Quantum Chemical Design of Multi-Component Perovskite Oxides for Energy Conversion Devices

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H_2 fuel cells => clean electric power generation

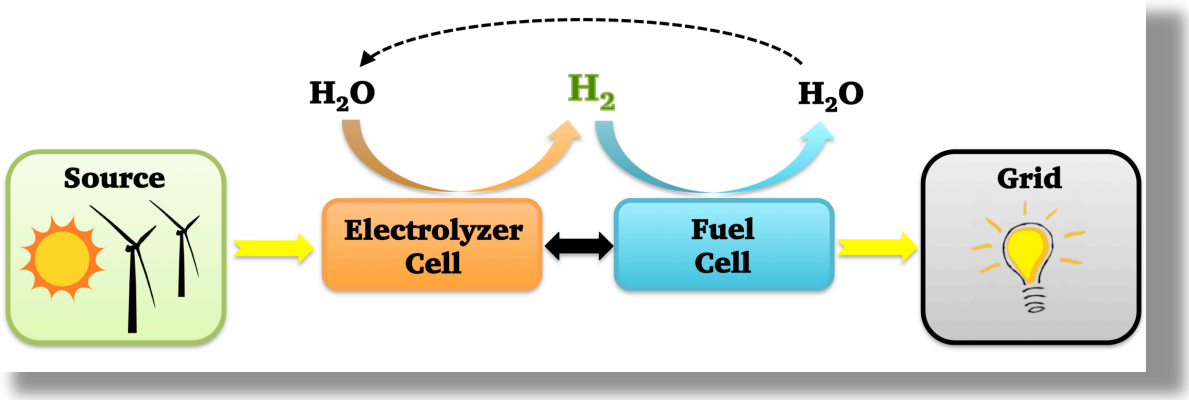
- FCs are electrochemical devices that convert fuels (**chemical energy**) into **electrical energy**

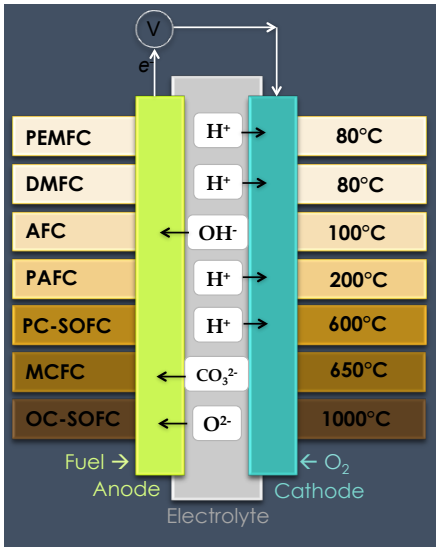
some examples:

- Alkaline FC

- PEM FC

- Solid Oxide FC





Proton-Conducting Electrochemical Cells

low cost oxides (no Pt)
Intermediate Temperatures (~500°C):

- higher mobility of H^+ wrt O^{2-}
- minimize degradation
- H_2 + fuels (FC)
- less electric demand than Low T (EC)

Proton-Conducting Solid Oxide Electrochemical Cells

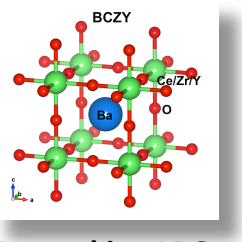
ELECTROLYTES

insulator

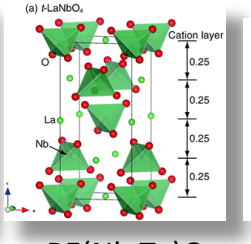
proton conductor

- oxygen vacancies V_O
- low H^+ migration barrier

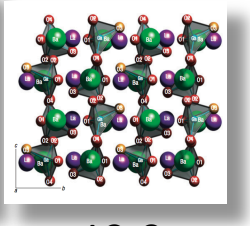
$H_2O + M\text{-}V_O\text{-}M + M\text{-}O\text{-}M \Rightarrow 2\cdot M\text{-}O(H)\text{-}M$



Perovskite ABO_3
$BaCeO_3/BaZrO_3$



$RE(Nb,Ta)O_4$



$AGaO_4$

ELECTRODE

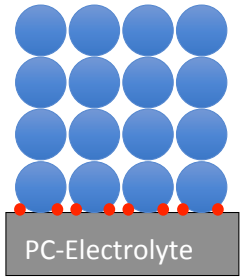
e^- conductor

catalytic activity

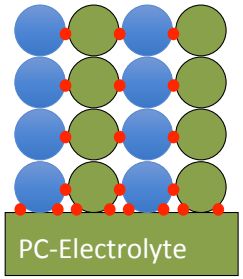
proton conductor

- Oxygen vacancies V_O
- Low H^+ migration barrier

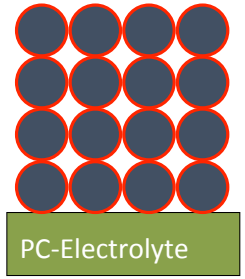
e^- (metal) or
MIEC (mixed e^-/O^{2-})



composite
electrode



IDEAL
mixed e^-/H^+



state-of-the-art

target system

MPECs

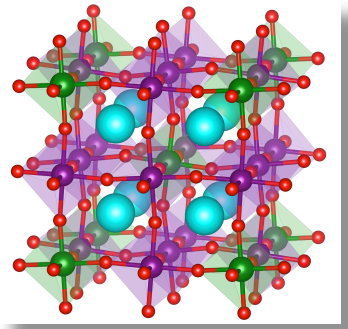
Induce e^- conductivity in PC-electrolytes

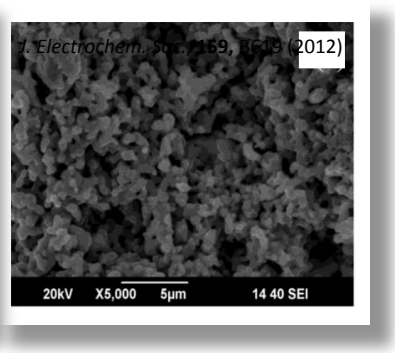
TCOs

Induce PC in MIEC materials

SFMO as Triple Conducting Oxide candidate

$Sr(Fe,Mo)O_3$





Outstanding electrocatalytic performance in symmetric OC-SOFCs

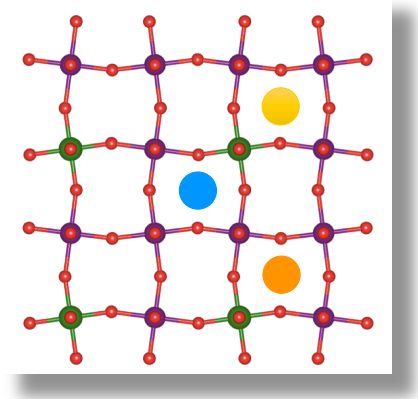
Redox stability, no poisoning

Excellent MIEC properties

- Non-stoichiometric
  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (δ=0.10)
- Low O^{2-} migration barrier (~0.3 eV)

Is also a good proton conductor ?

A-substitutions



Ionic Radii (Å)	
Sr^{2+}	1.44
Ba^{2+}	1.61
K^{+}	1.64

Ba^{2+} structural effects

K^{+} structural/electronic effects (p-doping)

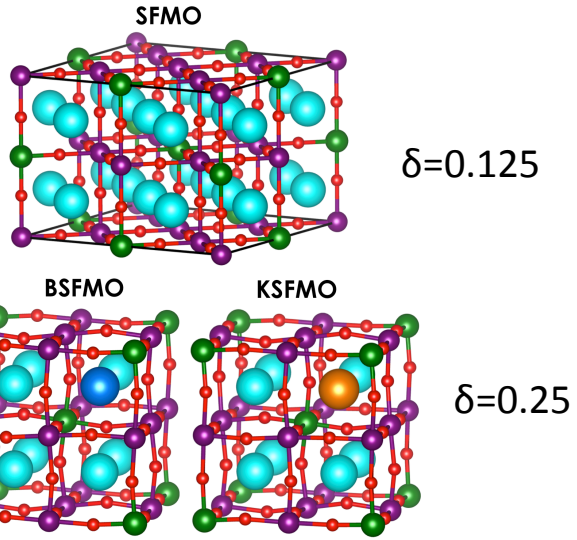
Ana B. Muñoz-García et. al *J. Am. Chem. Soc. 134,* 6826 (2012)
Ana B. Muñoz-García et. al *Phys. Chem. Chem. Phys.*, **15,** 6250 (2013)
Ana B. Muñoz-García et. al *Acc. Chem. Res.*, **47,** 3340 (2014)

computational strategy

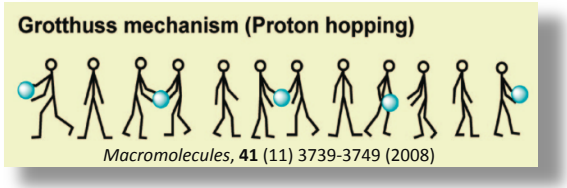
V_O formation M-O-M -> M-V_O-M + ½ O_2 $\Delta E_{form}V_o = E_{def} + 1/2\ E_{O2} - E_{host}$

Hydration H_2O + M-V_O-M + M-O-M -> 2 M-O(H)-M $\Delta E_{hydr}=E_{2OH}-E_{def} - E_{H2O}$

Transport M_a-O(H)-M_b + M_b-O-M_c -> M_a-O-M_b +M_b-O(H)-M_c $E_{transp}= E_{rot} + E_{jump}$



12.5% Ba/K substitution



Rotation → Fast

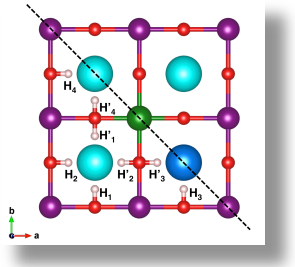
Proton Transfer → RDS

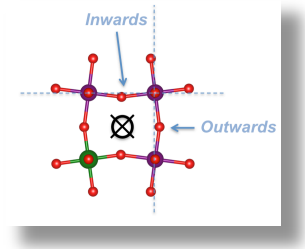
Chem. Soc. Rev., 2010, 39, 4370–4387

- DFT(PBE)+U
  - $(U-J)_{Fe}$=4.0 eV
- PWs- E_{cutoff} = 800 eV
- MEP & Transition States: CI-NEB

structure and energetics

Material	a(Å)	δ	$\Delta E_{form} V_O$ (eV)		ΔE_{hydr} (eV)
			Fe-O-Fe	Mo-O-Fe	
SFMO	7.872	0.125	-0.090	1.28	-0.328
BSFMO	7.948	0.25	0.023	1.42	-0.353
KSFMO	7.917	0.25	-0.297	0.619	**-1.166**

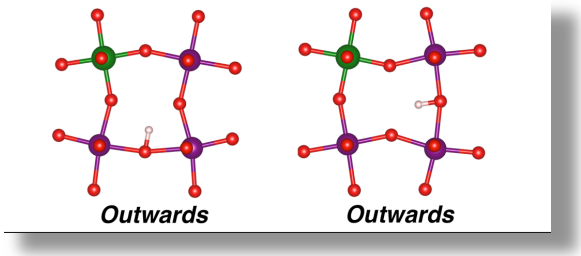




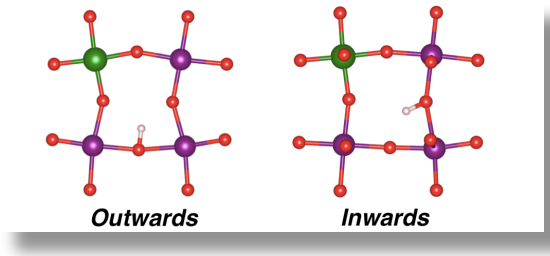
$\delta_{KSFMO} > \delta_{BSFMO} > \delta_{SFMO}$

ΔE_{hydr} ($BaCeO_3$) = **-1.63** eV

Solid State ionics , **259,** 1 (2014)



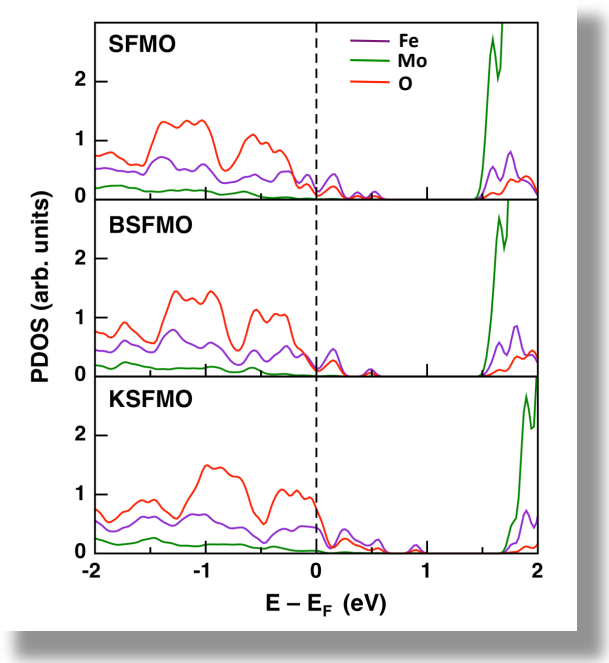
SFMO and BSFMO
- Mo-O(H)-Fe unstable
- Only *Outwards* Fe-O(H)-Fe



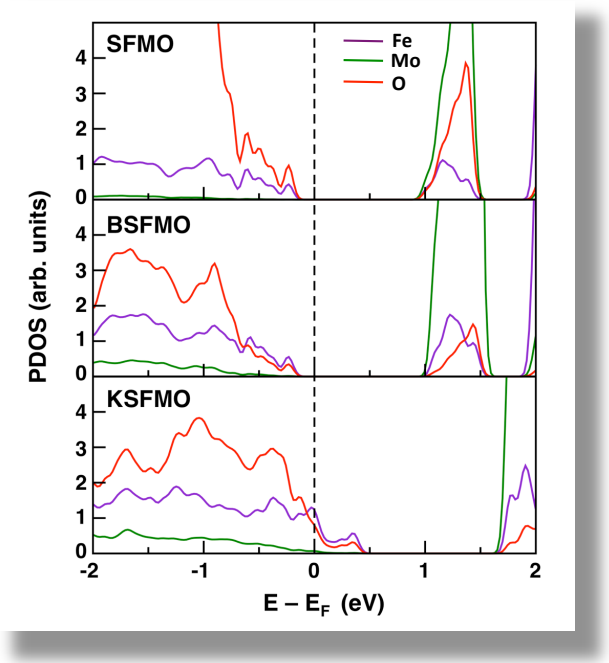
KSFMO
- Mo-O(H)-Fe stabilized by K
- Both *Outwards* and *Inwards* Fe-O(H)-Fe

electronic structure

dry



fully hydrated



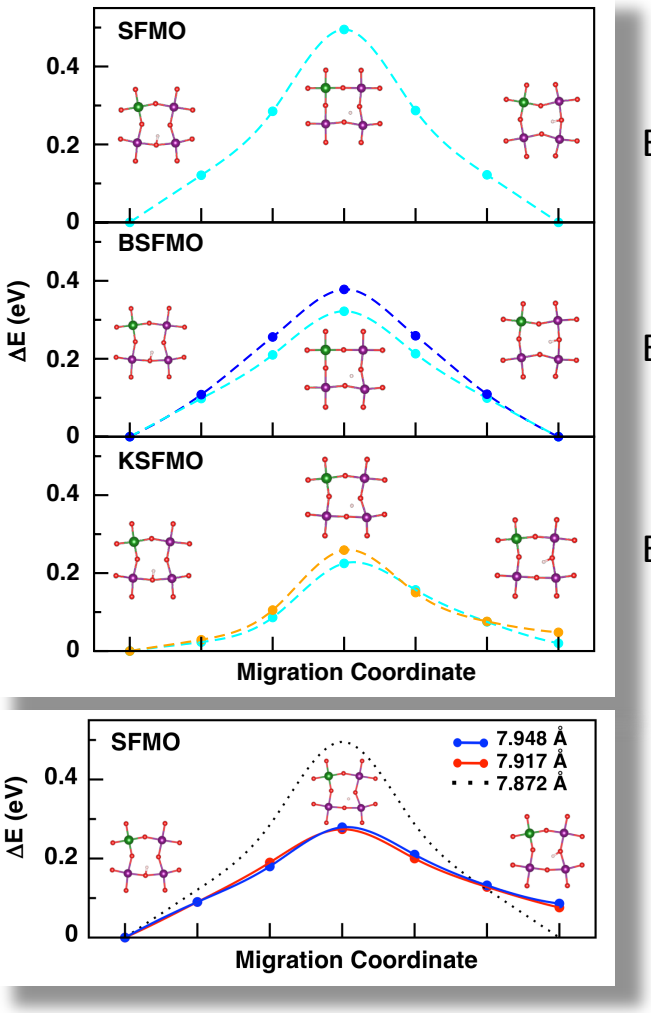
dry SFMO, BSFMO, KSFMO
MIEC

hydration affects carrier mobility in
SFMO and BSFMO

fully hydrated KSFMO likely performs as good electron conductor

Ana B. Muñoz-Garcia, Michele Pavone *Chem. Mater.* **2016**, *28, 490*

proton migration



E_{migr} in $BaCeO_3$ = 0.26 eV

Solid State ionics , **259,** 1 (2014)

E_{migr} = 0.495 eV

→ Concerted rotation

E_{migr} = 0.322/0.378 eV

→ Concerted rotation

E_{migr} = 0.225/0.259 eV

→ **NO** rotation

SFMO at BSFMO/KSFMO volumes

E_{migr} = 0.275 eV

→ **NO** rotation

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electrocatalytic capabilities

oxygen reduction reaction (ORR)

$$O_2 + 2H_2 \rightarrow 2H_2O$$

$$*O_2 + 1H^+ + 1e^- \rightarrow *OOH$$
$$*OOH + 1H^+ + 1e^- \rightarrow *O + H_2O$$
$$*O + 1H^+ + 1e^- \rightarrow *OH$$
$$*OH + 1H^+ + 1e^- \rightarrow * + H_2O$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

oxygen evolution reaction (OER)

$$2H_2O \rightarrow O_2 + 2H_2$$

$$* + H_2O \rightarrow *OH + 1H^+ + 1e^-$$
$$*OH \rightarrow *O + 1H^+ + 1e^-$$
$$*O + H_2O \rightarrow *OOH + 1H^+ + 1e^-$$
$$*OOH \rightarrow *O_2 + 1H^+ + 1e^-$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Nørskov computational NHE

$$\Delta G_{1-4} = \Delta E + (\Delta ZPE - T\Delta S) - eU$$

U=0 $\quad \mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2)$

$$U_{ONSET} \Rightarrow \Delta G_{1-4}^{ORR/OER} \leq 0$$

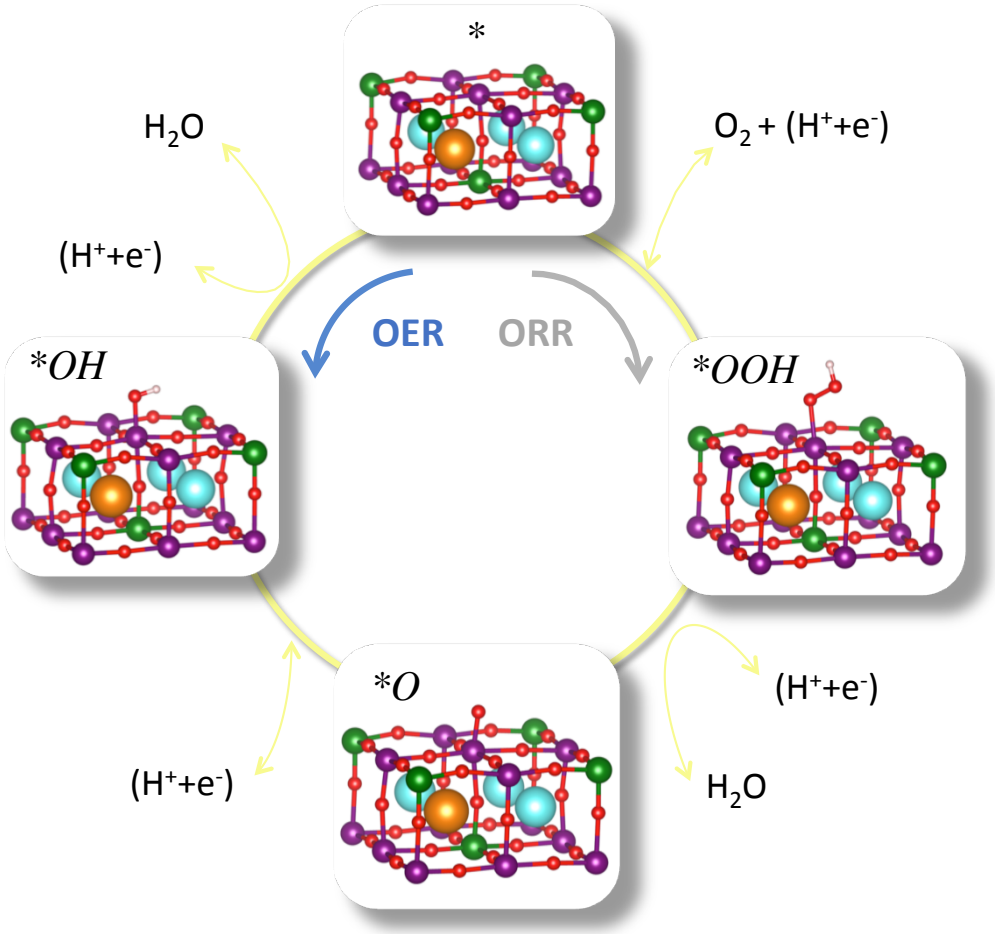
U≠0 $\quad \mu(H^+) + \mu(e^-) = \frac{1}{2}\mu(H_2) - eU$

$$\eta^{ORR} = 1.11V - U_{ONSET}$$

$$E^O_{H_2O/O_2} = 1.23V \Rightarrow E^{DFT}_{H_2O/O_2} = 1.11V$$

$$\eta^{OER} = U_{ONSET} - 1.11V$$

ORR/OER reaction pathways

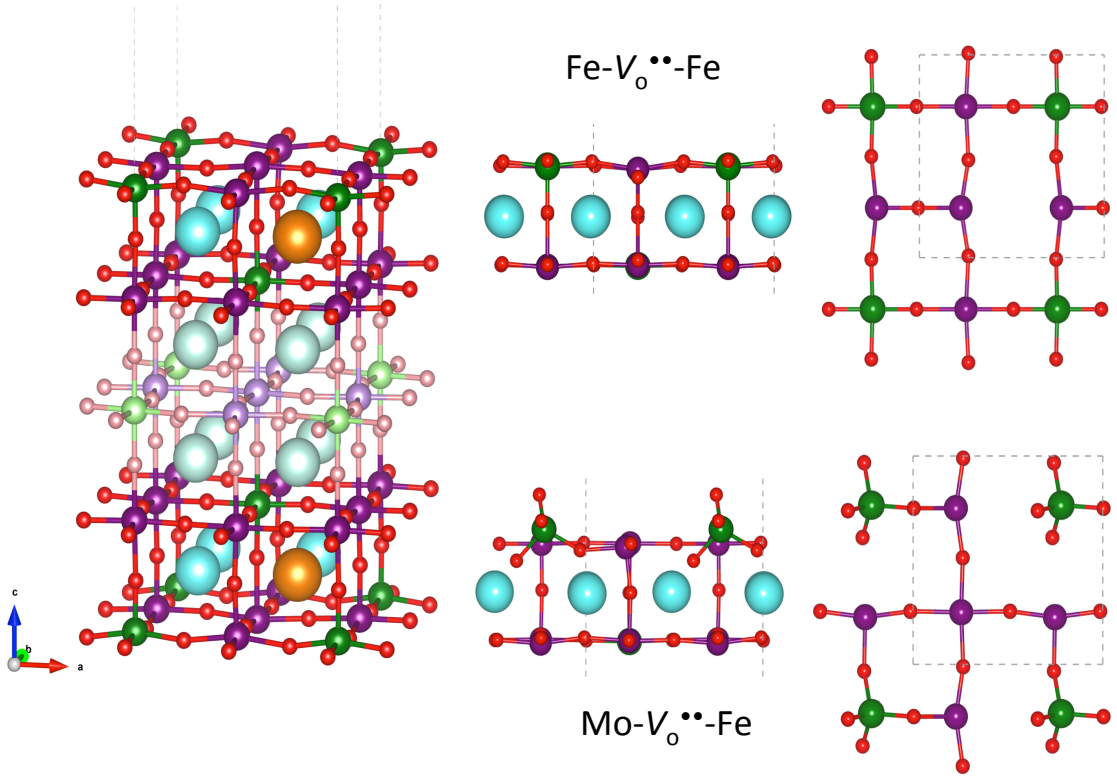


Stoichiometric
- Non-equivalent Fe
- Mo

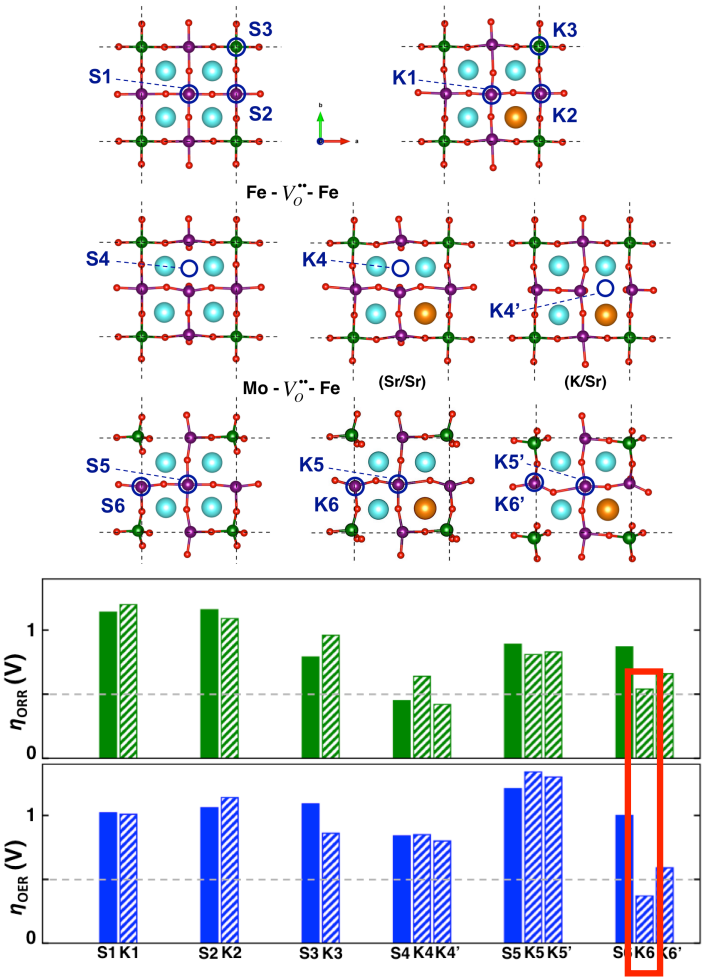
Non-Stoichiometric
- O_{Vac}
- Adjacent Mo, Fe

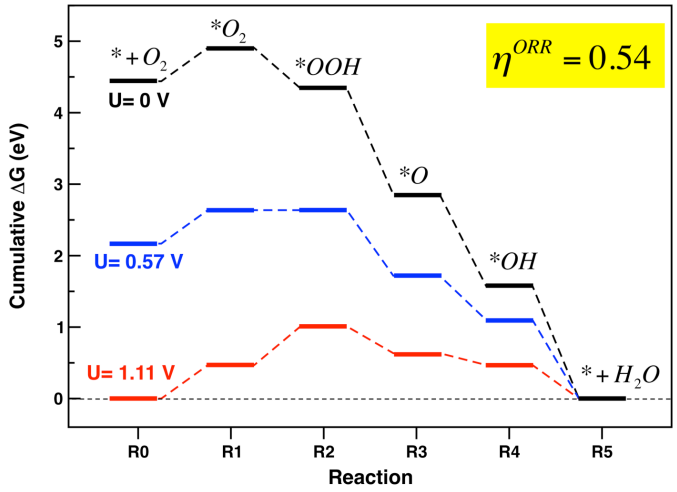
15 different pathways

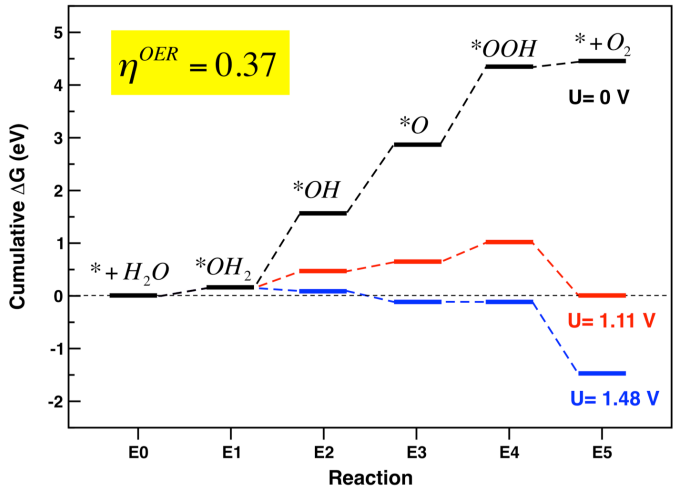
SFMO/KSFMO surface slab



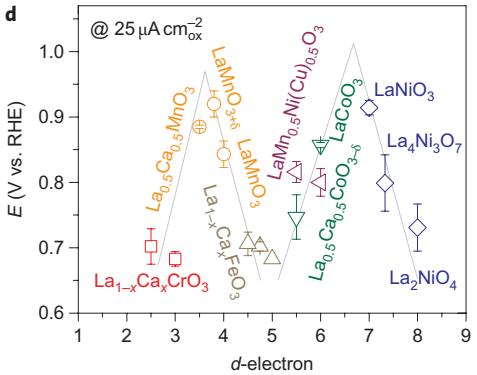
SFMO/KSFMO overpotentials





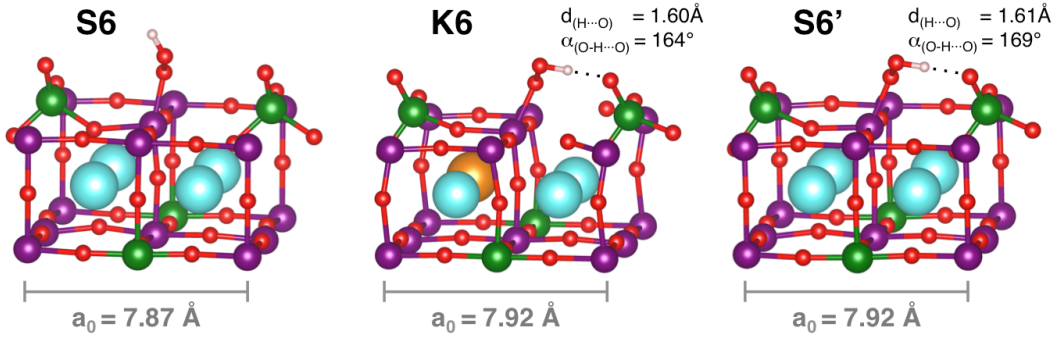


KSFMO key features



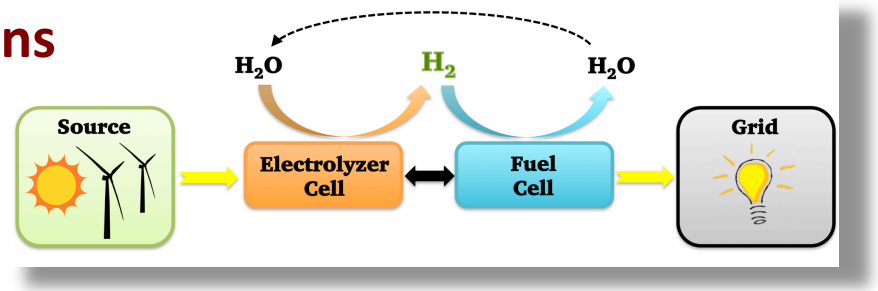
- Fe d occupancy is ideal for ORR
  - μ_{Fe} (K6) = 3.4 μ_B

J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J.B. Goodenough, Y. Shao-Horn, *Nat. Chem.* **2011**, 3, 546



- Stabilization of key reaction intermediate allows for convenient OER

PC-SOFC/EC: conclusions



TCO features of A-doped SFMO explored with first-principles calculations

- KSFMO presents the lowest $DE_{form}V_O$
- Only KSFMO is likely to be a good e^- conductor upon hydration
- KSFMO migration barriers are as low as those of $BaCeO_3$ (no concerted rotation)

Ana B. Muñoz-García
& M. Pavone
***Chem. Mater. 28, 490* (2016)**

Catalytic capabilities for OER/ORR explored using the TSHE

Ana B. Muñoz-García
& M. Pavone
***J. Mater. Chem. A.* 5, 12735 (2017)**

- Peculiar surface reconstruction of Mo-V_O-Fe
- Electronic structure of highly uncoordinated Fe is good for ORR in KSFMO
- OOH stabilization thanks to MoO_4 is good for OER in KSFMO

KSFMO proposed as bifunctional electrode for PC-SOFC/ECs

acknowledgements

- **Prof. Ana B. Muñoz-García** and **FPM3** group @ UNINA

First-Principles Modeling of Molecules ad Materials - July 2020

PON Ricerca e Innovazione 2014- 2020

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www.enea.it/it/Ricerca_sviluppo/lenergia/ricerca-di-sistema-elettrico