Understanding O_2 Electrocatalysis for Clean Energy Technologies

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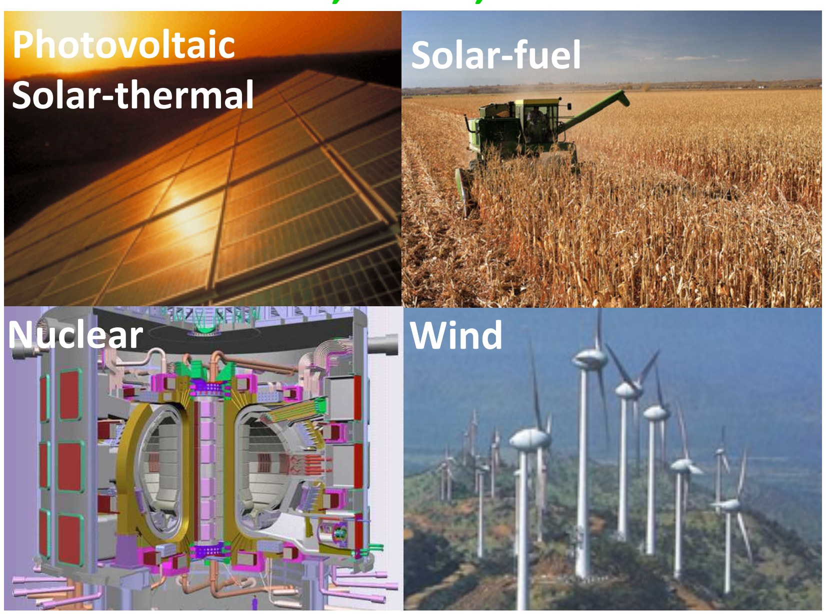
Energy Storage for a Sustainable Future

Current Energy Supply (~90% fossil)

→ Supply Challenge
→ Unsustainable
→ CO_2 emission

Future Energy Supply (no net carbon)

→ Efficient, clean, sustainable



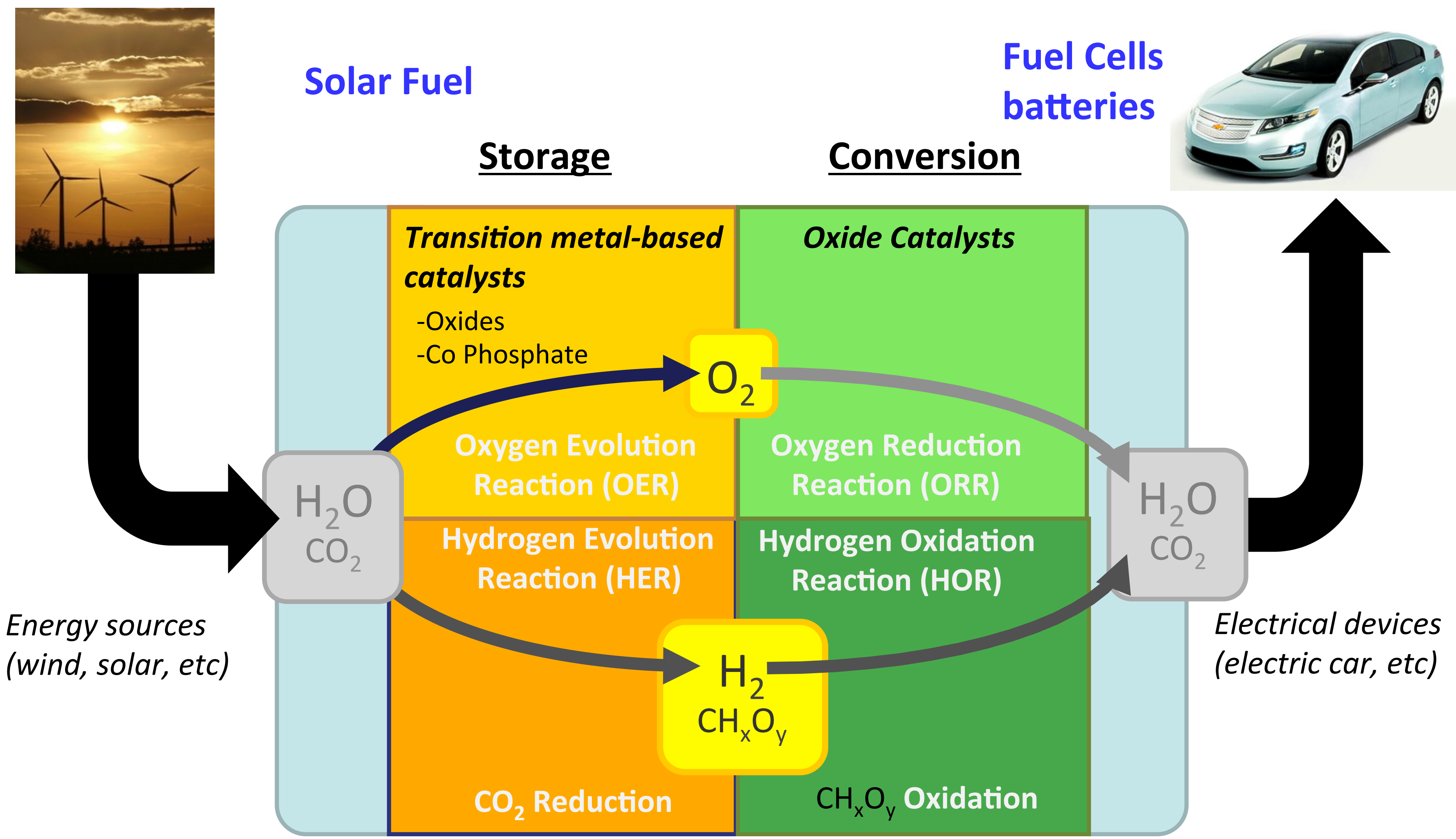
Bridge the gap

Energy
(1) Conversion
and
(2) Storage
Technologies

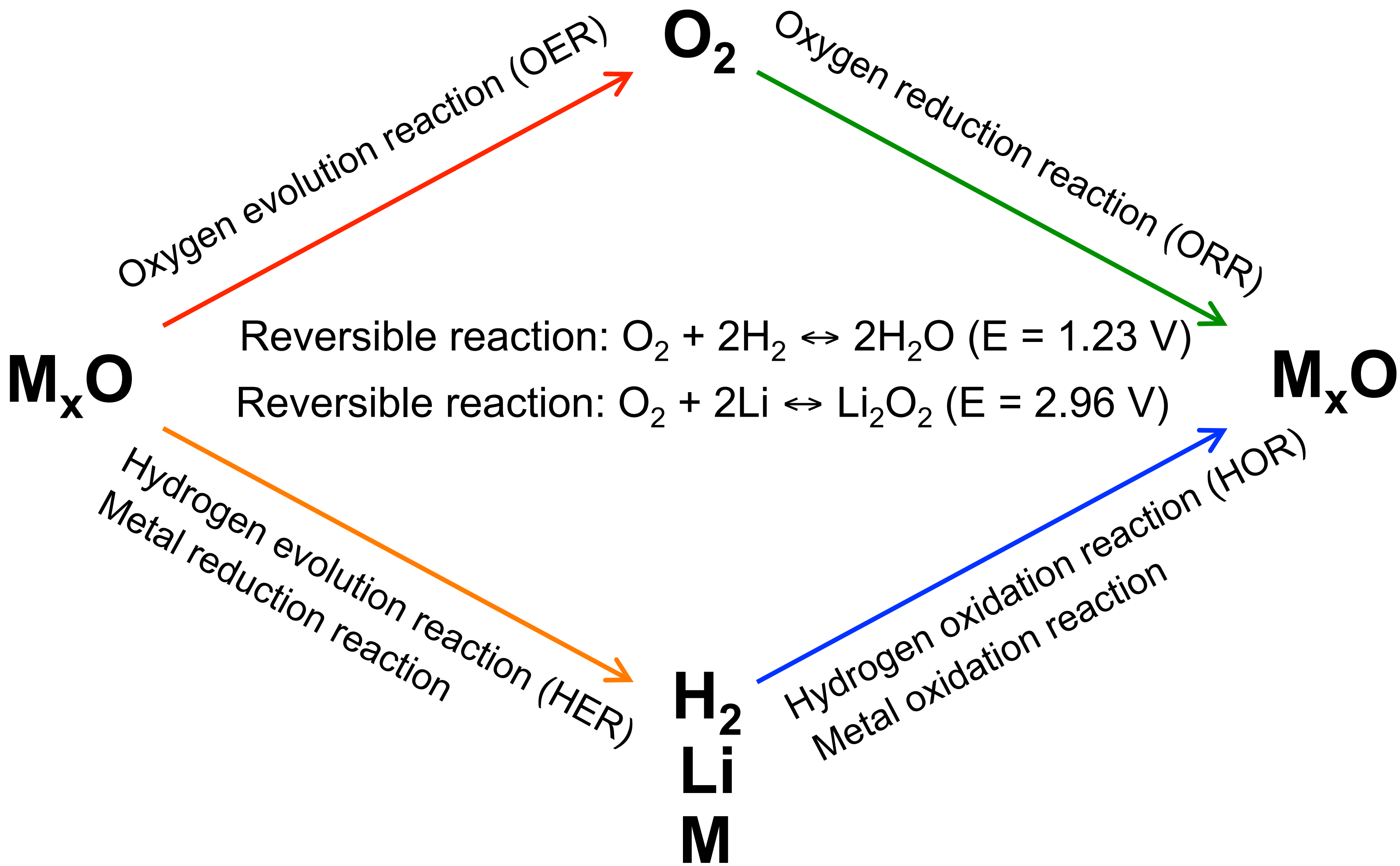
Oxygen Reduction and Evolution Critical to Clean Energy Technologies

Source: Reuter Pictures

Source: http://www.gm-volt.com

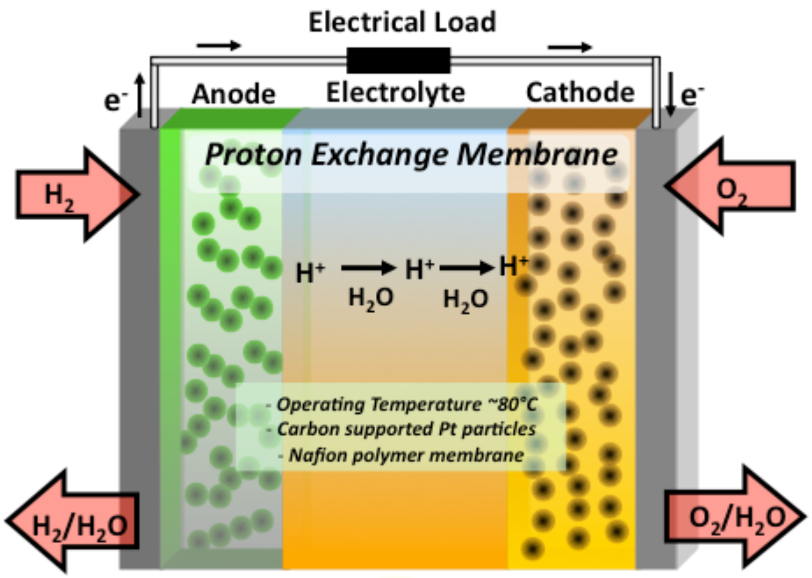


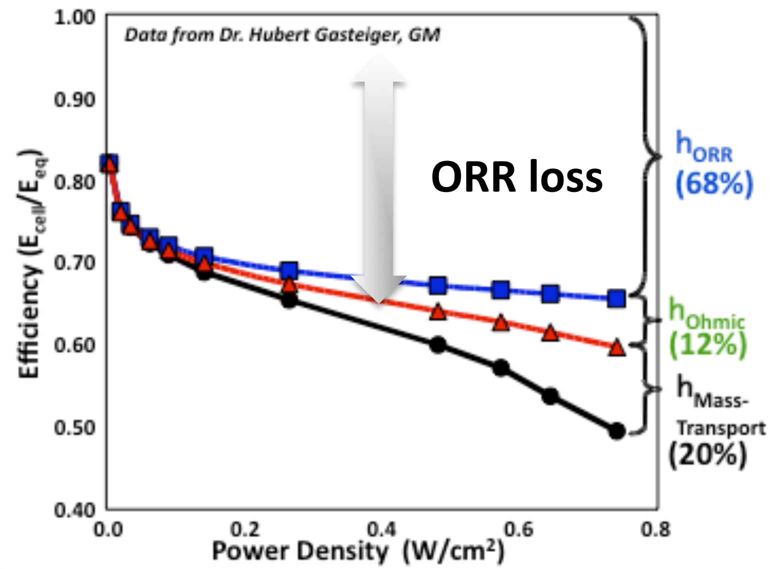
H_2/Li/M storage for clean energy technologies

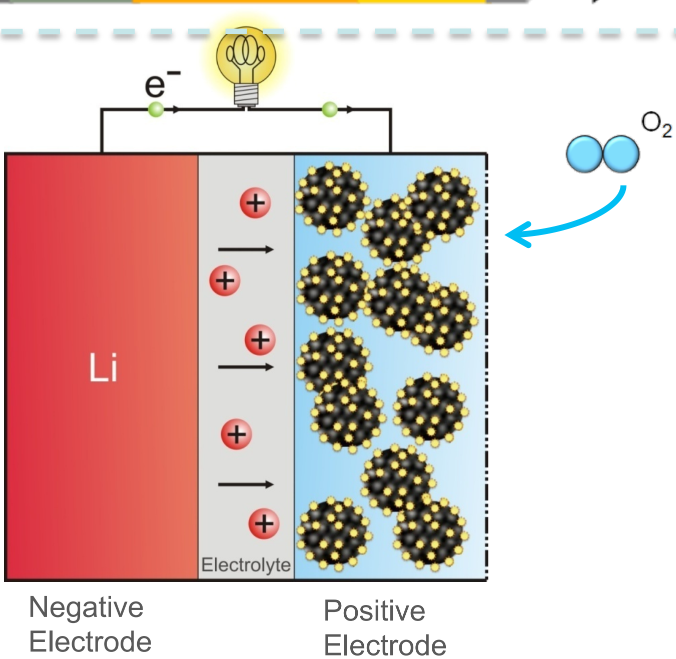


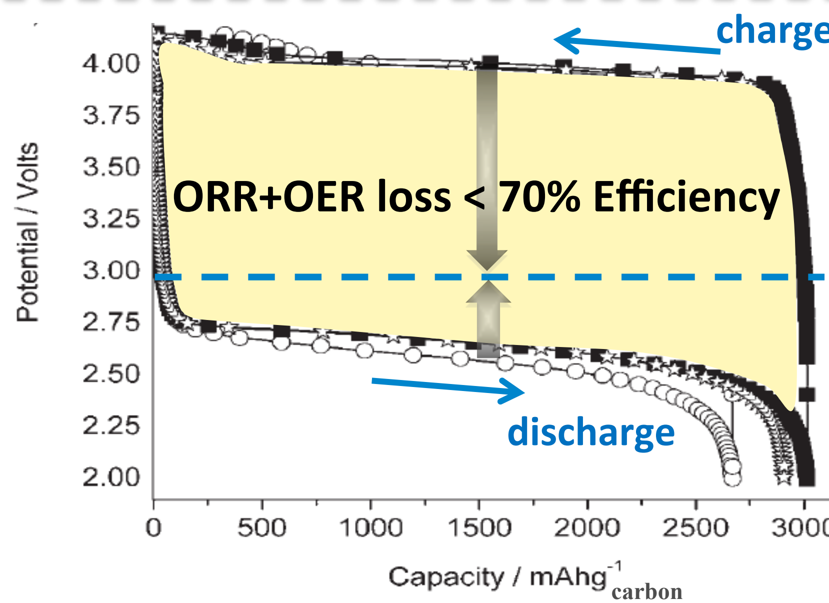
Understanding and using the redox of oxygen is at the heart of clean energy technology development

O_2 Electrocatalysis in Fuel Cells + Li-Air Batteries





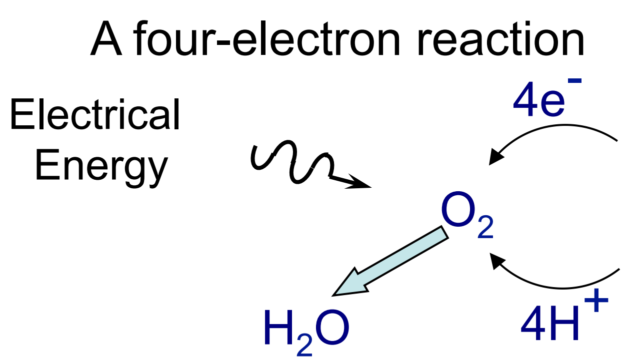




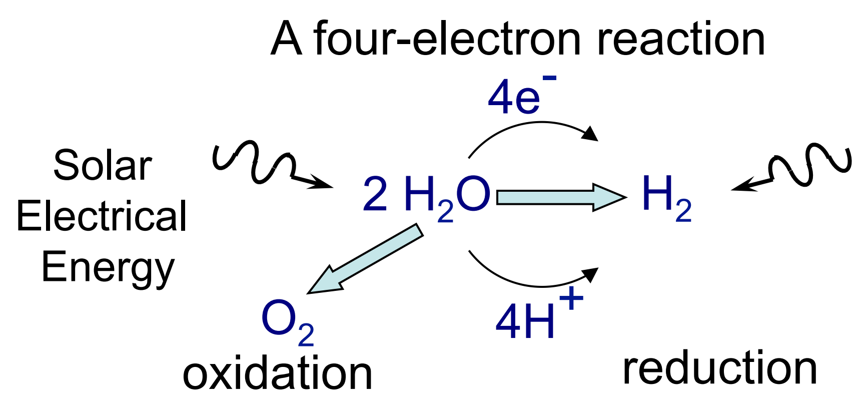
A. Débart et al, *Angew. Chem. Int. Ed.* *47* (2008) 4521

Scientific Challenges

Oxygen Reduction Reaction
(ORR)

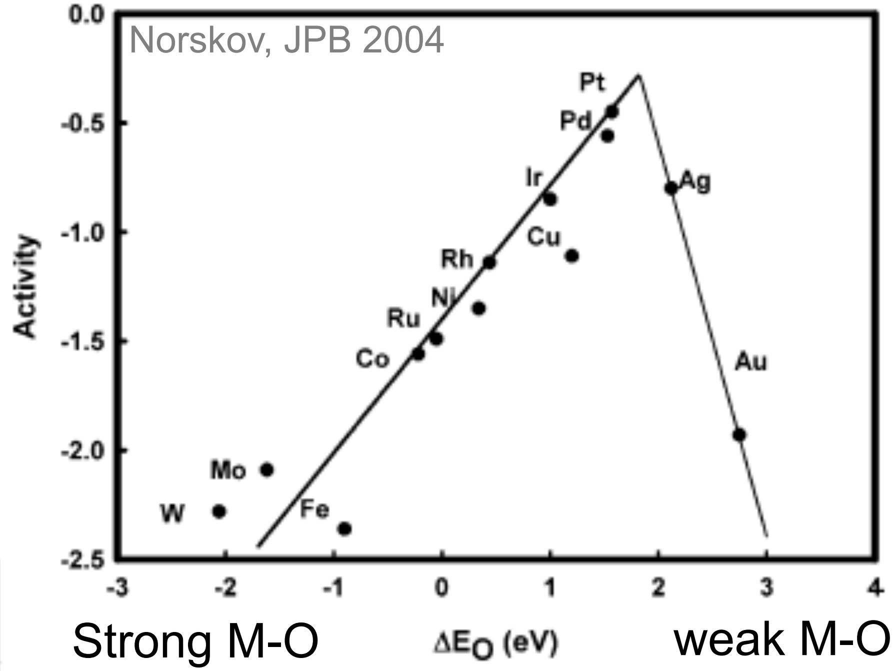


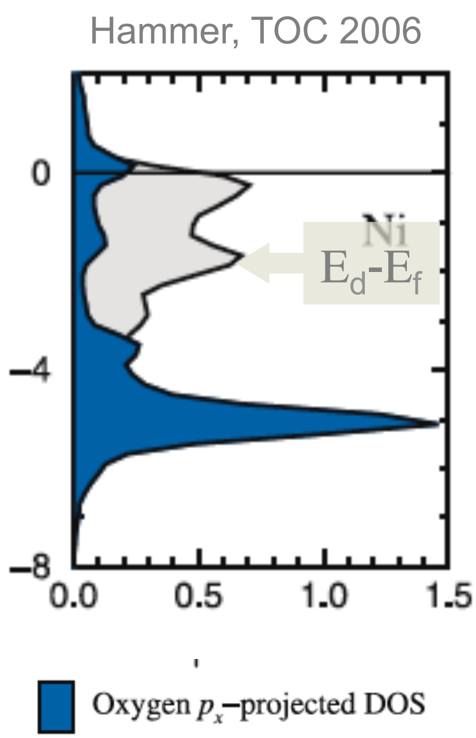
Oxygen Evolution Reaction
(OER)

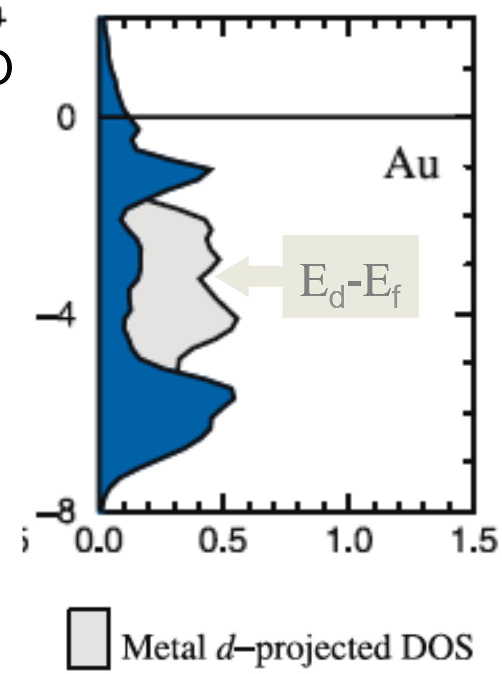


Understand catalytic processes at the molecular level
Design new catalysts and materials for energy storage

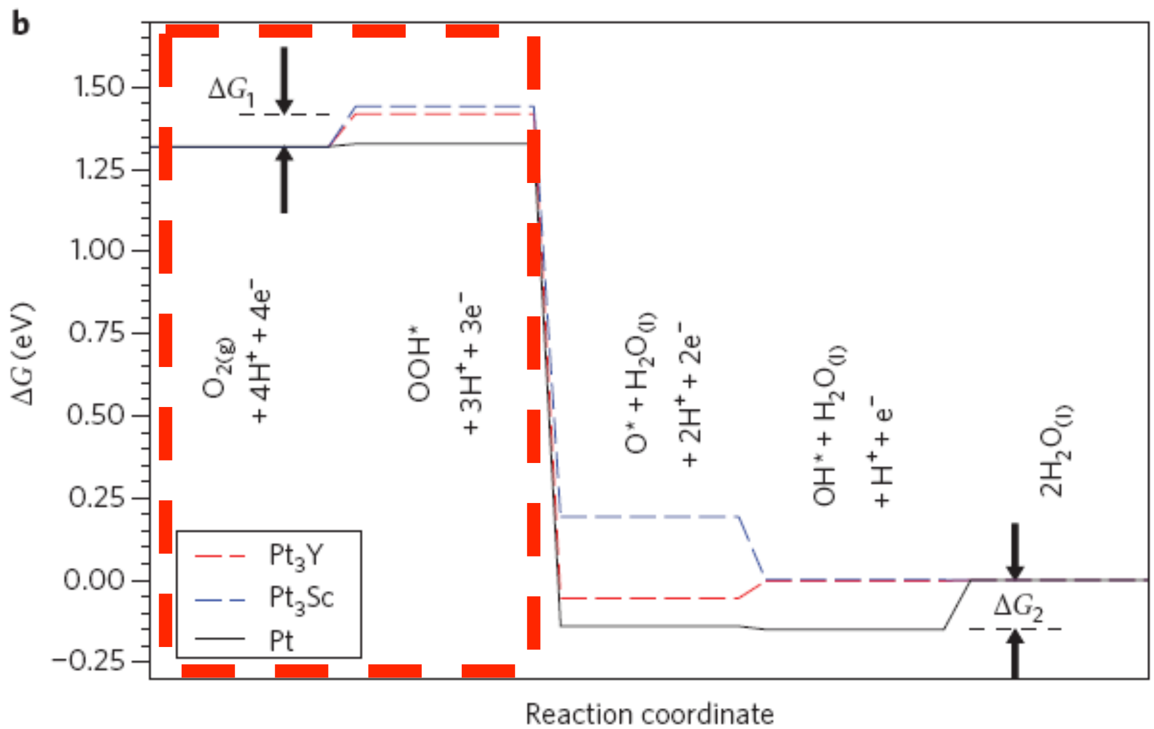
Electronic Structure => O Binding => ORR Activity

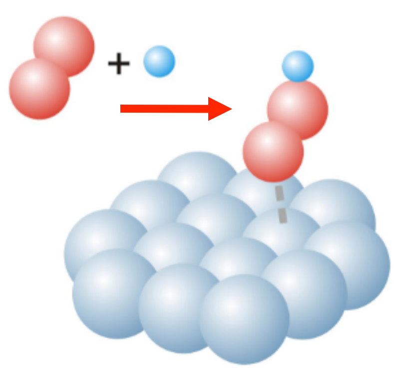






Current understanding of ORR mechanism on Pt

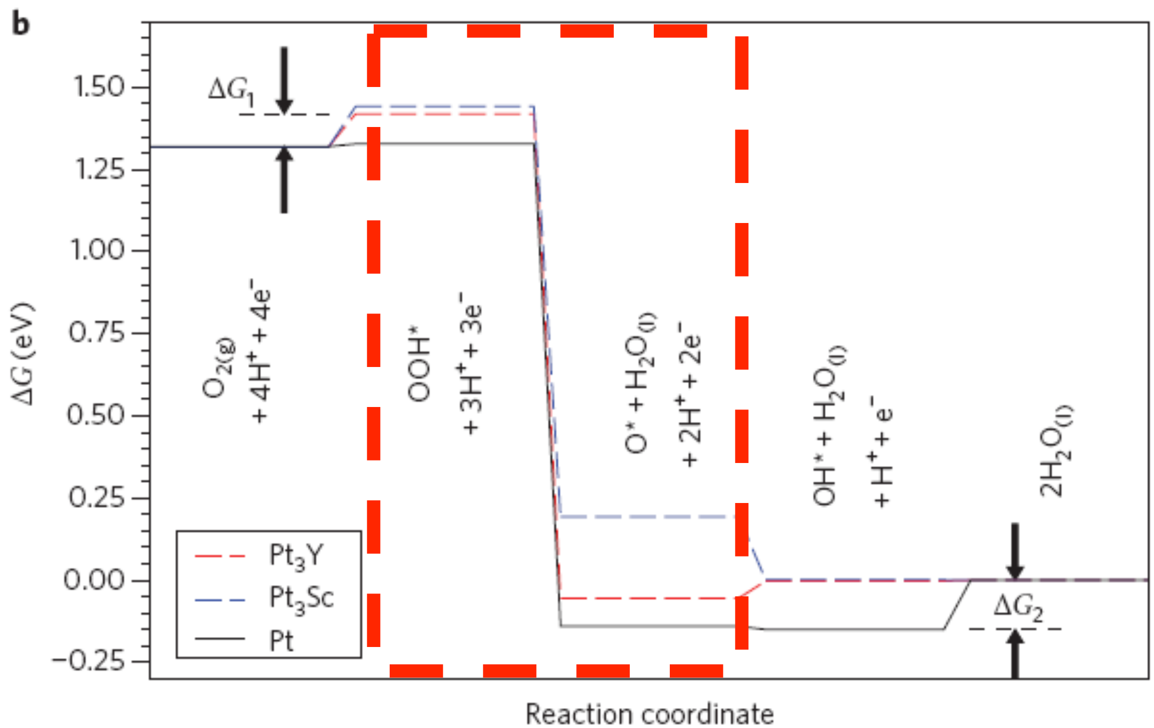


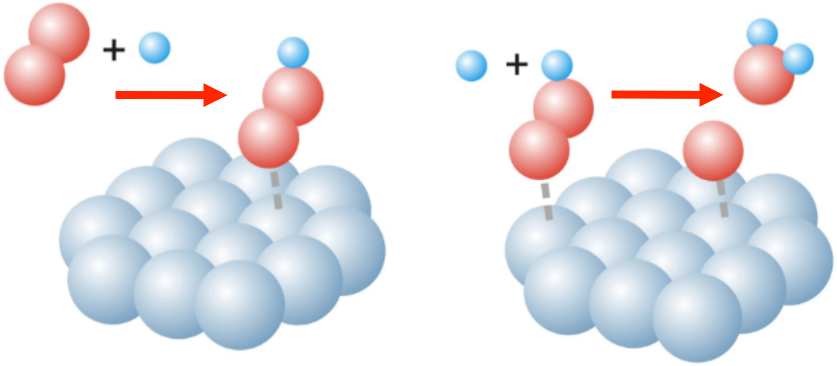


J.K. Norskov, et al, *J. Phys. Chem. B* **108** 46 (2004)

J. Greeley, et al, *Nature Chem* 1 (2009)

Current Understanding of ORR mechanism on Pt





J.K. Norskov, et al, *J. Phys. Chem. B* **108** 46 (2004)

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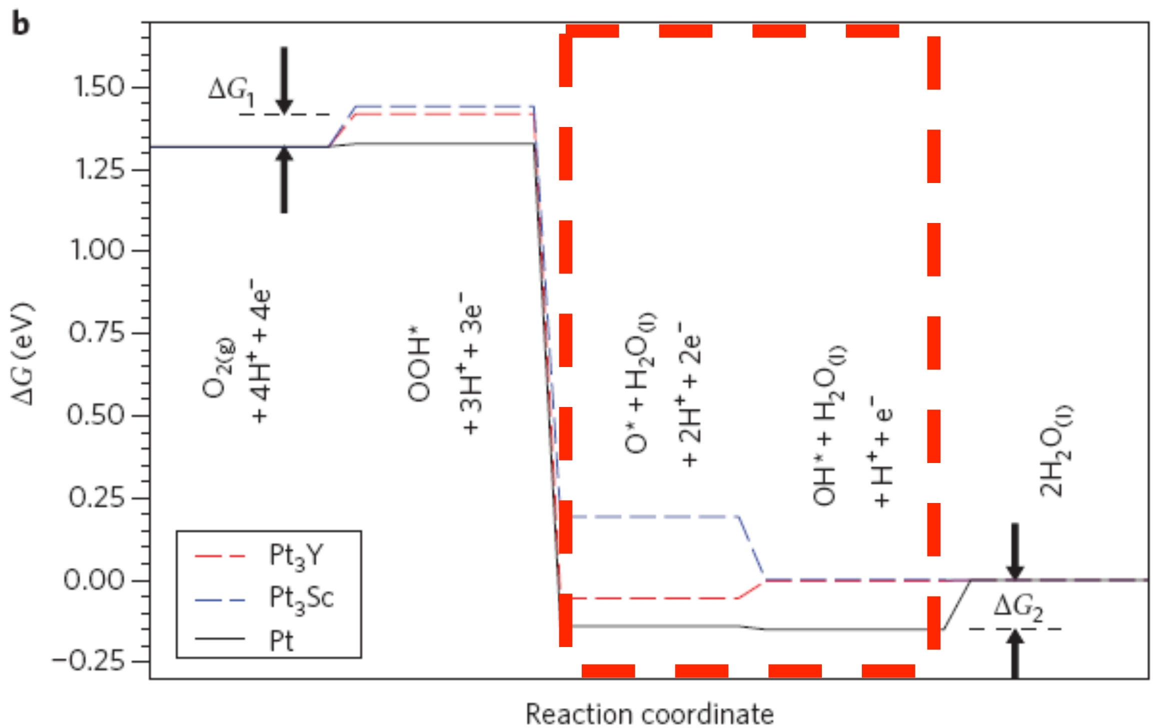
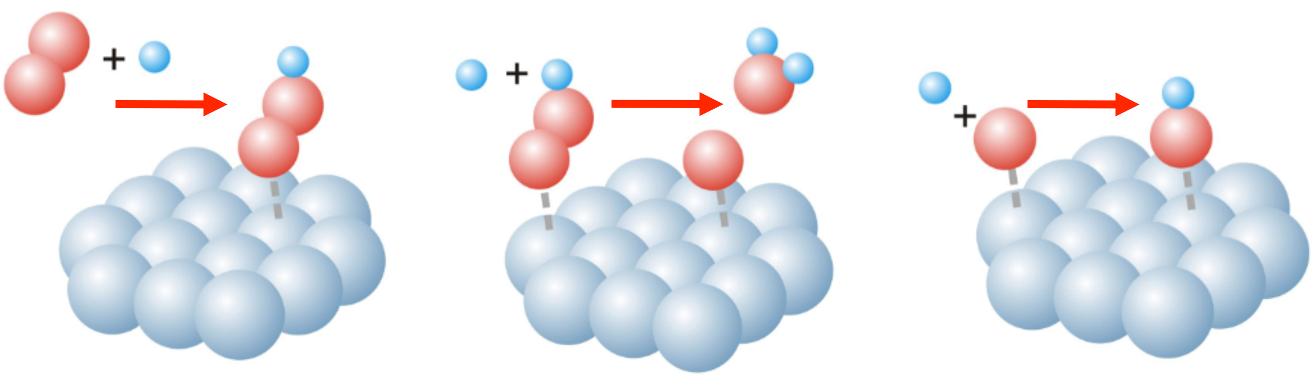
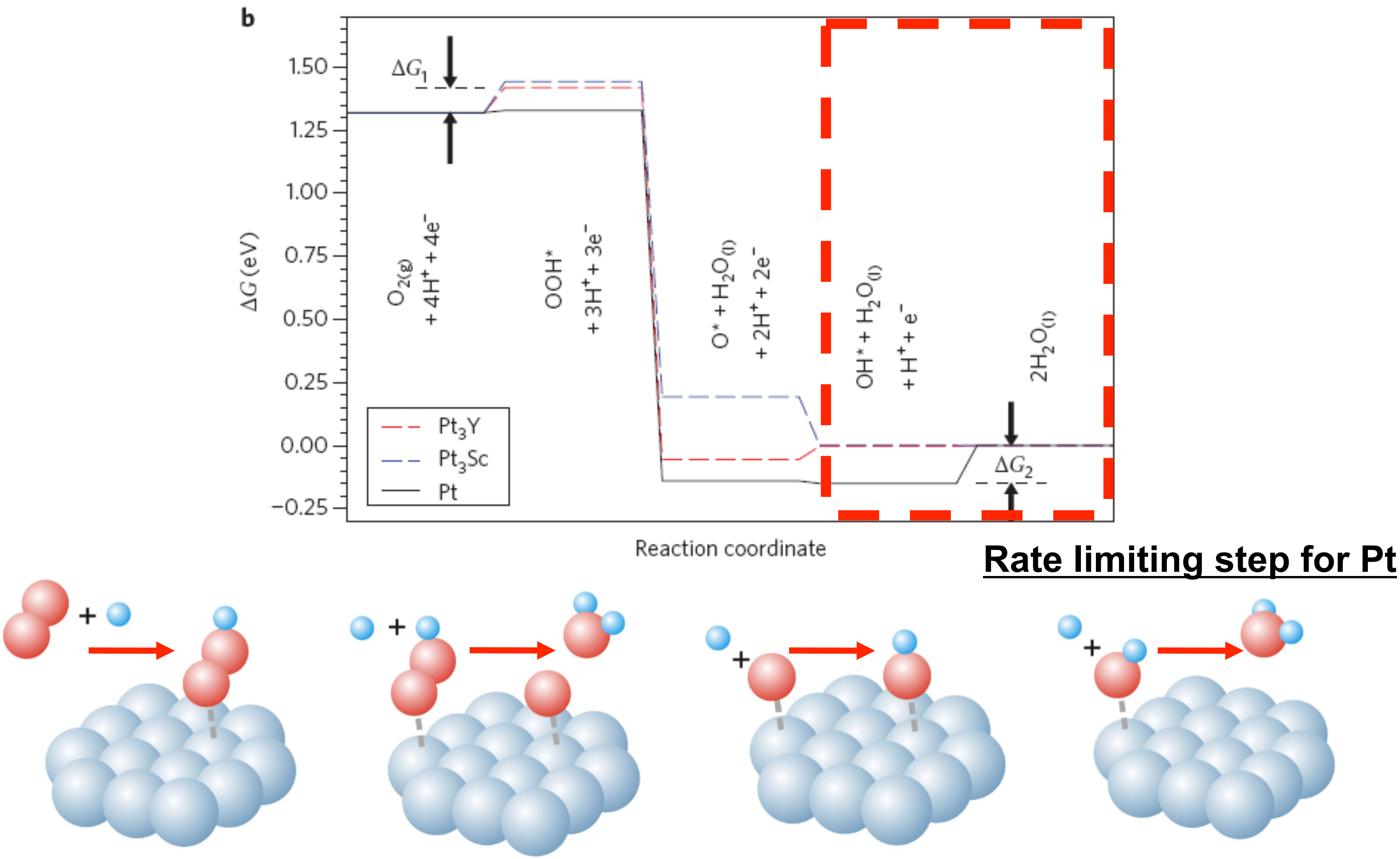




J.K. Norskov, et al, *J. Phys. Chem. B* **108** 46 (2004)

J. Greeley, et al, *Nature Chem* 1 (2009)

OH binding on Pt surface limits the ORR kinetics

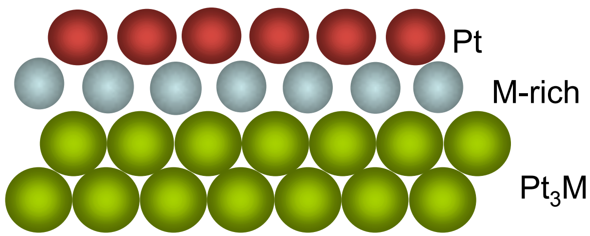


J.K. Norskov, et al, *J. Phys. Chem. B* **108** 46 (2004)

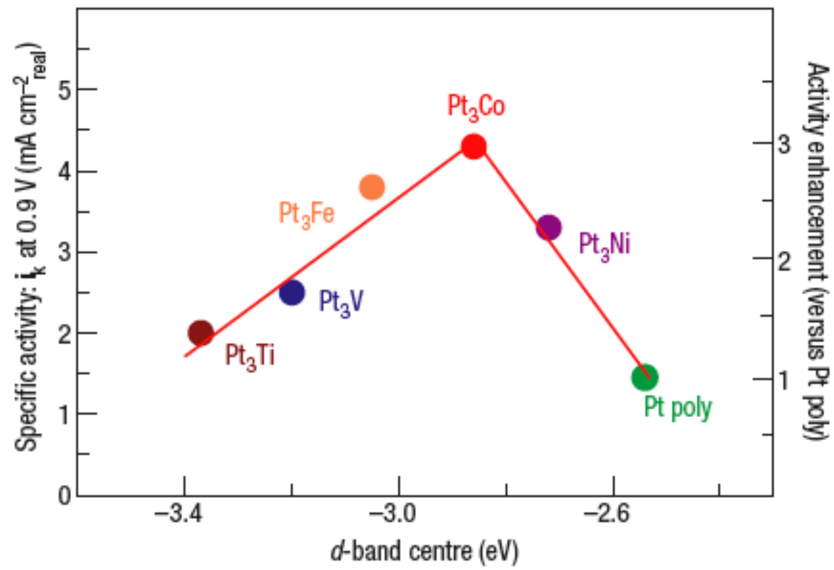
J. Greeley, et al, *Nature Chem* 1 (2009)

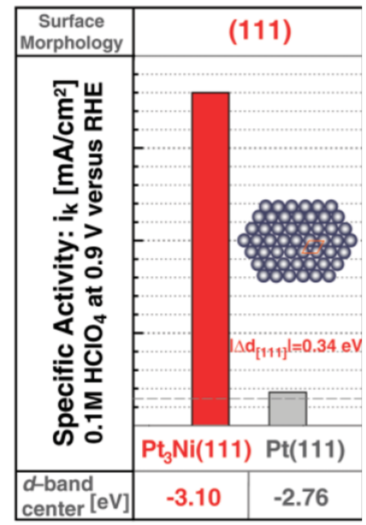
Modifying Surface Electronic Structure to enhance ORR activity on Pt-alloy surfaces

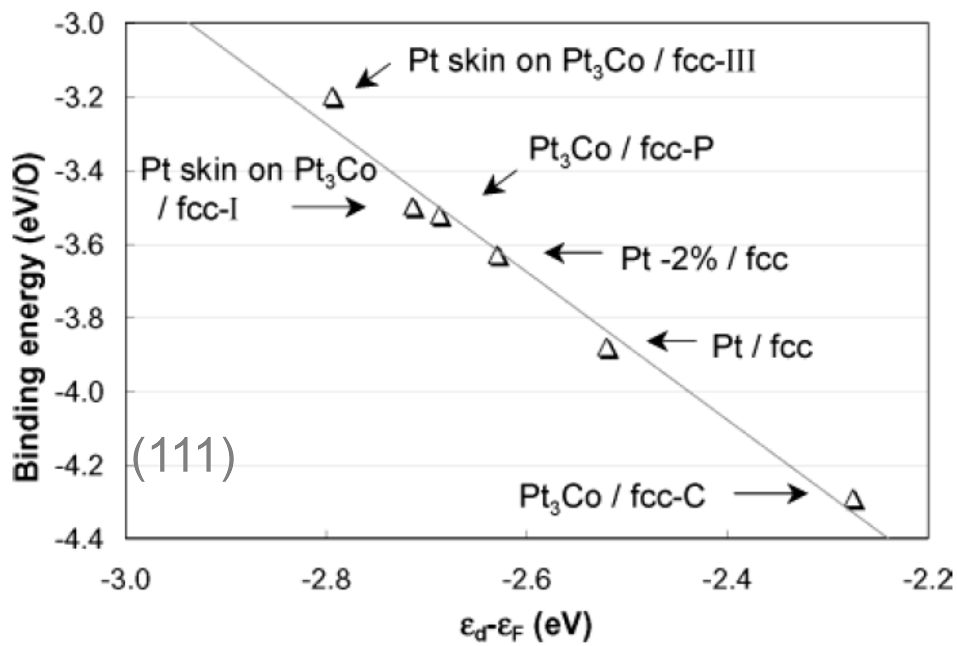
Pt Surface Segregation



Shortened Pt-Pt bond
Ligand effects



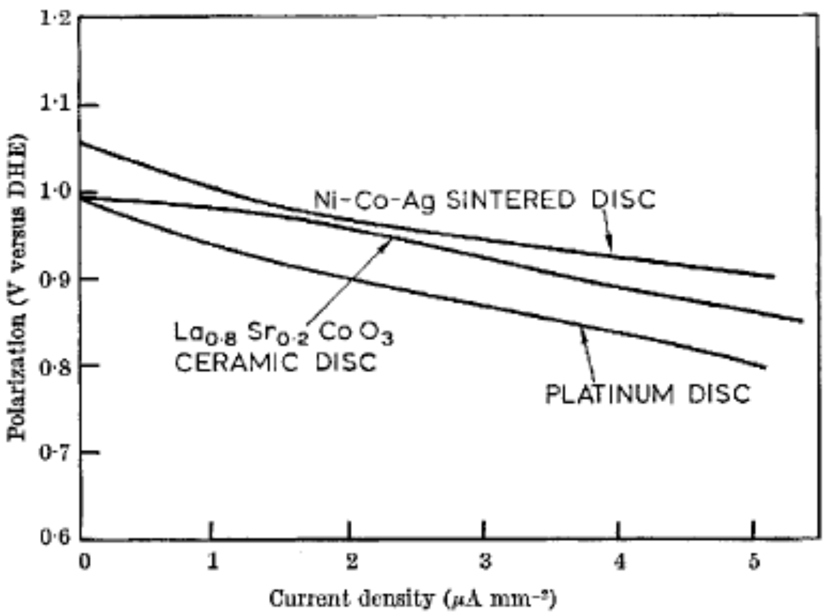


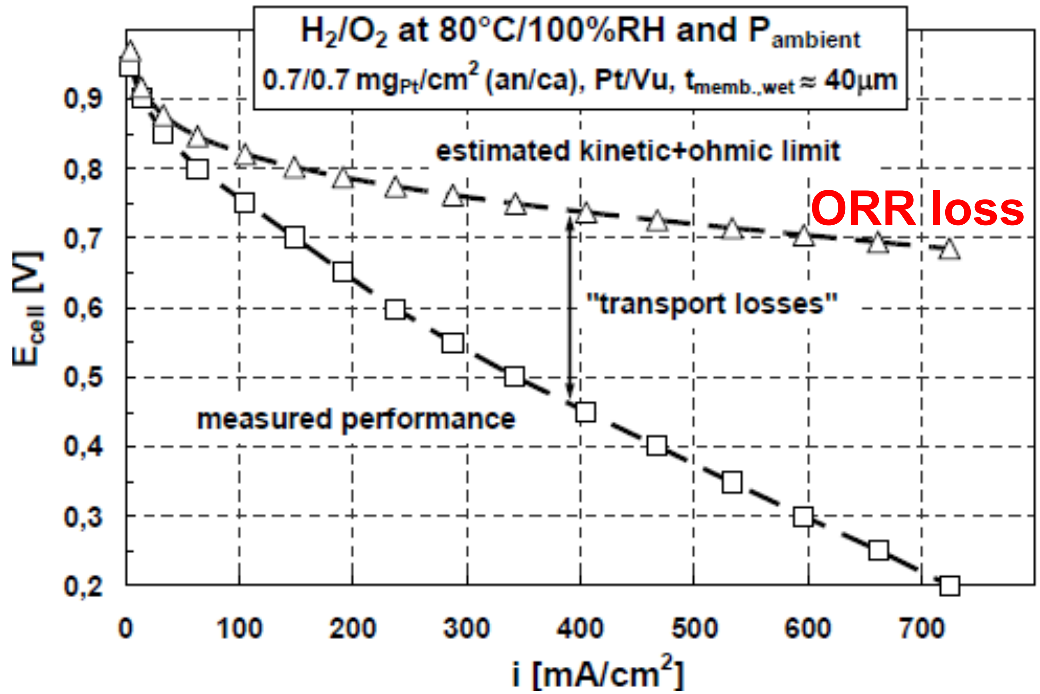


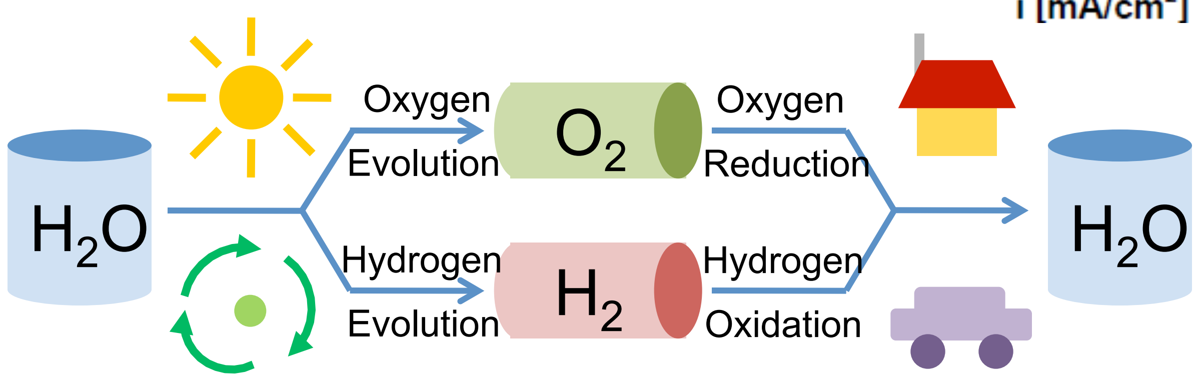
Norskov et al., Angew. Chem (2006) and JPCB 2004
Marvrikakis et al., JACS 2004
Marvrikakis and Novskov et al, PRL 1998
Kitchin et al. PRL 2004

Stamenkovic *et al*. Science 2007 and Nature Materials (2007)

Non-noble-metal-containing oxides for ORR at high PHs







D.B. Meadowcroft, *Nature* **226** 847 (1970)

A. Filpi, et al., *ECS Transactions* ***16*** (2008)

Perovskites for O_2 reduction and evolution

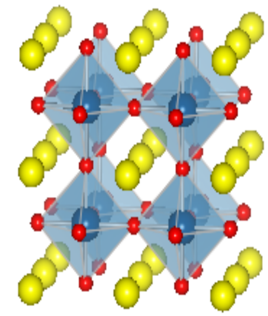
Objective

Search for ORR activity descriptor on oxide surfaces

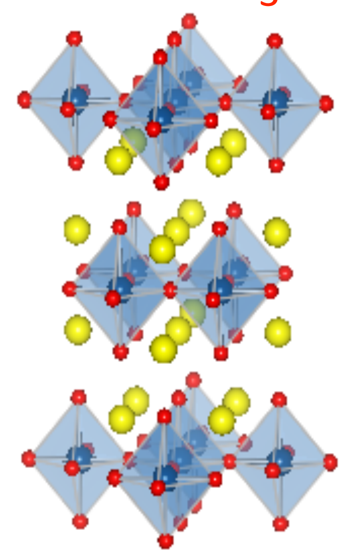
$$O_2 + 2H_2O + 4e \Leftrightarrow 4OH^-$$

Flexible Chemistry

-$LaBO_3$(B = Cr, Mn, Fe, Co, Ni)
-$La_{n+1}B_nO_{3n+1}$ (n = 1, 2, 3, and infinity)
-$LaA'BB'O_3$ (A- and B-site substitution)

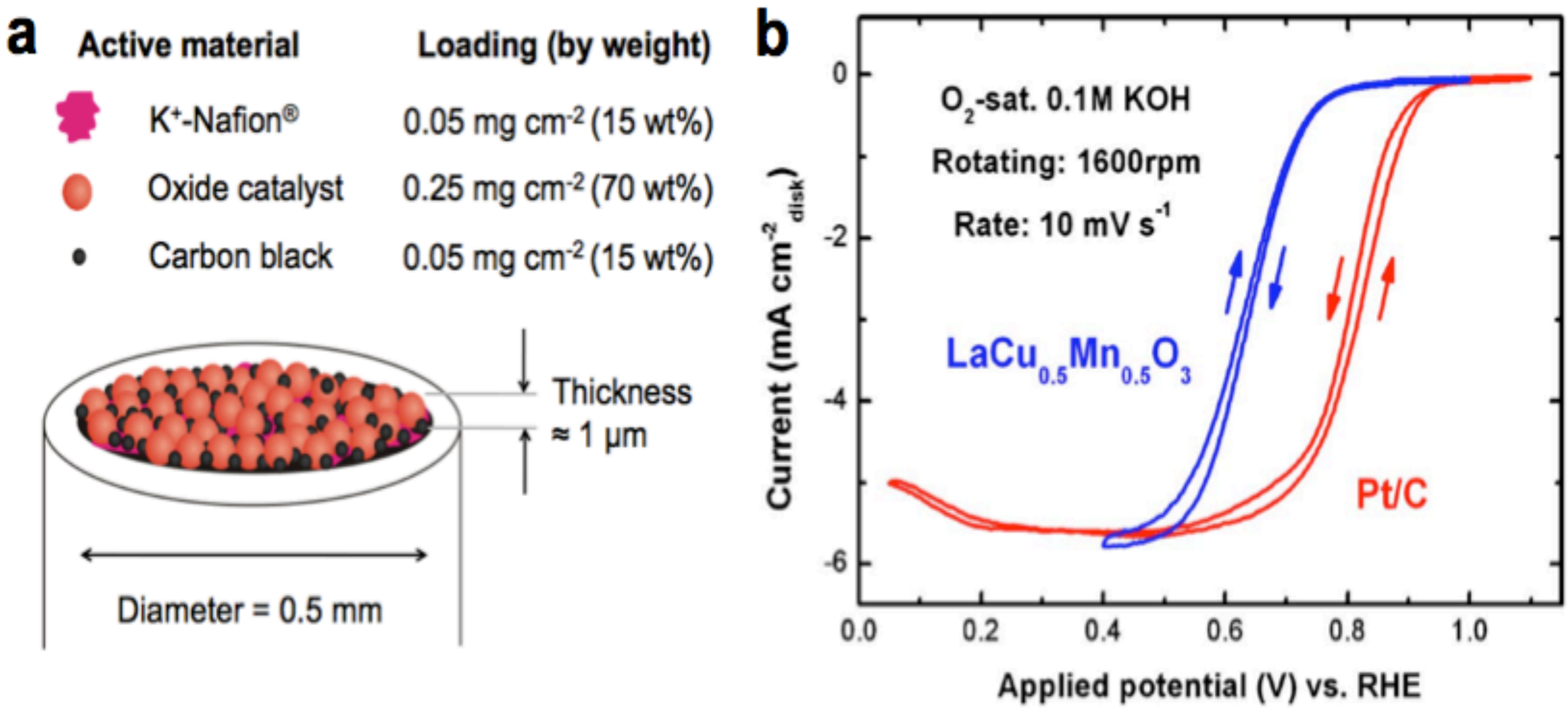


$LaB^{3+}O_3$



$La_2B^{2+}O_4$
(n=1)

How to assess ORR/OER activity on perovskite powder

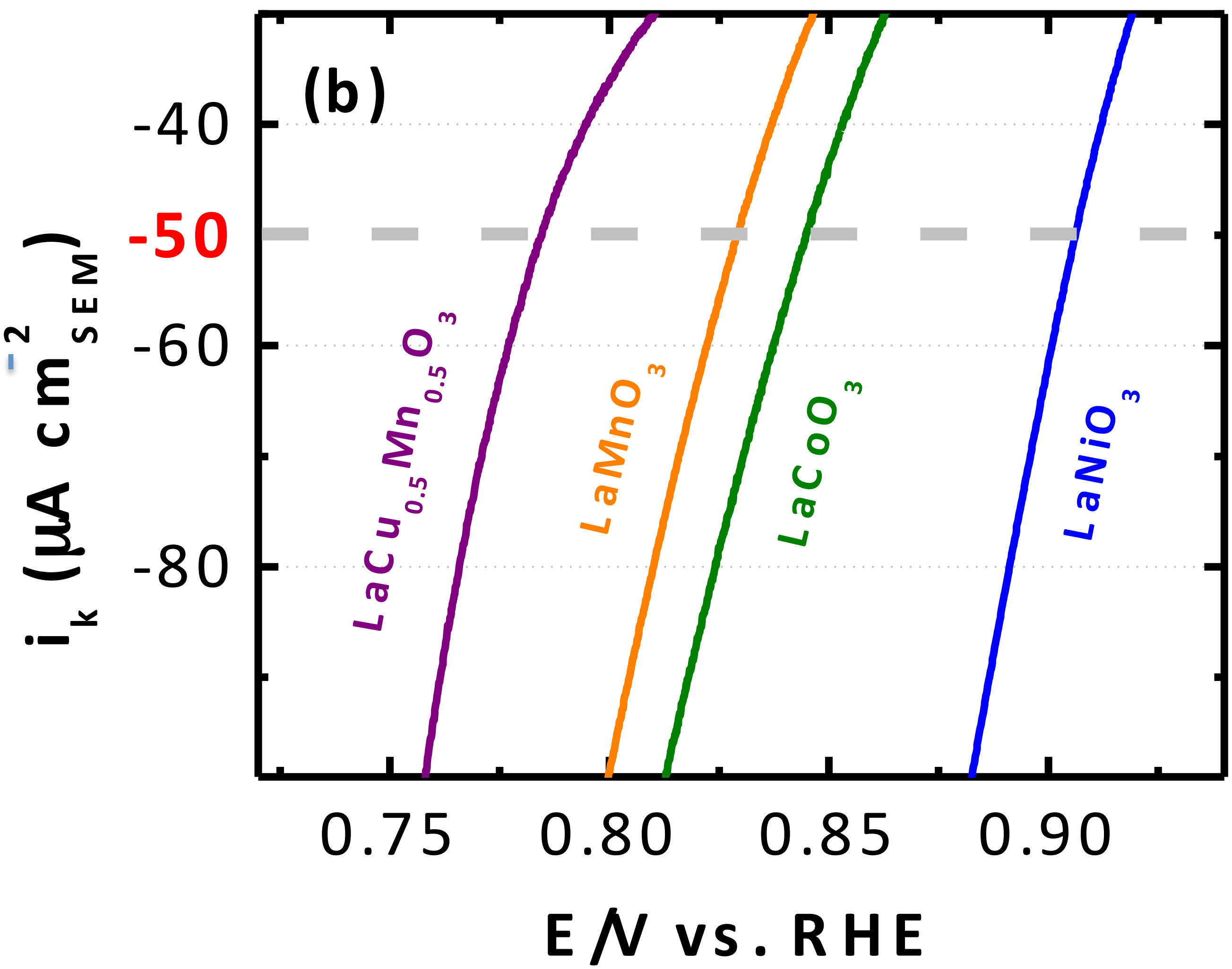


Intrinsic ORR activity can be estimated from thin films of oxide powder

Suntivich, J., H.A. Gasteiger, N. Yabuuchi and Y. Shao-Horn, Journal of the Electrochemical Society, 8, B1263-B1268 (2010).

Intrinsic ORR activity of perovskites vary greatly

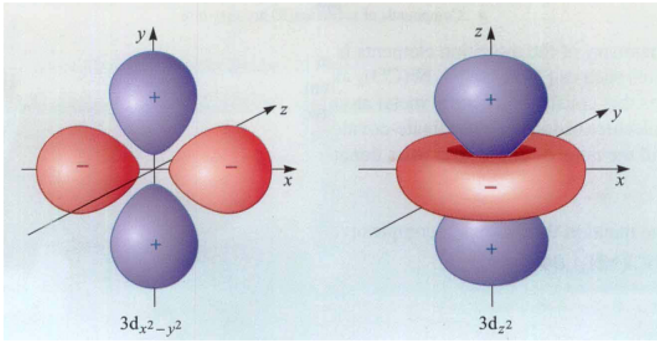
Up to ~4 orders of magnitude



Suntivich, J. et al., Nature Chemistry, 2011

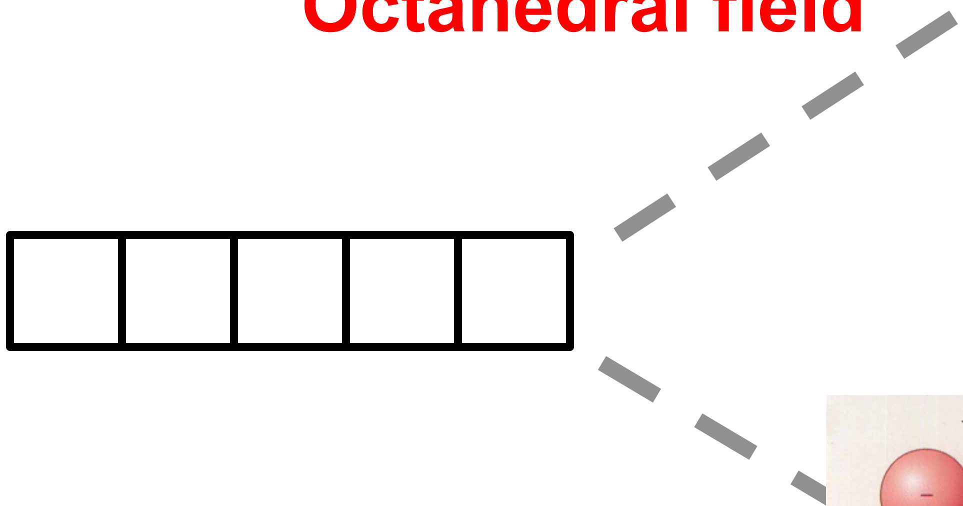
Two types of antibonding d-electrons for TM ions

Octahedral field

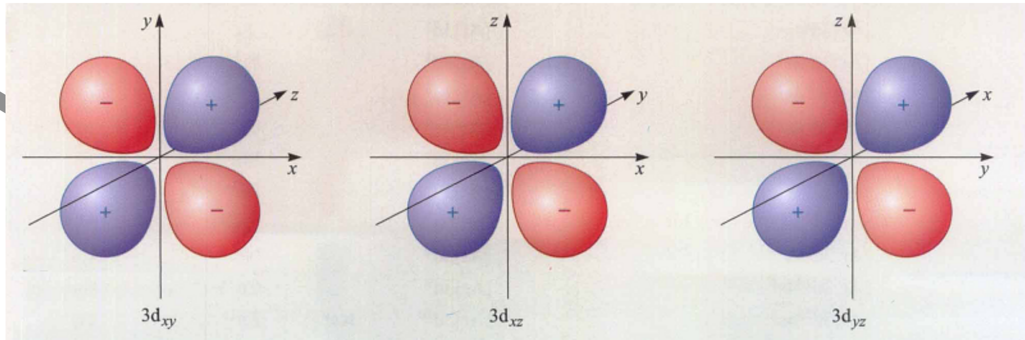


σ^*

Stronger hybridization E_g



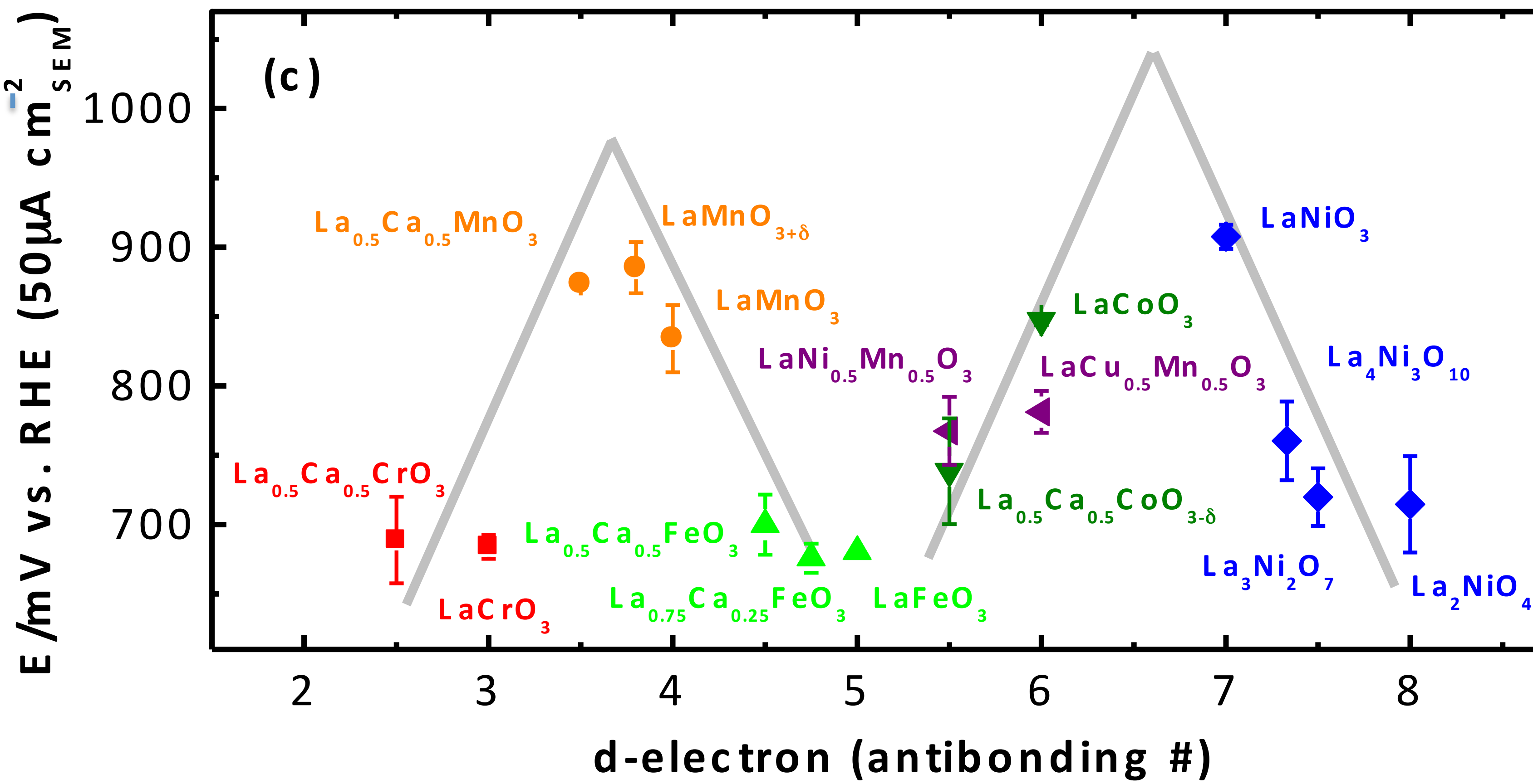
d-orbitals



Weaker hybridization T_{2g} π^*

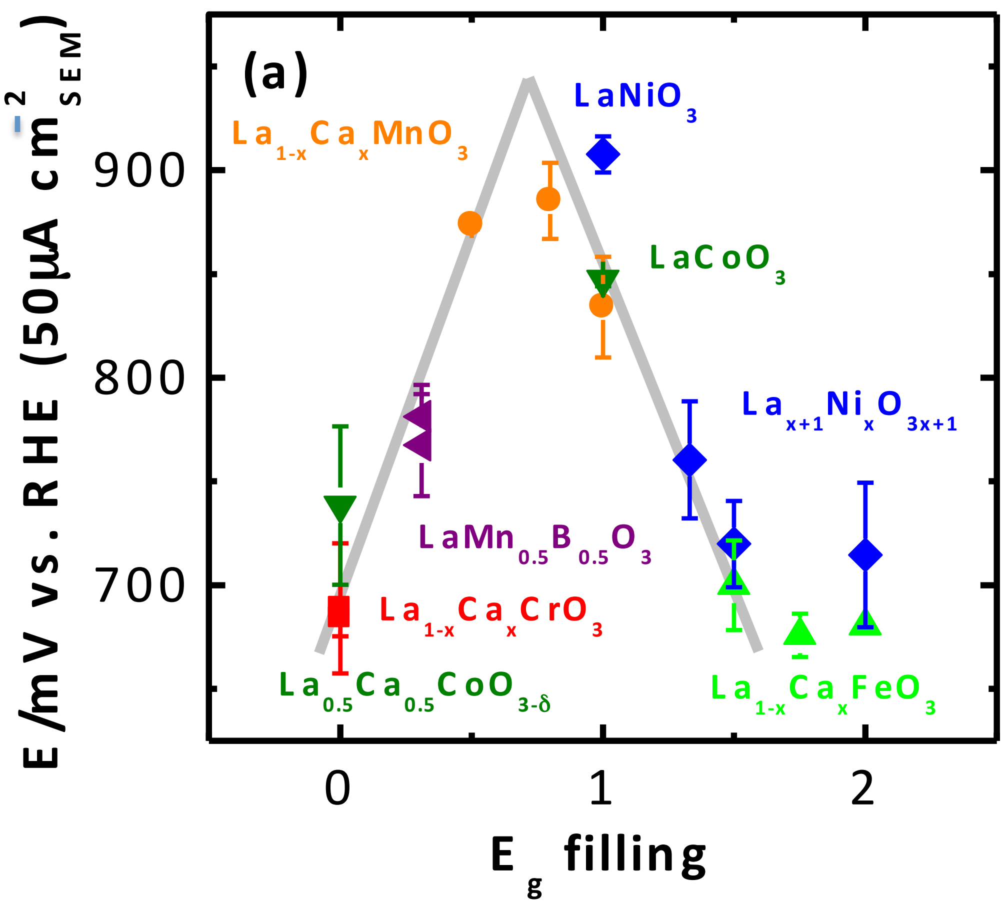
Janes, R., Moore, E.A., Metal-Ligand Bonding (2004)

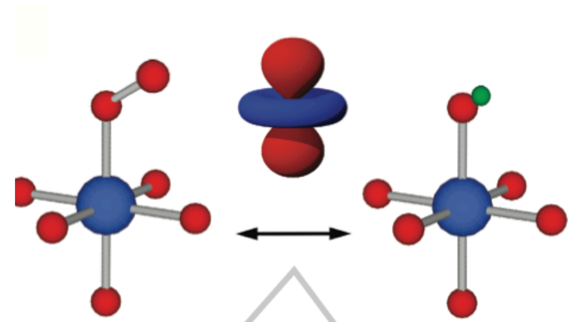
d-electron of B ions ≠ ORR descriptor



Suntivich, J. et al., Nature Chemistry, 2011

Using E_g filling as a primary descriptor of ORR activity





For example

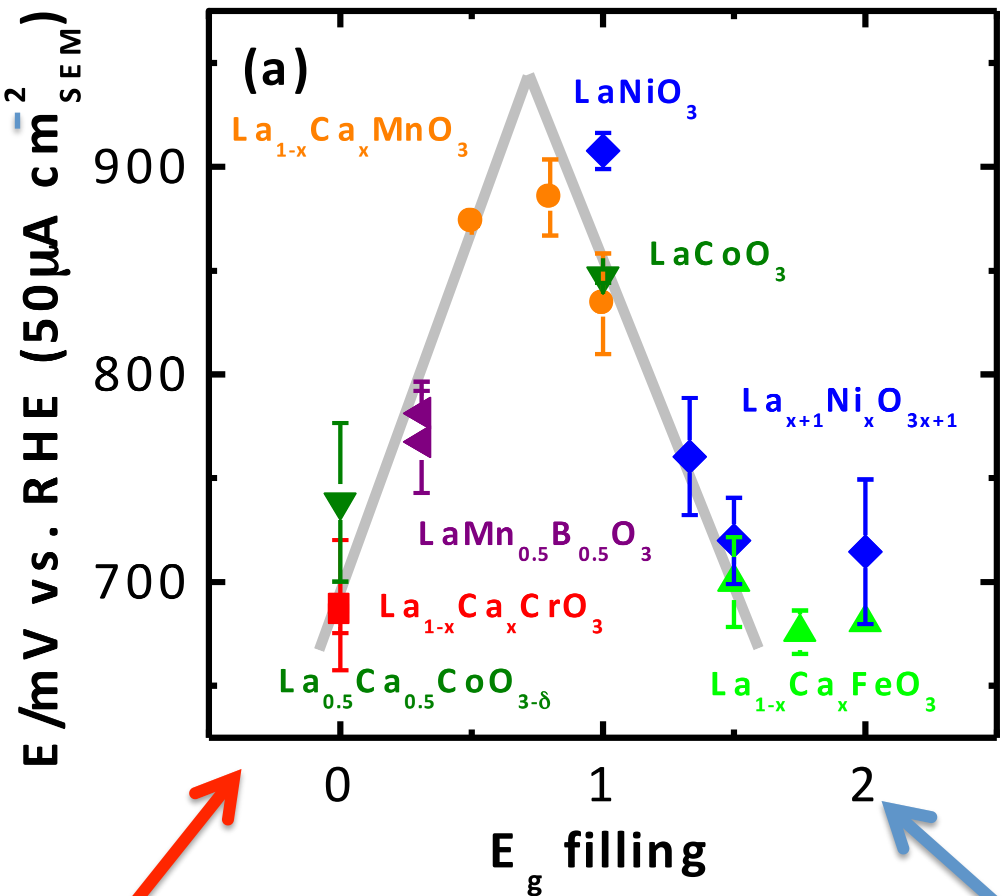
$LaMnO_3 \rightarrow t_{2g}{}^{3}e_g{}^{1} \rightarrow d^4$

$La_{1-x}Ca_xMnO_3 \rightarrow t_{2g}{}^{3}e_g{}^{1-x} \rightarrow d^{4-x}$

$La_2NiO_4 \rightarrow t_{2g}{}^{6}e_g{}^{2} \rightarrow d^8$

Suntivich, J. et al., Nature Chemistry, 2011

Using E_g filling as a primary descriptor of ORR activity

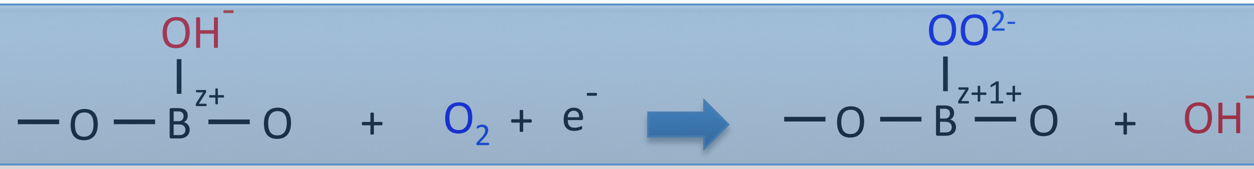


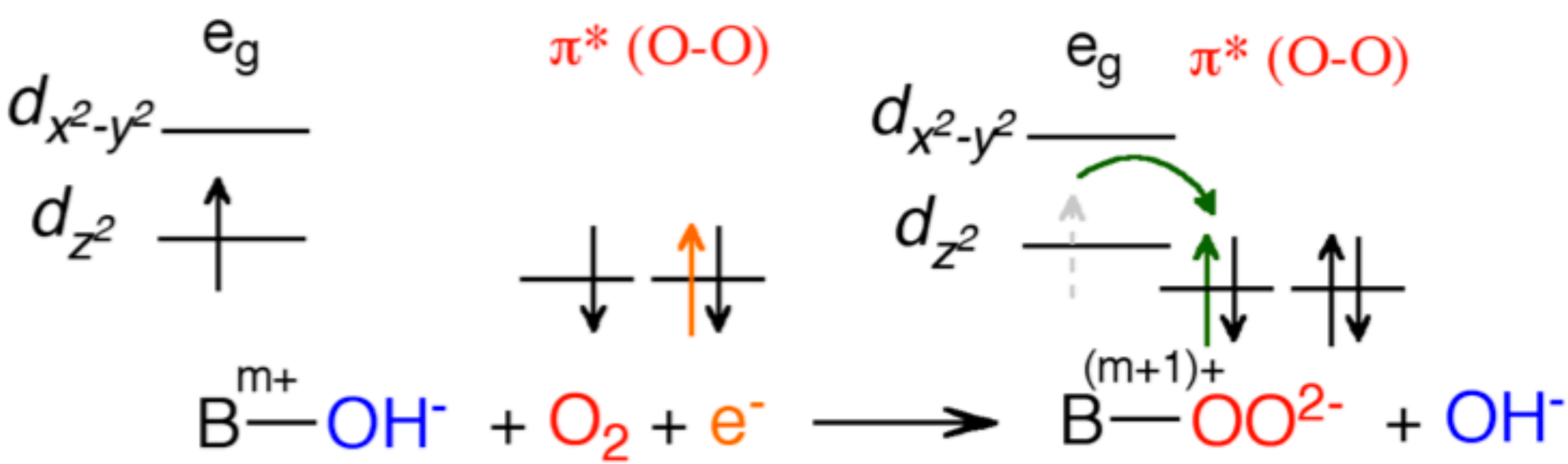
Binding of O_2 on M too strong
Surface hydroxide regeneration limiting

Binding of O_2 on M too weak
displacement of OH- species by $O^{2-}_{2,ads}$ limiting

ORR mechanism for perovskites

surface hydroxide displacement:

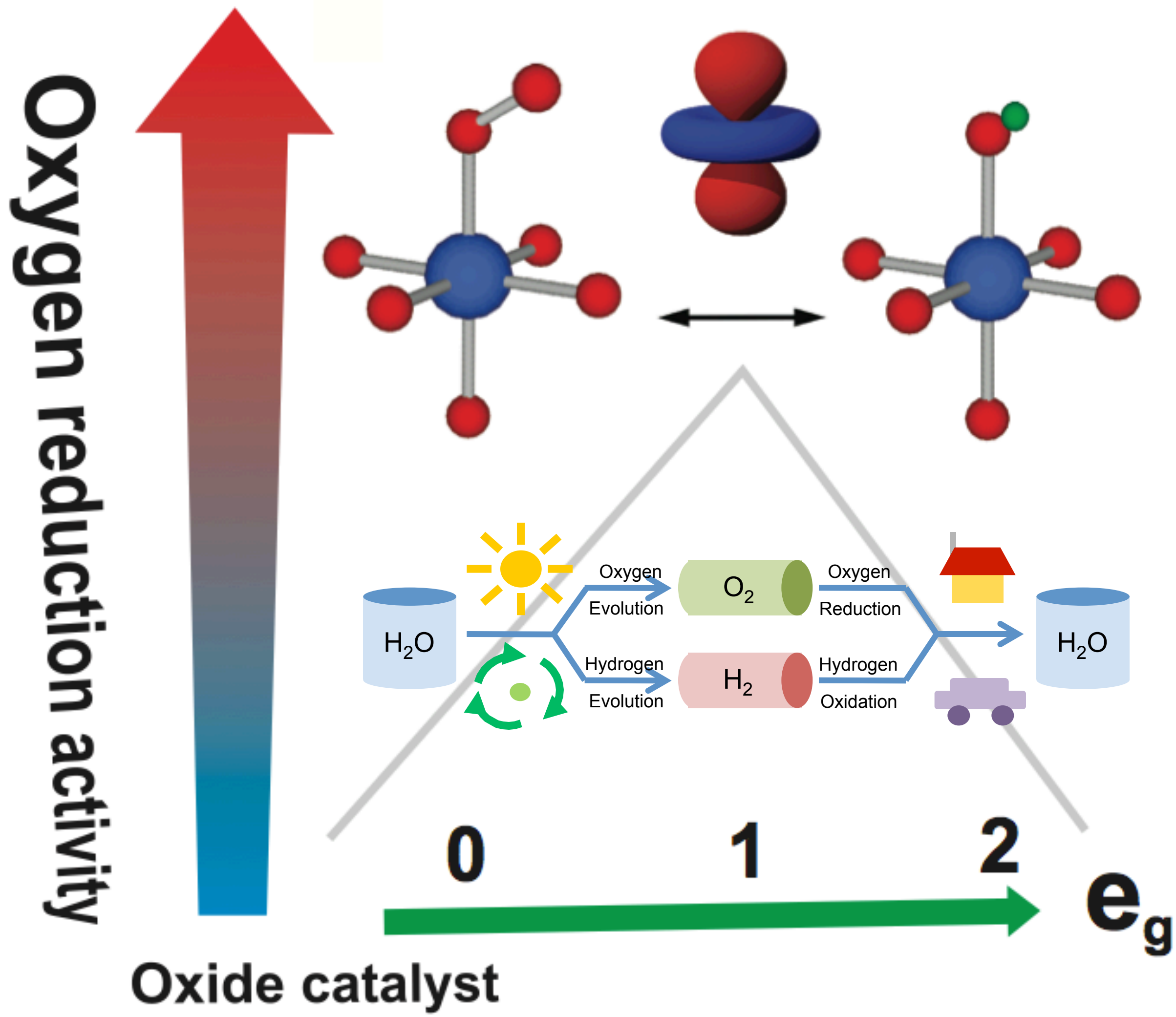




JB Goodenough, FC Handbook 2003 (vol. 2, pg. 521)

Suntivich, J. et al., Nature Chemistry, 2011

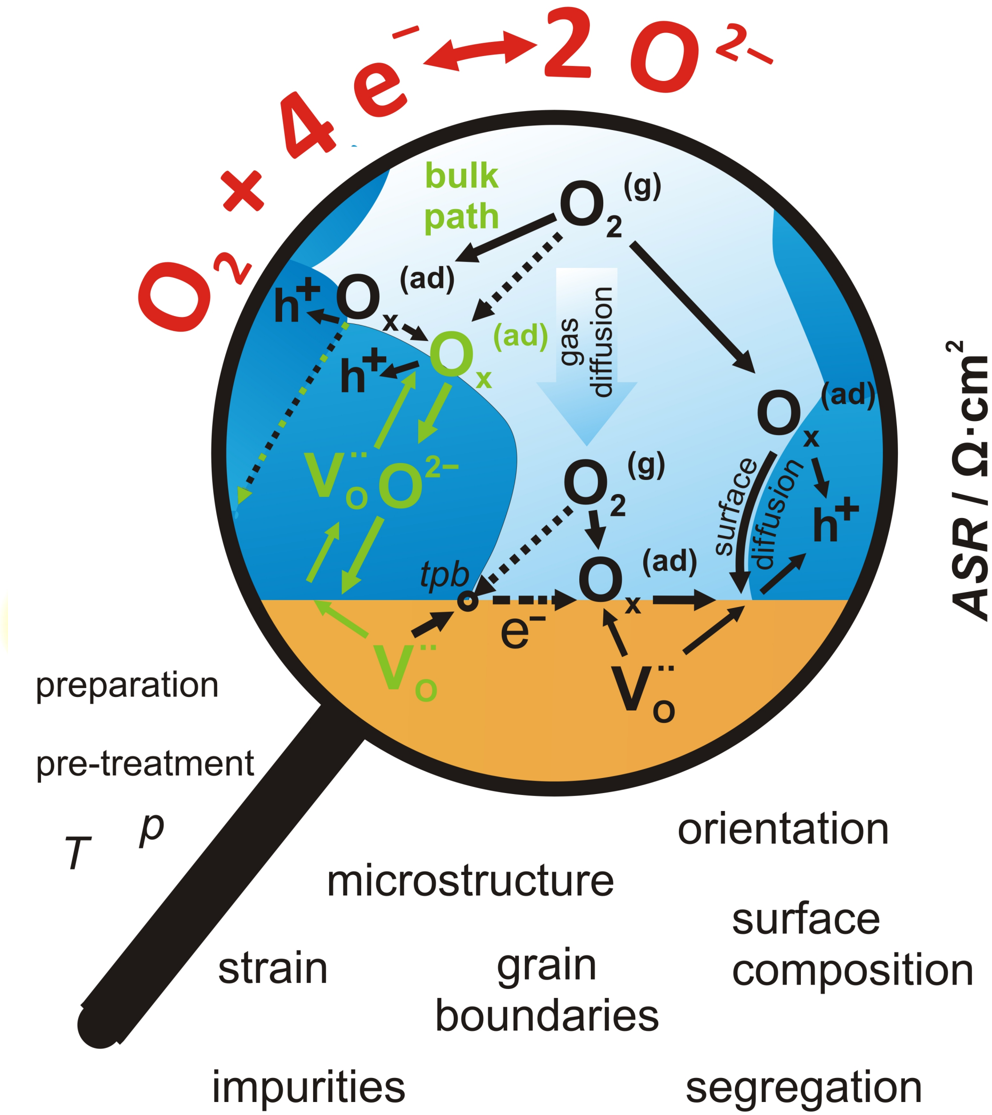
Perspectives and open questions

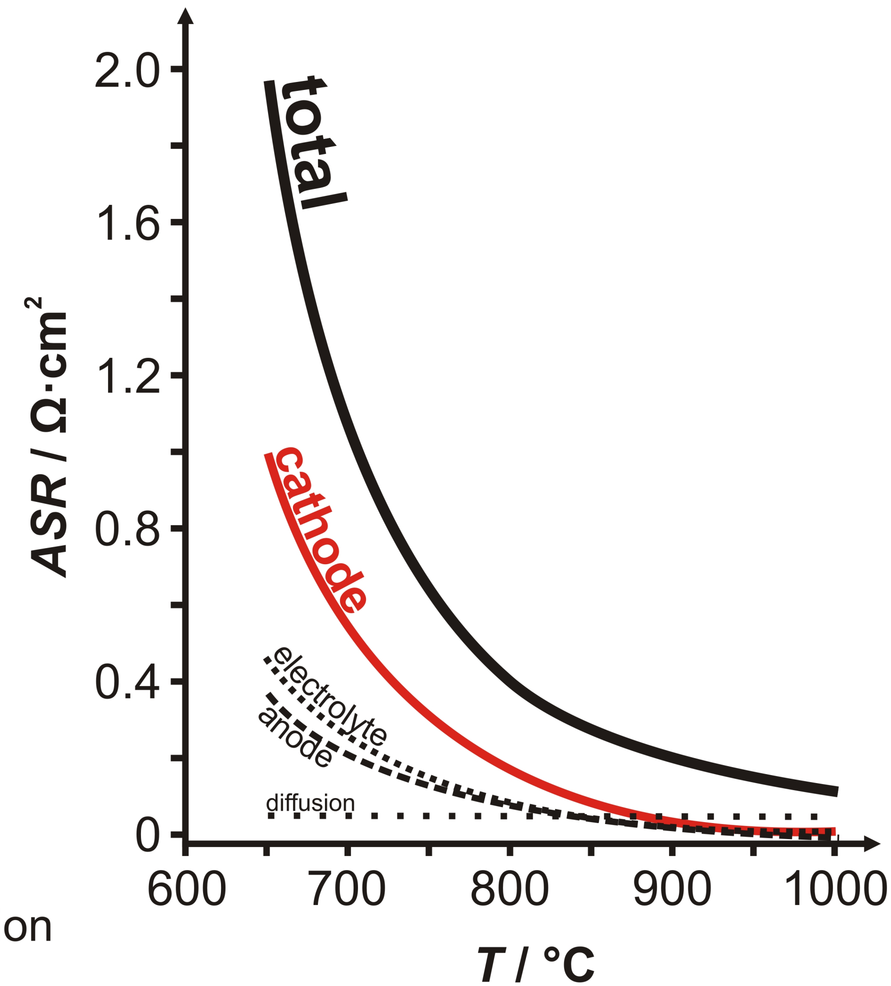


Would the ORR descriptor found for perovskites be applicable for all oxides?
Would the ORR descriptor influence OER activity?

Suntivich, J. et al., Nature Chemistry, 2011

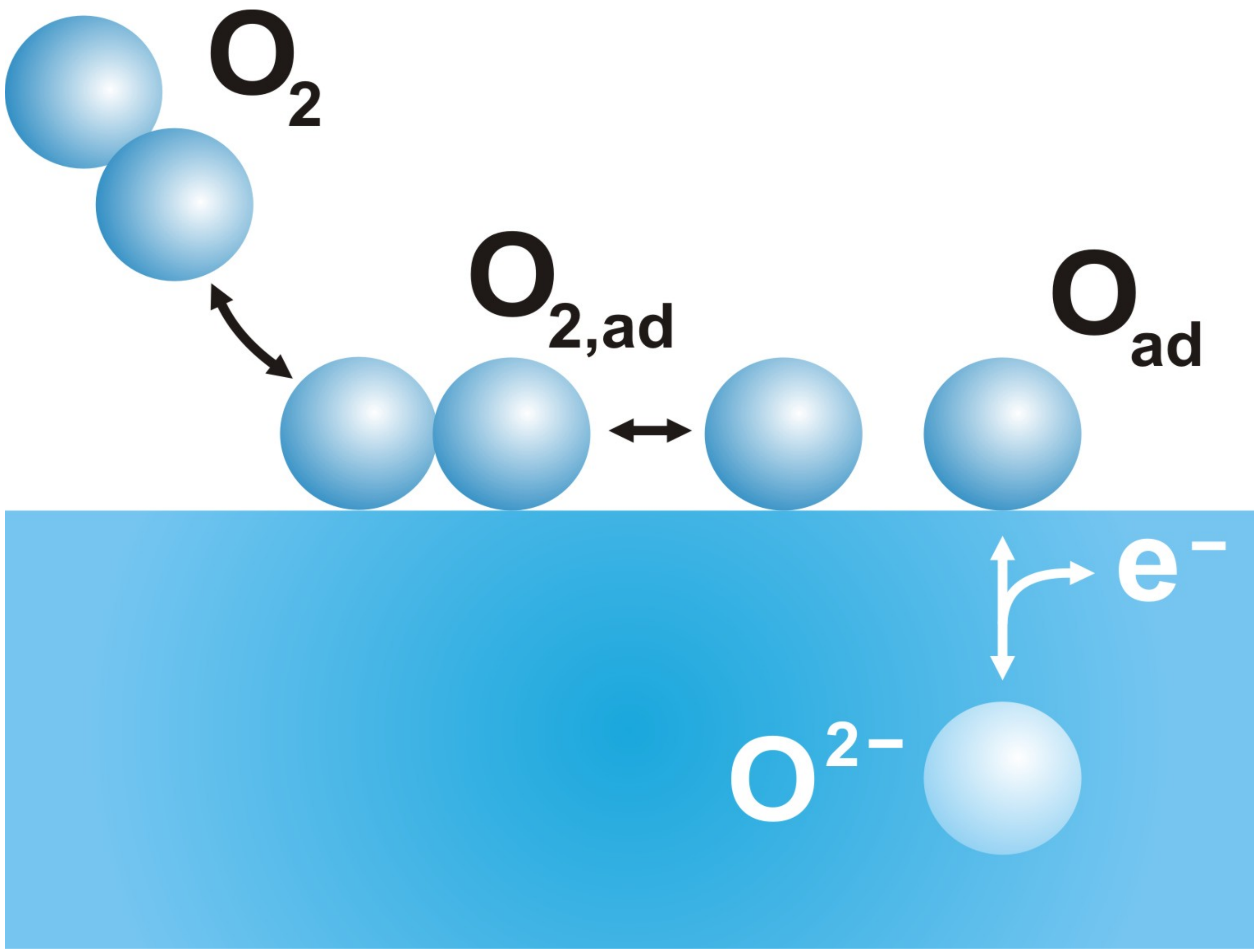
Challenges in ORR/OER at high temperatures





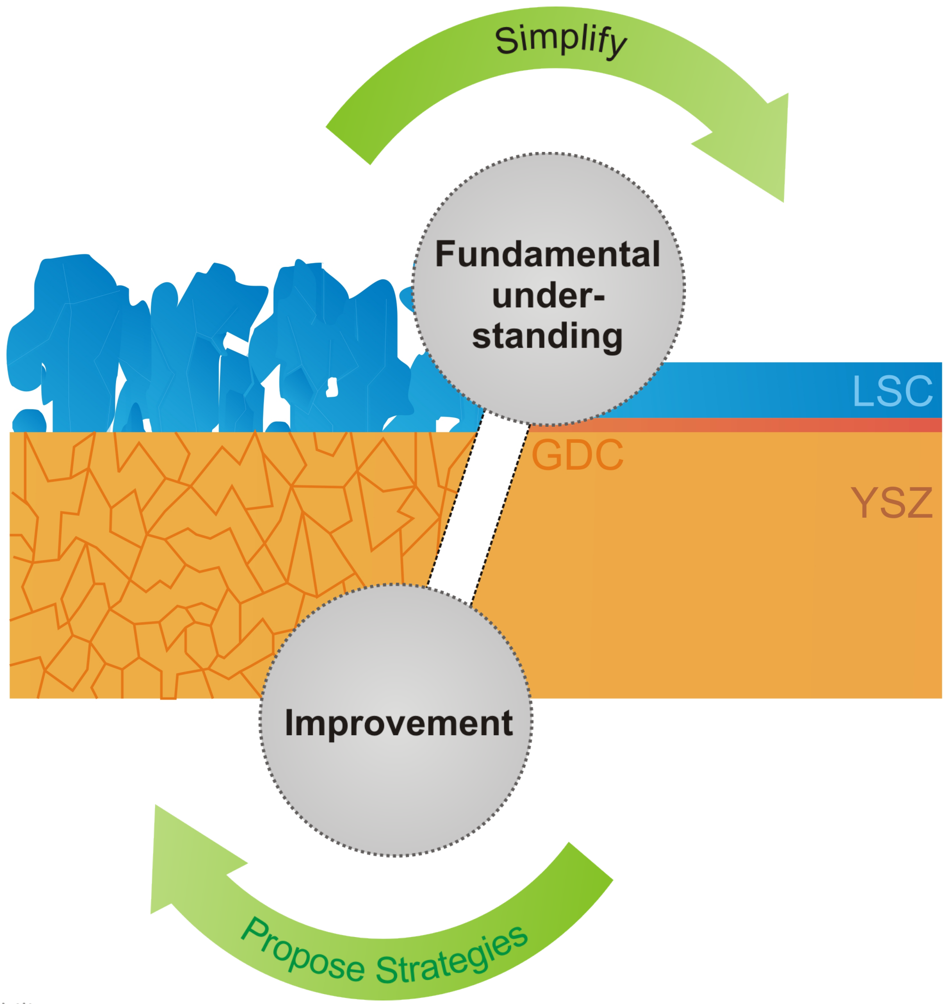
[1] Webpage RWTH Aachen, [2] M. Mogensen, P. V. Hendriksen, in: High Temperature Solid Oxide Fuel Cells – Fundamentals, Design, and Applications, Elsevier 2003

High-Temperature ORR/OER on Perovskites



$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$

Reduced Complexity: a Model System Approach



New cathode [1] development

Powder properties/ Microstructure

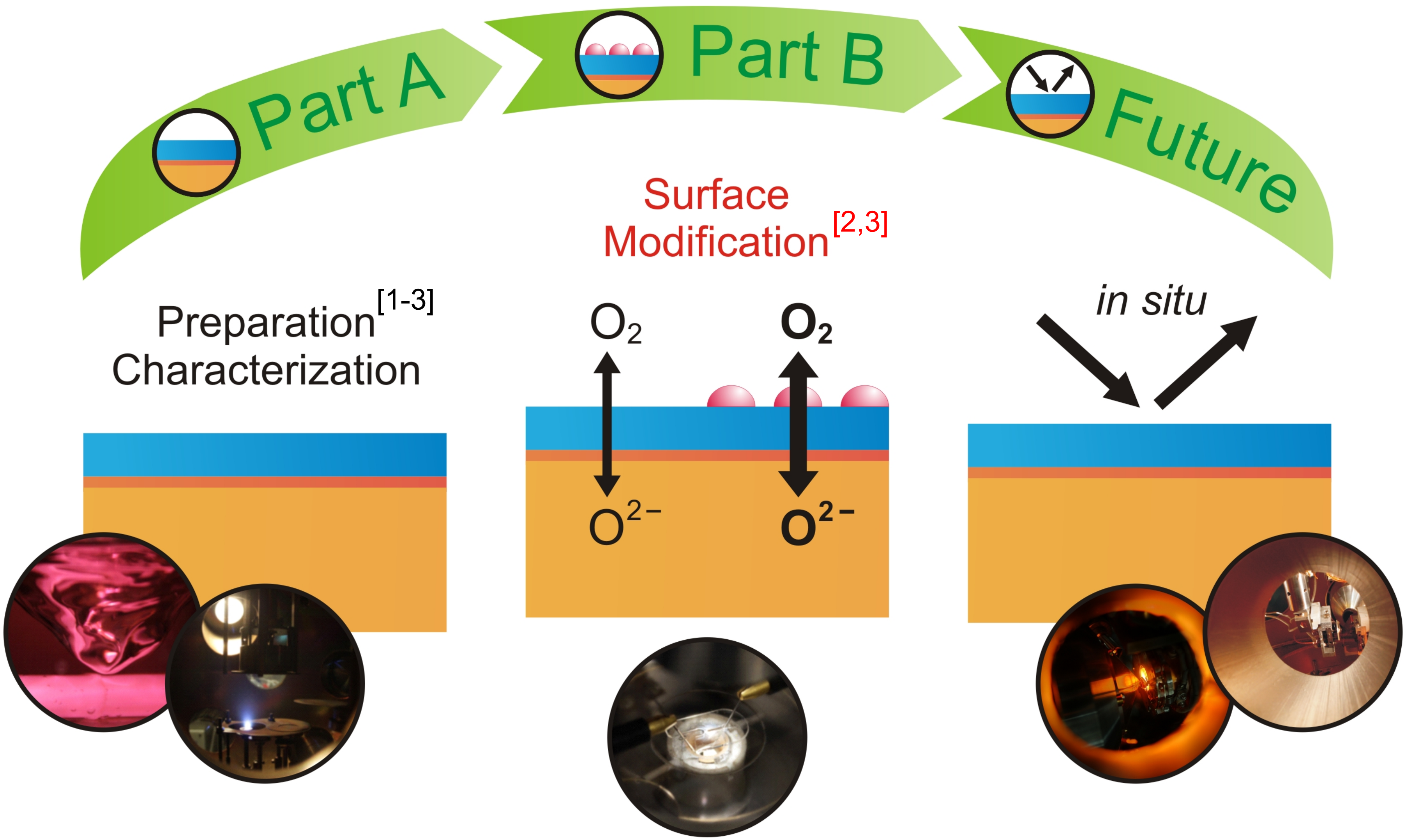
Cell design / Processing

Durability

[1] F. Tiez, A. Mai, D. Stover, Solid State Ionics 179, 2008, 1509-1515

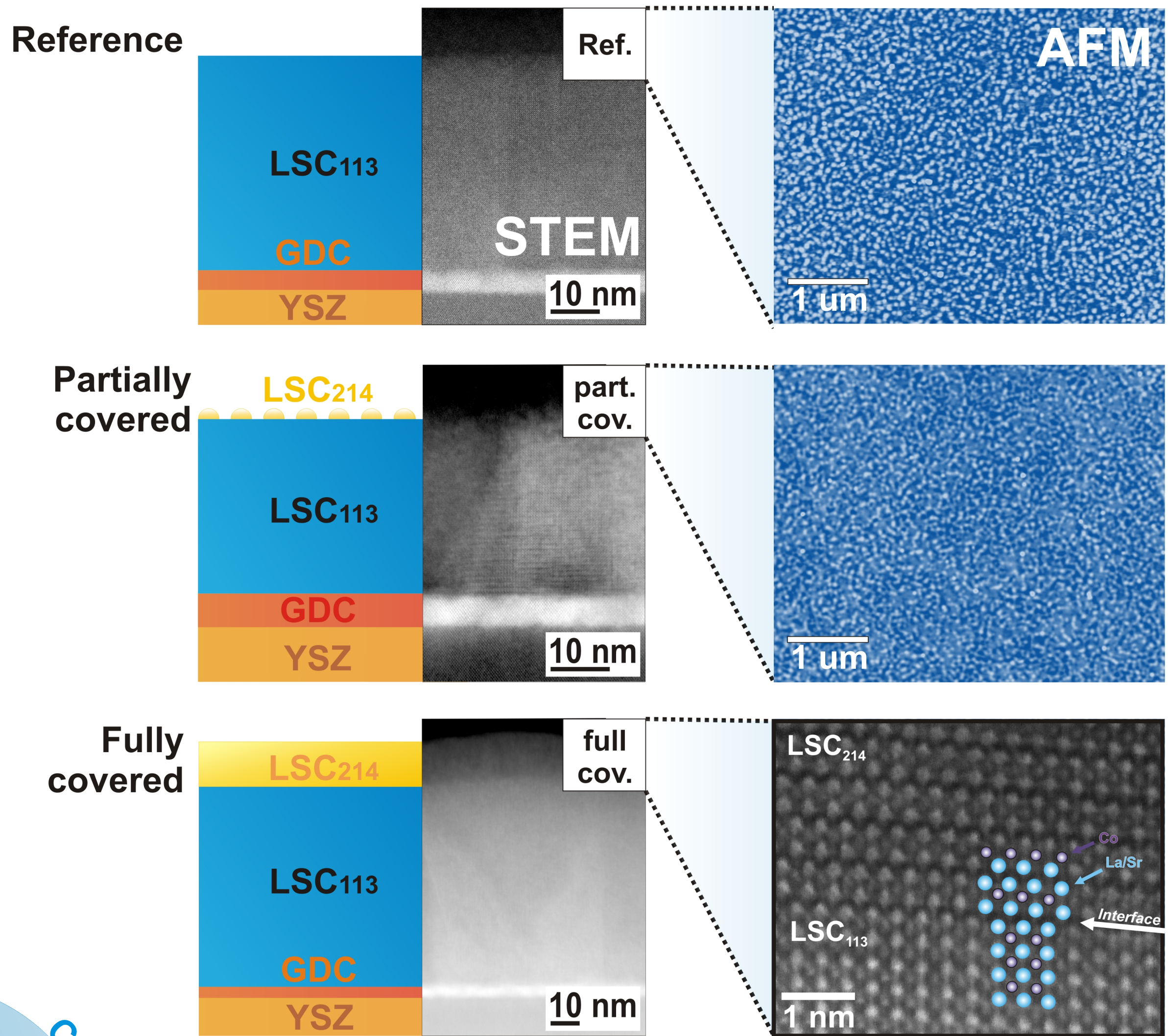
LSC = $La_{0.8}Sr_{0.2}CoO_{3-\delta}$, GDC = Gadolinium doped Ceria, YSZ = Yttria-stabilized Zirconia

Understanding surfaces to enhance ORR/OER activity



[1] G. J. la O' et al., Angew. Chem. Int. Ed. 2010, 49, 5344-5347, [2] E. J. Crumlin, E. Mutoro et al., JPCL 1, 2010, 3149,
[3] E. Mutoro et al., Energy Environ. Sci., 2011, in press (doi:10.1039/C1EE01245B)

Surface decoration: 113-$La_{0.8}Sr_{0.2}CoO_3$/214-$(La_{0.5}Sr_{0.5})_2CoO_4$



STEM:
D. Leonard
A. Borisevich
(ORNL)

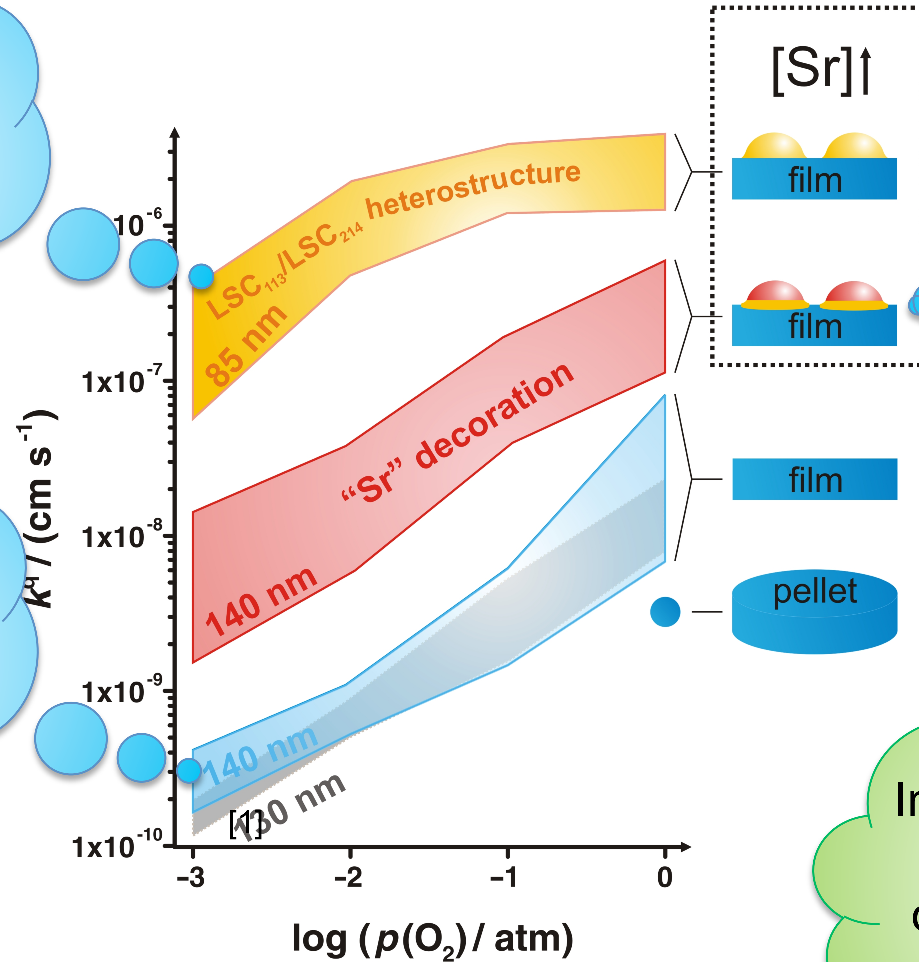
Collaboration

E. J. Crumlin, E. Mutoro et al., JPCL 1, 2010, 3149

Surface decoration enhances ORR/OER activity

214 surface addition greatly enhances ORR activity

Films more active for ORR/OER than powder

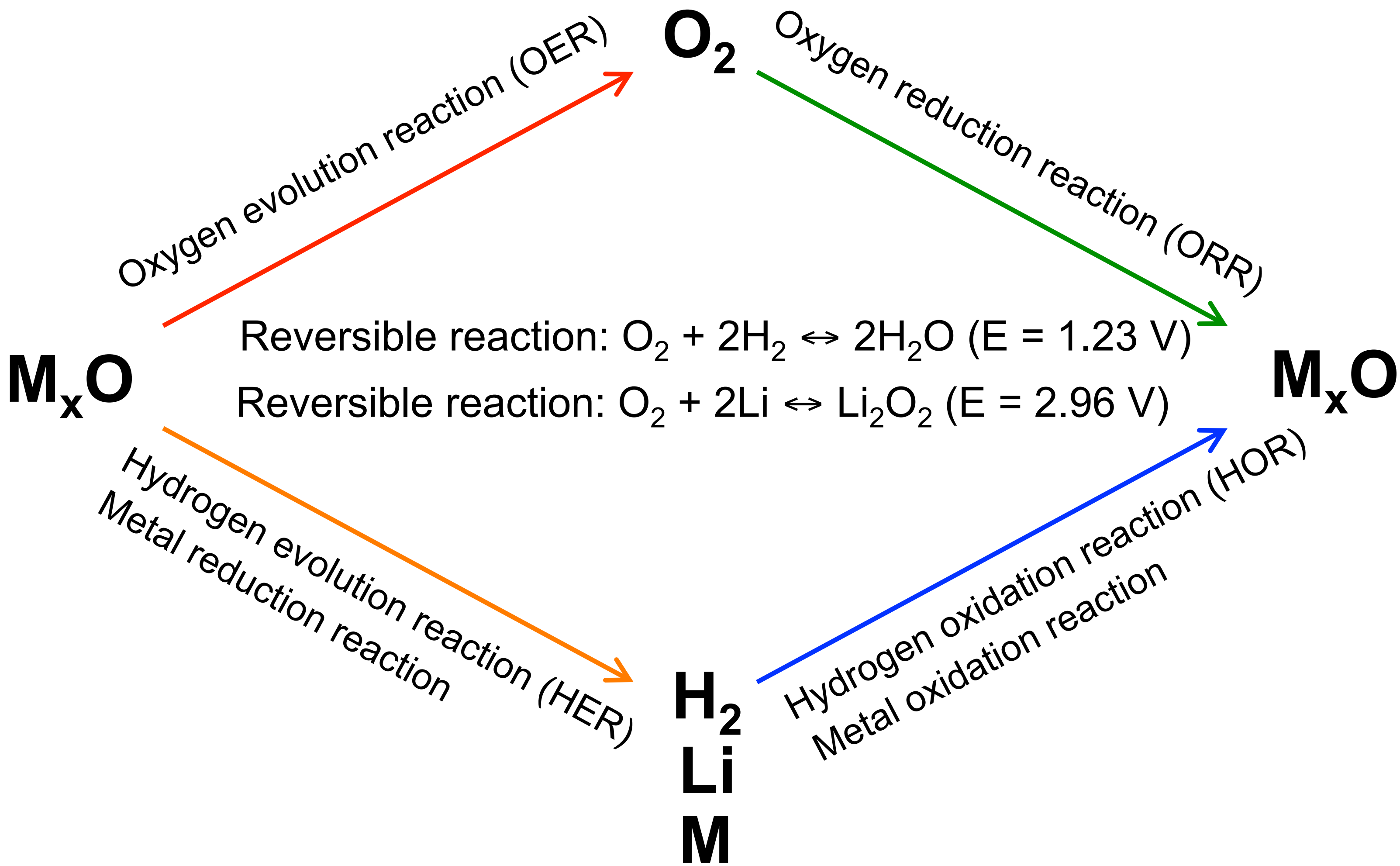


Sr-rich surface phases can activate LSC

Information of surface composition under operating conditions necessary

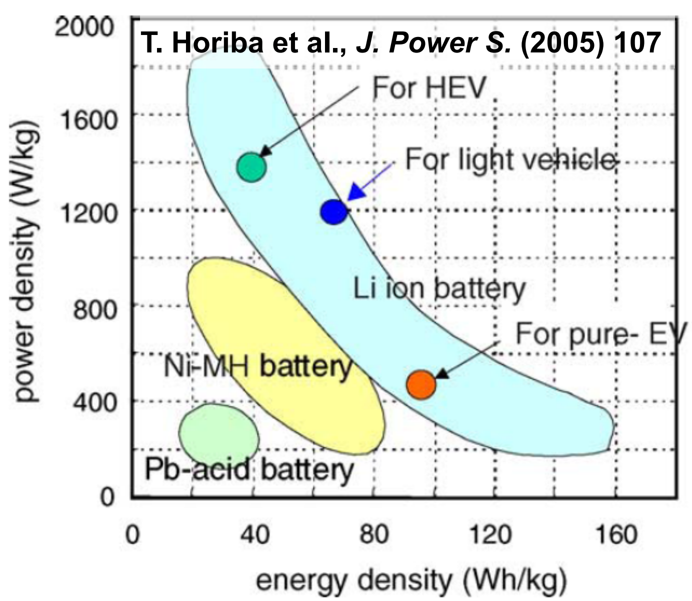
[1] E. Mutoro et al., Energy Environ. Sci., 2011, in press (doi:10.1039/C1EE01245B), E. J. Crumlin, E. Mutoro et al., JPCL 1, 2010, 3149, [2] G. J. la O' et al., Angew. Chem 2010.

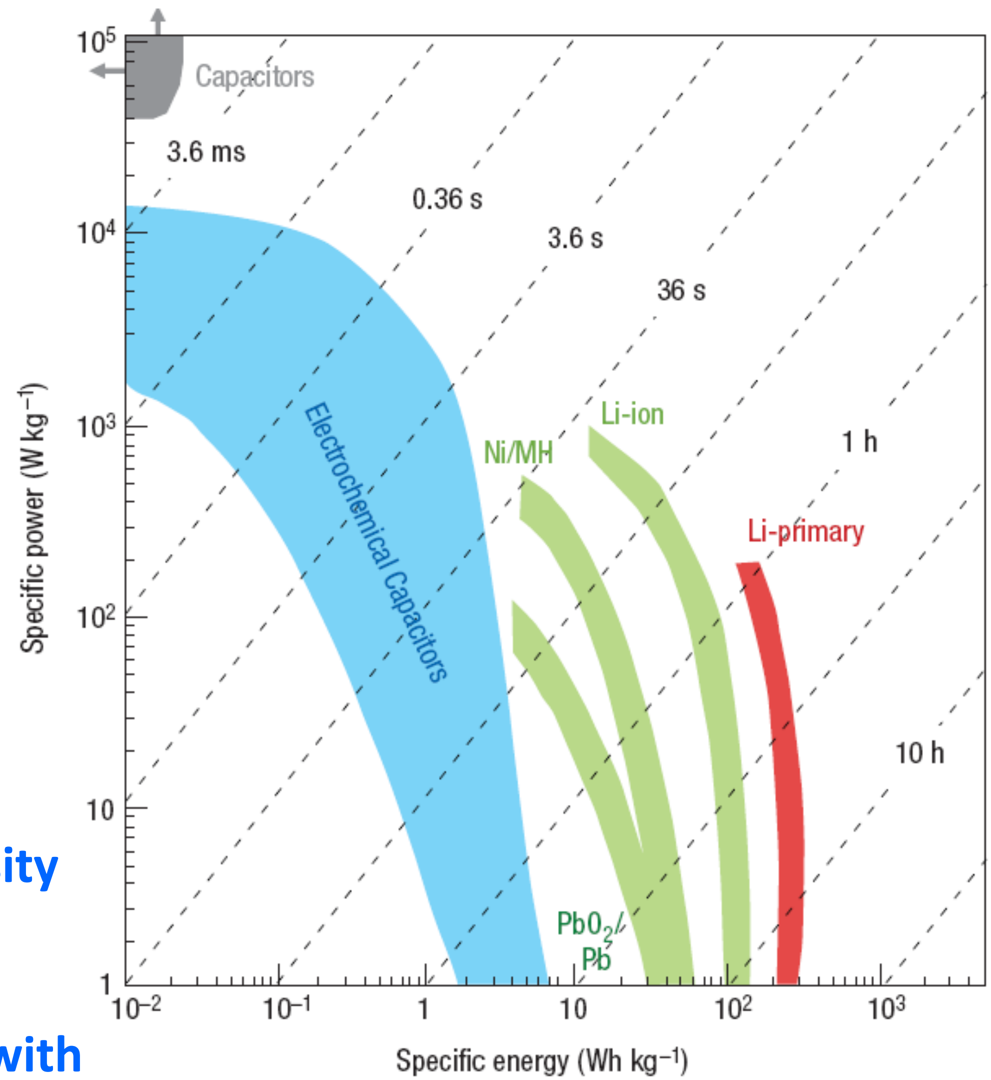
H_2/Li/M storage for clean energy technologies



Understanding and using the redox of oxygen is at the heart of clean energy technology development

Exploring redox of oxygen for new lithium storage technologies





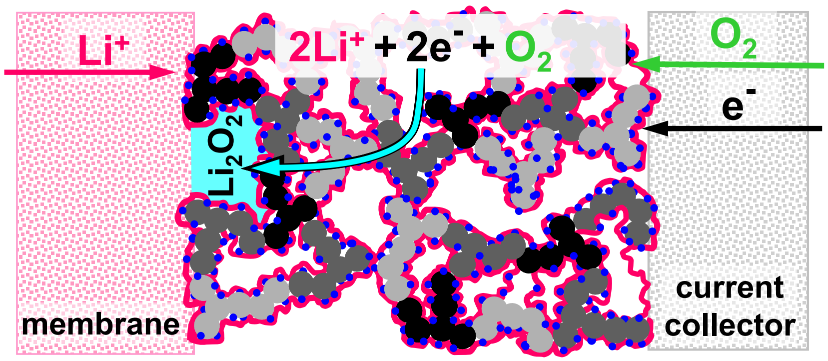
Simon and Gogotsi, Nature Materials, 2008

- **Energy and Power Gap**
  - High energy and high power density systems for hybrid vehicles

- **New energy storage technologies with much higher energy densities for electric vehicles**

Li-air batteries offering ~5 fold in gravimetric energy vs. Li-Ion batteries

$O_2 + 2Li \leftrightarrow Li_2O_2$ (E = 2.96 V)

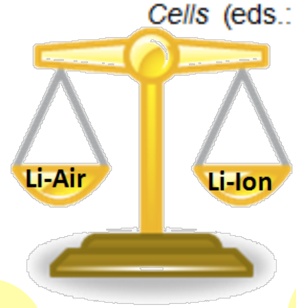


assumptions:

0.36 g_{carbon}/cm^3 [*)], 15% ε_{carbon}, 25% $\varepsilon_{electrolyte}$, 60% ε_{Li2Ox}

	Li_2O_2	Li_2O	$LiCoO_2$
Q_s wrt. C [mAh/g_{carbon}]	4600	6000	
Q_s wrt. C+Li_2O_x [$mAh/g_{(C+Li2Ox)}$]	900	1350	160
average discharge voltage [V]	2.75	2.75	3.9
E_s wrt. C+Li_2O_x [$Wh/kg_{(C+Li2Ox)}$]	2450	3700	620

*) W. Gu, D.R. Baker, Y. Liu, H.A. Gasteiger; in: *Handbook of Fuel Cells* (eds.: W. Vielstich et al.); Wiley (2009): *vol. 6*, p 631



Li-Air

Estimated gravimetric energy

~ 3000 $Wh/kg_{Li2Ox\text{-}cathode}$

Projecting on the cell level – 1/3

~ 1000 $Wh/kg_{Li\text{-}air\ cell}$

Li-Ion ($LiCoO_2$)

Estimated gravimetric energy

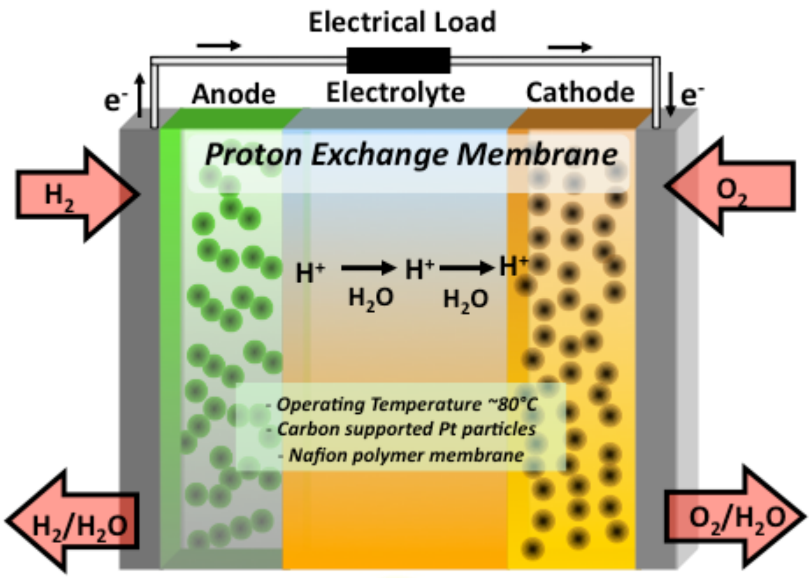
~ 620 $Wh/kg_{LiCoO2\text{-}cathode}$

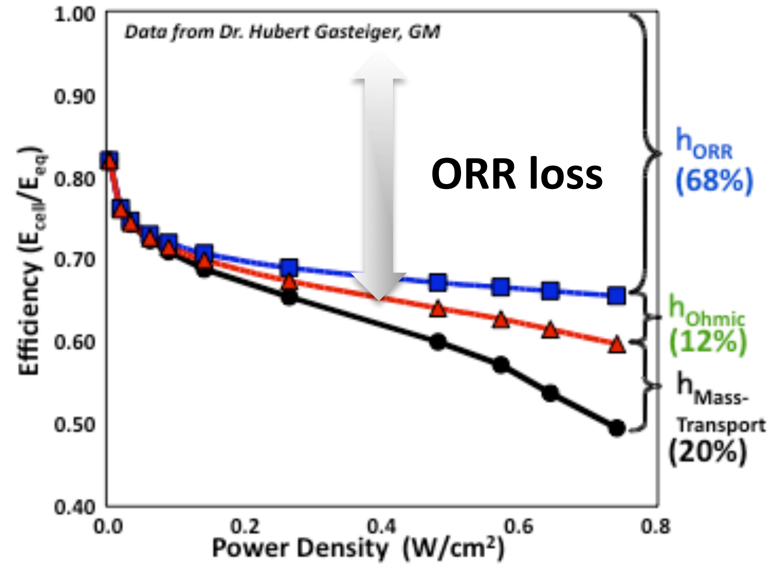
Projecting on the cell level – 1/3

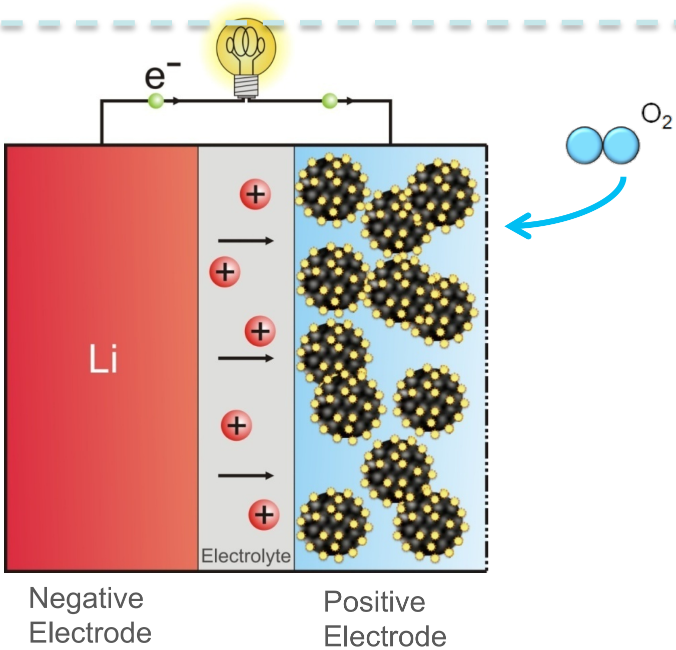
~ 210 $Wh/kg_{LiCoO2\ cell}$

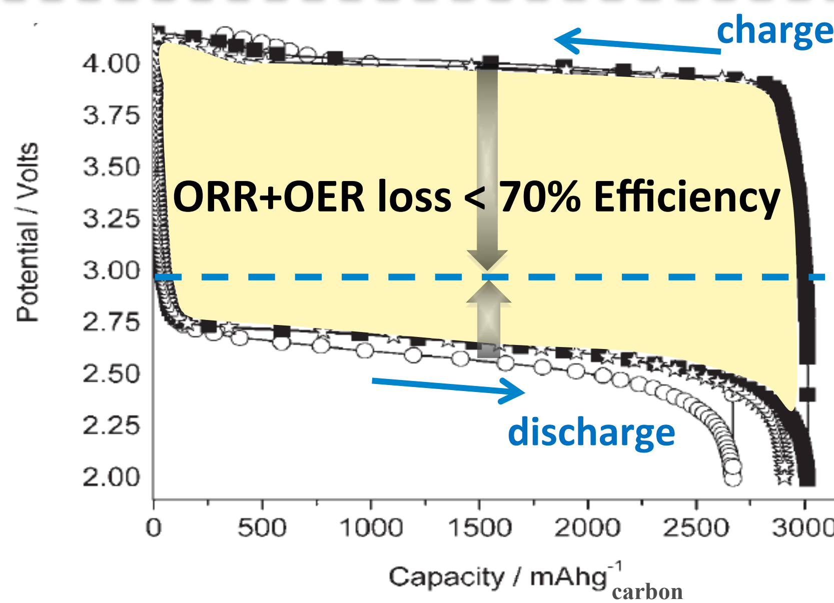
Lu et al, ESSL 2010

Using O_2 electrocatalysis for Lithium Storage









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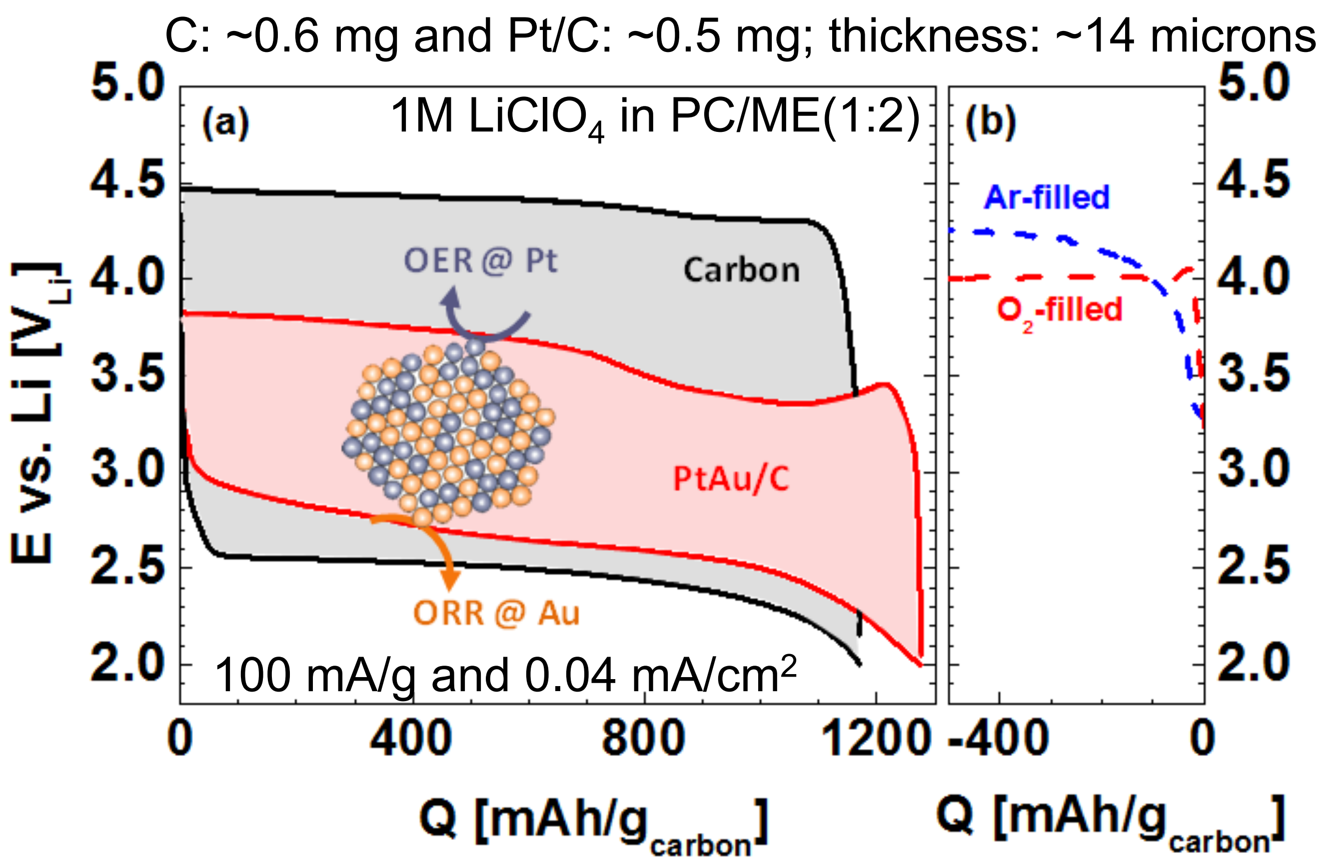
PtAu/C exhibits record round-trip efficiency to date



Achieved record round-trip efficiency: 75%

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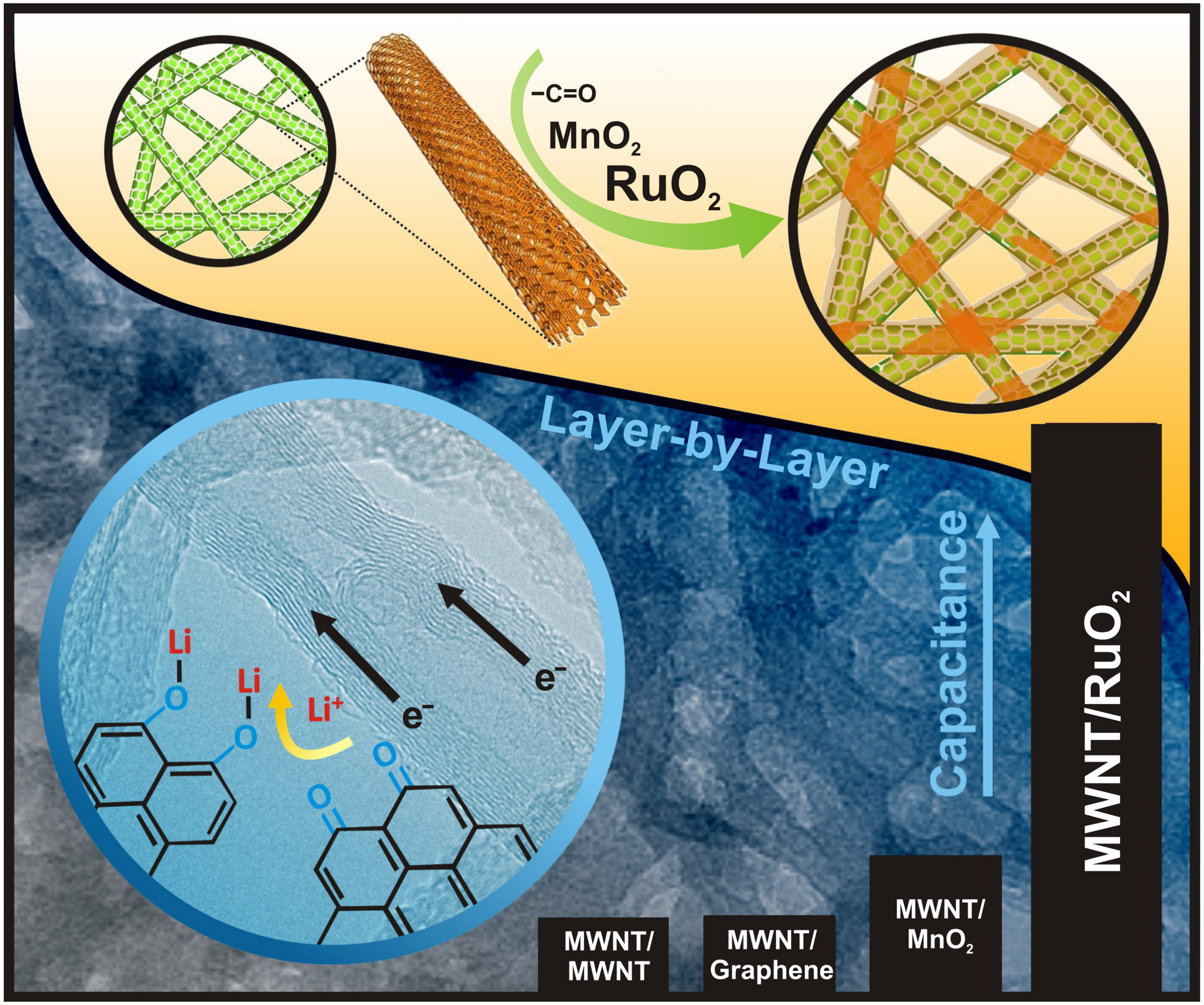
Functionalized O-MWNTs for High-Power Lithium Storage



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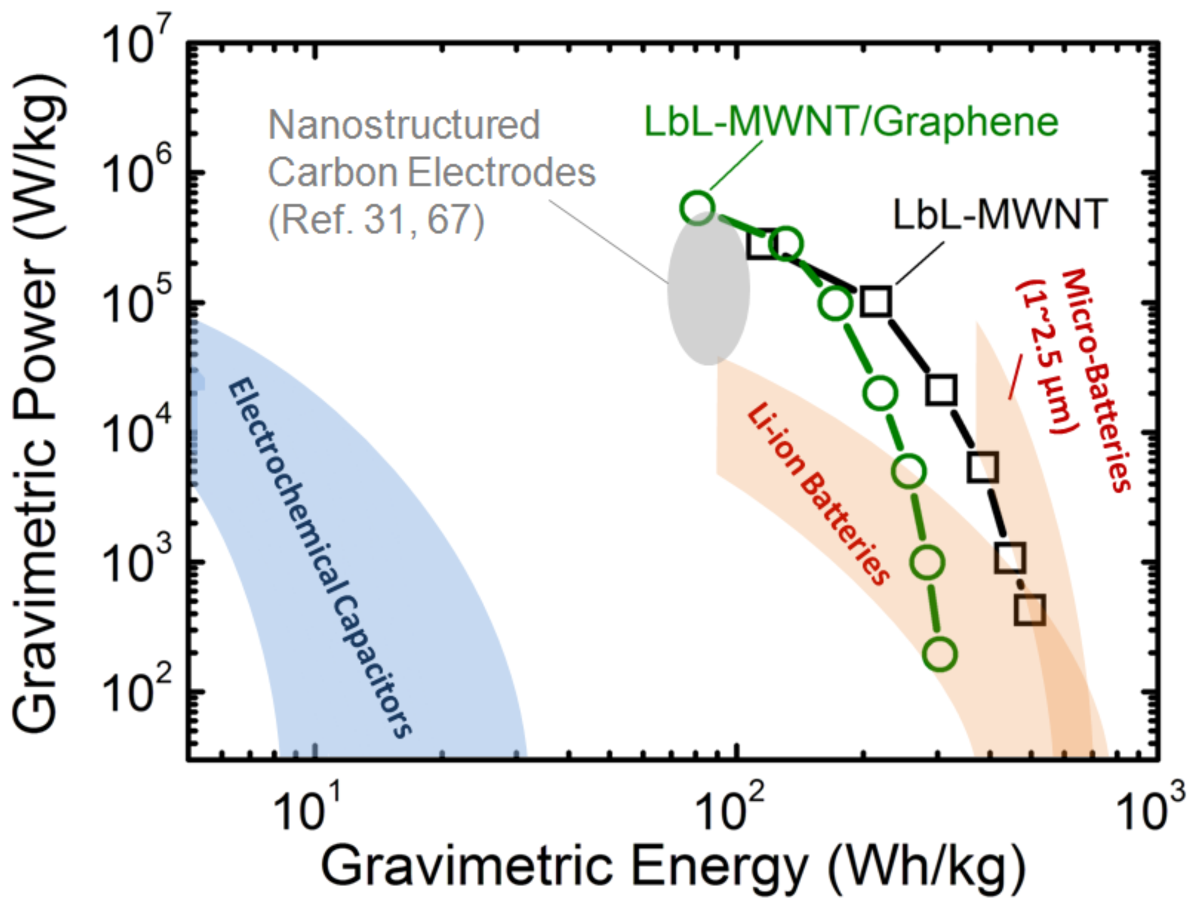
Functionalized O-MWNTs for high-power lithium storage



5-10x increase in power relative to Li-ion batteries

5-10x increase in energy relative to supercapacitors

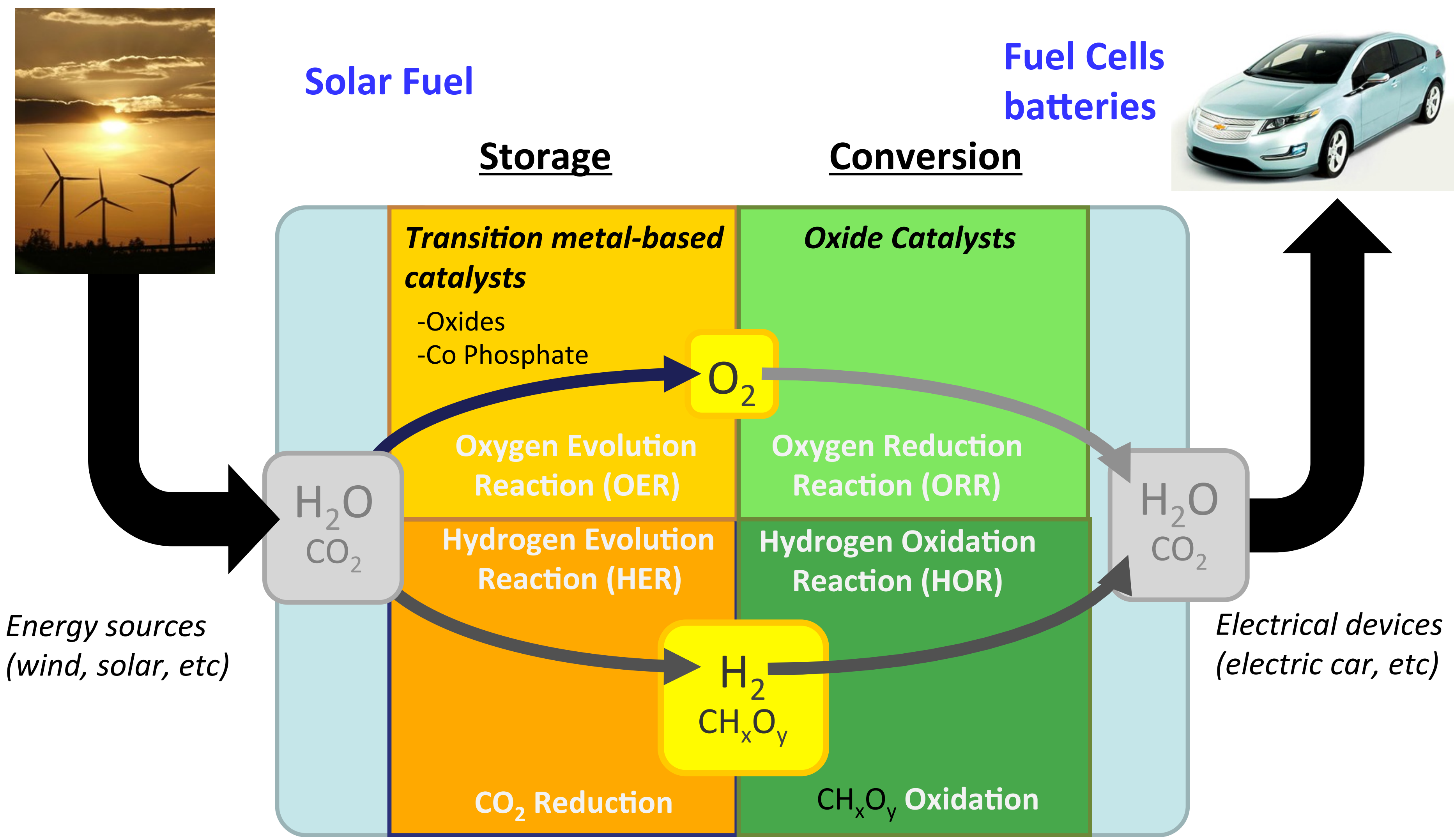
Demonstrated high energy, power and lifetime of nanostructured electrodes for thin-film energy storage
Technology licensed to Contour Energy Systems, CA

S.W.Lee, B.M. Gallant, H. R. Byon, P.T. Hammond, Y. Shao-Horn, *Energy and Environment Science, 2011*

Oxygen Reduction and Evolution Critical to Clean Energy Technologies

Source: Reuter Pictures

Source: http://www.gm-volt.com



Acknowledgments

O_2 electrocatalysis at high PHs, Jin Sunvtich (MIT), H. A. Gasteiger (TUM)
Mechanism discussion: **J.B. Goodenough (**UT-Austin)
Toyota Motor Company
DOE BES Catalysis (DE-FG02-05ER15728)
Chesonis Family Fellowship

O_2 electrocatalysis for Li-air, Yi-Chun Lu, David Kawabi, Pierre Claver, Hubert A. Gasteiger (TUM) Zhichuan Xu, Jonathon Harding, Ethan Crumlin, Robert McGuire
XANES, Jigang Zhou, Lucia Zuin (Canadian Light Source Inc)
XPS: Azzam Mansour (NSWC)
NP synthesis: Kimberley Hamad-Schifferli (MIT)
DOE EERE (BATT Program)
MIT-Ford Alliance
National Science Foundation MRSEC program

O_2 electrocatalysis at HTs, Eva Mutoro, Ethan J. Crumlin (MIT)
STEM: **A. Borisevich , D. N. Leonard** (ORNL)
PLD: **M. D. Biegalski, H. M. Christen** (ORNL), **C. Ross** (MIT)
In situ APXPS: **H. Bluhm, Z. Liu, M. Grass** (ALS)
German Research Foundation
(Research Fellowship)
DOE BES (SISGR DE-SC0002633)
King Abdullah University
of Science and Technology
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and Minerals in Dharam, Saudi Arabi