Ab initio study of diffusivity and ionic conductivity of $Ln_2NiO_{4+\delta}$(Ln=La, Nd, Pr) mixed conductor

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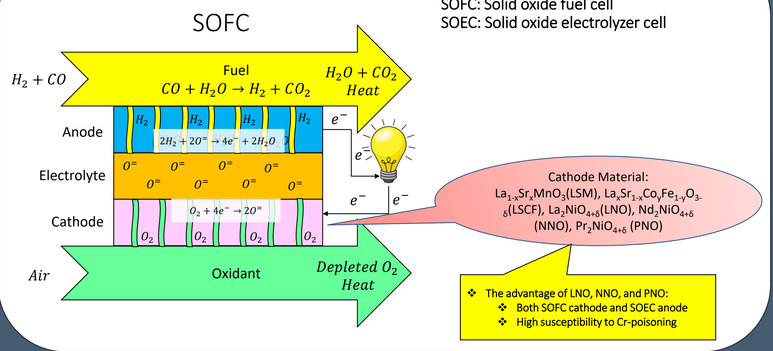
Introduction



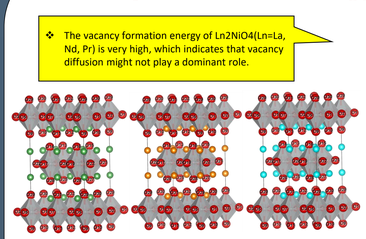
SOFC: Solid oxide fuel cell
SOEC: Solid oxide electrolyzer cell

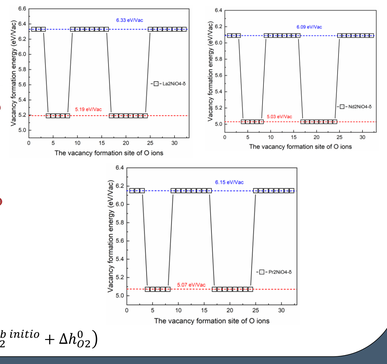
Cathode Material:
$La_{1-x}Sr_xMnO_3$(LSM), $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$(LSCF), $La_2NiO_{4+\delta}$(LNO), $Nd_2NiO_{4+\delta}$ (NNO), $Pr_2NiO_{4+\delta}$ (PNO)

- The advantage of LNO, NNO, and PNO:
  - Both SOFC cathode and SOEC anode
  - High susceptibility to Cr-poisoning

Vacancy formation energy ($Ln_2NiO_{4-\delta}$)

- The vacancy formation energy of Ln2NiO4(Ln=La, Nd, Pr) is very high, which indicates that vacancy diffusion might not play a dominant role.



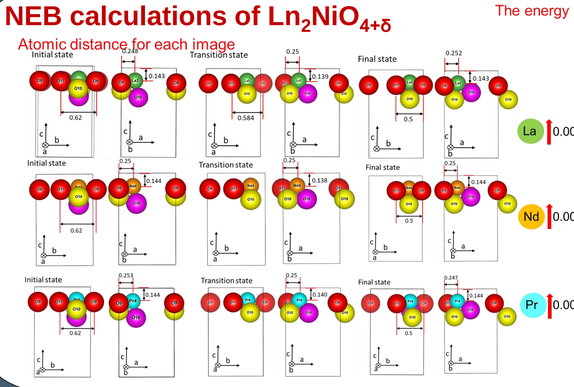


$$Ln_{16}Ni_8O_{32} \xrightarrow{-O} Ln_{16}Ni_8O_{31}$$

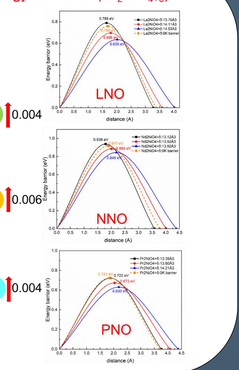
$$\Delta E_{Vf} = E^{ab\ initio}_{Ln16Ni8O31}(vac) - E^{ab\ initio}_{Ln16Ni8O32} + \frac{1}{2}\left(E^{ab\ initio}_{O2} + \Delta h^0_{O2}\right)$$

NEB calculations of $Ln_2NiO_{4+\delta}$

Atomic distance for each image



The energy barrier of ($Ln_2NiO_{4+\delta}$)



Objective of the work

Diffusion mechanism of the $Ln_2NiO_{4+\delta}$ structure

Vacancy diffusion? Interstitial diffusion?

Ab initio study of energy barrier, diffusion coefficient, and ionic conductivity

Extrapolation of the temperature-dependent energy barrier

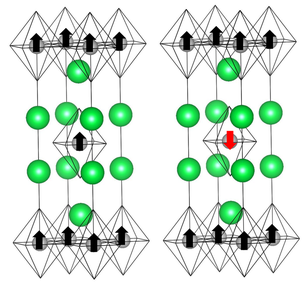
GOAL:

Develop a novel Cathode material with high ionic conductivity and electronic conductivity

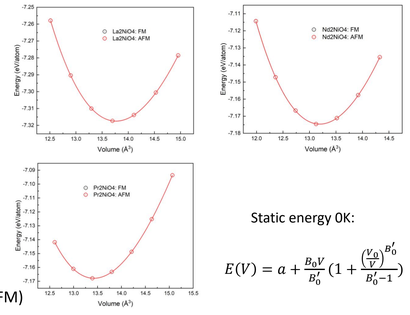
Action items:

- ❑ Calculations of the Vacancy formation energy
- ❑ Calculations of the thermal expansion coefficient
- ❑ Extrapolation of the temperature-dependent energy barrier
- ❑ Prediction of the diffusion coefficient and ionic conductivity ($Ln_2NiO_{4+\delta}$, δ=0.125)

Equation of state of Ln_2NiO_4 (Ln=La, Nd, Pr)



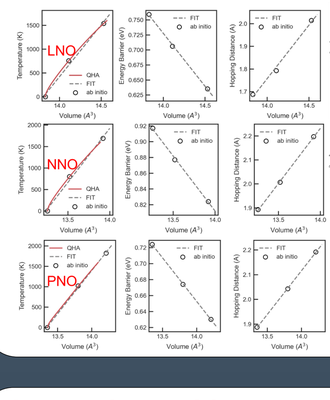
Ferromagnetic (FM) Anti-ferromagnetic(AFM)



Static energy 0K:

$$E(V) = a + \frac{B_0 V}{B_0'}\left(1 + \frac{\left(\frac{V_0}{V}\right)^{B_0'}}{B_0' - 1}\right)$$

Temperature-dependent properties-$Ln_2NiO_{4+\delta}$



$$D(V) = y_{Va}\delta(V)^2 v_0 \exp\left(-\frac{\Delta E_b(V)}{k_B T}\right)$$

$$\sigma = \frac{Nq^2 D(V)}{V k_B T}$$

$$v_0 = k_B T/h$$

$$y_{Va} \approx \frac{n_{V_{O^-}}}{n_{O^{2-}}}$$

v_0: vibration frequency

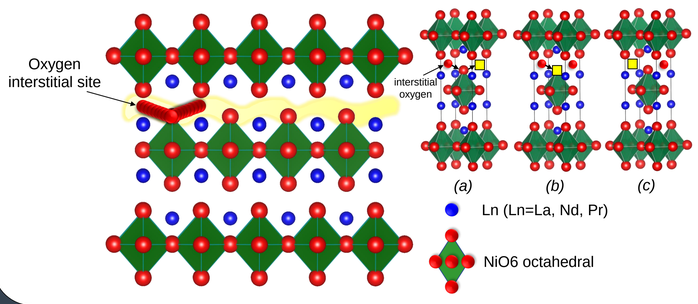
δ: hopping distance

y_{Va}: vacancy fraction

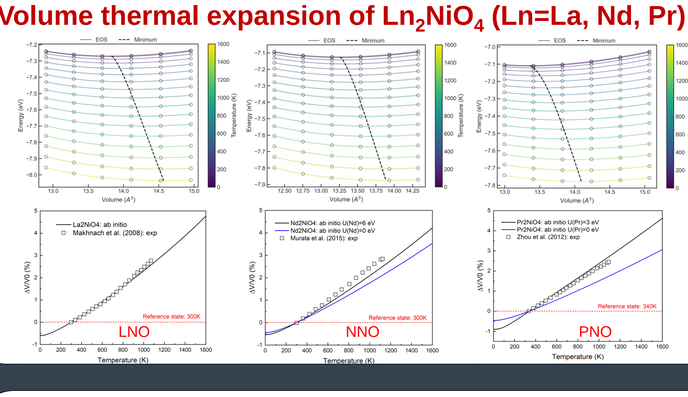
$n_{V_{O^-}}$: the # of interstitial oxygen vacancy

$n_{O^{2-}}$: the # of oxygen ion

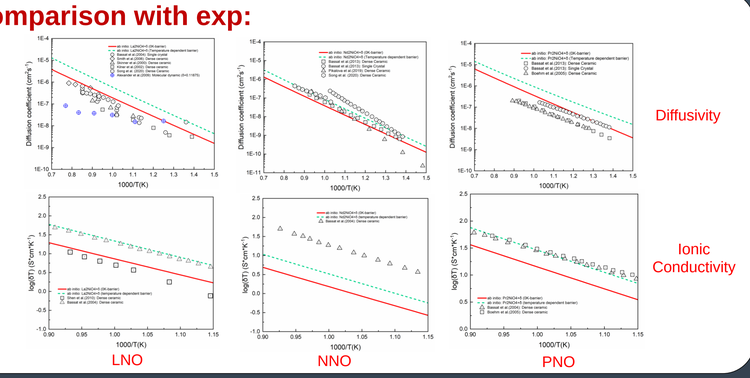
Oxygen migration path ($Ln_2NiO_{4+\delta}$)



Volume thermal expansion of Ln_2NiO_4 (Ln=La, Nd, Pr)



Comparison with exp:



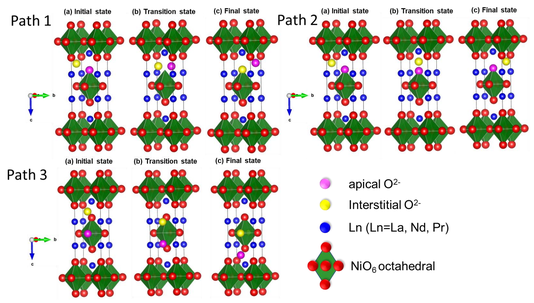
Computational details

Ab initio calculations:

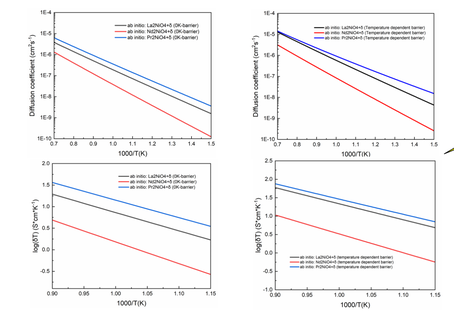
- ❑ Vienna ab initio simulation package (VASP)
- ❑ Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional
- ❑ Monkhorst-Pack k-point meshes with density not less than 5000 pra (per-reciprocal-atom))
- ❑ The DFT+U approach was adopted in the present work
  - ❖ d-element Ni: U=6 eV (adopted the value from Staykov et al.)
  - ❖ f-element Nd: U=6 eV (fitted the EDOS result produced by HSE06 function), Pr=3 eV (adopted the value from Staykov et al.)

Ref. Staykov, A., Nguyen, T., Akbay, T. and Ishihara, T., 2022. Oxygen Reduction Reaction and Electronic Properties of LnO-Terminated Surfaces of Pr2NiO4 and La2NiO4. *The Journal of Physical Chemistry C*, *126*(17), pp.7390-7399.

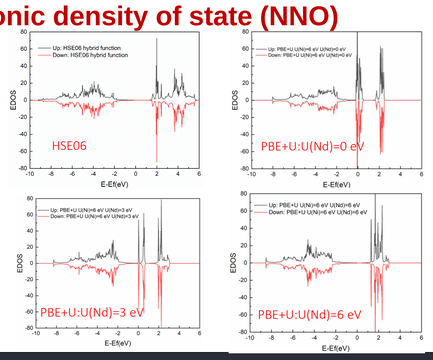
Selected diffusion paths



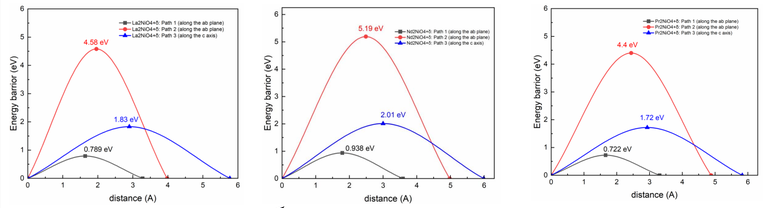
Comparison between different A-site elements



Electronic density of state (NNO)



Energy barrier of different paths



- The diffusion of the oxygen ion along the path 1 has the lowest energy barrier

Conclusions

- The vacancy diffusion might not play a dominant role for the Ln2NiO4 materials due to the high vacancy formation energy.
- After the investigation of different possible pathways, it can be concluded that the interstitial O^{2-} of the $Ln_2NiO_{4+\delta}$ should migrate parallel to the ab plane instead of the c direction, as the energy barrier along the ab plane is lower.
- The ranking of the diffusion coefficient and ionic conductivity of $Ln2NiO_{4+\delta}$, from the highest to the lowest, is $Pr2NiO_{4+\delta}$, $La2NiO_{4+\delta}$, and $Nd2NiO_{4+\delta}$.

Acknowledgments

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