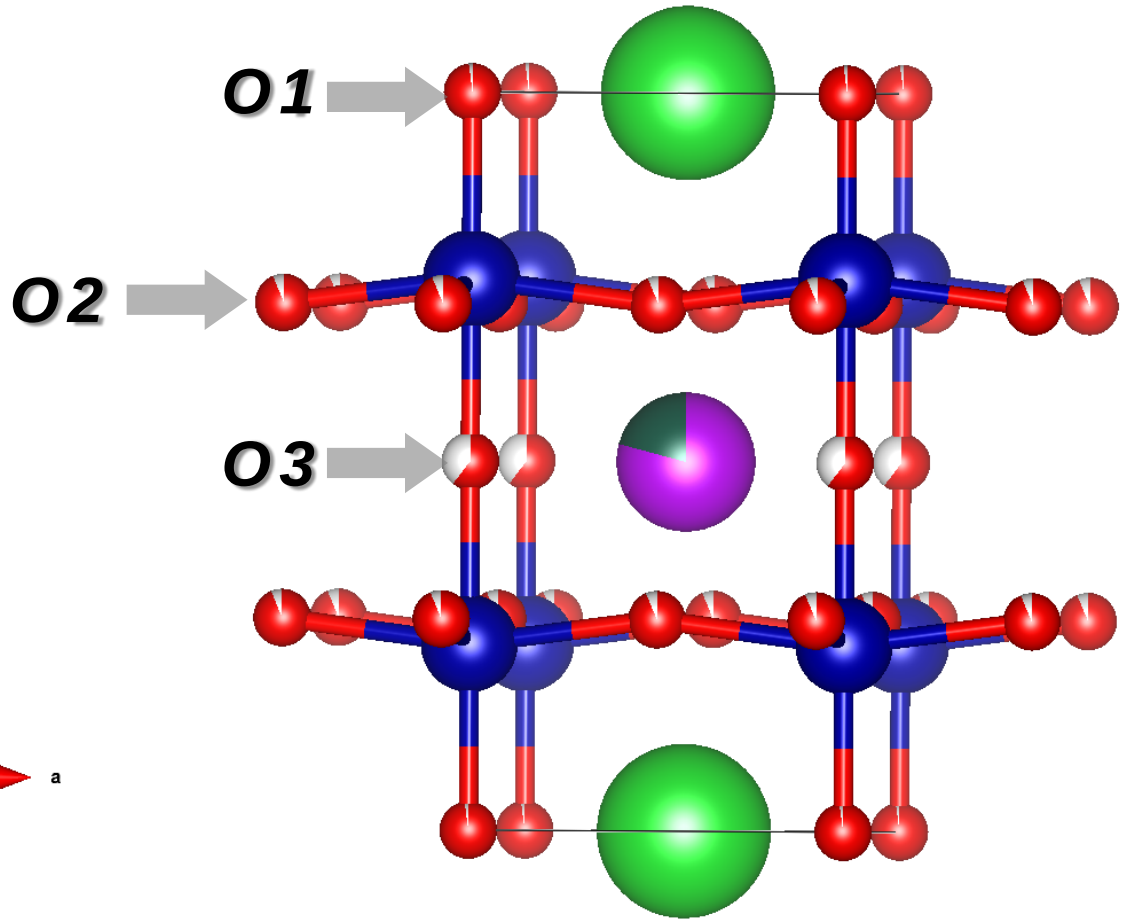
Increased stability with increasing La-content.
x>0.3 stable in 1.5 bar steam at 700°C

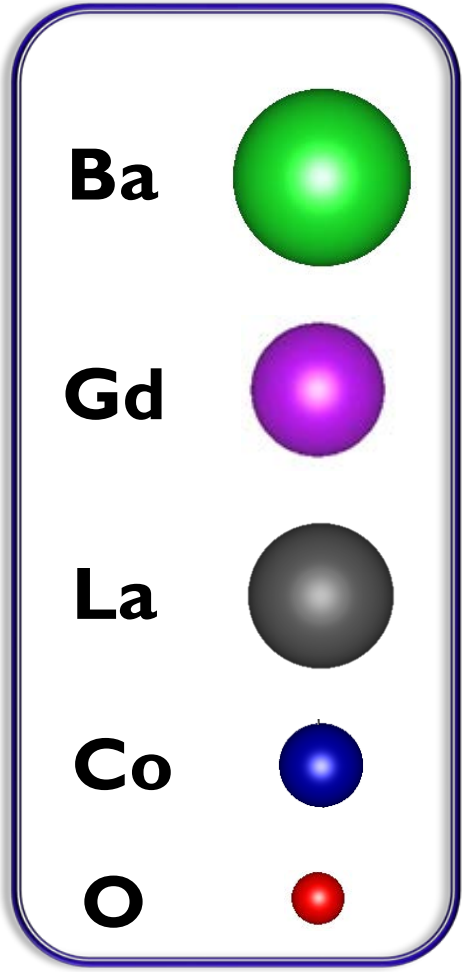
$Ba_{1-x}La_xGd_{0.8}La_{0.2}Co_2O_{6-\delta}$, x = 0-0.5

- Nomenclature:
  - $Ba_{0.7}Gd_{0.8}La_{0.5}Co_2O_{6-\delta}$ abbreviated as BGLC785
- Commercial production by Marion Technologies using combustion synthesis
  - Single phase powders displaying double perovskite structure obtained for all compositions
- Characterization
  - Structural analysis by XRD – high temperature and synchrotron
  - Electrochemical characterization for both electrocatalytic activity and bulk electrical conductivity
  - Thermogravimetry for non-stoichiometry data and defect model fitting

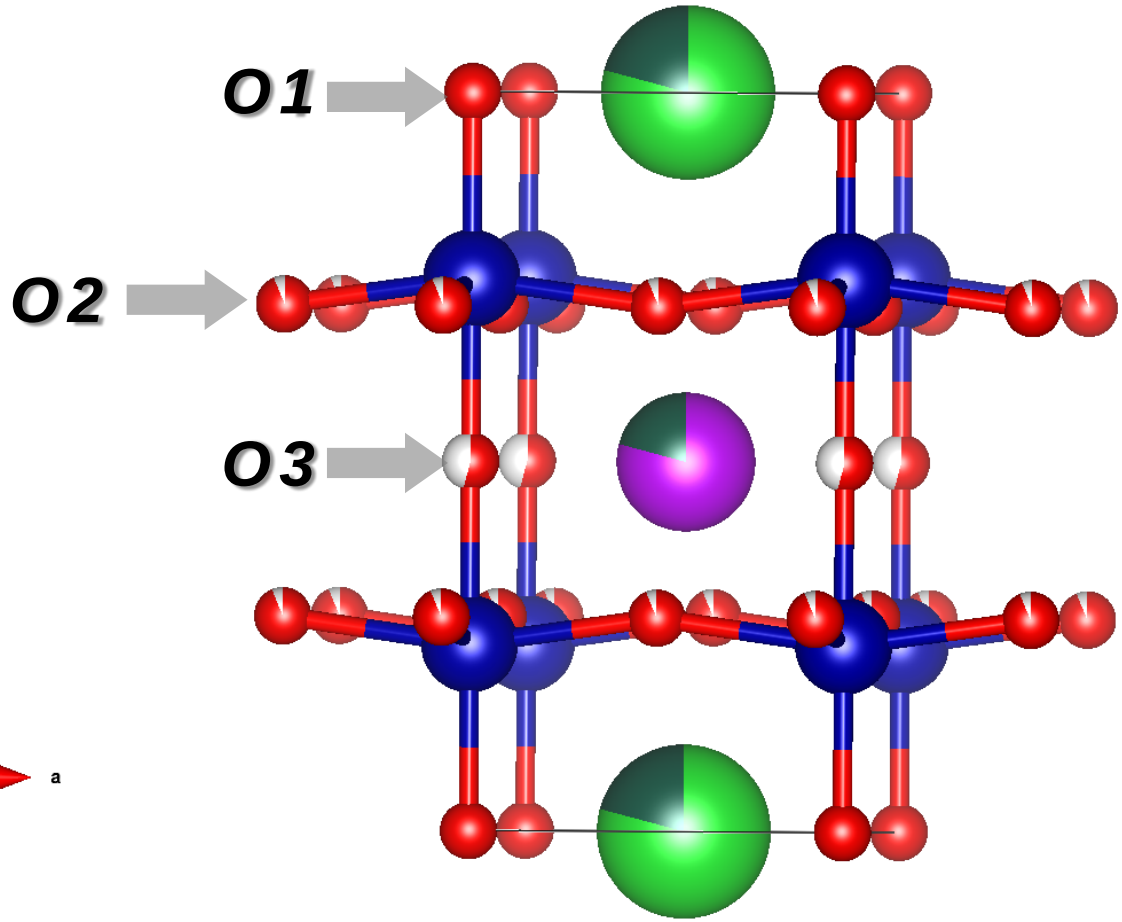
Structural characterization

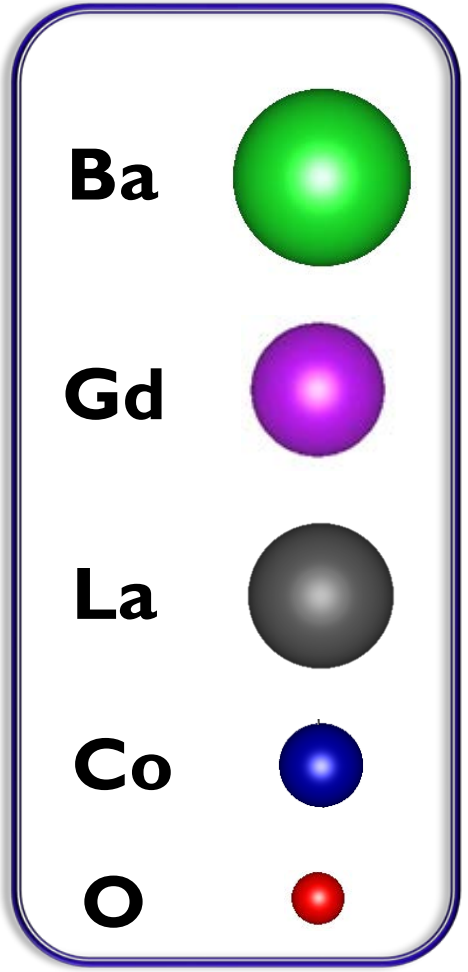
BGLC1082 (x = 0)



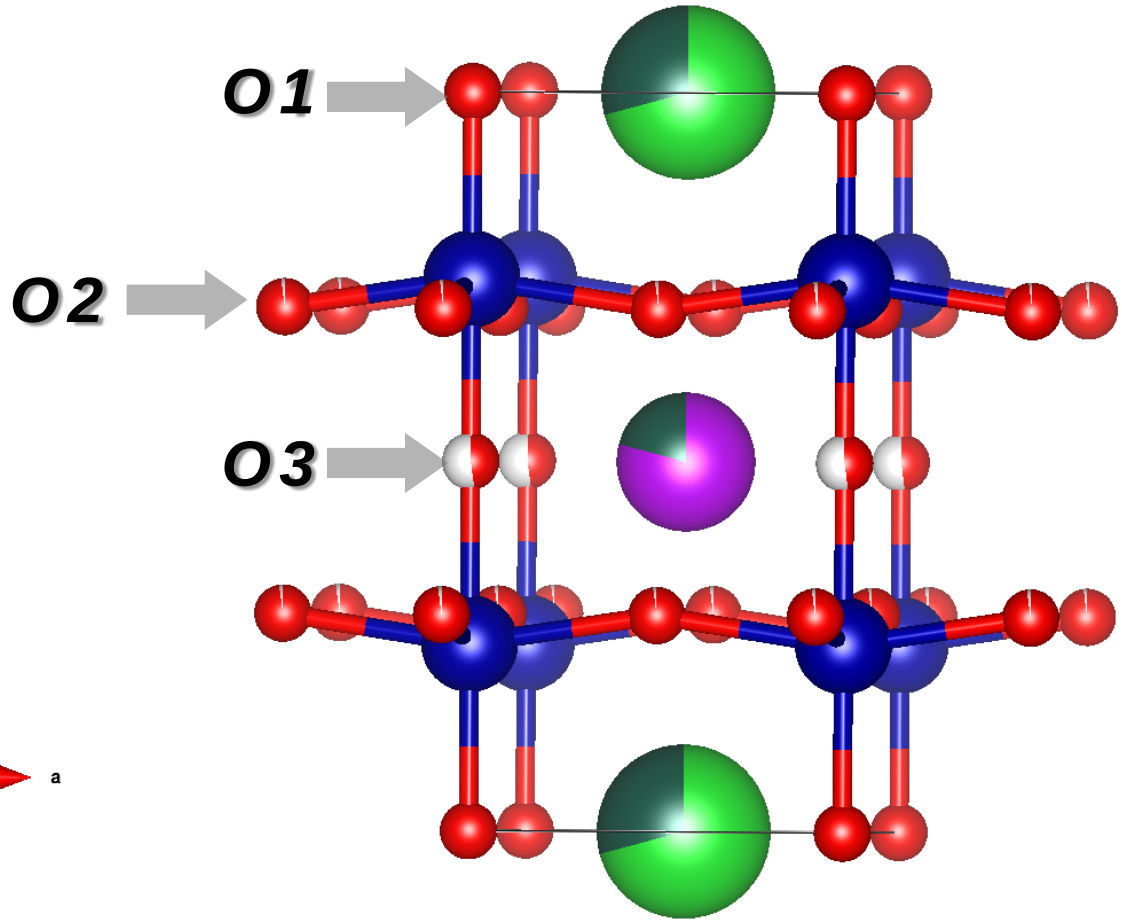


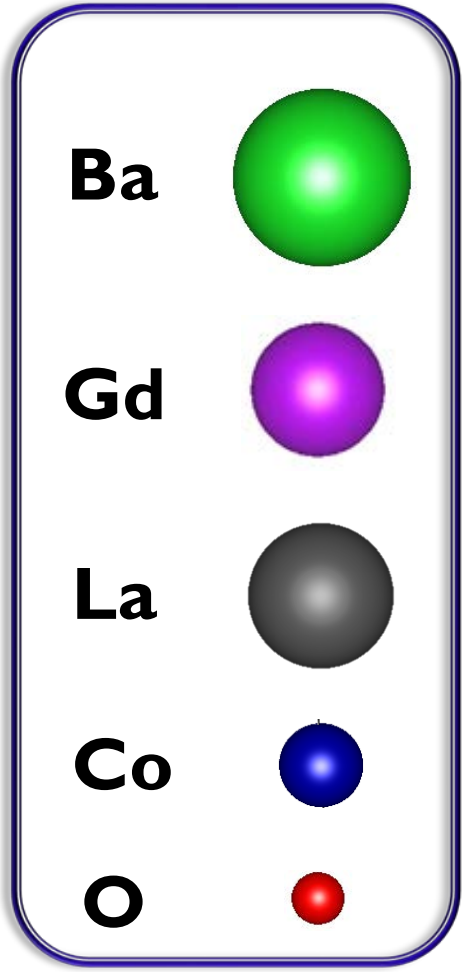
BGLC884 (x = 0.2)





BGLC785 (x = 0.3)

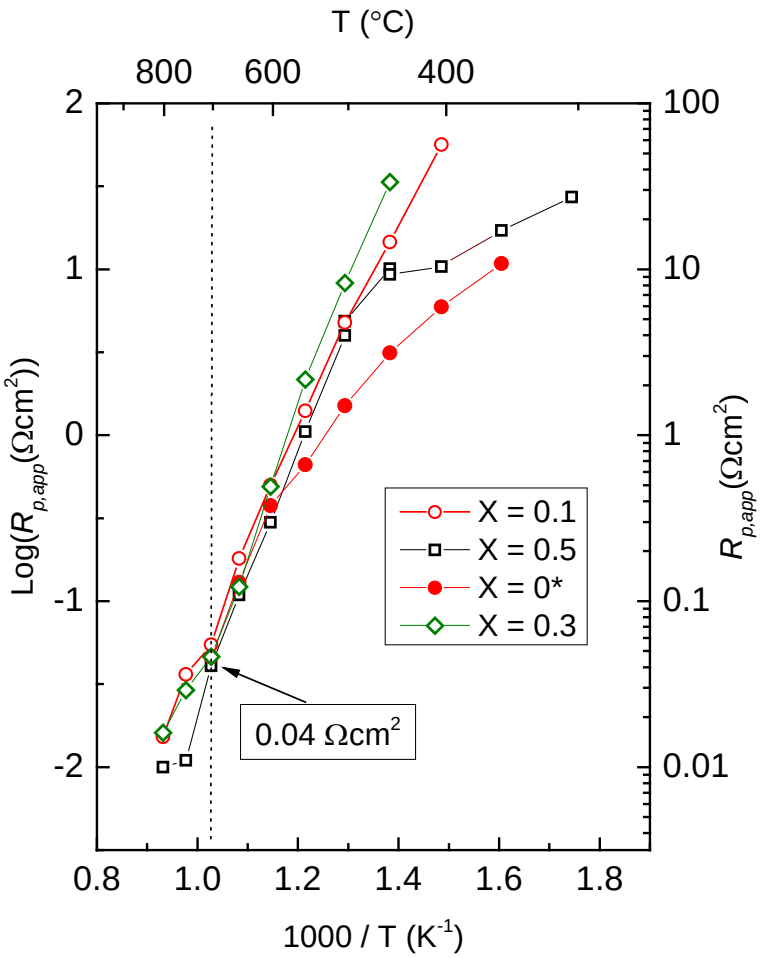




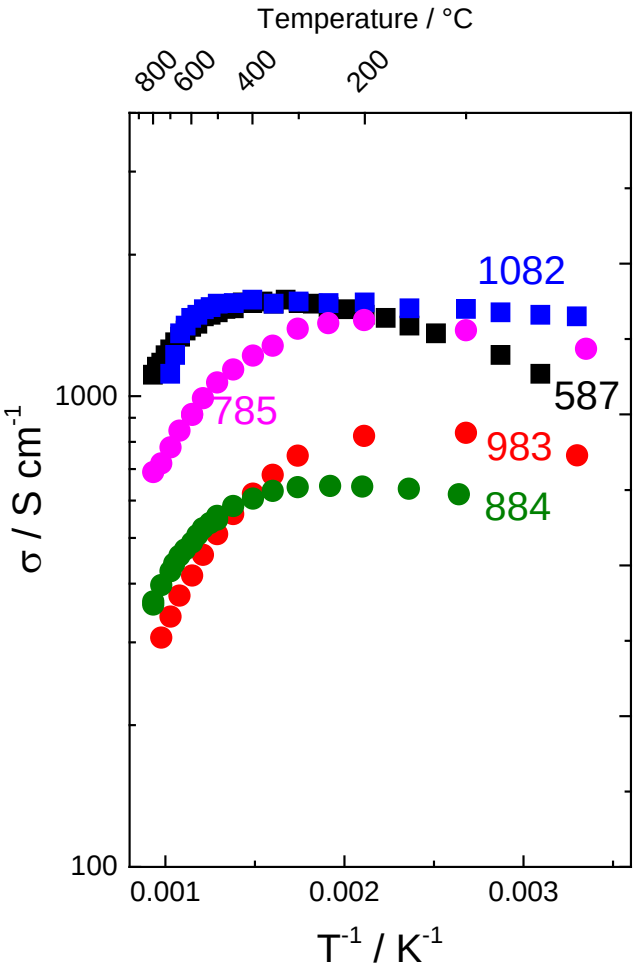
Electrochemical characterization

All BGLC compositions show high electrochemical activity, but no clear trend is evident

Polarization resistances



Electrical conductivities



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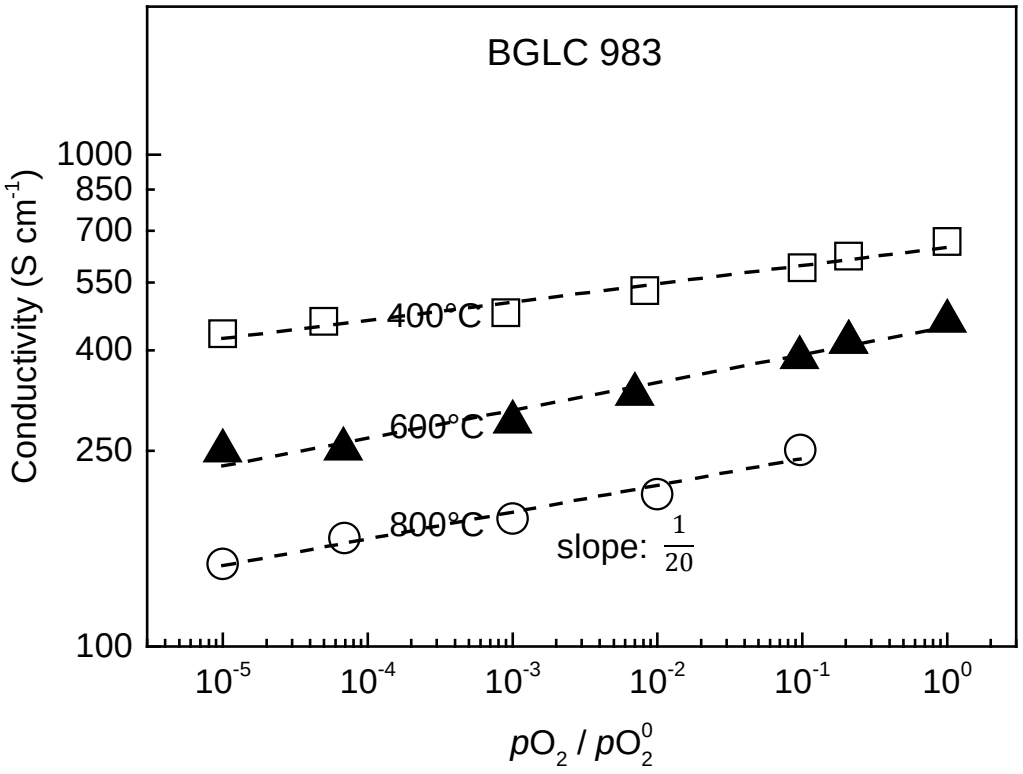
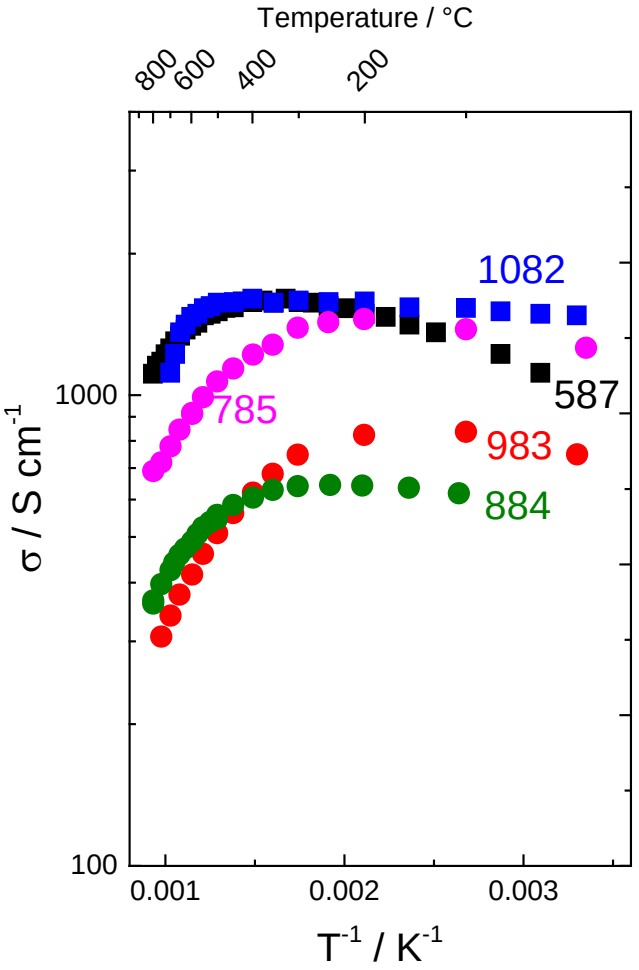
pO_2-dependency of conductivity

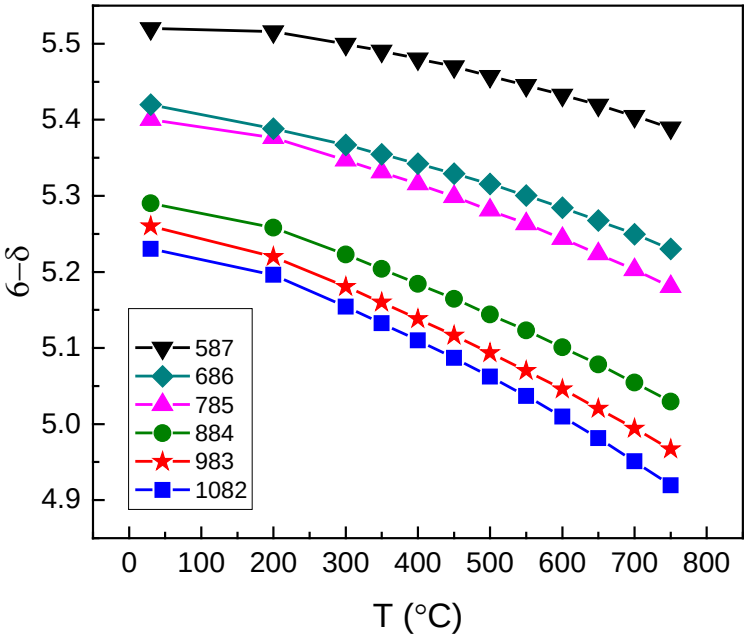


Electrical conductivities of BGLC

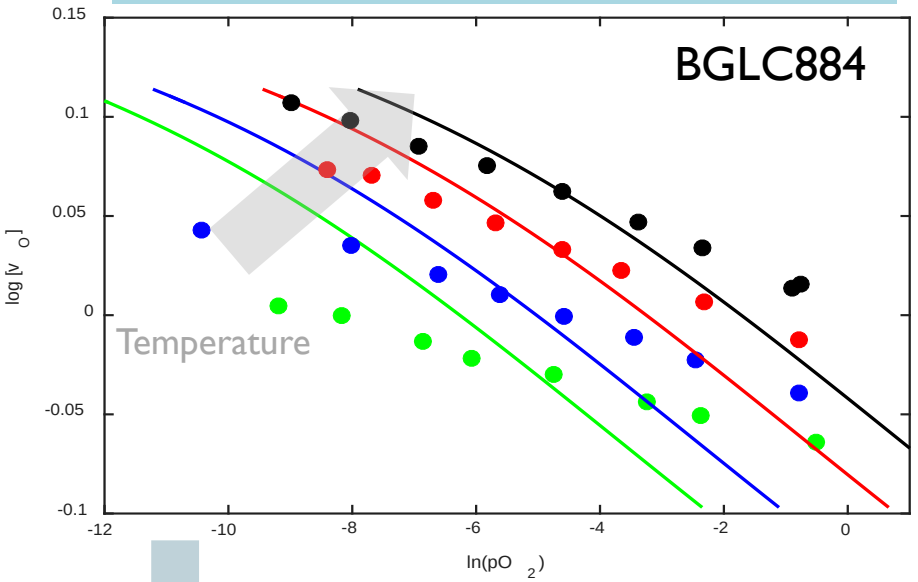


Large oxygen non-stoichiometry in all compositions

Oxygen non-stoichiometry in 0.15 atm O_2



Oxygen non-stoichiometry from 450 to 750 °C



Simple defect chemistry cannot account for the experimental data

Developing a new defect chemical model from the basis of a fully oxidized double perovskite

Ref. state: $BaLnCo_2O_6$

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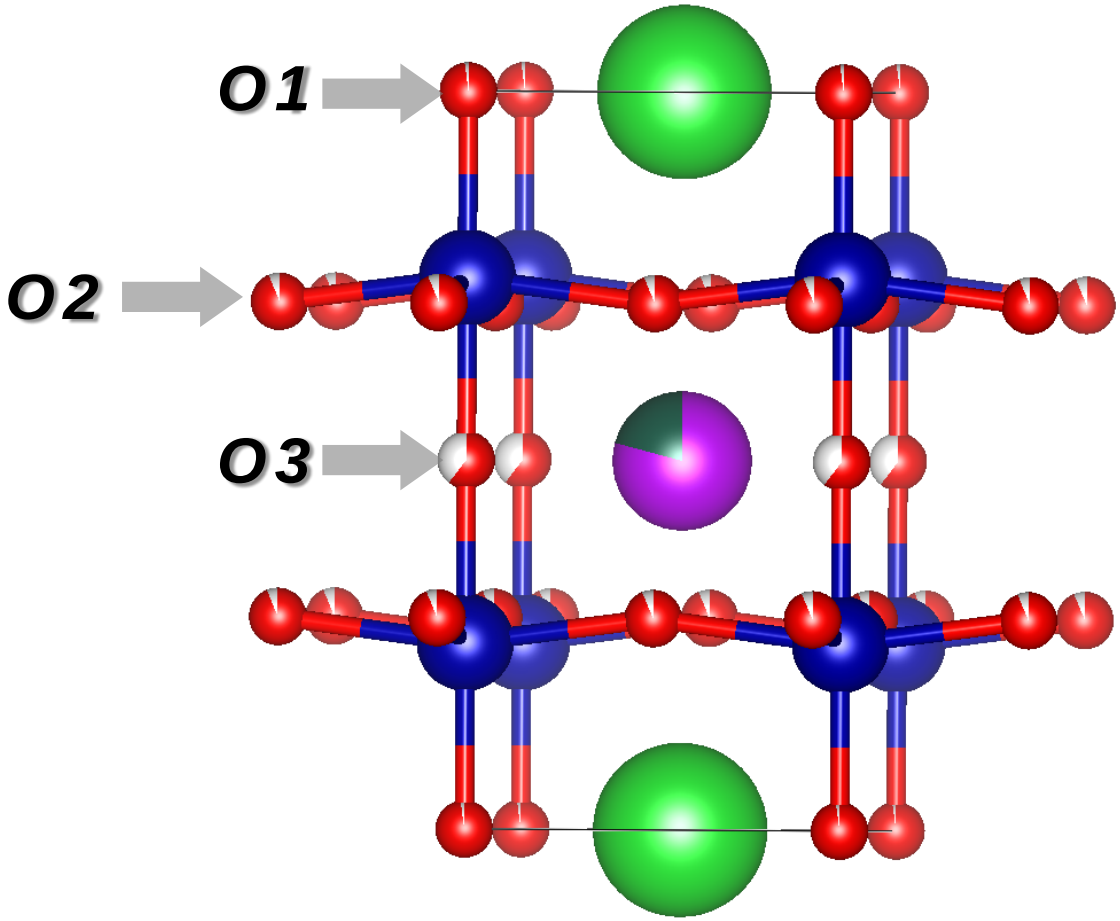
3 specific O-sites

Oxygen site balances:

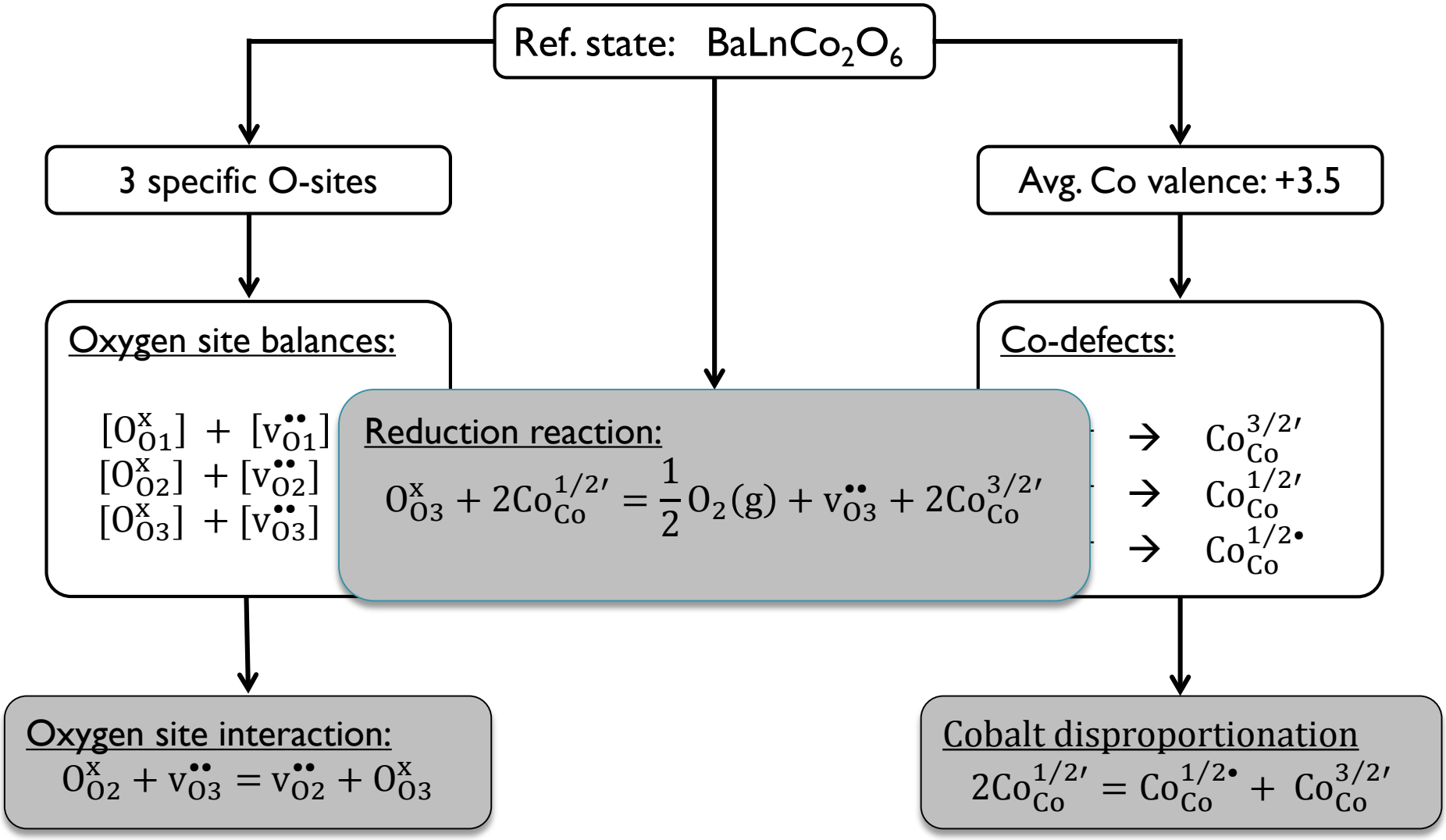
$$[O_{O1}^{x}] + [v_{O1}^{\bullet\bullet}] = 1$$
$$[O_{O2}^{x}] + [v_{O2}^{\bullet\bullet}] = 4$$
$$[O_{O3}^{x}] + [v_{O3}^{\bullet\bullet}] = 1$$

Oxygen site interaction:

$$O_{O2}^{x} + v_{O3}^{\bullet\bullet} = v_{O2}^{\bullet\bullet} + O_{O3}^{x}$$



Developing a new defect chemical model from the basis of a fully oxidized double perovskite



Governing Equations for $Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$

Equilibrium reactions

Reduction reaction:

$$K_{red} = \frac{[\mathrm{v}_{O3}^{\bullet\bullet}]\left[\mathrm{Co}_{Co}^{3/2\prime}\right]^2}{[\mathrm{O}_{O3}^{x}]\left[\mathrm{Co}_{Co}^{1/2\prime}\right]^2} p_{O_2}^{1/2}$$

Cobalt disproportionation:

$$K_{disp} = \frac{\left[\mathrm{Co}_{Co}^{1/2\bullet}\right]\left[\mathrm{Co}_{Co}^{3/2\prime}\right]}{\left[\mathrm{Co}_{Co}^{1/2\prime}\right]^2}$$

Oxygen interaction

$$K_{Oint} = \frac{[\mathrm{v}_{O2}^{\bullet\bullet}][\mathrm{O}_{O3}^{x}]}{[\mathrm{v}_{O3}^{\bullet\bullet}][\mathrm{O}_{O2}^{x}]}$$

Site balances:

$$\delta = [\mathrm{v}_{O2}^{\bullet\bullet}] + [\mathrm{v}_{O3}^{\bullet\bullet}]$$

$$[\mathrm{O}_{O2}^{x}] + [\mathrm{v}_{O2}^{\bullet\bullet}] = 4$$

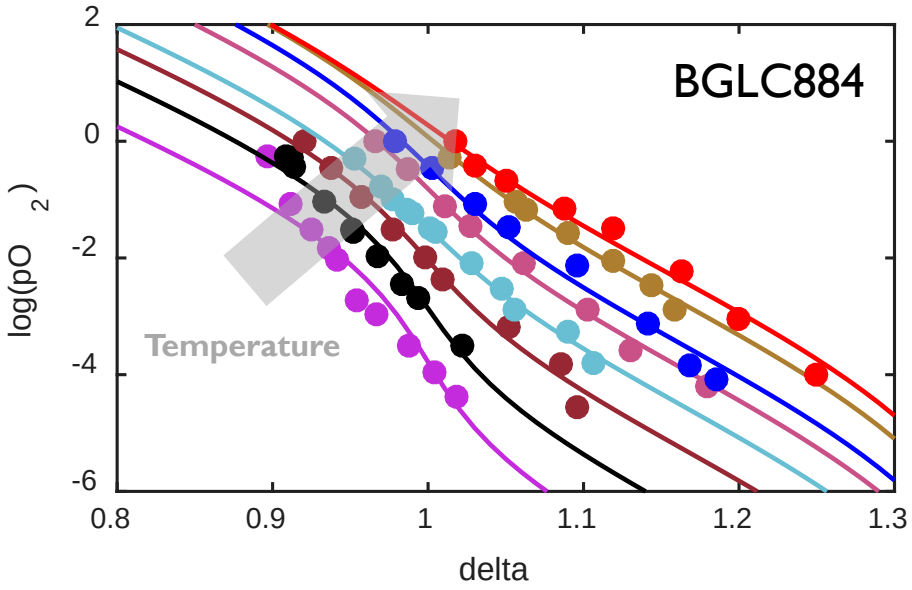
$$[\mathrm{O}_{O3}^{x}] + [\mathrm{v}_{O3}^{\bullet\bullet}] = 1$$

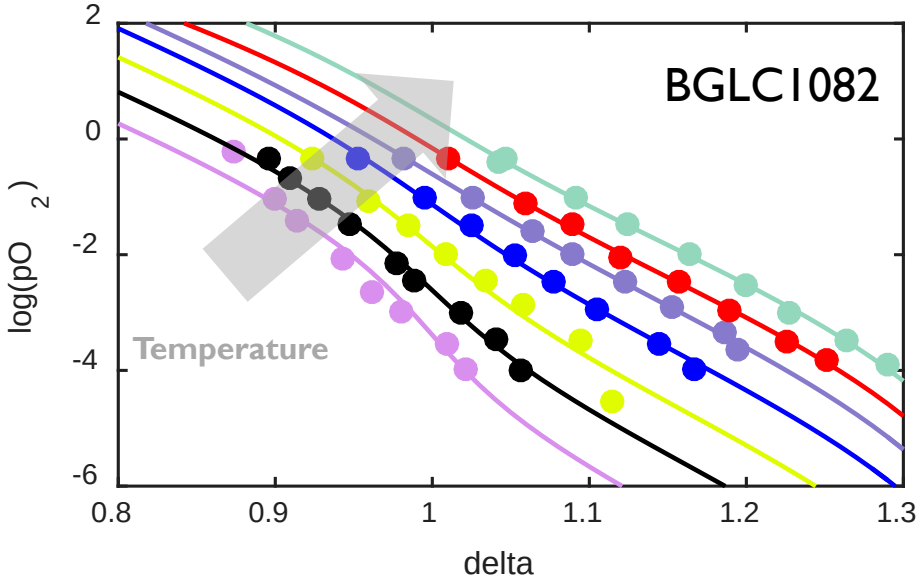
$$\left[\mathrm{Co}_{Co}^{1/2\bullet}\right] + \left[\mathrm{Co}_{Co}^{1/2\prime}\right] + \left[\mathrm{Co}_{Co}^{3/2\prime}\right] = 2$$

Electroneutrality:

$$\frac{3}{2}\left[\mathrm{Co}_{Co}^{3/2\prime}\right] + \frac{1}{2}\left[\mathrm{Co}_{Co}^{1/2\prime}\right] = \frac{1}{2}\left[\mathrm{Co}_{Co}^{1/2\bullet}\right] + [\mathrm{La}_{Ba}^{\bullet}] + 2\delta$$

The defect model is in good agreement with experimental data

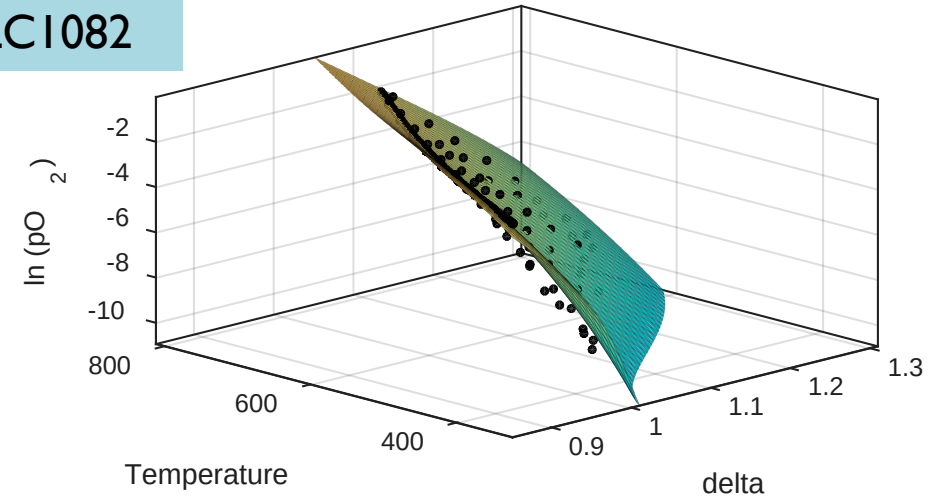




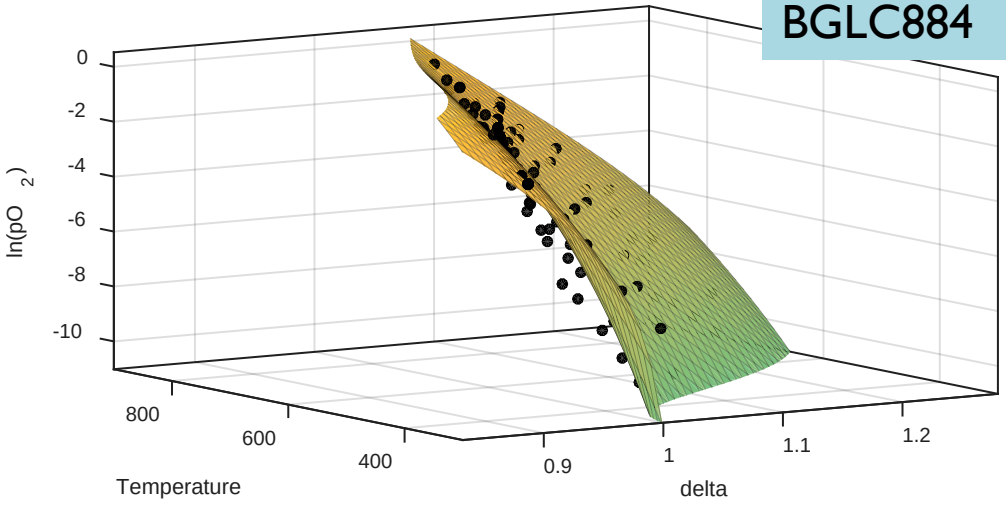
Full 3D defect chemical modelling

BGLC1082

	ΔH (kJ/mol)	ΔS (J/molK)
Reduction reaction	37 ± 3	58 ± 2
Co disproportionation	44(fixed)	0(fixed)
Oxygen interaction	49 ± 2	-3 ± 1

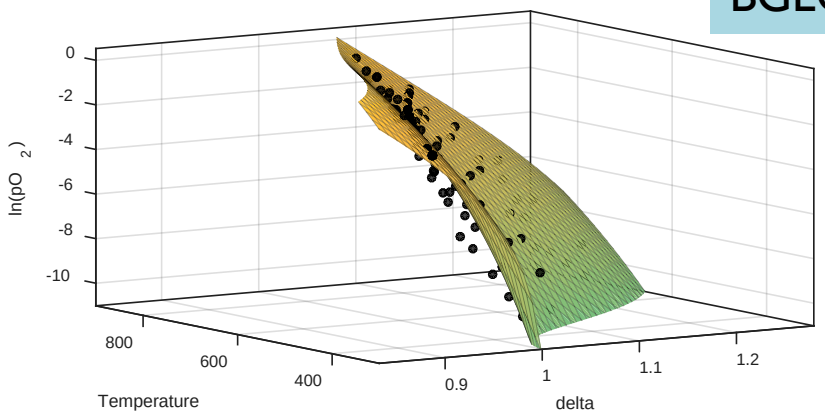


BGLC884



	ΔH (kJ/mol)	ΔS (J/molK)
Reduction reaction	35 ± 4	68 ± 3
Co disproportionation	44 (fixed)	0 (fixed)
Oxygen interaction	60 ± 5	1 ± 2

Reduction enthalpies from TG-DSC in reasonable agreement with our defect model



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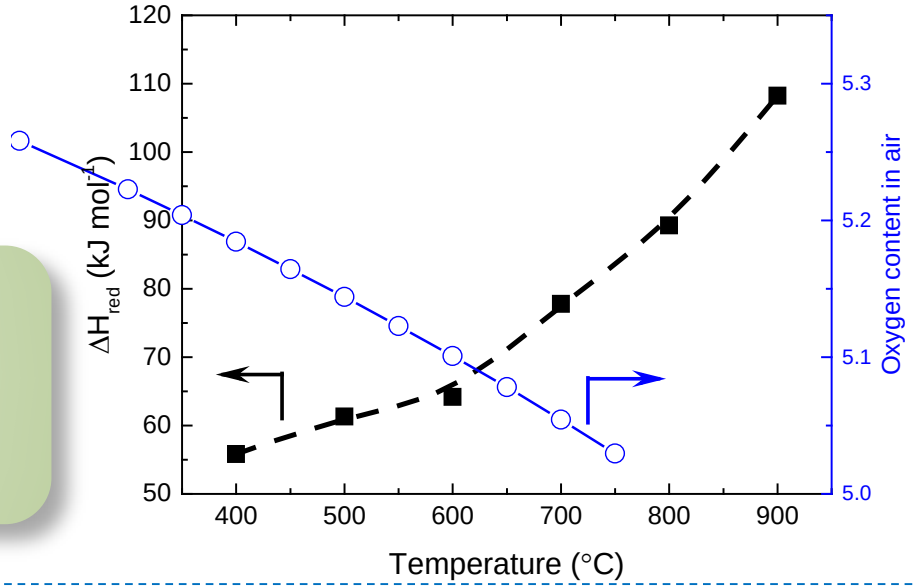

Increasing reduction enthalpy with temperature indicates a change in mechanism as all O1-sites are exhausted

Conclusions

- Partial La-substitution seems to increase stability towards steam while maintaining high electrochemical activity
- As of yet, no clear trends are apparent in the electrochemical activity of BGLC as a function of La-content
- A defect model using a fully oxidized double perovskite as the reference structure has been developed
  - Uses all structural information available
  - Can accommodate La-substitution
  - Assumes electronic degeneracy between the two cobalt atoms in each unit cell
- More data is needed to fully describe the oxygen ordering, cobalt charge disproportionation and potential proton incorporation mechanisms

Acknowledgements

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