Study of Defect Chemistry in $(La_{1-x}Ca_x)FeO_{3-\delta}$ perovskite with Computational Thermodynamics

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Ion Transport Membrane: $(La_{1-x}Ca_x)FeO_{3-\delta}$

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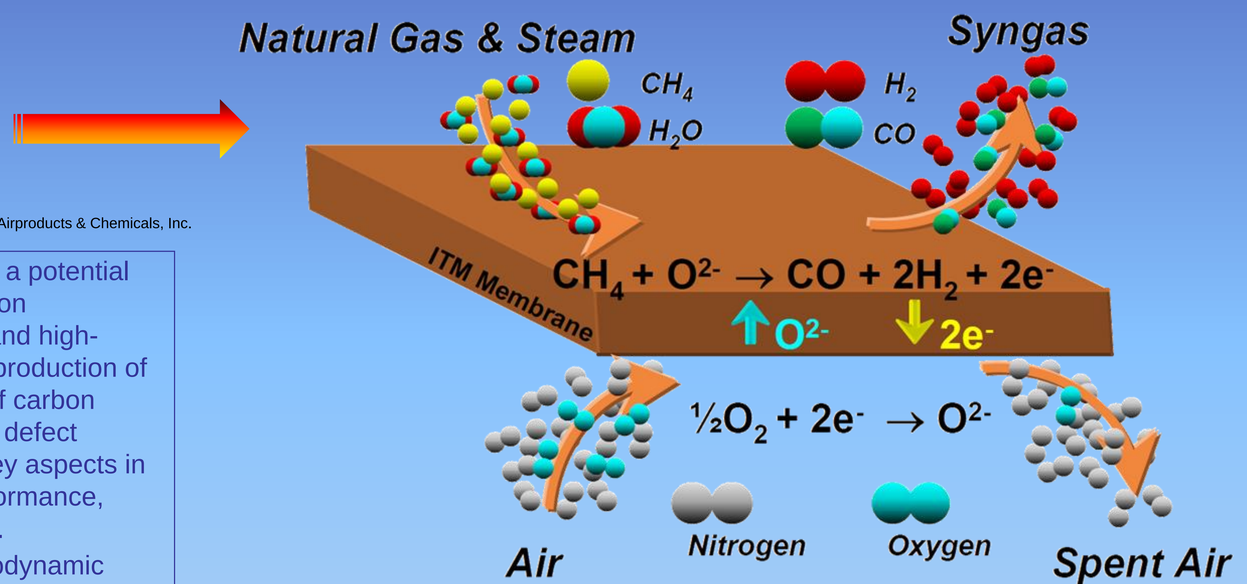

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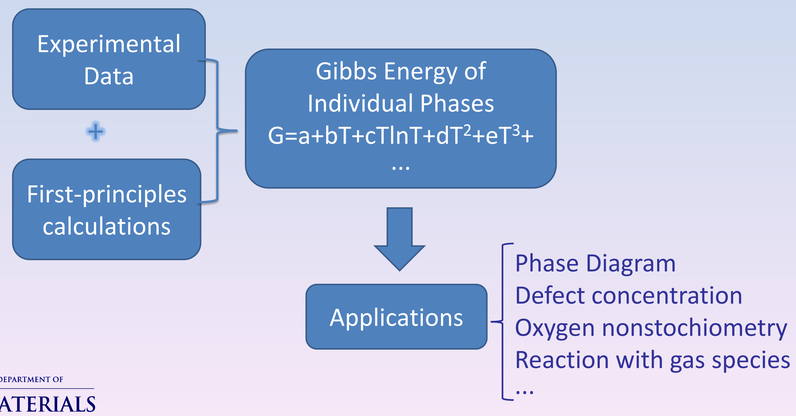
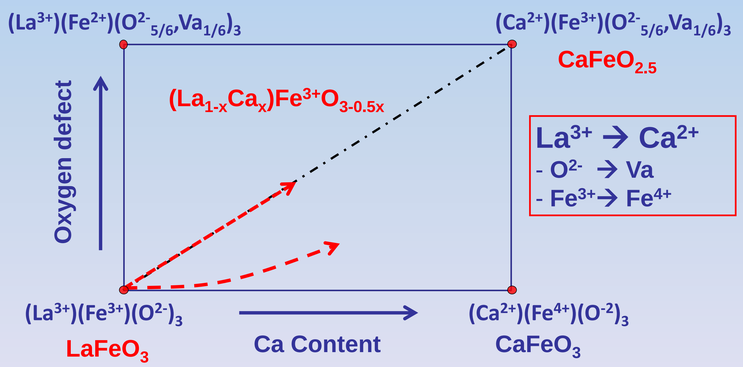
- Ion Transport Membrane is studied as a potential candidate material for the gas separation membrane. It could provide low-cost and high-quality oxygen, and it will improve the production of the synthesis gas, which is a mixture of carbon monoxide and hydrogen. However, its defect chemistry and energetics, which are key aspects in understanding its electrochemical performance, have not been completely investigated.
- Therefore, develop an accurate thermodynamic model is required to predict its defect mechanism and stable condition for operation based on the CALPHAD method and defect analysis

Thermodynamic modeling

- CALPHAD (CALculation of PHAse Diagram) method
  - Thermodynamic modeling using CALPHAD approach involves calculation of Gibbs energy descriptions of various phases in the system of interest. Data from experiments and first-principles calculations are used to evaluate the model parameters which can be used to predict properties outside of the original data range.



Defect Analysis for $(La_{1-x}Ca_x)FeO_{3-\delta}$



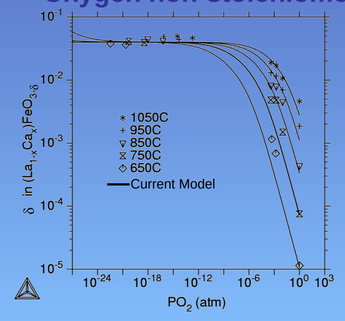
- Ca substitution results in the formation of Fe^{4+} or oxygen vacancy due to the charge neutrality condition
  - In oxidizing atmosphere: $\delta \approx (x - y_{Fe+4})/2$
  - With decreasing PO2: $\delta \approx x/2$
- Suggested sublattice model for $(La_{1-x}Ca_x)FeO_{3-\delta}$ phase

  $(La^{3+},Ca^{2+},Va)(Fe^{2+},Fe^{3+},Fe^{4+},Va)(O^{2-},Va)_3$

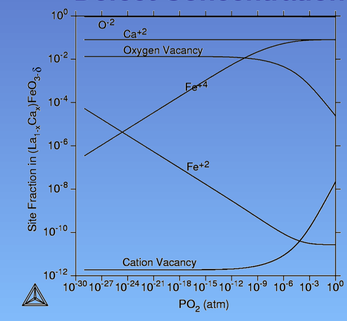
Results and Discussions

x=0.08 in $(La_{1-x}Ca_x)FeO_{3-\delta}$

Oxygen non-stoichiometry

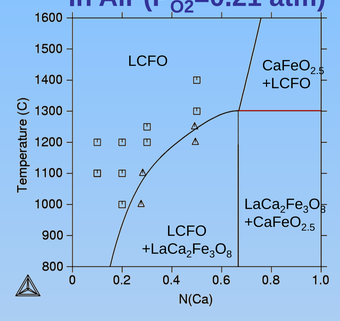


Defect Concentration

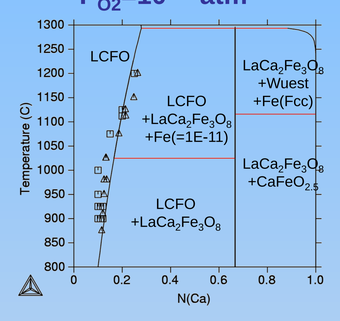


$LaFeO_{3-\delta}$-$CaFeO_{3-\delta}$ phase diagram

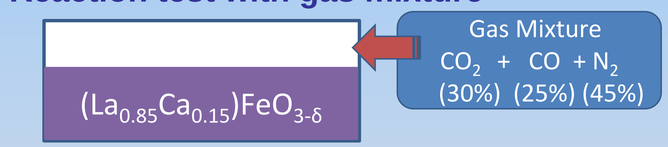
In Air (P_{O2}=0.21 atm)

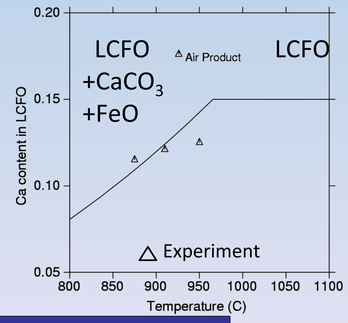


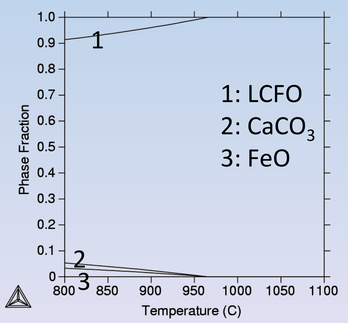
$P_{O2}=10^{-14}$ atm



Reaction test with gas mixture







Summary

Thermodynamic model of $(La_{1-x}Ca_x)FeO_{3-\delta}$ has been developed

- Fe^{+4} and oxygen vacancy are considered as a major defect in oxidizing and reducing atmosphere, respectively
- Calculated oxygen nonstoichiometry results are in good agreement with experiment, and phase diagrams in differnet oxygen partial pressures and reaction with gas mixture are predicted