ORR/OER reaction pathways



SFMO/KSFMO surface slab



SFMO/KSFMO overpotentials





KSFMO key features



• Fe d occupancy is ideal for ORR

-
$$\mu_{\rm Fe}$$
 (K6) = 3.4 $\mu_{\rm B}$

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 H_2O H_2 H_2O H_2O

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 BaCeO₃ (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 MoO₄ is good for OER in KSFMO

KSFMO proposed as bifunctional electrode for PC-SOFC/ECs

CASE 3: *DFT-based calculations to investigate the surface reactivity of transition emtal oxides*

- ZrO₂ and Fe-doped ZrO₂ for ORR in PEMs <u>Collaboration with TUM</u>: Madkikar, Menga, Harzer, Mittermeier, Siebel, Wagner, Merz, Schuppler, Nagel, Muñoz-García, Pavone, Gasteiger, Piana
- CuFeO₂ delafossite for CO₂ photoconversion to fuels

Defective ... but effective!

Fe-doped ZrO₂ as ORR catalysts in PEMFCs

- Communication in J. Electrochem Soc (2017) ^[1]
 - Enhanced ORR activity with Fe-doped ZrO₂ catalysts wrt single components (Fe:Zr ratio 0.02-0.08, particle size < 10 nm)
- Open questions:
 - Nature of Fe coordination
 - Understanding of active sites
 - Catalyst performance in PEMFC?



 Main exp. results relevant to our DFT modeling

- ★ Dominant presence of isolated Fe³⁺ (No Fe⁰, FeC, Fe₂O₃)
- ★ Fe-containing ZrO_2 much more active than ZrO_2 or Fe (sites?, V_O)
- ★ Decrease of H_2O_2 yield for increasing catalyst loading (H_2O)



[1] Madkikar, Mittermeier, Gasteiger, Piana. J. Electrochem. Soc, 164, F831-F833 (2017)

- Joint experimental and theoretical effort:
 - XPS, NEXAFS and ⁵⁷Fe Mössbauer Spectroscopy
 - Activity of carbon-supported catalysts: RRDE & single-cell PEMFC
 - DFT

Structural models and computational details



- ZrO₂ tetragonal
- (011) surface ^[1]
- 48 f.u. (144 atoms)
- $\mathbf{Fe}_{zr} \rightarrow \sim 2\%^{\text{TOT}} \sim 6\%^{\text{SURF}}$ (at.)





Pristine vs Fe-doped ZrO₂

- V_o formation energy
- O_2 adsoprtion \rightarrow active sites
- OOH formation (1st PCET)
- H₂O vs H₂O₂ formation (2nd PCET)



DFT-PBE+U – PBC U-J (Zr d, Fe d) = 4.0 eV ^[2,3] PW-E_{cut}= 800 eV $3x3x1 \Gamma$ k-points mesh PCETs : TSHE

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

[1] Christensen et al. PRB, 58, 8050 (1998) [2] Muñoz-García et al. ACS Appl. Mat. Inter., 7, 21662 (2015) [3] Muñoz-García et al. JMCA., 5, 12735 (2017)

Fe oxidation state, surface patterns & V_{o}



Active sites for O₂ adsoprtion





Product formation & selectivity



CuFeO₂ for solar fuel production





- Low efficiencies (chained losses)
- High Overpotentials
- Poor stability

Product	Half-cell reaction	E ^o vs NHE (V)
нсоон	CO_2 + 2 H ⁺ + 2 e ⁻ \rightarrow HCOOH	-0.58
со	CO_2 + 2 H ⁺ + 2 e ⁻ \rightarrow CO + H ₂ O	-0.51
H₂CO	$\mathrm{CO_2} + 4 \ \mathrm{H^+} + 4 \ \mathrm{e^{\text{-}}} \rightarrow \mathrm{H_2}\mathrm{CO} + \mathrm{H_2}\mathrm{O}$	-0.48
CH₃OH	CO_2 + 6 H ⁺ + 6 e ⁻ \rightarrow CH_3OH + H_2O	-0.39
CH₄	CO_2 + 8 H ⁺ + 8 e ⁻ \rightarrow CH_4 + 2 H ₂ O	-0.24
H ₂	2 H ₂ O + 2 e [.] →H ₂ + 2 OH [.]	-0.41

Acqueous media

- Poor selectivity
- Competition with HER
- High PCET kinetically hindered

CuFeO₂

- E_a=1.52 eV
- $p-doped \rightarrow IPCE 14\%$, HCOOH production ^[1]
- CuFeO₂/CuO tuned to HCOOH/acetate ^[2]
 - CO₂ activation on CuFeO₂ surface?
 - Reaction Mechanism?
 - It is possible to go beyond HCOOH?



Onset Potentials



Routes for methanol production



- Enhance CO route by stabilizing 1° PCET on O (1b)
- For 1st PCET on C route find the way to stabilize adsorbed H₂CO (4a)

Electrocatalysis: conclusions & perspectives

- ★ DFT picture compatible with experimental outcomes
- ***** Fe_{Zr} in ZrO_2 is Fe^{3+} (HS)
- **\star** Fe induces V_O in ZrO₂
- ★ Different nature of active sites for ORR
 - ★ ZrO_2 → surface Zr
 - ★ Fe:ZrO₂ → Fe-V₀Zr and Zr-V₀-Zr
- ★ Product selectivity explained
 - ★ 1st PCET make (mainly) stable OOH species in both materials
 - * 2^{nd} PCET forms H_2O_2 on ZrO_2 and H_2O (with some H_2O_2) in Fe: ZrO_2



- \star Surface oxygen vacancies needed to activate CO_2
- ★ In agreement with experiments, our calculations predict that HCOOH is the main CO₂RR product

ORR on

Fe-doped ZrO₂

- ★ Lowest U_{ONSET}
- ★ HCOOH desorption
- **★** Promising features to get to methanol:
 - \star CO stable on CuFeO₂
 - ★ Low U_{ONSET}

Density Functional Embedding Theory

Problem: To treat a localized feature (*e.g.* impurity, vacancy, etc.) embedded in an infinite background.Challenge: Need explicit treatment of electron correlation, beyond that provided by Kohn-Sham DFT.





Strategy: Model as a finite cluster in a QM-based effective extended crystal potential v_{emb} .

Partition of the total system into a cluster region (*I*) and background/environment (*II*)

$$E_{tot}[\rho_{tot}] = E_{cluster}[\rho_{cluster}] + E_{env}[\rho_{env}] + E_{int}[\rho_{cluster}, \rho_{env}]$$

$$V_{emb}[\rho_{cluster}, \rho_{env}] = \frac{\delta E_{int}}{\delta \rho_{cluster}}$$

• Accurate QM for cluster region (e.g., CASPT2, MRSDCI)

• Embedding potential: low level QM method, e.g. DFT

C. Huang, M. Pavone, E. A. Carter J. Chem. Phys. 2011, 134, 154110

beyond DFT => oxygen reduction on Al(111)

- a benchmark case: O₂ approaching an ideal Al (111) surface => discrepancy between experiment and theory.
- experiments consistently suggest the existence of an energy barrier preventing low-energy sticking.
- conventional KS-DFT shows no such barrier.

We employed a density-fuctional embedding theory

- Al(111) surface slab described with LDA (VASP)
- O₂ and O₂-Al_n clusters with CASPT2 (MOLCAS)





F. Libish, C. Huang, P. Liao, M. Pavone, E. A. Carter Phys. Rev. Lett. 2012 109, 198303

O₂ on Al(111)



F. Libish, C. Huang, P. Liao, M. Pavone, E. A. Carter Phys. Rev. Lett. 2012 109, 198303

O₂ on Al(111)



	No. of atoms				
Site	1st layer	2nd layer	Orientation	$E^{\text{barrier}} \pm \delta \text{ (meV)}$	$L_{\text{Al-O}_2}^{\text{barrier}}$ (Å)
bridge	8	6		560 ± 10	2.4
	8	6	\bot	450 ± 30	2.7
fcc	6	6		430 ± 20	2.4
	6	6	\bot	360 ± 10	2.9
hcp	6	6		410 ± 10	2.5
	6	6	\bot	410 ± 20	2.9
top	7	3	I	660 ± 20	2.6
	7	3	\perp	660 ± 20	2.8
experiment				$\lesssim 600$	



- ECW predicts correct barrier heights
- Analysis shows the origin is a CT

F. Libish, C. Huang, P. Liao, M. Pavone, E. A. Carter Phys. Rev. Lett. 2012 109, 198303

Density Functional Embedding Theory (DFET) for molecular and extended covalent systems

- So far ECW have only be applied for systems with well defined partitions
- There are problems for covalent systems and dangling chemical bonds

dehydrogenation energies (eV)

	ONIOM (PBE0:LDA)	Embed (PBE0:LDA)	PBEO
(a)	3.42	3.50	3.55
(b)	5.05	5.05	5.05
(c)	4.79	4.65	4.71
(d)	5.30	5.00	4.98

C. Huang, A. B. Muñoz-Garcia, M. Pavone J. Chem. Phys. 145, 244103, 2016

Density Functional Embedding Theory (DFET) for molecular and extended covalent systems

electron densities for the graphene partitions

C. Huang, A. B. Muñoz-Garcia, M. Pavone J. Chem. Phys. 145, 244103, 2016

DFT-based embedding: conclusions and perspectives

- DFET allows for multi-scale ab initio calculations of complex systems, focusing the computational efforts for post-HF level of theory on a limited portion of the total system
- An effective scheme can be exploited to study covalent extended systems as for example graphene, carbon nanotube
- DFET study of complex molecular systems where long range electronic polarization effects are not described by ONIOM or QM/MM
- DFET for spectroscopic properties: solid state NMR
- DFET for molecular dynamics

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