The Role of Fe Charge State on the Defect and Crystal Structure of \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta} \) (\( 0 \leq x \leq 1 \)) under SOFC Operating Conditions: A Combined Density Functional Theory and Thermodynamics Approach

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1. Motivation
- Ultimate Goal: Computationally design new materials with high oxygen vacancy concentration \((c_{\text{vac}})\), i.e., a high oxygen nonstoichiometry (\(\delta\)), at SOFC operating conditions.
- Focus of this study: Establish a method to accurately calculate the oxygen vacancy concentration of a known perovskite system, LSF (La\(_{1-x}\)Sr\(_x\)FeO\(_{3-\delta}\)), and compare with experimental results [1].
- The main challenge is to predict the free energy of oxygen vacancy formation \((\Delta G_{\text{vac}})\) at SOFC operating conditions.
  - For non-interacting vacancies, \(\Delta G_{\text{vac}} = f(T, p)\) only
  - For interacting vacancies, \(\Delta G_{\text{vac}} = f(T, p, \delta)\)
- \(\delta\) depends on:
  - Crystal structure,
  - La/Sr ratio in LSF,
  - Oxygen chemical potential, \(\Delta m(O) = f(T, p)\).
  - Charge state/magnetic moment of Fe [2]

2. Fe Charge State Calculation for \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta} \) (\( 0 \leq x \leq 1 \))
- \(2\delta \frac{Fe^{3+}}{Fe^{4+}} + \frac{1}{2} Fe^{2+} + V_{\text{O}}^0 + 2Fe^{3+}\)

3. Computational Approach
- Computational studies were performed using Density Functional Theory and Thermodynamics.
- \( U = 3 \) was selected to give Fe magnetic moment and lattice parameters comparable with experimental results for LaFeO\(_3\) and SrFeO\(_3\).
- DFT+U was used to minimize all the crystal structure energies and predict the magnetic moment on Fe.
- DFT+U was used to calculate the oxygen vacancy formation energy in supercells with varying size and a single oxygen vacancy, mimicking a broad range of oxygen nonstoichiometry.

4. \( \Delta E_{\text{vac}} \) with \( \uparrow x \) on Fe\(^{x+}\)
- The magnetic moment on Fe is used to describe classical charge state on Fe in Fe-O complexes.
- The magnetic moment on Fe in SrFeO\(_3\) (3.61\(\mu_B\)) is assigned with a classical charge state of +4. The magnetic moment on Fe in LaFeO\(_3\) (4.23 \(\mu_B\)) is assigned with charge state of +3. Then a linear interpolation gives the intermediate charge states.
- DFT calculation show that the vacancy formation energy increases with decreasing charge on Fe in different Fe-O complexes.
- Oxygen vacancies are preferentially formed near high oxidation state Fe cations, if the LSF structure has mixed Fe charge states.

5. \( V_{\text{O}}^0 \) is Generated Near Higher Fe\(^{x+}\)

6. Thermodynamic Extension
- To account for SOFC operating conditions, we used [6,7]:
  \[
  \Delta G_{\text{vac}} = \Delta G_{\text{vac}}(T, p) + \frac{1}{2} \Delta G_{\text{O}}(T, p)
  \]
  \[
  \Delta G_{\text{O}} = \Delta G_{\text{O}}^{\text{perfect}} + \frac{1}{2} \Delta G_{\text{O}}^{\text{defective}}
  \]
  \[
  \Delta G_{\text{O}}^{\text{perfect}} = \text{Perfect crystal structure}
  \]
  \[
  \Delta G_{\text{O}}^{\text{defective}} = \text{Crystal structure with one oxygen vacancy.}
  \]
  \[
  \text{Chemical potential of oxygen at SOFC operating conditions [8,9],}
  \]
  \[
  \mu_{\text{O}}(T, p) = \mu_{\text{O}}^{\text{perfect}} + \mu_{\text{O}}^{\text{defective}} = \mu_{\text{O}}^{\text{perfect}} - \frac{1}{2} \mu_{\text{O}}^{\text{defective}}
  \]
  \[
  E_{\text{B}}^{\text{DF}} = \text{DFT calculated energy of a single oxygen molecule.}
  \]
  \[
  \Delta \mu_{\text{O}}^{\text{perfect}}(T, p) = \text{Connection energy of oxygen from 0 K, isolated molecule to standard state (298.15 K, 1 atm).
  }
  \]
  \[
  \mu_{\text{O}}^{\text{perfect}} = \mu_{\text{O}}^{\text{perfect}} - \mu_{\text{O}}^{\text{defective}} - \Delta \mu_{\text{O}}^{\text{defective}}(T, p, \delta)
  \]
  \[
  \frac{\Delta E_{\text{vac}}}{\Delta \mu_{\text{O}}^{\text{perfect}}(T, p, \delta)} = \text{The interactive vacancy concentration (c) was calculated as a function of vacancy formation energy via [10]:}
  \]

7. \( \Delta G_{\text{vac}} \) is \( c_{\text{vac}} \) Dependent

8. \( c_{\text{vac}} \) Induces Phase Transformations
- In this work a combined thermodynamics and DFT approach was used to predict oxygen vacancy concentrations and crystal structures at SOFC operating conditions.
- In LSF, the oxygen vacancies are formed near the Fe site, especially in structures with a high Fe charge state.
- Recommendations:
  - Stabilize the rhombohedral structure instead of the cubic structure (Fig. 7b).
  - Stabilize Fe\(^{3+}\) in octahedral not square pyramidal coordination (Fig 5).

References:

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