Ab initio Modeling of Cation Diffusion in $La_{1-x}Sr_xMnO_{3\pm\delta}$ for Solid Oxide Cell Electrodes Applications

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Motivation

Cation diffusion can directly or indirectly influence degradation of LSM/YSZ.
- Diffusion of cations from the interfaces to surfaces under current load.
- May increase the number of TPB and improve the performance in a short time
- Leads to increase of the interface resistance in the long-term operation due to morphological and compositional evolution near the LSM/YSZ interfaces

Backhaus SSI 2008

The interface degradation was identified as:
1. loss of LSM coverage
2. loss of three-phase-boundary (TPB) length.

Miyoshi SSI 2002

LMO morphological instability upon annealing

Annealing at 1273 K for 300 h

Develop quantitative theoretical models based on *ab initio* energetics to assess cation diffusivity in bulk LSM vs T and P(O₂)

- Cation interdiffusion of LSM/YSZ interfaces.
- Property assessment of diffuse interfaces

Diffusion Model (Random Walk Diffusion)

$$D_{Mn}^{Self} = [def - complex] \frac{Z}{6} \cdot a_0^2 \cdot v_0 \cdot \exp\frac{\Delta S_{migration}}{k_b} \cdot \exp\frac{-(\Delta E_{migration})}{k_b T}$$

Fixed constants

Carrier concentration of defects (clusters) vs. P(O₂) and T:
- Point defect equilibrium model
- Defect interactions for defect clusters

Fitting parameters: v_0 and $\Delta S_{migration}$

Migration barriers of the cation diffusion pathways obtained from DFT NEB calculations

Equilibrium Defect Chemistry

LaMnO₃±δ T=873K, 973K, 1073K, 1173K, 1273K, 1473K
Lee and Morgan PCCP 2012

La₀.₈Sr₀.₂MnO₃±δ T=873K, 973K, 1073K, 1173K, 1273K

This work

873K   1073 K   1273 K

Lee and Morgan PCCP 2012

Concentration of defect complexes involved in cation diffusion in LSM is calculated based on the DFT interaction energies

e.g., for V_A'''-V_B''' defect complex in LSM,:

$$V_A''' + V_B''' \rightarrow V_A'''\text{-}V_B'''$$

$\Delta G_{association} \approx \Delta E_{association} (+0.4 \text{ eV from DFT})$

$\rightarrow [V_A'''\text{-}V_B'''] = [V_A''']\cdot[V_B''']\cdot\exp(-\frac{\Delta E_{association}}{k_b T})$, where $[V_A'''] = [V_B''']$ from LSM point defect model

B-site Cation Diffusion Pathways

4 Mn diffusion pathways

80-atom 2√2a×2√2a×2a supercell (a: perovskite lattice constant)

Pathway 1 (V_A-V_B)
Palcut, PCCP 2008; Miyoshi, PCCP 2009; Harvey, EES 2012

Reaction Coord.

Pathway 2 (Curved V_B)
De Souza J Mater Chem 1999 (Classical MD)

Reaction Coord.

Pathway 3 (2ⁿᵈ NN V_B)
De Souza J Mater Chem 1999 (Classical MD)

Reaction Coord.

Pathway. 4 (V_O-V_B)
This work

at low P(O₂)

Reaction Coord.

A-site Cation Diffusion Pathways

Sr-hop   La-hop

2.4 eV   2.9 eV

- Direct 1ˢᵗ NN A-site vacancy migration
- Lower migration barriers of Sr than that of La in La₀.₇₅Sr₀.₂₅MnO₃ despite a larger ionic radius
- Sr-V_A repulsion increases the effective Sr migration energy to be about 3.2 eV, close to the effective La migration energy. *Puchala, Lee, and Morgan, JES 2012*
- Calculated DFT migration barrier for La in LaMnO₃±δ : 2.8 eV

Cation Self-diffusion Coefficients vs. T and P(O₂)

Set $\Delta S_{migration}$ = 4.5k_b and attempt frequency v_0 = 10¹³ Hz

- **T dependence at P(O₂)=0.2 atm**

Exp. data (●) and the B/W figure from *Miyoshi PCCP 2009*

D_{Mn}^* (LMO), ΔE_a=1.5eV
D_{La}^* (LMO) ΔE_a=2.5eV
D_{Mn}^* (LSM) ΔE_a=2.2eV

P(O₂)=0.2 bar

$D_{eff,Mn}$ in LaMnO₃ (this study)

1. Y in YCrO₃ [16]
2. La in LaCrO₃ [17]
3. Ca in La₀.₇₉Ca₀.₂₁CrO₃ [18]
4. Ca (g.b.) in La₀.₇₉Ca₀.₂₁CrO₃ [18]
5. Cr in La₀.₇₉Ca₀.₂₁CrO₃ [19]
6. Cr (g.b.) in La₀.₇₉Ca₀.₂₁CrO₃ [19]
7. Cr in La₀.₉₀Sr₀.₁₀CrO₃ [19]
8. Cr (g.b.) in La₀.₉₀Sr₀.₁₀CrO₃ [19]
9. La, Sr, Mg in La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₃ [20]
10. Y, Cr in La₀.₅Sr₀.₅FeO₃, Cr in LaFeO₃ [21]
11. Y in LaFeO₃ [21]
12. Fe in LaFeO₃ [22]
13. Co in LaCoO₃ [23]
14. Sr in BaTiO₃ [24]
15. Zr in BaTiO₃ [24]
16. Pr in LaMnO₃ [26]
17. **Mn in LaMnO₃ [27]**
(Broken line: Diffusion couple)

Exp.	ΔE_a
D_{Mn}^*(LMO) *Miyoshi PCCP 2009*	0.6 eV
D_{Mn}^*(LMO) *Palcut, JPCC, 2007*	2.9±0.4 eV
D_{Pr}^*(LMO) *Palcut, SSI, 2008*	1.3±0.1 eV

Model (This work)	ΔE_a
D_{Mn}^*(LMO)	1.5 eV
D_{La}^*(LMO)	2.5 eV
D_{Mn}^*(LSM)	2.2 eV

- **P(O₂) dependences of D_{Mn}^***

T=1473 K   Slope → 0.5   Slope → 1   This work

Miyoshi PCCP 2009 LaMnO₃ T=1523 K   Mn Sectioning / Mn Residual   This work   Cr Sectioning / Cr Residual

D[V_A-V_B], D[V_B-V_O] LaMnO₃
D[V_A-V_B], D[V_B-V_O] La₀.₇₅Sr₀.₂₅MnO₃
T=1073 K

- Model predictions capture the experimental P(O₂) dependences (transition of slopes)
  - P(O₂) dependences governed by nonideality of cation vacancies
- Decrease of D_{Mn}^* with decrease of P(O₂), due to lower cation vacancy concentration
- Predict to change from D_{Mn}^* (V_A-V_B) at higher P(O₂) to D_{Mn}^* (V_O-V_B) at lower P(O₂), due to change of dominant point defect population

Summary

Developed an *ab initio*-based cation diffusion model to quantitatively predict cation self-diffusion coefficients of La₁₋ₓSrₓMnO₃±δ vs. a wide range of T and P(O₂)

- Good agreement with experimental LaMnO₃±δ D_{Mn}^* T and P(O₂) dependences
- Results support the Mn_B-V_A-V_B model as the dominant Mn diffusion pathway at high P(O₂)
- Predict to have a crossover of D_{Mn}^*(V_A-V_B) vs. D_{Mn}^*(V_B-V_O) at intermediate/low PO₂
- LaMnO₃ D_{Mn}^* [V_A-V_B] is 2~3 orders magnitude greater than La₀.₇₅Sr₀.₂₅MnO₃ due to higher cation vacancy conc.
- Predicted apparent activation energies (ΔE_a's) at P(O₂) = 0.2 bar
  - D_{Mn}^* : **1.5 eV** in LaMnO₃±δ ; between the reported exp. values **0.6 eV** (Radio-isotope diffusion)
  - D_{La}^*: **2.5 eV** in LaMnO₃±δ vs. exp. Pr Impurity diffusion in 1.3±0.1 eV (Palcut PCCP 2008)
  - ΔE_a of D_{Mn}^* vs. Sr doping: **1.5 eV** in LaMnO₃±δ vs. **2.2 eV** in La₀.₇₅Sr₀.₂₅MnO₃

Future Work
- Extend to model cation interdiffusion of LSM/YSZ interface
- The formalism can be applied to other SOFC perovskite systems (e.g. LSCF, LSC, BSCF)
- Impurity diffusion (Y, Zr, Pr, Co, etc.) in LSM

Acknowledgement

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