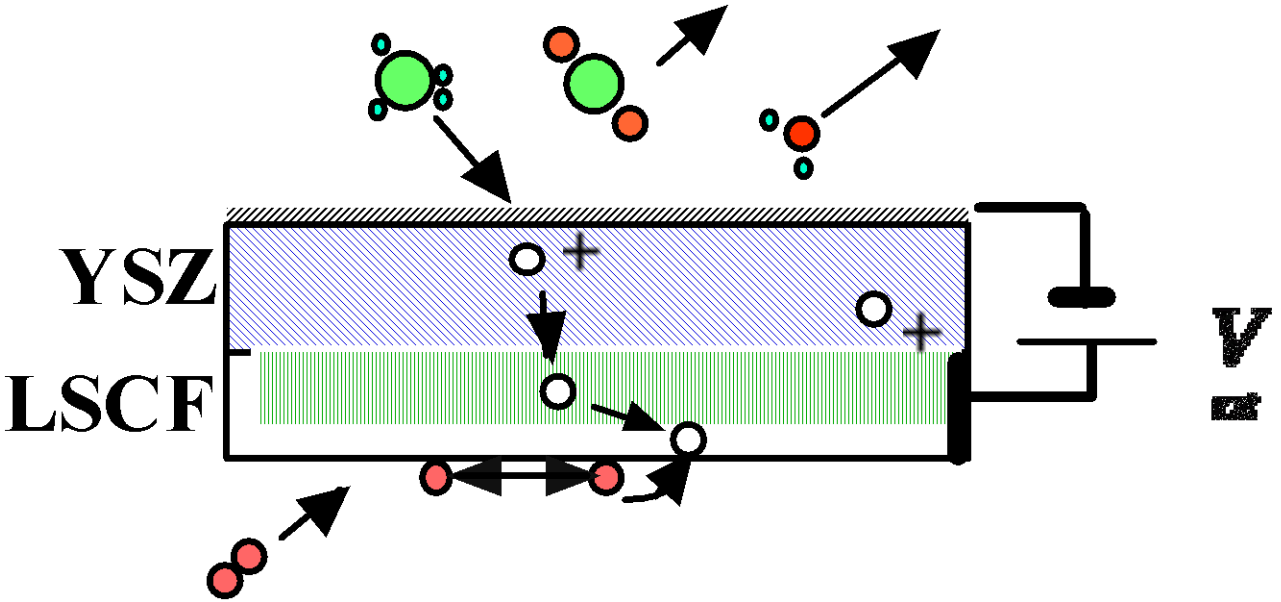


Origin and Effects of Sr Segregation in LSM and LSCF

Walter Harrison, Stanford University
Leonardo Technologies, Inc.

Bottom line:

- **May be inhibiting fuel cell operation**
  … but could be eliminated!

Arises from polar surfaces of crystal.

Will put in context of doping
and bulk charge neutrality.

Doping crystals is tricky!

- Most familiar case, semiconductors
- Si(P)

  Silicon neutral. Substitute P

  Equivalent to adding proton to nucleus - ‘theoretical alchemy’

  Bulk charge density, diverging energy

  Neutralized by electrons

  Basis of industry!

Equally familiar to us: $ZrO_2(Y)$

- Y^{3+} for Zr^{4+} Holes in valence band?

- Band gap too large

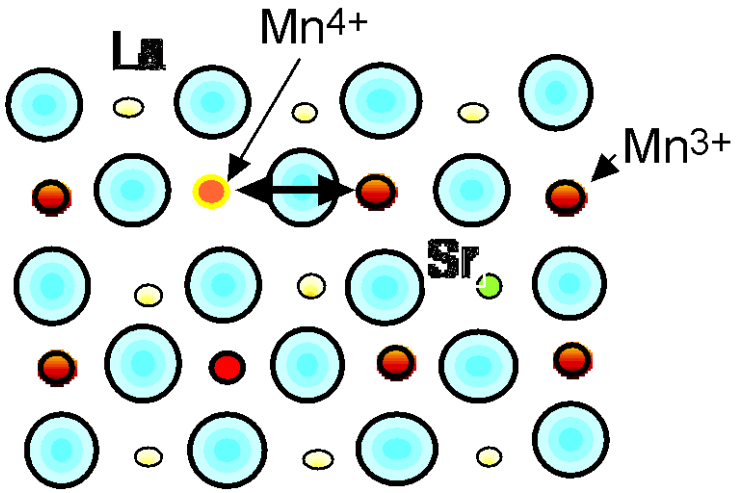
  Oxygen vacancy, V_O^{2+}
- Our electrolyte!

LSM Still another case

- $La^{3+}Mn^{3+}O_3^{2-}$, Sr^{2+} for La^{3+}
- Promote Mn^{3+} to Mn^{4+} for neutrality

  Like semiconductor, but no bands!
- Polaron hopping
- LMO and SMO

  are insulating!



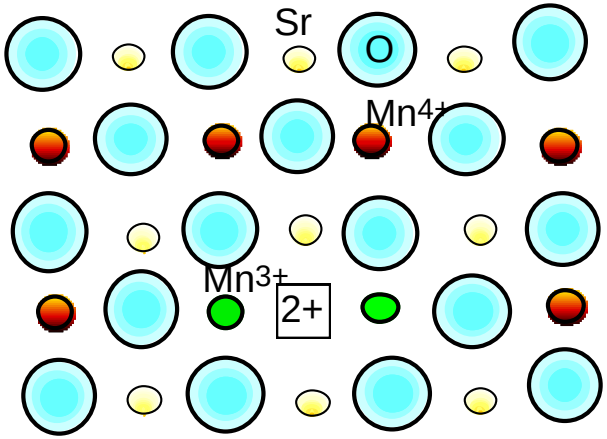
- Another world!

- Even oxygen vacancies different

  $SrMn^{4+}O_3$

  Oxygen vacancy $\rightarrow$ two Mn^{3+}

Mn^{3+} level lower by 0.5 eV next to vacancy



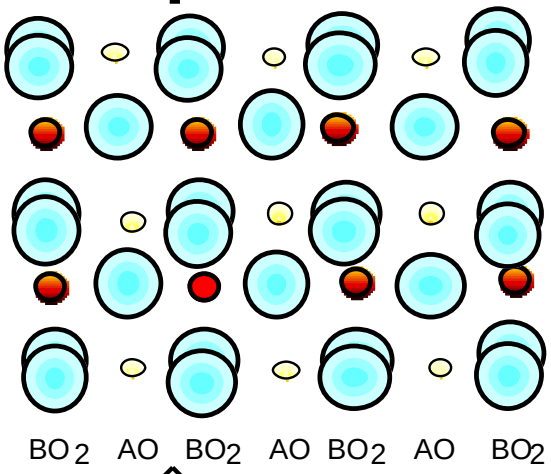
Vacancy complex is neutral !

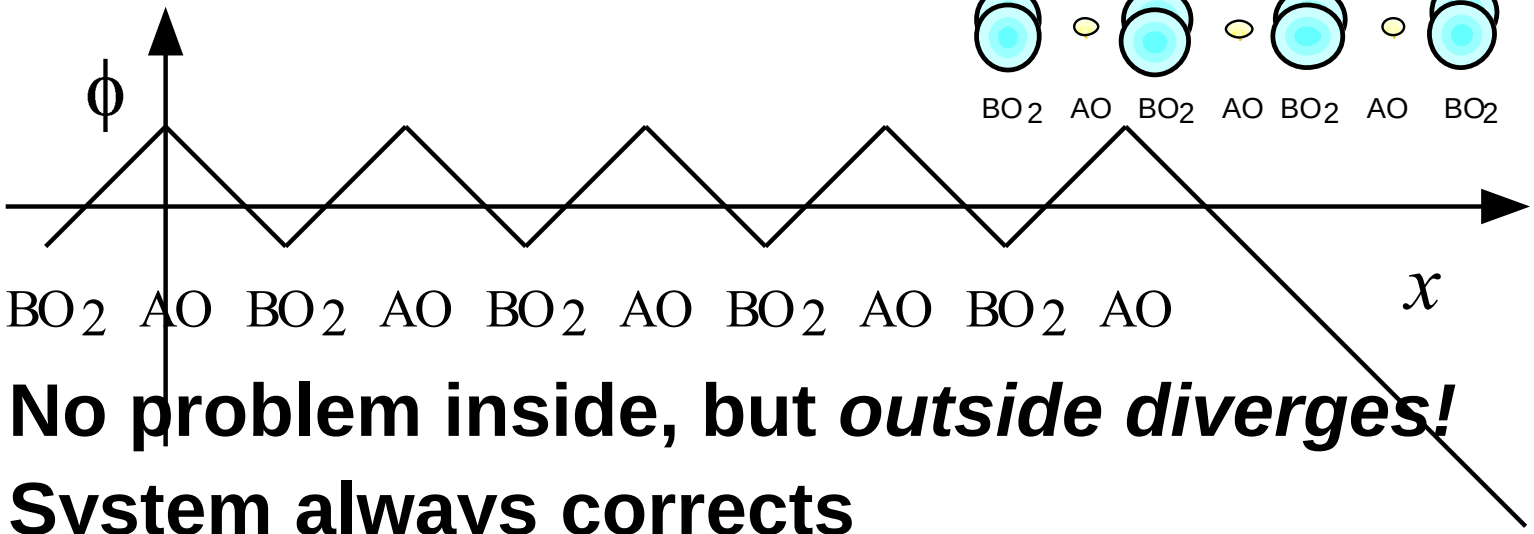
Polar Surfaces

- $LaMnO_3$

  Alternate $Mn^{3+}O^{2-}_2$ and $La^{3+}O^{2-}$ planes

  Potential alternates

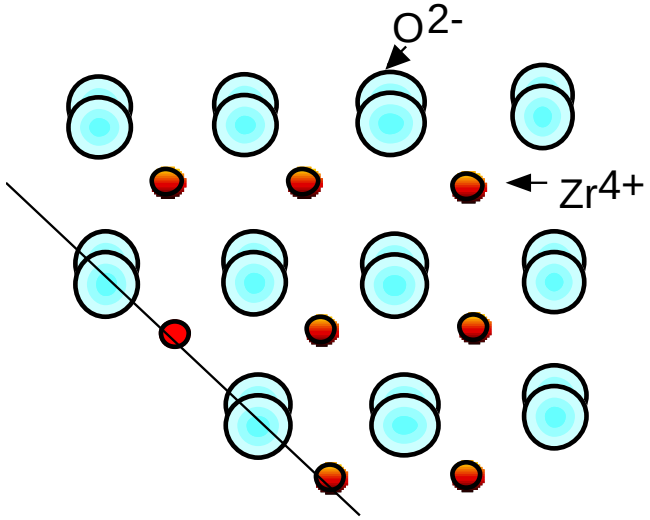




- **No problem inside, but *outside diverges!***
- **System always corrects**

- YSZ Alternates 4+,4-
- (100) planes.

  Chooses (110) surfaces!

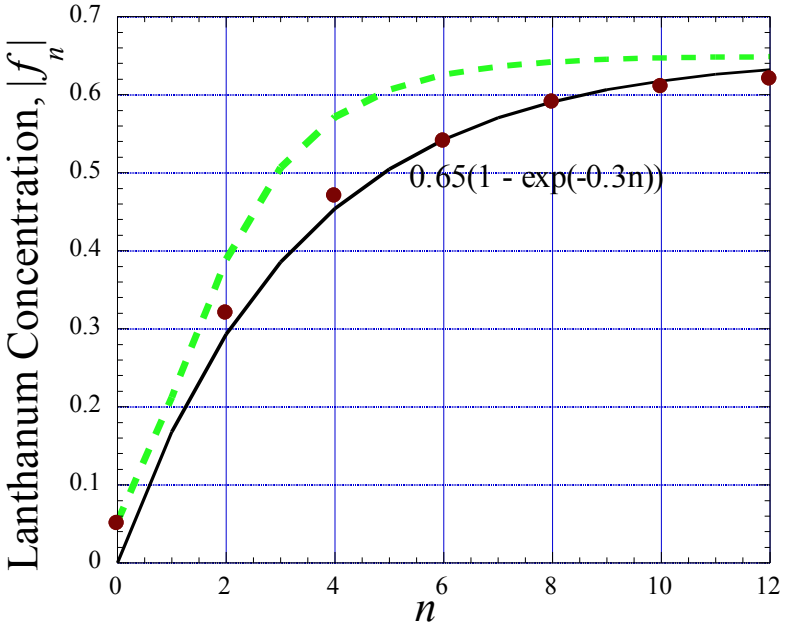


- LSM. LSCF

  Perovskite structure

  No neutral planes (at least simple ones)
- Turns out but by Sr segregation

0.04



Hani Dulli,, P. A. Dowben, S.-H. Liou,, and E. W. Plummer, *Surface segregation and restructuring of colossal-magnetoresistant manganese perovskites, $La_{0.65}Sr_{0.35}MnO_3$,* Phys. Rev. B **62**, R14629 (2000).

- Minimize electrostatic energy

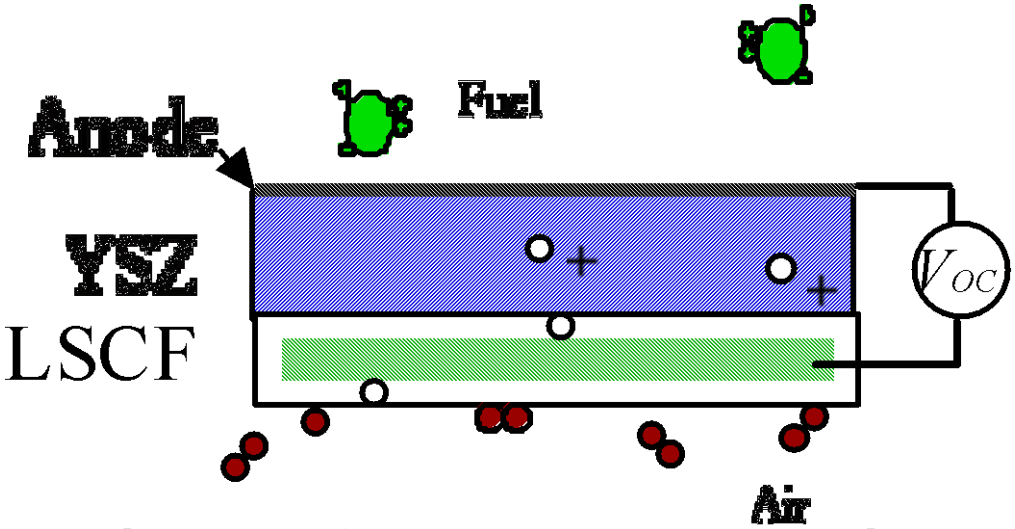
W. A. Harrison , *The origin of Sr segregation,,,* Phys. Rev. B **83**, 15543 7 (2011). (arXiv:1101.541 4)

- Applies also to LSCF,

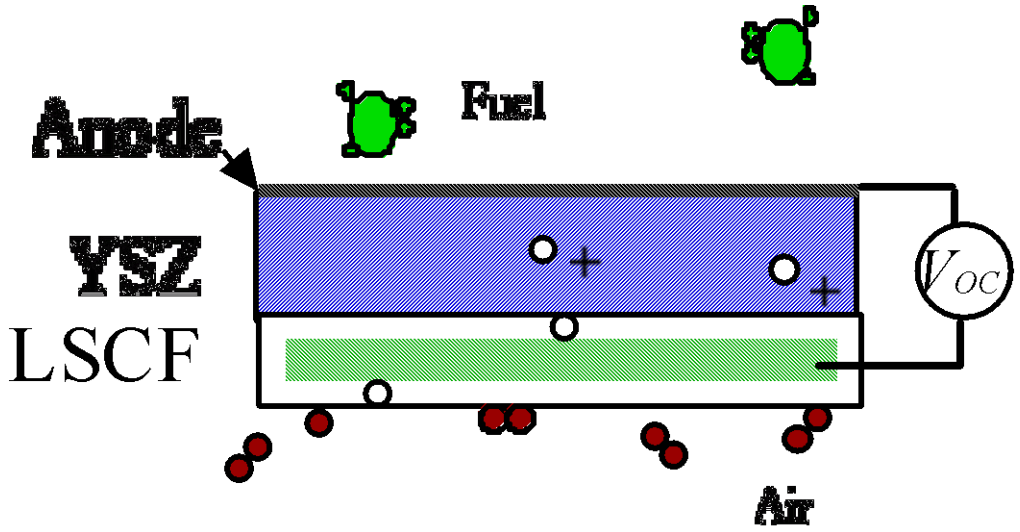
  and LSCF-YSZ interface

- Result: Surface is insulating

Combine with YSZ, fuel cell.



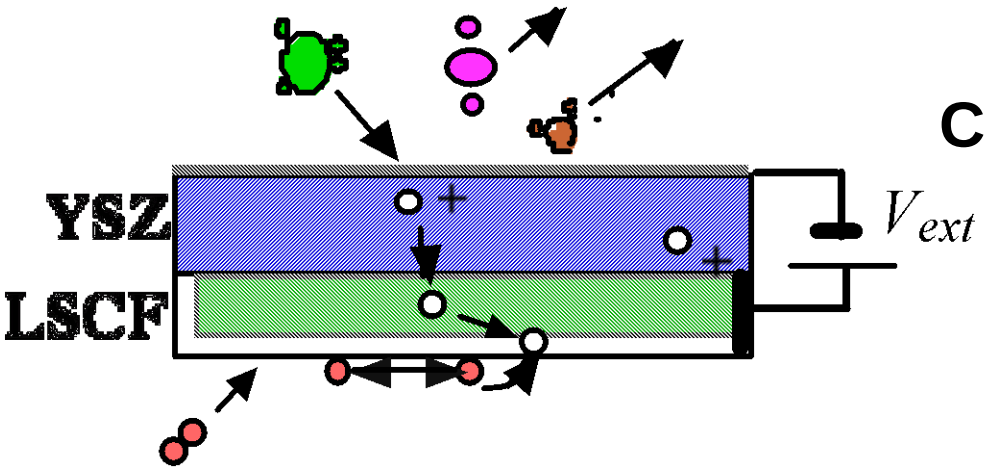
Open circuit: no flow, two worlds



- **Just enough to make V_{OC}**
- **Close circuit: all transfer at interface**

Vacancies flow, but need two Mn^{3+}, 0.04^2

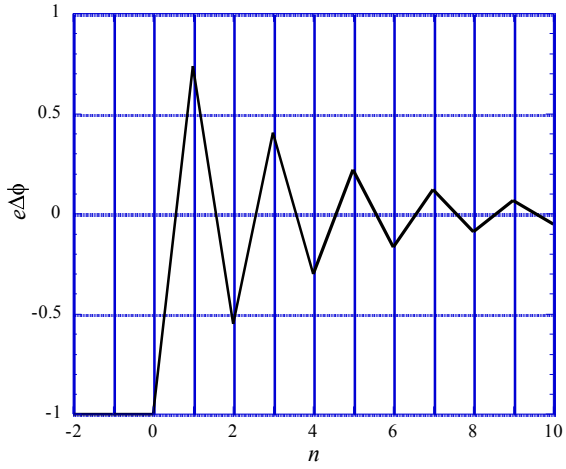
Possible Solution

- If neutralize interface, stop segregation?
- Need replace 1/4 of La by K in one plane.
- 

Charging!

Vacancy Segregation

- **Potential near surface:**



- **Vacancy distribution**