Semiconductors for water splitting: Material design principles

Role of materials computation

Traditionally

- Predict new phases of materials, or guide experiments
- Provide additional detail or explain existing experiments
- Test a hypothesis or theory that cannot be tested experimentally

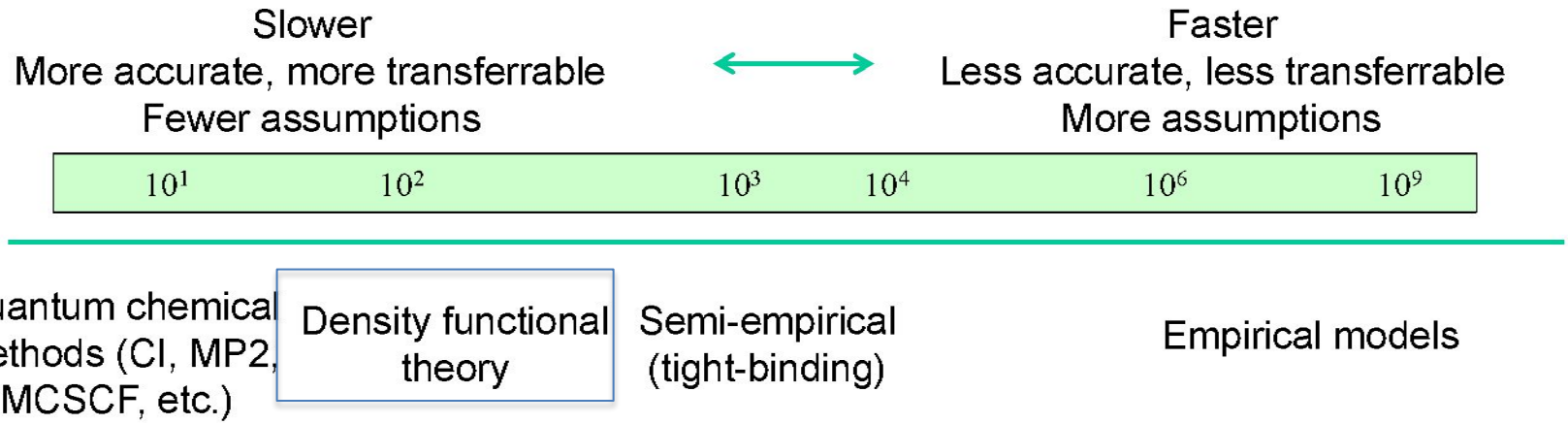
Modern days

- Guide experimental efforts by screening candidate materials (perhaps in an industrial setting)
- Model to build your intuition about a material or process

All materials modeling is empirical

- All models for materials are constructed from experimental observations
- When using them to make predictions, you can only say something new in regimes where your model is not explicitly fitted to experiment observations
- The latter can be very challenging – be afraid!

Accuracy vs Time trade-off

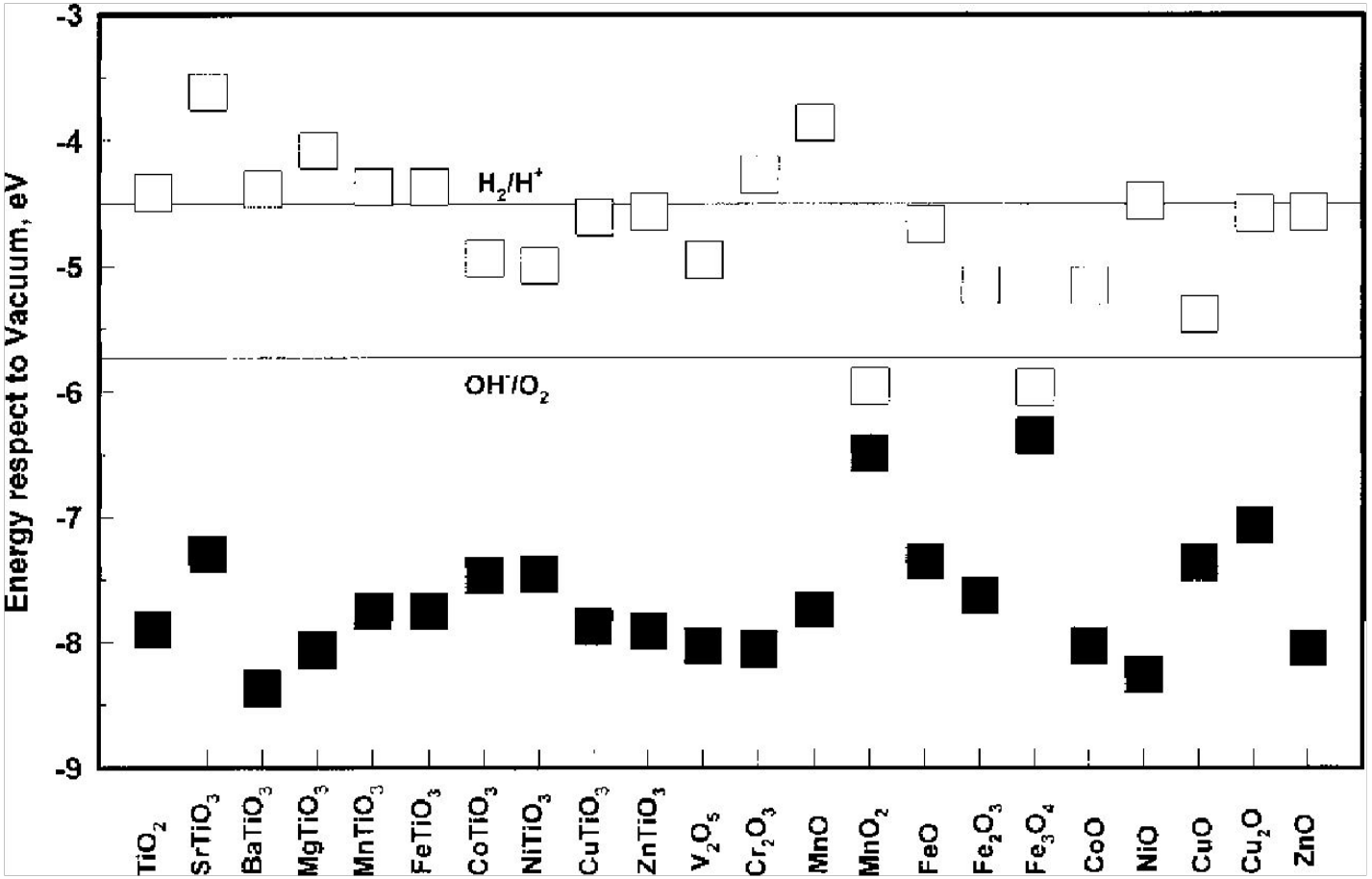


Screening for new candidates

- Requirements for a good PEC material
  - Stable
  - Suitable band gap
  - Appropriate band positions
  - Suitable mobility of charge carriers

- Catalyze hydrogen and oxygen evolution

Energy level diagrams



Butler-Ginley scheme

- Mulliken scale
  - Average of electron affinity and ionization energy

- Geometric mean of electronegativity
  - Mid-gap state

$$E_{VB} = -X_{GM} - E_g/2$$
$$E_{CB} = -X_{GM} + E_g/2$$

Can we find out locate these band positions?

- Exercise 1:

- Let us locate the band positions for TiO_2, ZnO and $SrTiO_3$.
- Band gaps:
  - TiO_2 – 3.2 eV
  - ZnO – 3.2 eV
  - $SrTiO_3$ – 3.4 eV

- Electronegativity
- Ti 3.45 O 7.53 Zn 4.45 Sr 2.0

- TiO_2
  - VB -7.4 eV
  - CB -4.2 eV
- ZnO
  - VB -7.38
  - CB -4.18

Can we find out locate these band positions?

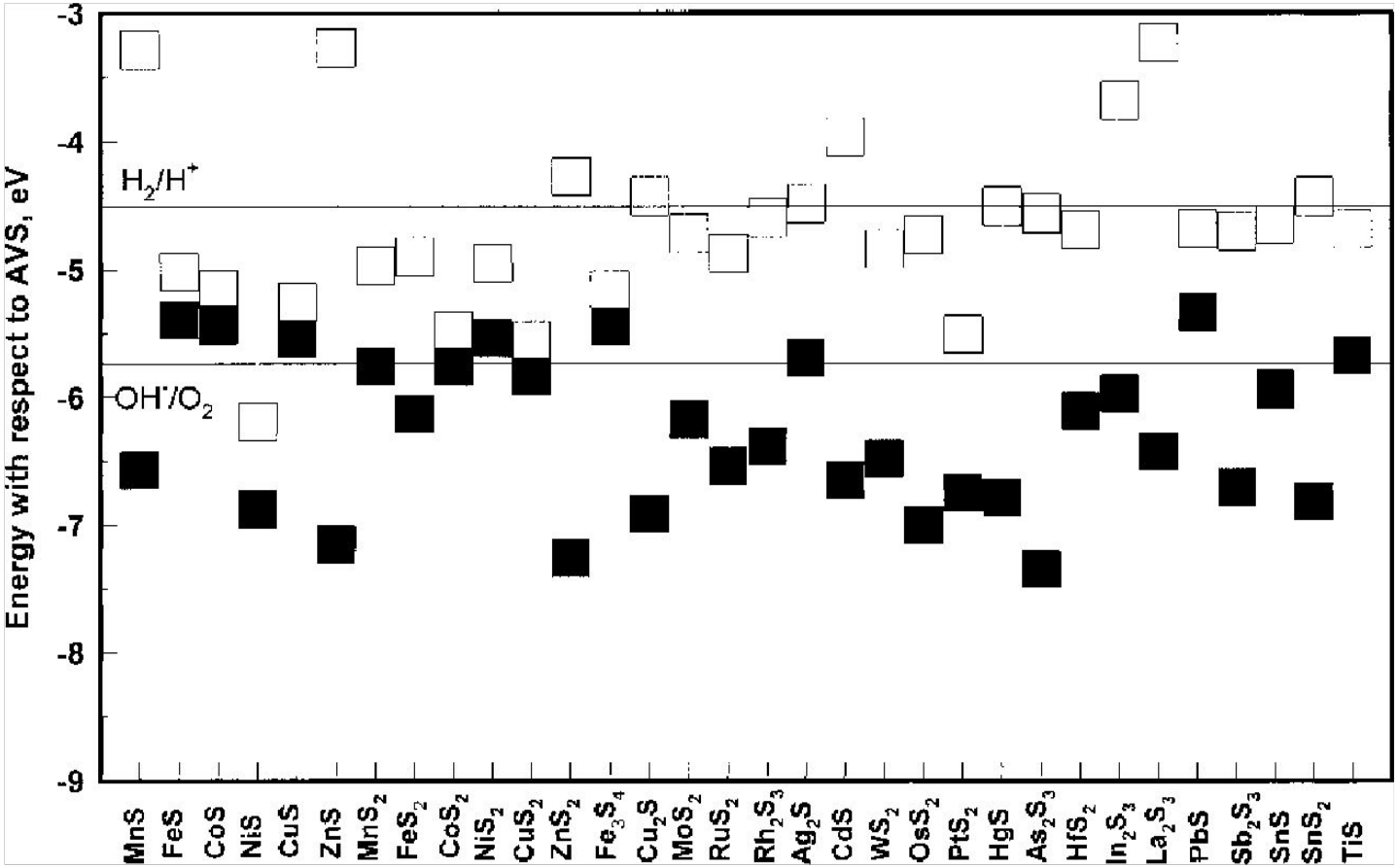
- Exercise 2:

- Let us locate the band positions for ZnS, ZnS_2 and TiS_2
- Band gaps:
  - TiS_2 – 0.7 eV
  - ZnS – 3.6 eV
  - ZnS_2 – 2.70 eV

- Electronegativity
- Ti 3.45 S 6.22 Zn 4.45

- TiS_2
  - VB -5.46
  - CB -4.76

Sulfides


Energy with respect to AVS, eV
-3
-4
-5
-6
-7
-8
-9
H_2/H^+
OH^-/O_2
MnS
FeS
CoS
NiS
CuS
ZnS
MnS_2
FeS_2
CoS_2
NiS_2
CuS_2
ZnS_2
Fe_3S_4
Cu_2S
MoS_2
RuS_2
Rh_2S_3
Ag_2S
CdS
WS_2
OsS_2
PtS_2
HgS
As_2S_3
HfS_2
In_2S_3
La_2S_3
PbS
Sb_2S_3
SnS
SnS_2
TiS

Stability

1. Structure relaxation and calculation of the total energy: RPBE.
Linear programming for calculating the heat of formation:

Stability of the compound with respect to its possible constituents

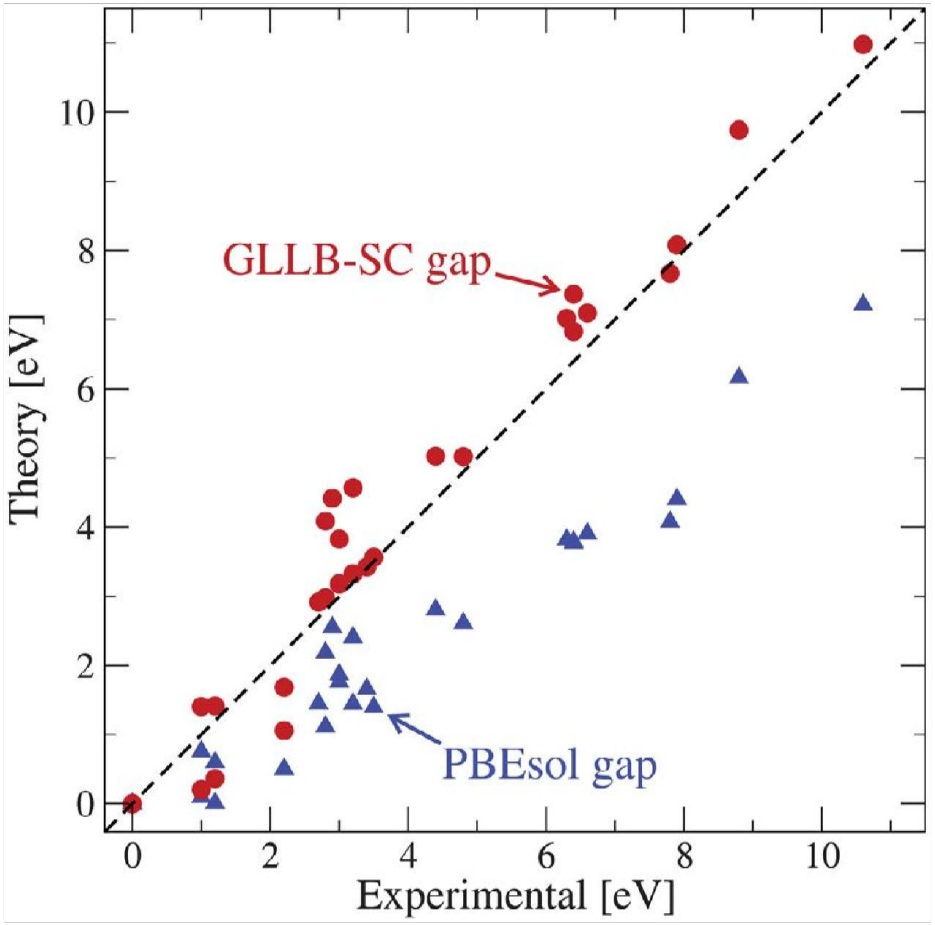
Calculate band gap

Calculation of the bandgap:

GLLB-SC (Gritsenko *et al.*, *Phys. Rev. A* **51**, 1944 (1995)).

- $E^{QP} = E^{KS} + \Delta_{xc}$
- Gap estimated within an error 0.5 eV.
- Error using PBEsol: 1.5 eV

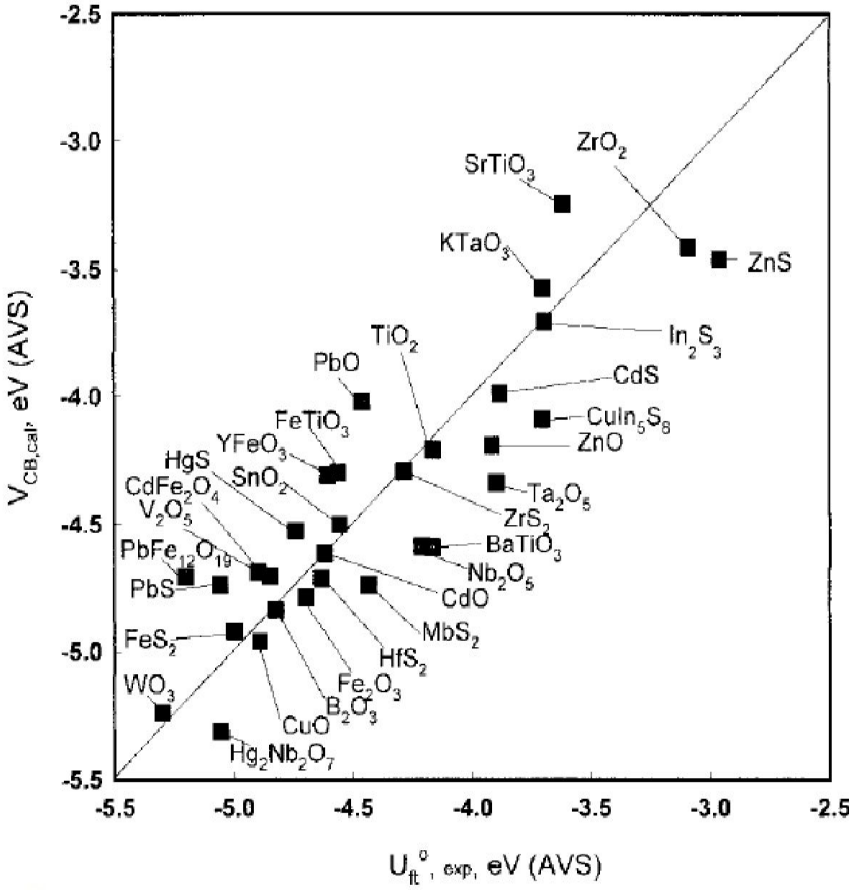
Improving band gaps



I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci **5**, 5814 (2012).

Band positions

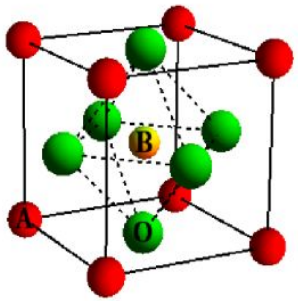
(Butler *et al.*, *J. Electrochem. Soc.* **125**, 228 (1978)).



Materials for screening

																He
											B	C	N	O	F	Ne
Li	Be					H					Al	Si	P	S	Cl	Ar
Na	Mg										Ga	Ge	As	Se	Br	Kr
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te	I	Xe
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb	Bi	Po	At	Rn
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg					

Excluded elements:
- Non Metals;
- Radioactive, toxic.



Screening of candidates:
- **52** different **elements**;
- Different **anions** (O, N, S, F, Cl, …);
- Different periodic structures (**perovskite**, rutile, spinel).

AB + (O_3, O_2N, ON_2, N_3, O_2S, O_2F, OFN) = 19000 combinations!

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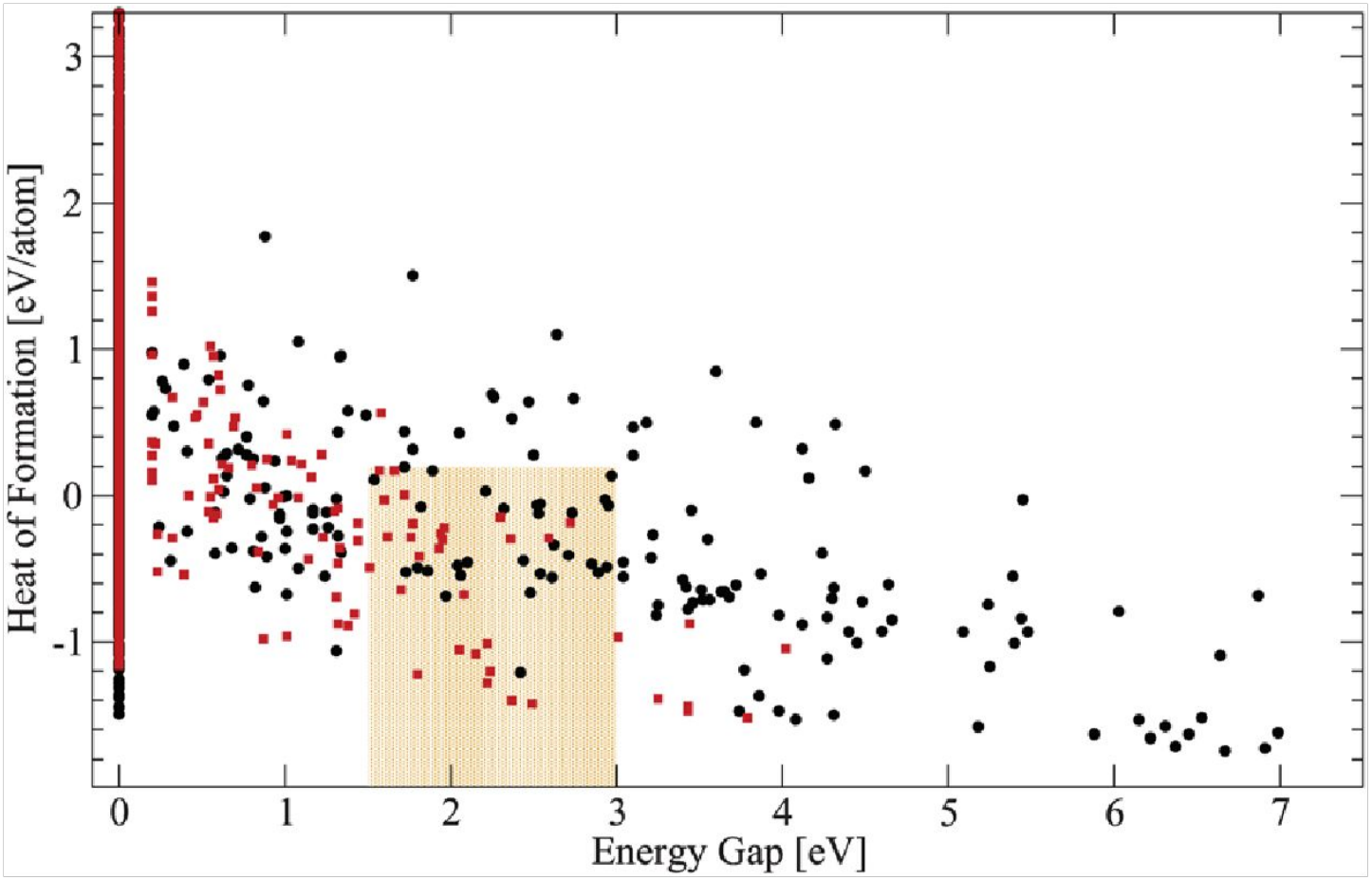
Stability vs Band gap issue



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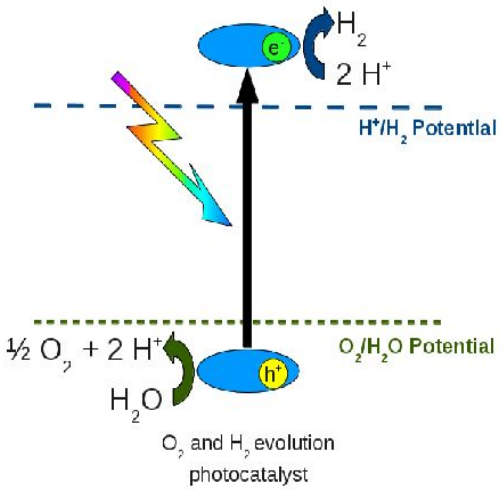
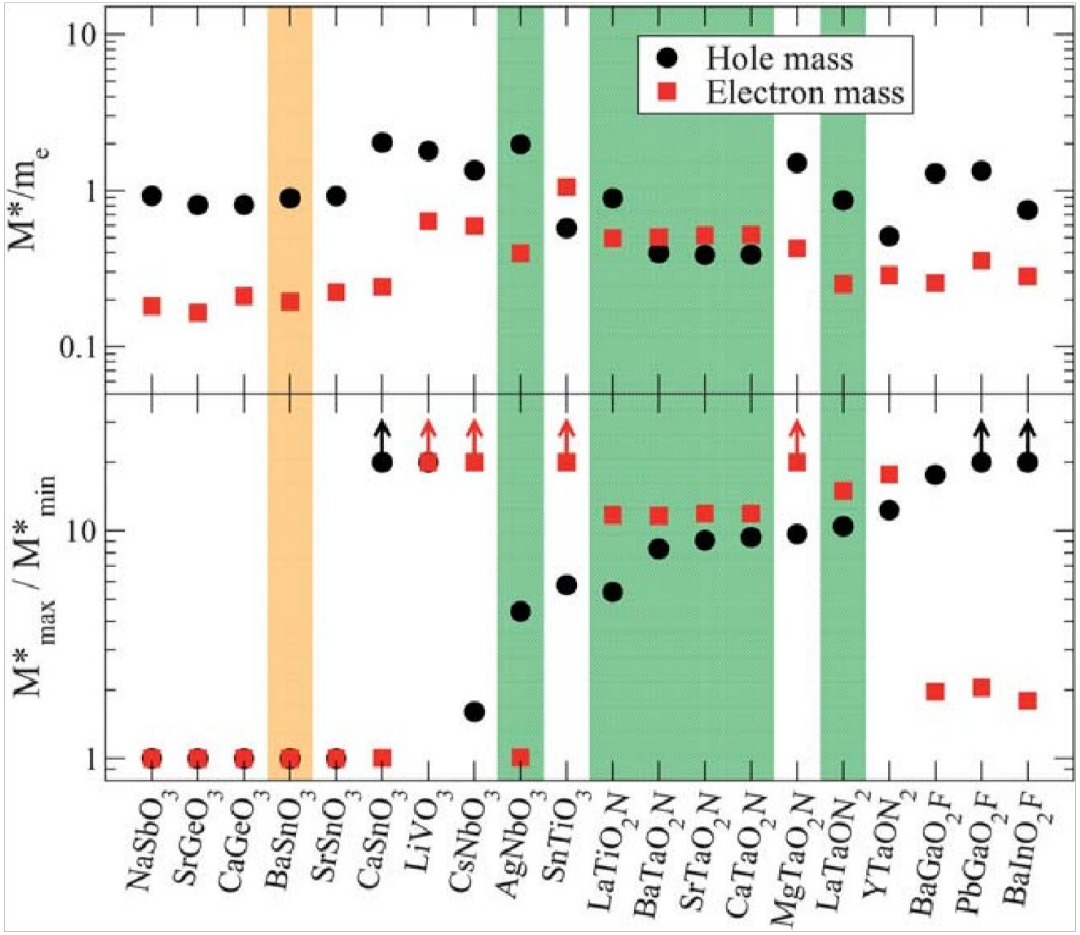
Candidates



20 candidates!

Known and successful materials:
$AgNbO_3$, $LaTiO_2N$, $BaTaO_2N$,
$SrTaO_2N$, $CaTaO_2N$, $LaTaON_2$

Additional criteria



Screening for new candidates

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Electrolytic water splitting

$$H_2O(l) + * \rightarrow OH^* + H^+ + e^-,$$

$$OH^* \rightarrow O^* + H^+ + e^-,$$

$$O^* + H_2O(l) \rightarrow OOH^* + H^+ + e^-,$$

$$OOH^* \rightarrow * + O_2(g) + H^+ + e^-.$$

Two simple concepts

For each elementary step:

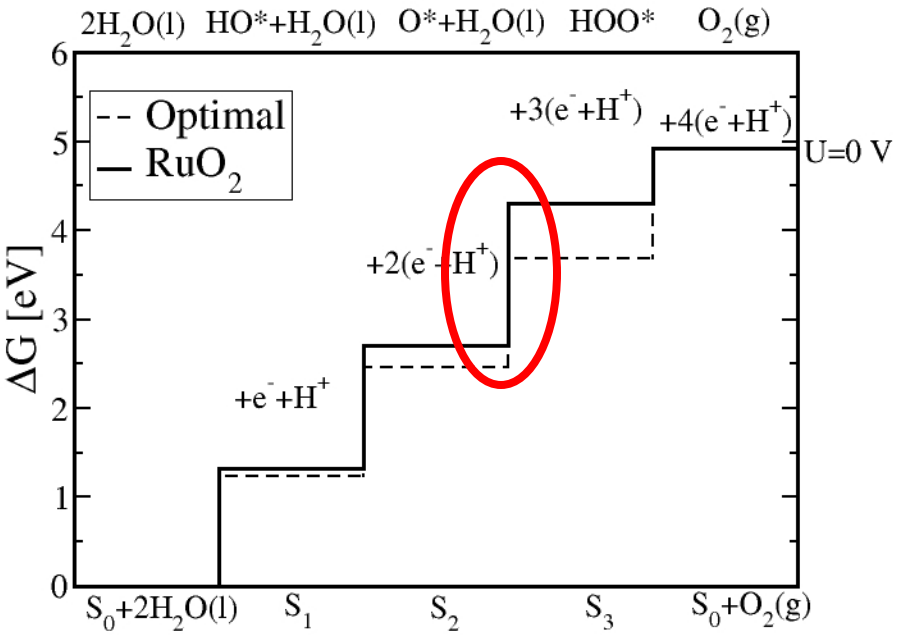
$\Delta G(U) = \Delta G_0 - eU$

The limiting potential, U_0, where this step is exergonic:

$\Delta G(U_0)=0 <=> U_0=\Delta G_0/e$

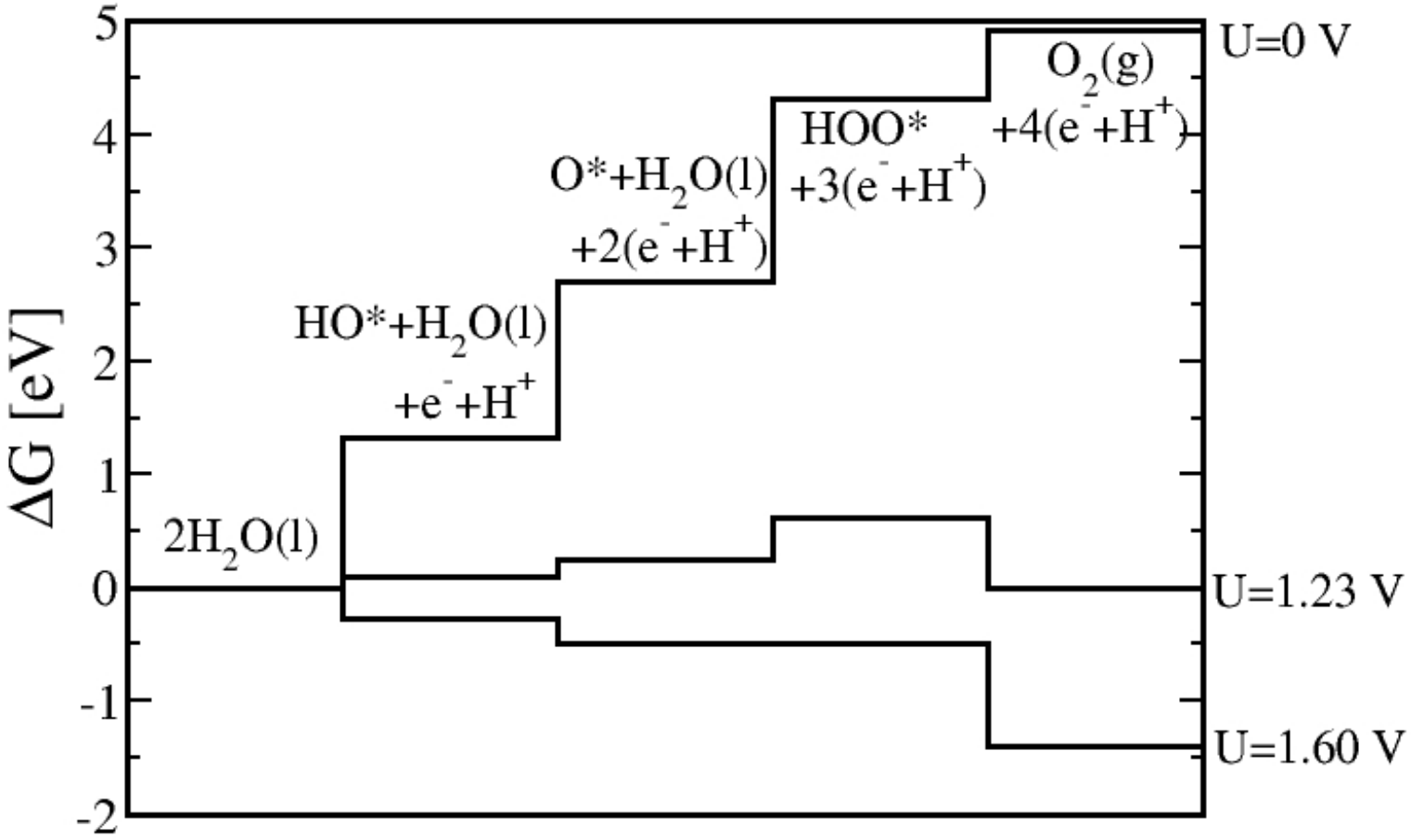
The theoretical overpotential:

$\eta = U_0-1.23\ V$

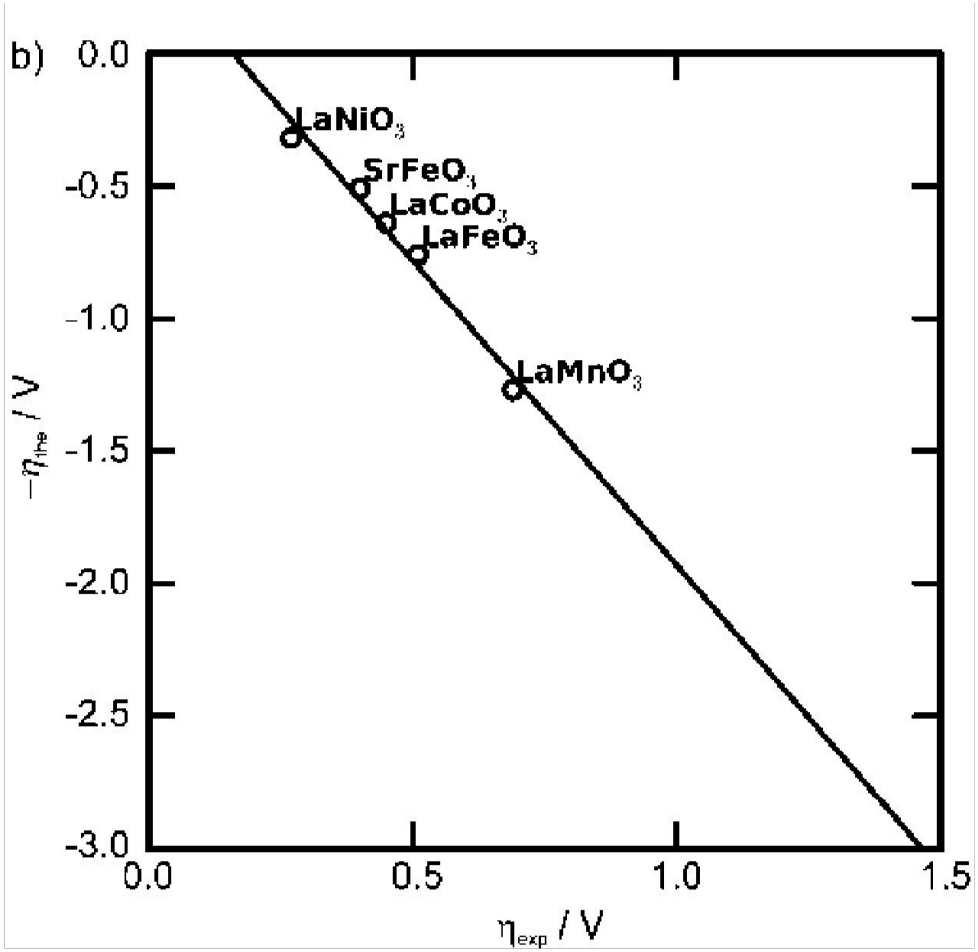


J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Kitchin, T. Bligaard, and H. Jonsson, J. Phys. Chem. B **108**, 17886 (2004).

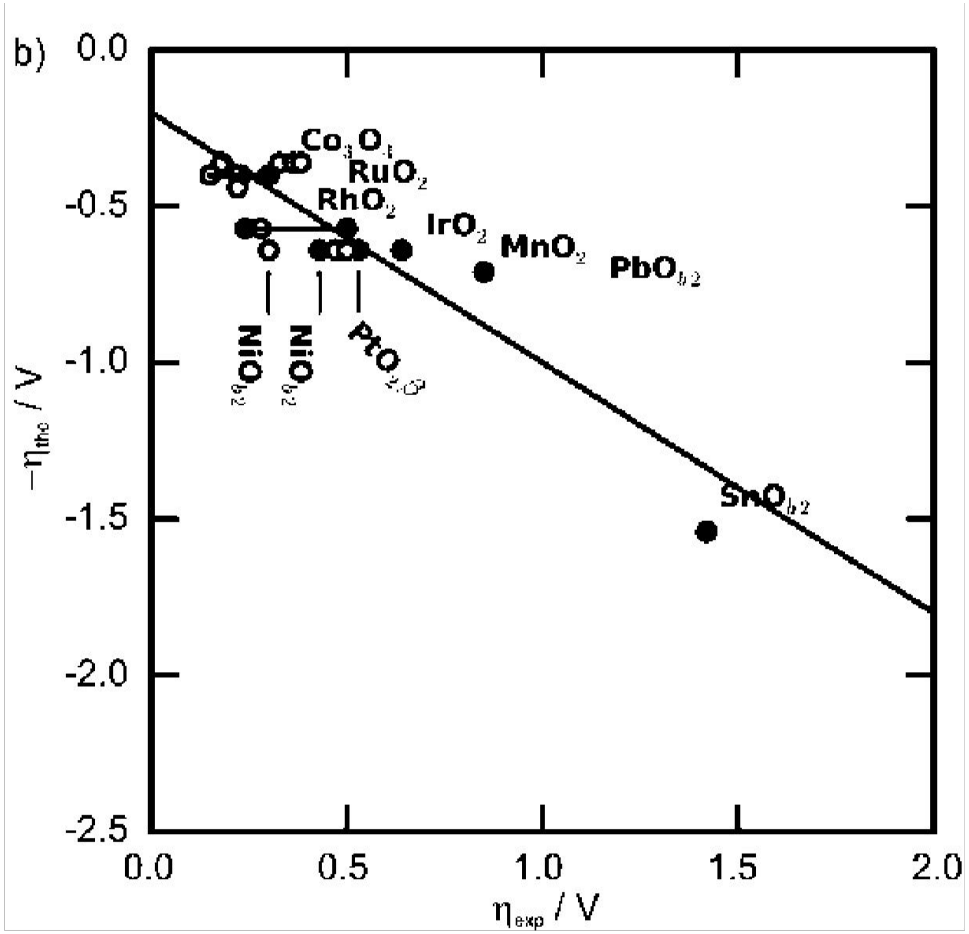
Free energy diagram on RuO_2



Electrolytic water splitting on pervoskites



Rutile and spinel oxides

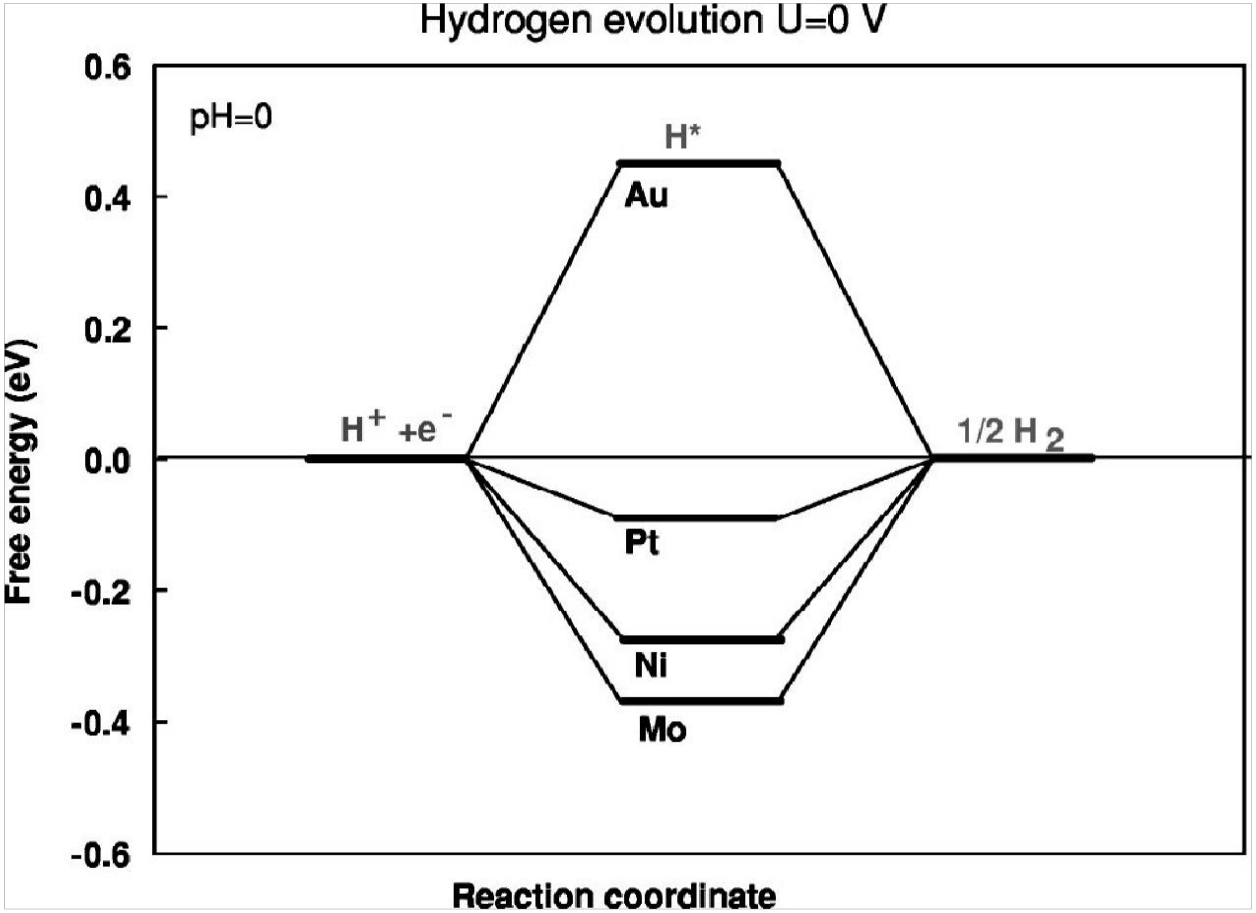


Hydrogen evolution

$$* + 2H^+ + 2e^- \leftrightarrow H^* + H^+ + e^-$$

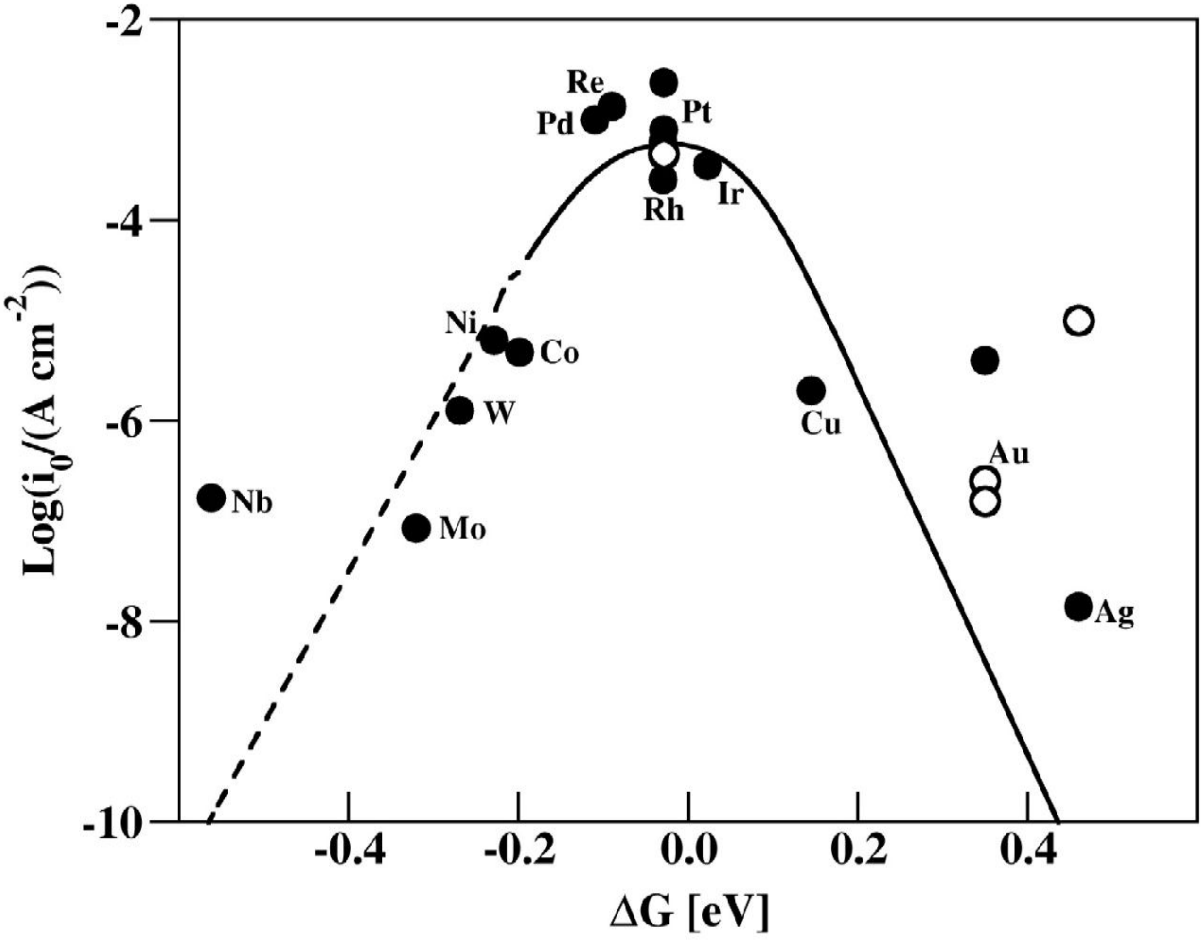
$$H^* + H^+ + e^- \leftrightarrow * + H_2(g)$$

Free energy diagram

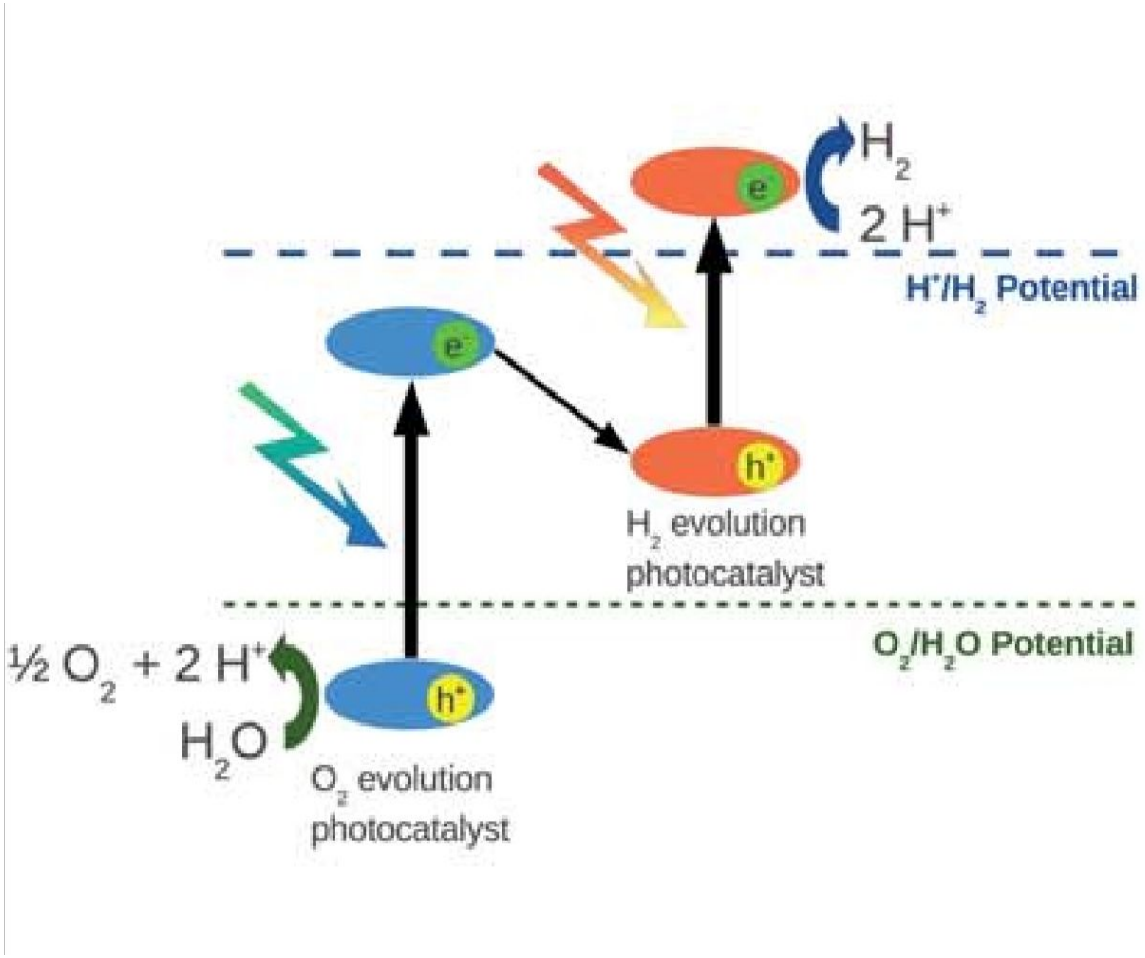


J.K. Nørskov, T. Bligaard, A. Logadottir, J.R. Kitchin, J. Chen, S. Pandelov, and U. Stimming, J. Electrochem. Soc. **152**, J23 (2005).

Hydrogen evolution volcano



Tandem scheme



Conditions for tandem scheme

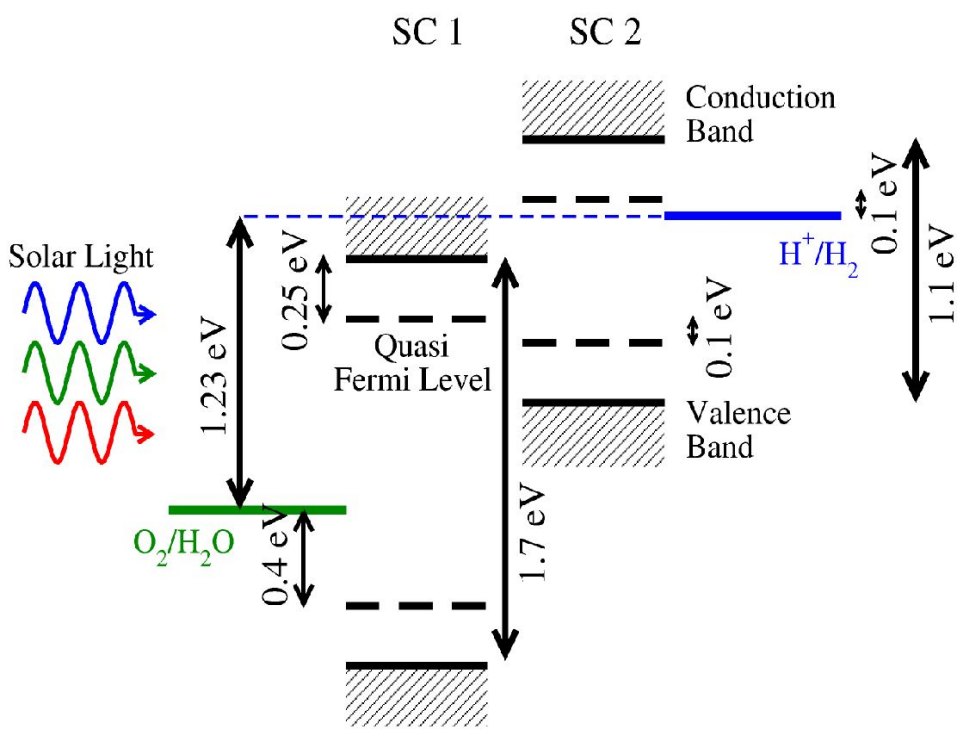
First semiconductor

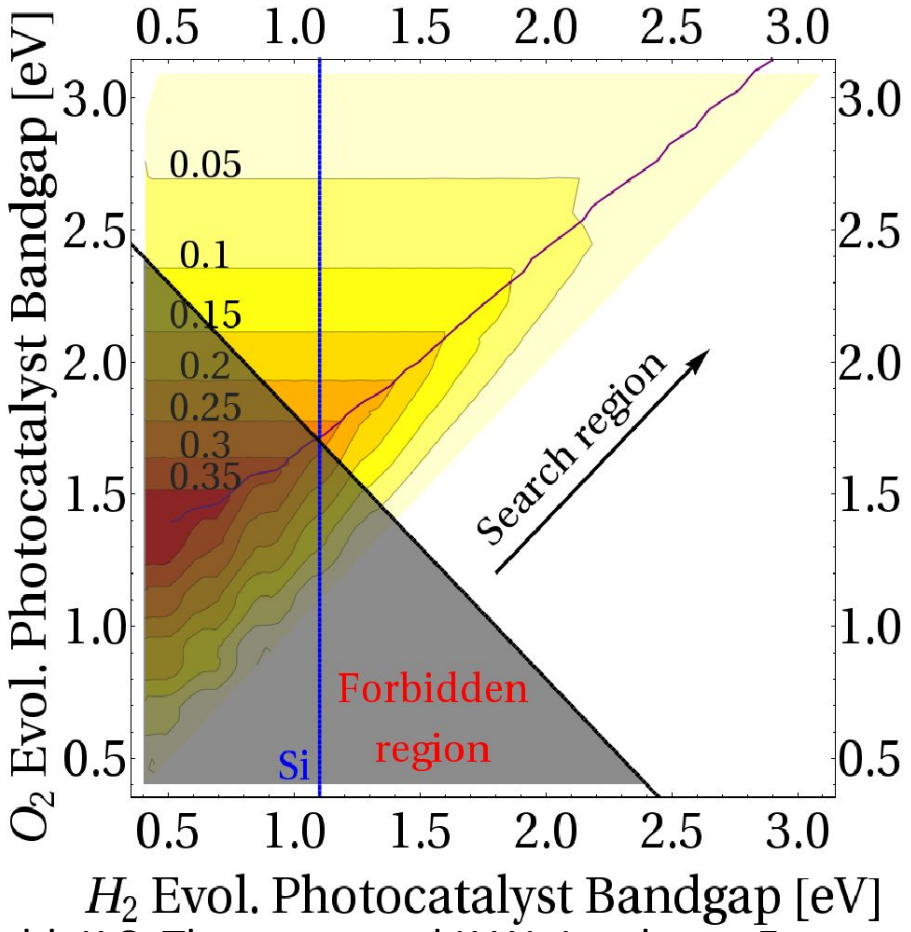
- Valence band appropriate for oxygen evolution
- Conduction band appropriate for second semiconductor VB

Second semiconductor

- Conduction band appropriate for hydrogen evolution

Tandem cell





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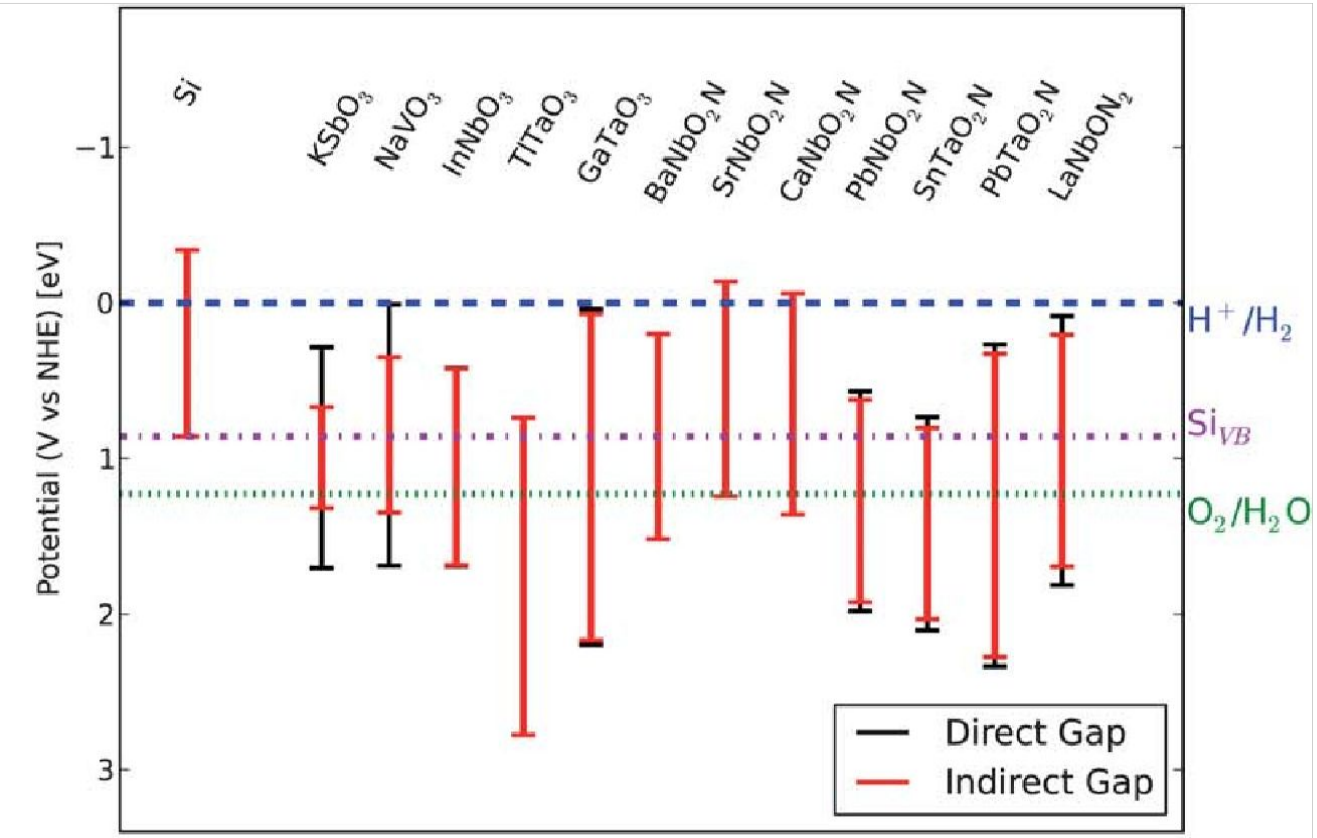
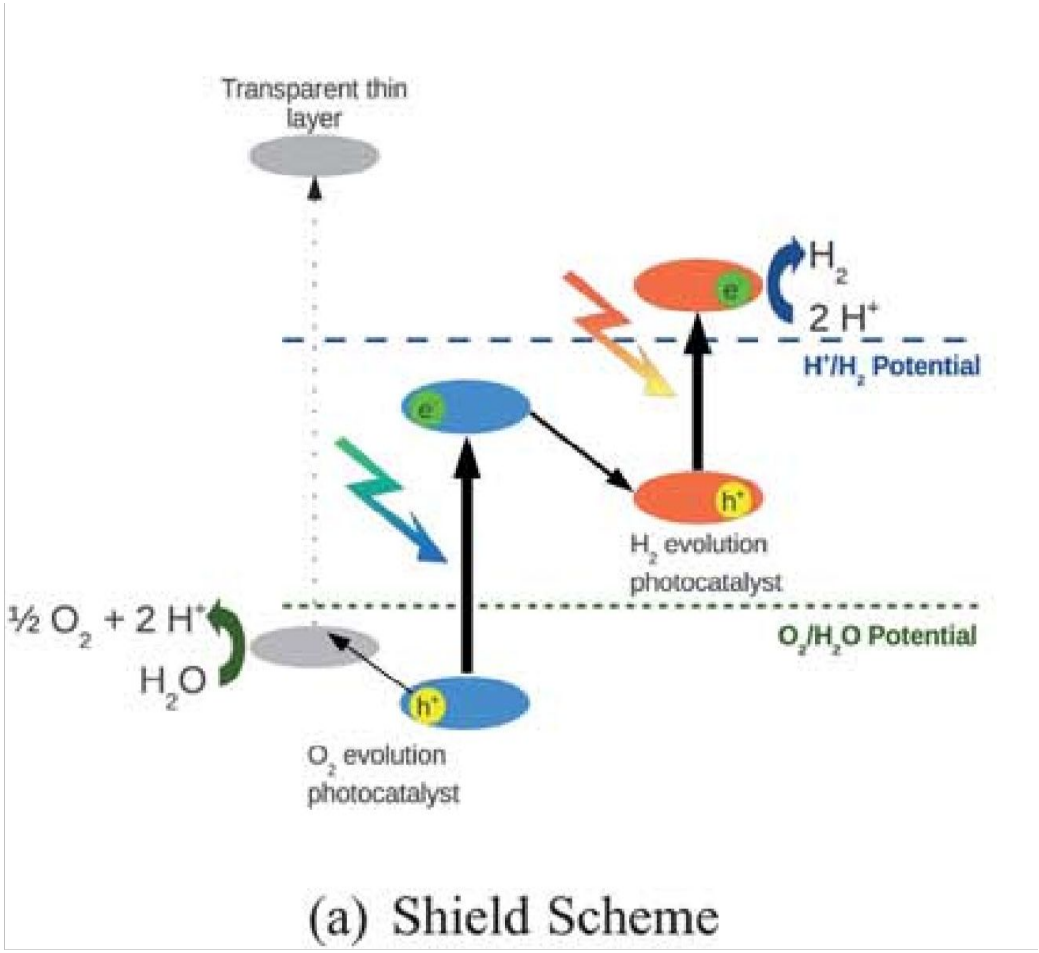
Tandem cell



(b) Candidates for Tandem Cell WS

Transparent shield

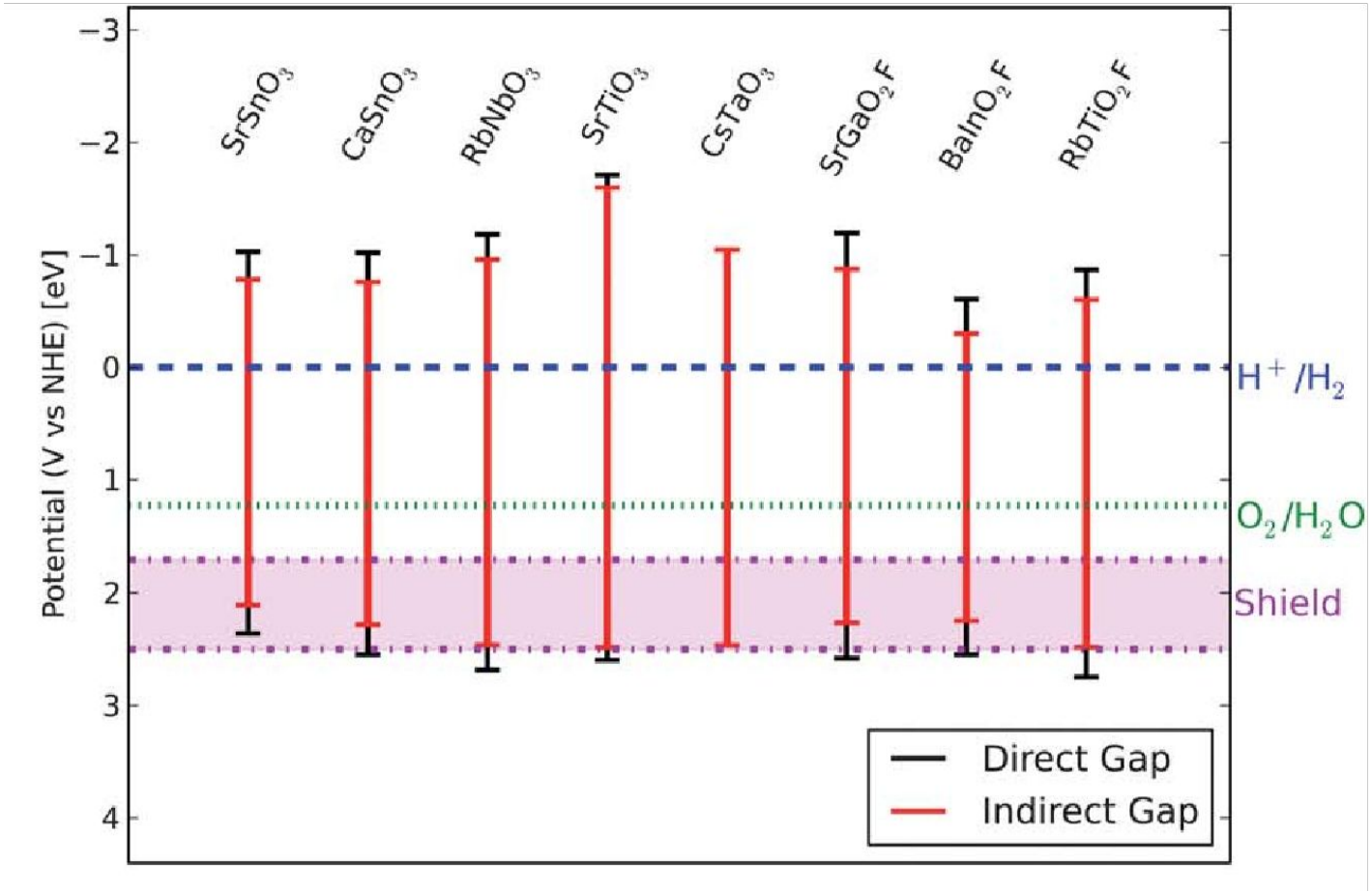


(a) Shield Scheme

Conditions for transparent shield

- Must be transparent
  - High band gap
- Valence band level between the edges of the photocatalyst and oxygen evolution for hole mobility

Candidates for transparent shield



Database

Database: https://cmr.fysik.dtu.dk