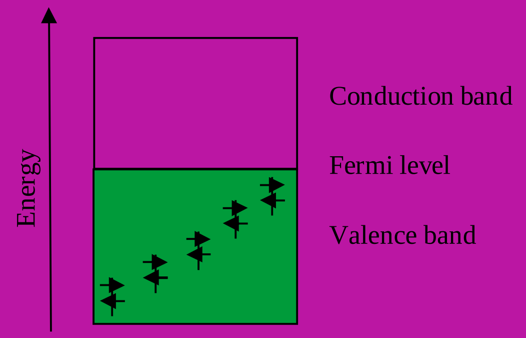
Module B2: Material Substitution

AAE-E3120 Circular Economy for Energy Storage



Prof. Annukka Santasalo-Aarnio

Aalto University
School of Engineering

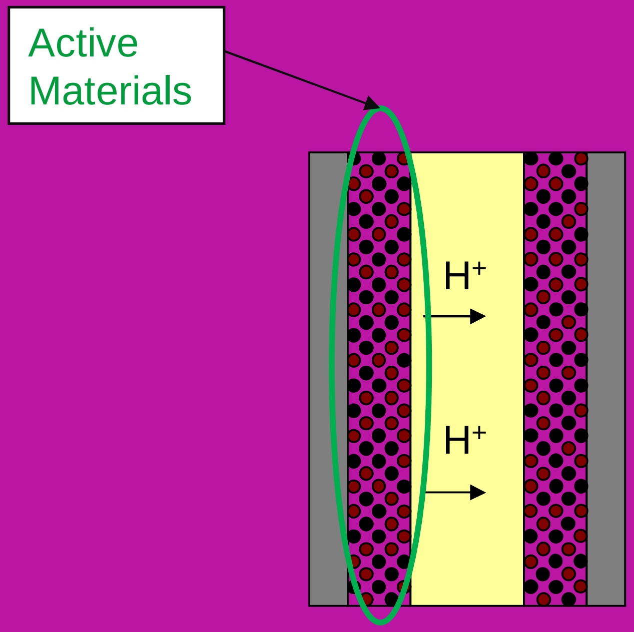
Learning outcomes

- **Recognize the material choice effect to degradation mechanisms of the system**
    - What are the frame of active materials we can select?

- **Develop new design for recycling approach for energy storage application and justify with scientific argumentation**
    - High activity (how to ensure that with active material selection?)

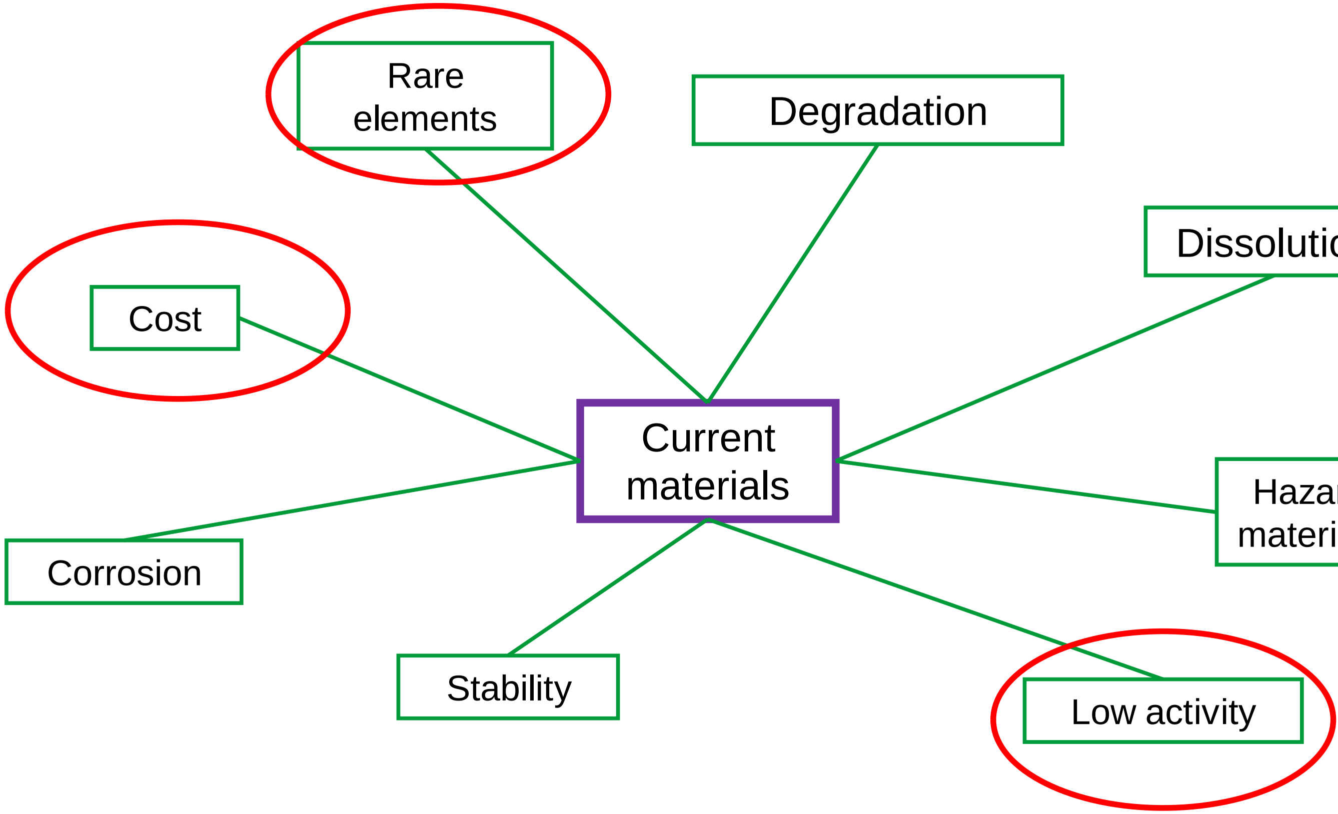
Active materials

- In electrochemical systems



Why have we selected problematic materials for the active materials?

Challenged with active materials



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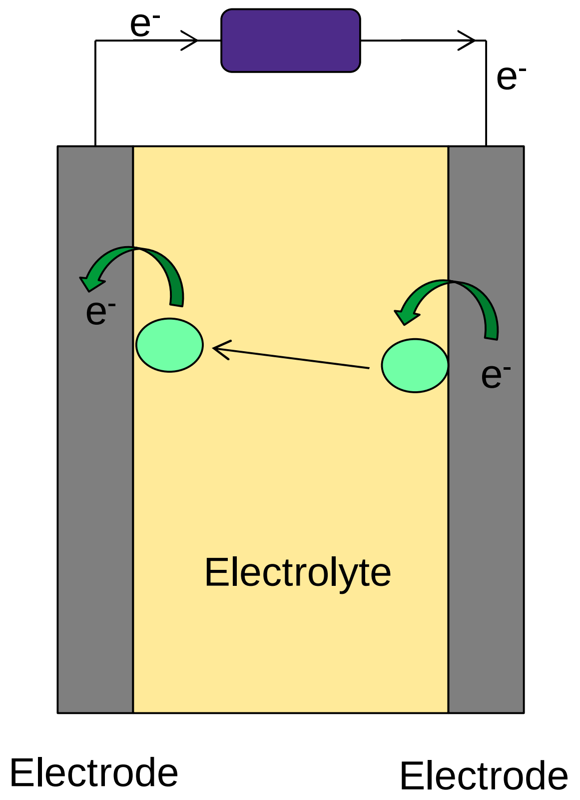
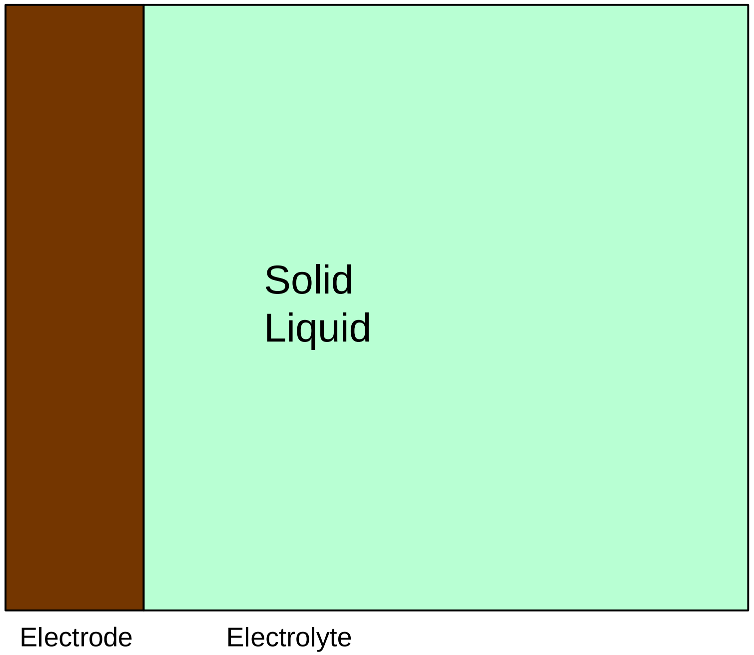
Development for active materials

Electrochemical cell



Reaction on two phase boundary



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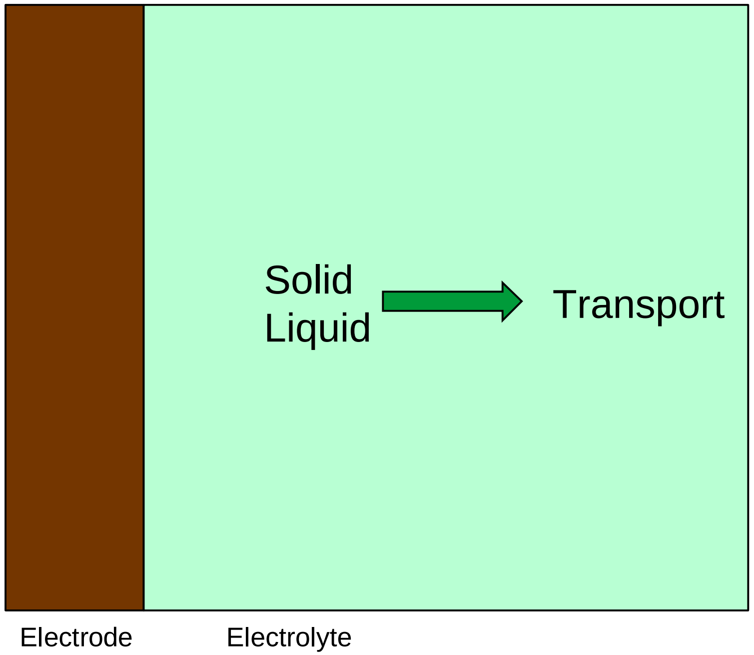
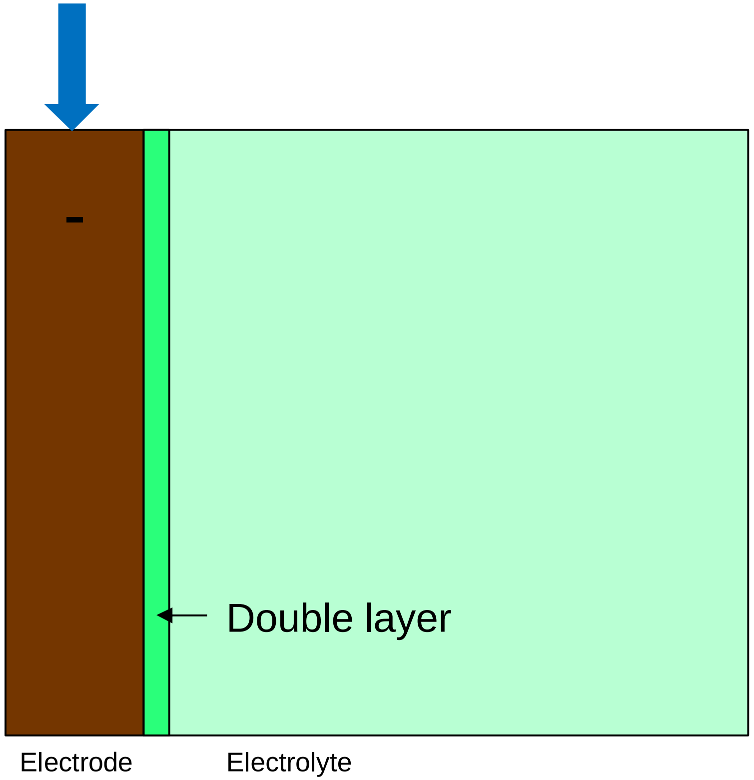
Reaction on two phase boundary

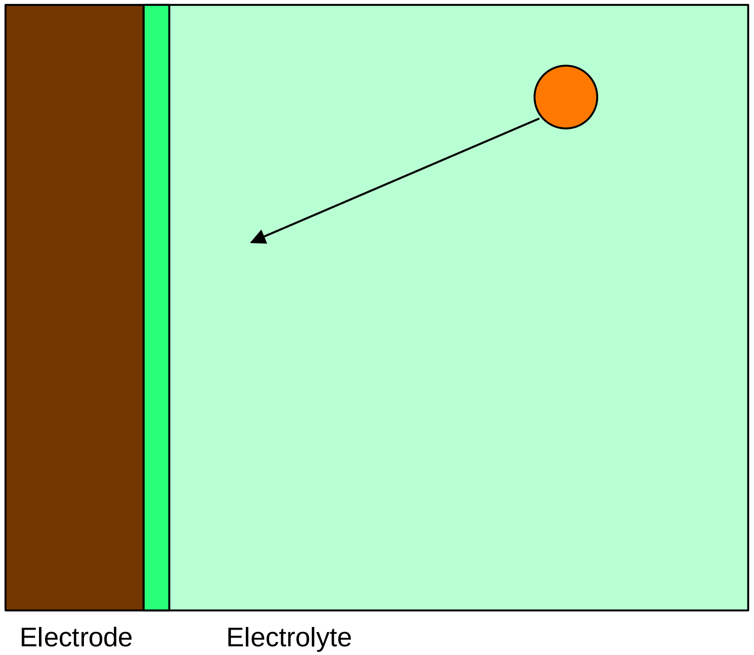


When voltage is applied



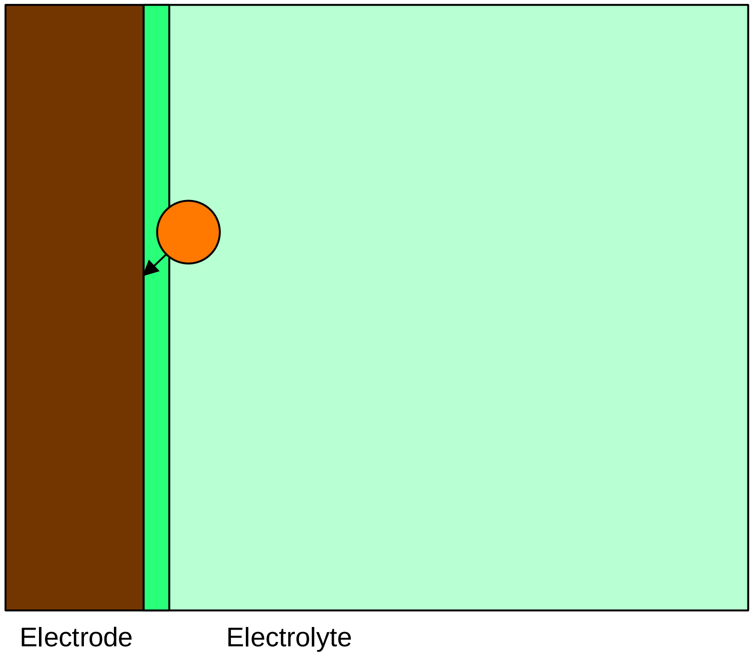
Ions in the electrolyte (if liquid) will organize to the electrode surface and create a Double Layer

Reaction on two phase boundary



Diffusion
vicinity of the electrode

Reaction on two phase boundary



Adsorption
to the electrode

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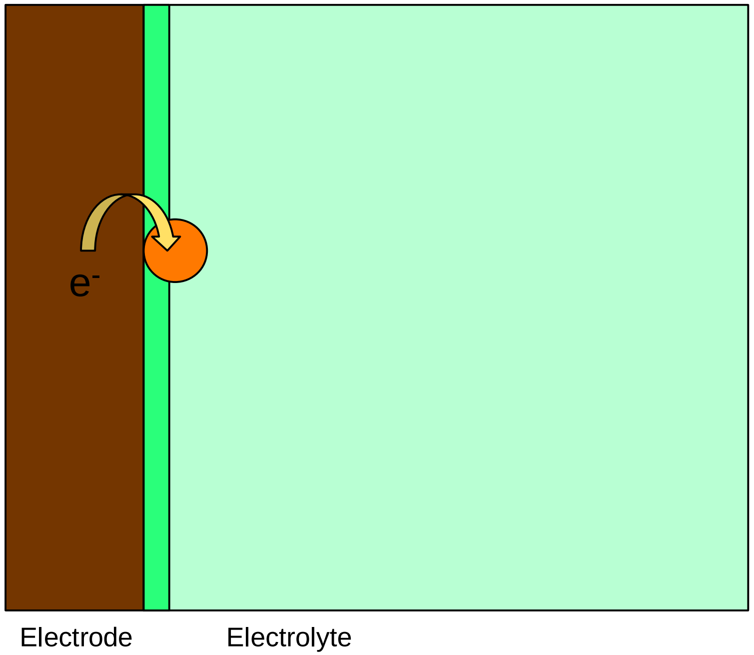
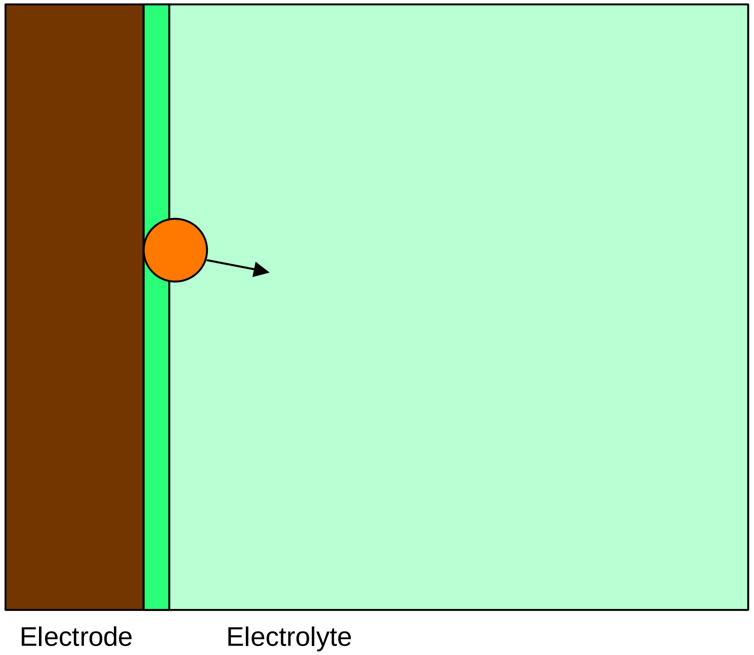
Reaction on two phase boundary



Reaction:
electron transfer

Reaction on two phase boundary



Desorption
From the electrode

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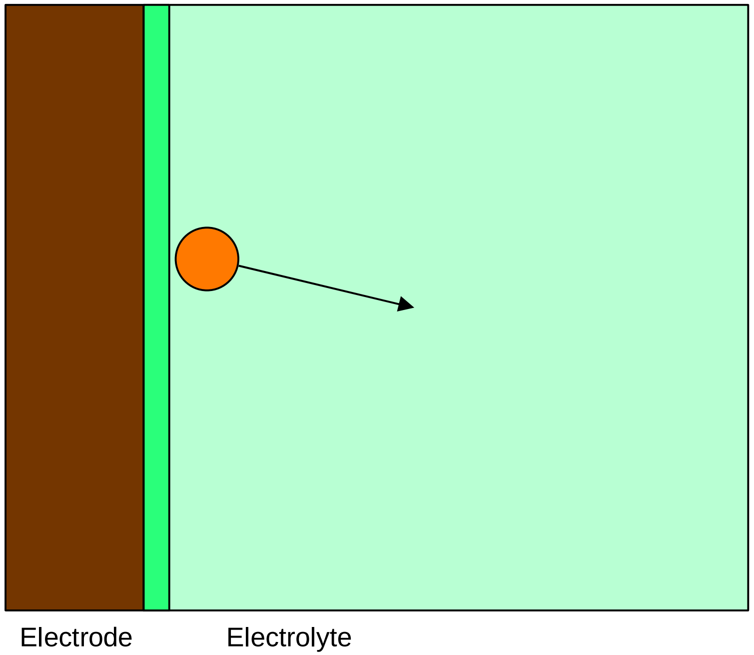
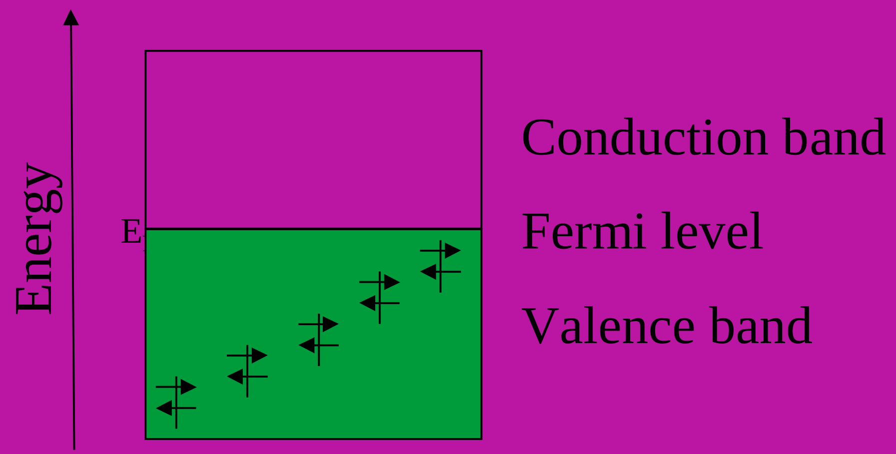
Reaction on two phase boundary



Diffusion
Back to the bulk

Active materials

- Requirement for catalyst materials



Why have we selected problematic materials for the active materials?

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Active materials

Lecture Journal

What is a catalyst?

Electrocatalyst?

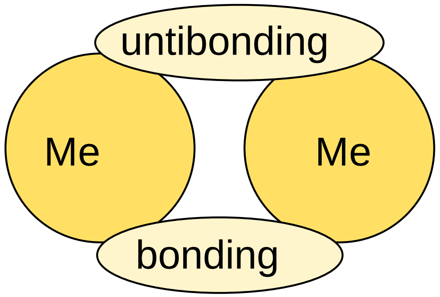
Active materials

Lecture Journal
What is a catalyst?
Electrocatalyst?

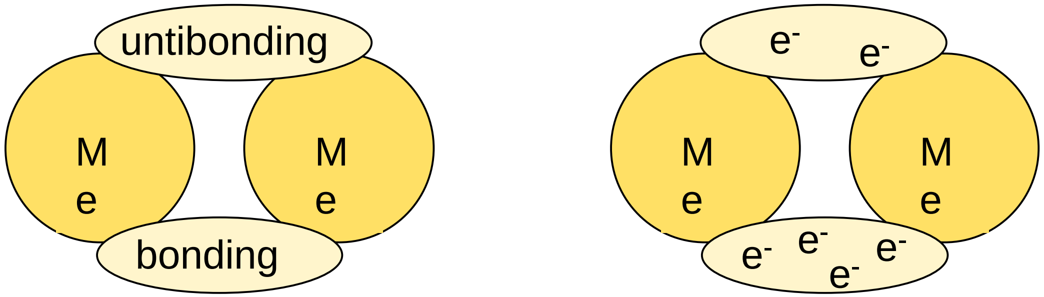
Electrocatalyst

A material working a catalyst in a reaction involving an electron transfer.

Metal atoms



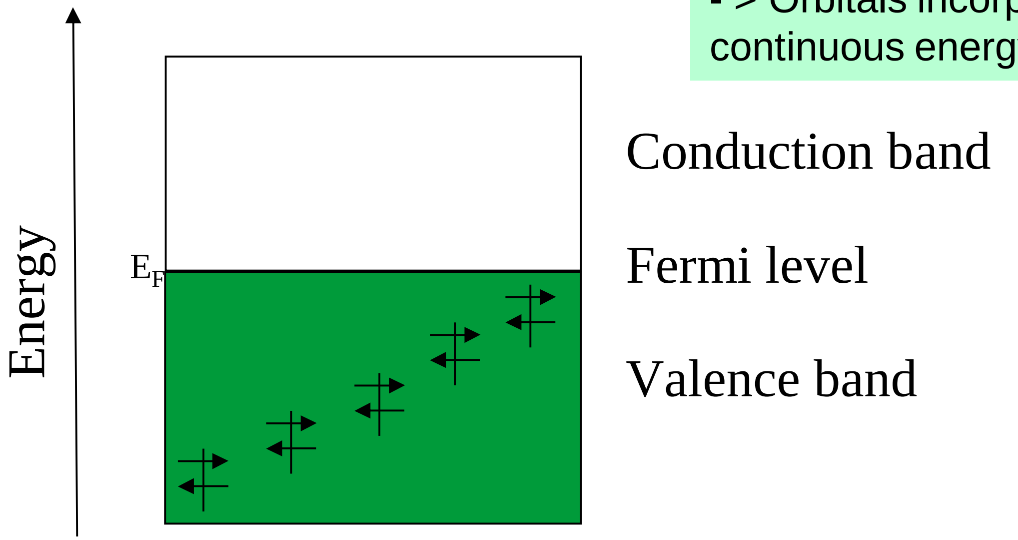
Metal atoms



If there are more electrons on the bonding orbital – the bond is stable

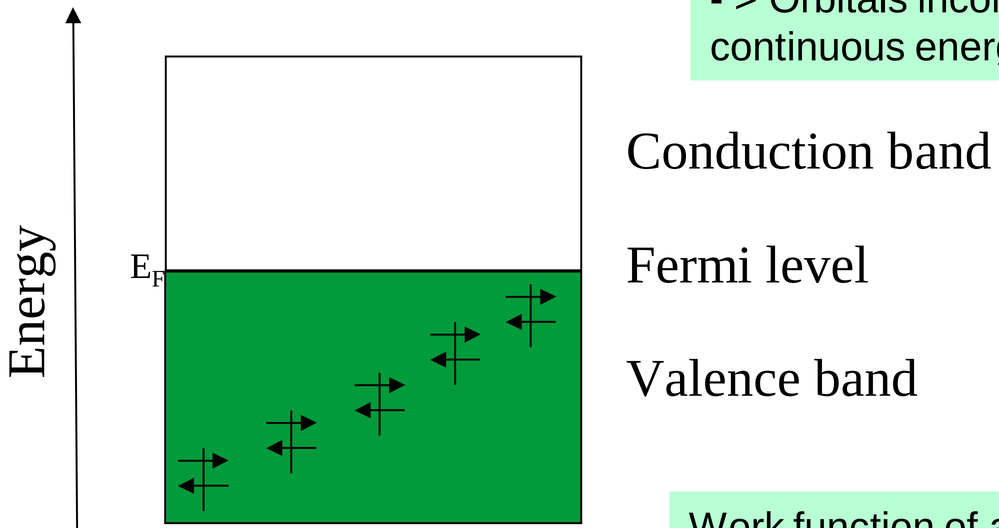
Metal Electrode

Formed of many metal atoms
- > Orbitals incorporate to
continuous energy bands



Metal Electrode

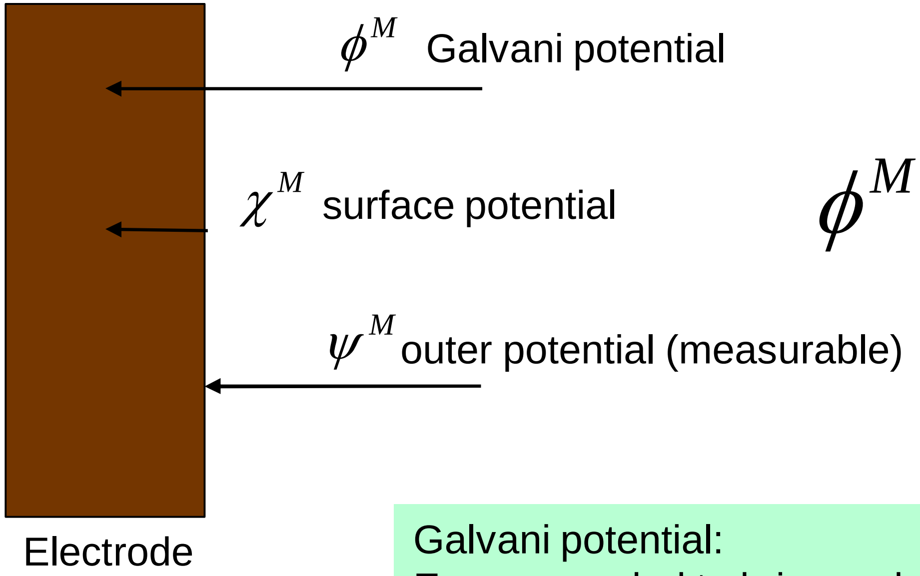
Formed of many metal atoms
- > Orbitals incorporate to continuous energy bands



$$E_F^M = -\Phi^M = \tilde{\mu}_e^M$$

Work function of a uncharged metal: The electrical work needed to remove an electron from the Fermi level of the metal to vacuum

Electrode potential



$$\phi^M = \chi^M + \psi^M$$

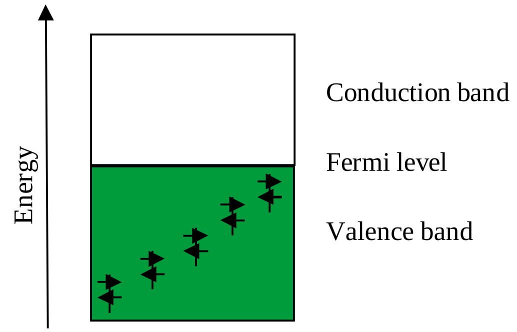
Galvani potential:
Energy needed to bring a charged particle from the vacuum to the inner part of the metal

Metal Electrode

$$E_F^M = -\Phi^M = \tilde{\mu}_e^M$$

Work function of uncharged electrode is?

$$\Phi^M =$$



Uncharged electrode

$$\tilde{\mu}_e^M = \mu_e^M - F\chi^M$$

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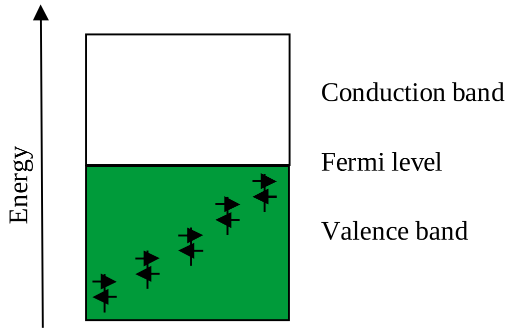
Metal Electrode

$$E_F^M = -\Phi^M = \tilde{\mu}_e^M$$

Work function of uncharged electrode is?

$$\Phi^M = F\chi^M - \mu_e^M$$



Uncharged electrode

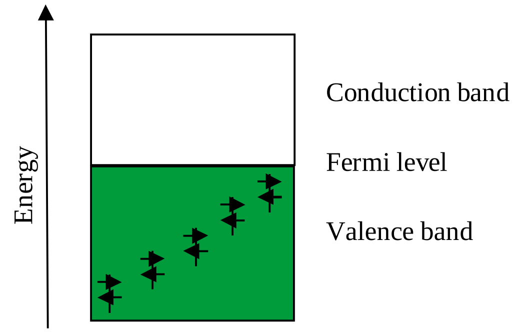
$$\boxed{\tilde{\mu}_e^M = \mu_e^M - F\chi^M}$$

Metal Electrode

$$E_F^M = -\Phi^M = \tilde{\mu}_e^M$$

Work function of uncharged electrode is?

$$\Phi^M = F\chi^M - \mu_e^M$$



Uncharged electrode

$$\tilde{\mu}_e^M = \mu_e^M - F\chi^M$$

Work function of a metal effects

- Surface potential -> Adsoprtion of molecules on the electrode

Work Function

Work function of a metal effects

- Surface potential -> Adsoprtion of molecules on the electrode

$$\Phi^M = F\chi^M - \mu_e^M$$

Different metals

	Φ (eV)
Pt	6.35[1]
Au	5.10[1]
Zn	4.3[1]

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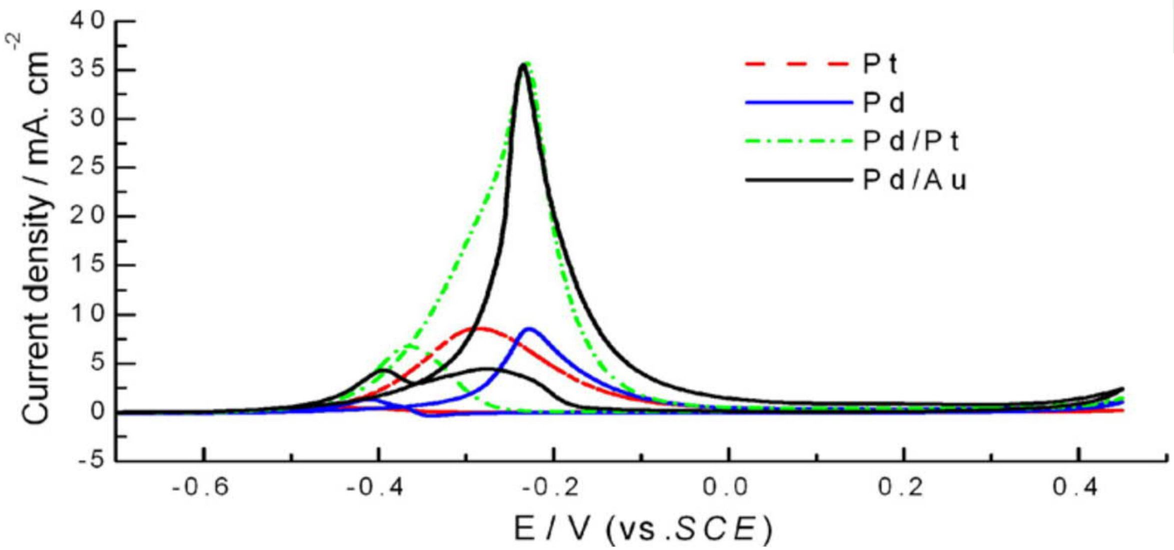
D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, Boca Raton 1999/2000.

Work Function – how that effects performance?

	Φ /eV
Pd	5.0
Pt	6.35



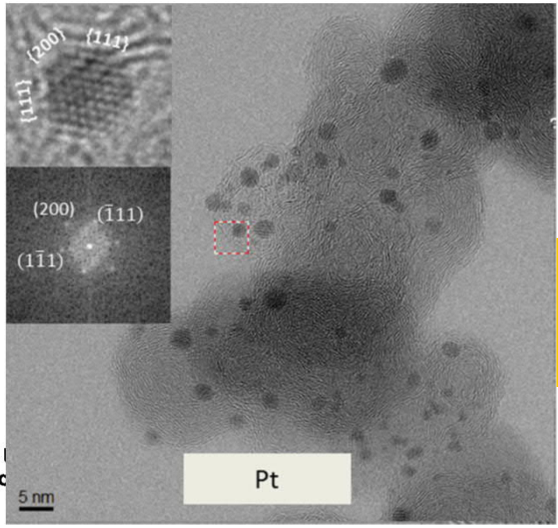
J. Zhang et al. Electrochem. Commun. 9 (2007) 1298.

Surface orientation

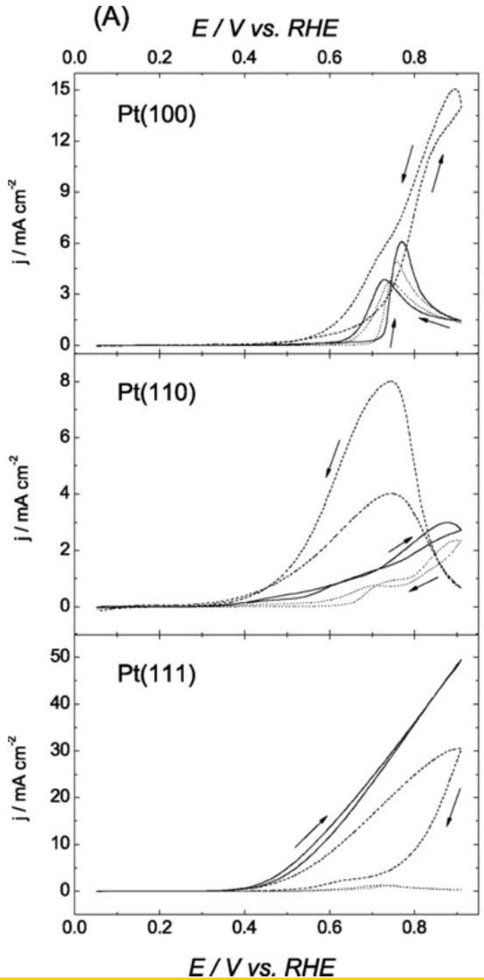
Crystalline structures

	Φ (eV)
Pt(100)	5.82[1]
Pt(110)	5.85[2]
Pt(111)	6.07[1]

1) M. Salmerón et al. Phys. Ref. B 28 (1983) 6758.
2) D. R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 80th ed., CRC Press, Boca Raton 1999/2000.



E. Sairanen et al. / Applied Catalysis B: Environmental 148–149 (2014) 11



Methanol (solid line), 2-Propanol (dashed line) and 50/50 mixture (thin line) oxidation in 0.1 M $HClO_4$ electrolyte on different surface orientations.

A. Santasalo et al. Electrochem. Acta 54 (2009) 6576.

Work Function – how to modify?

- Alloying metals effects the work function of the electrode

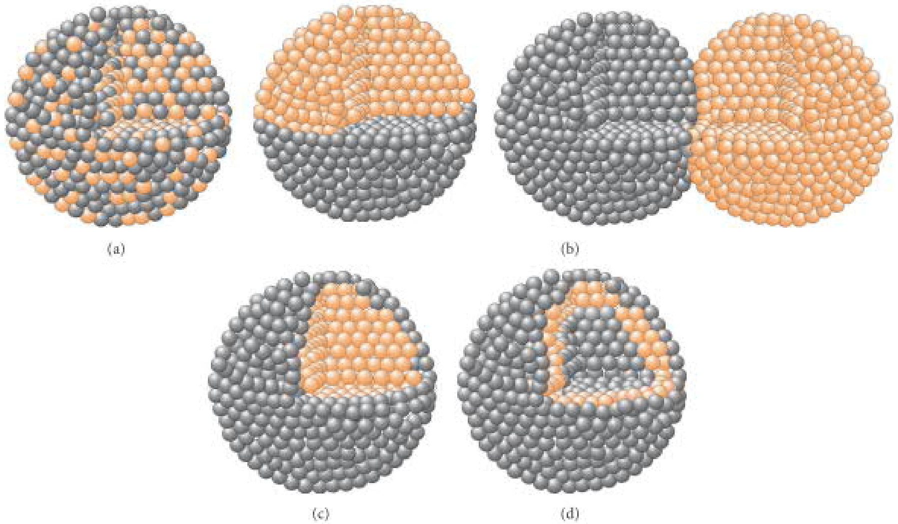
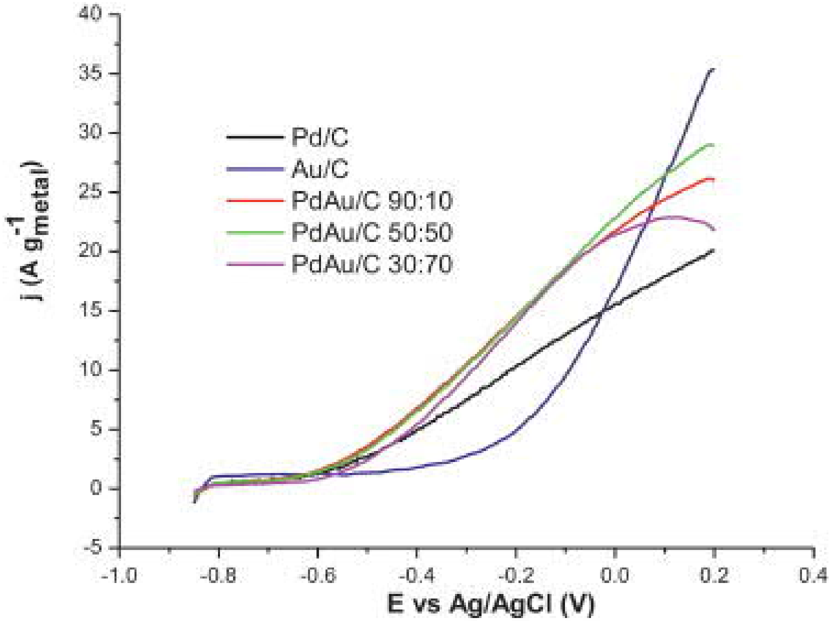


FIGURE 2: Schematic illustration of bimetallic NPs with different structures (a) alloy, (b) heterostructure, (c) core-shell, and (d) multishell structure.

Anna Zielińska-Jurek, Journal of Nanomaterials
Volume (2014), http://dx.doi.org/10.1155/2014/208920

Work Function – performance?



Ethanol oxidation in alkaline media (1 M KOH) on different catalyst. Au/C is gold nanoparticle catalyst on carbon support.

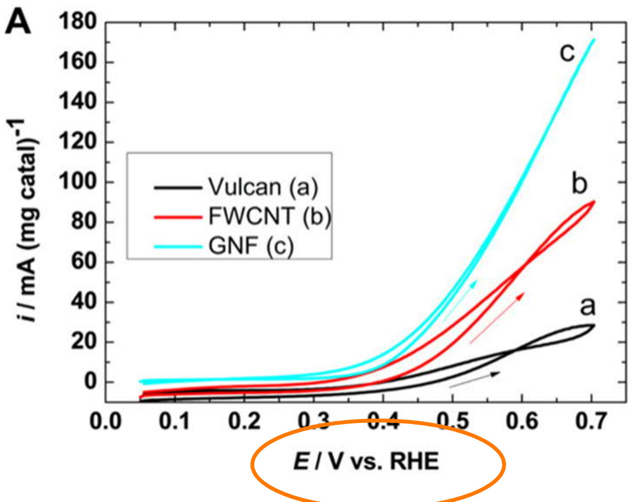
Lecture Journal

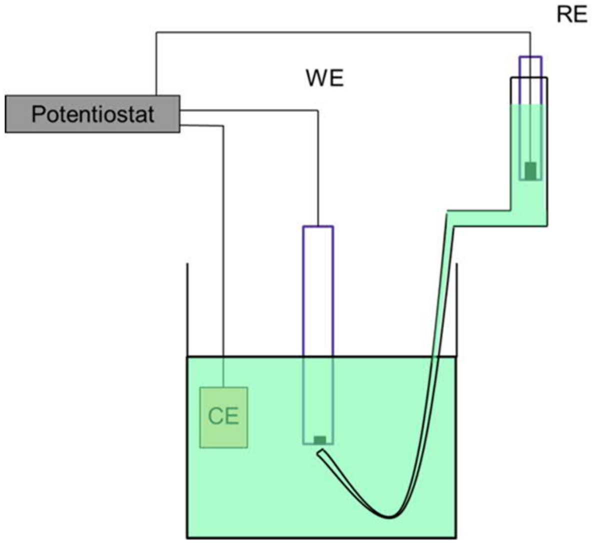
What would be the best catalyst for this particular reaction?

A. Geraldes *et al.* Electrochimica Acta 111 (2013) 455.

How to interpret the catalyst material data?

3 Electrode set up:
To study individual electrode reaction



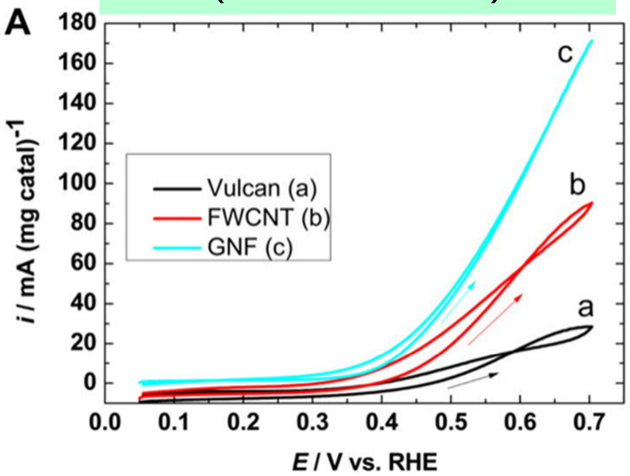


In electrochemical cell:
25 ºC
0.1 M $HClO_4$ + 1 M MeOH

A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

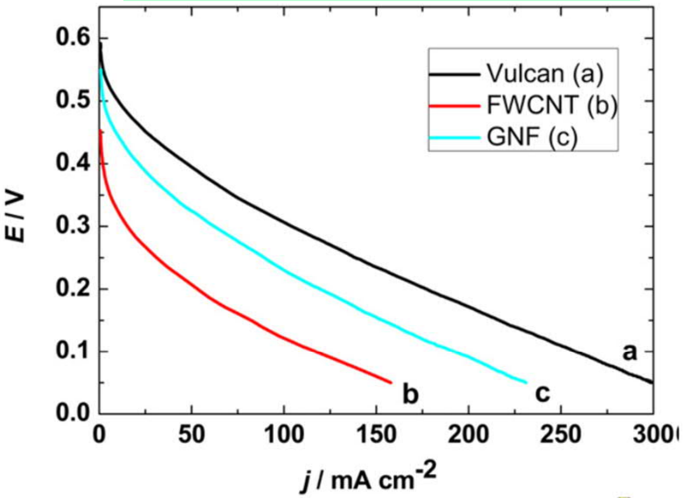
How to interpret the catalyst material data?

3 Electrode system
(anode reaction)

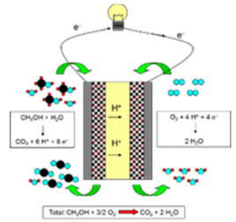


In electrochemical cell:
25 ºC
0.1 M $HClO_4$ + 1 M MeOH

2 Electrode system
(anode + cathode)

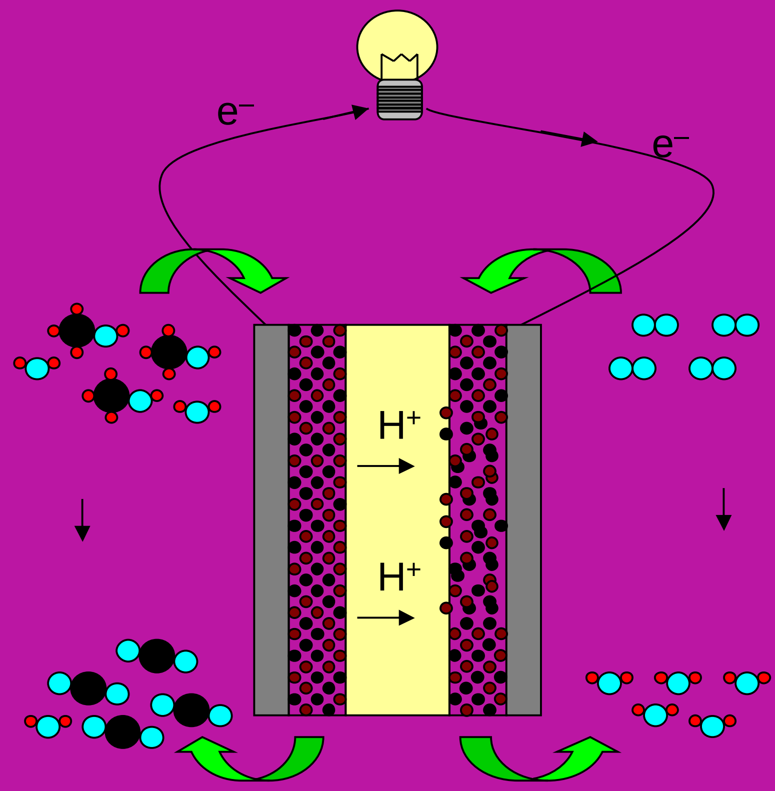


Single cell fuel cell:
70 ºC
1 M MeOH



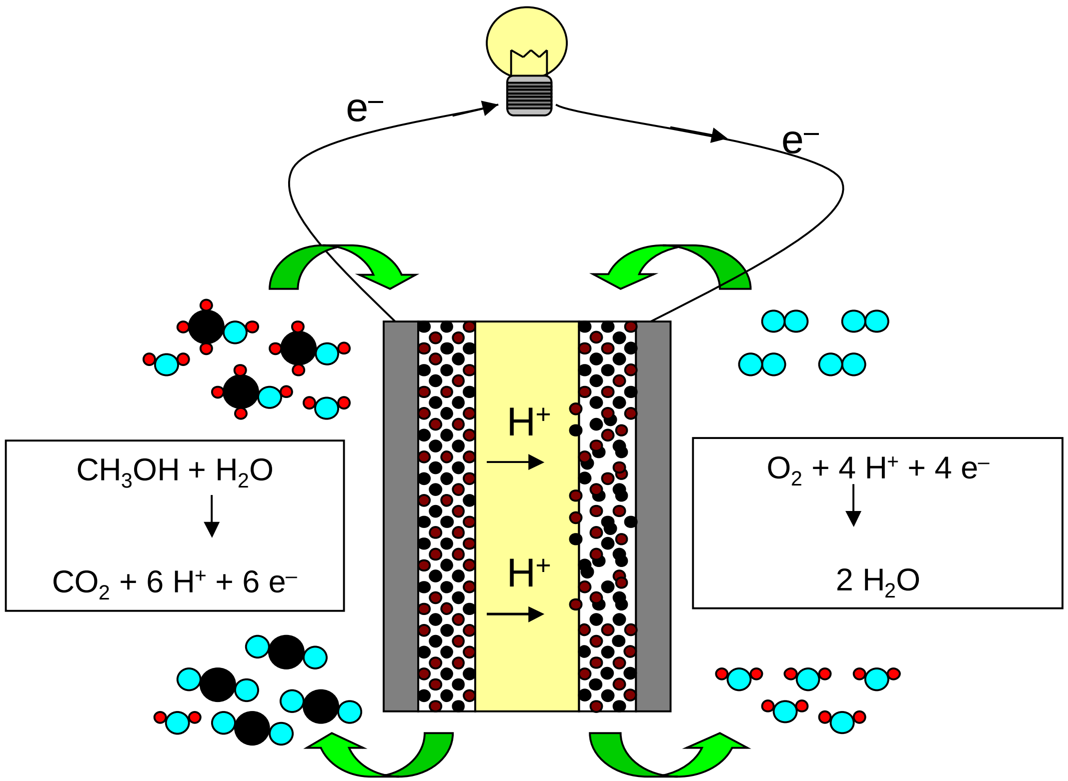
A. Santasalo-Aarnio et al. International Journal of Hydrogen Energy, 37 (2012) 3415-3424.

Catalyst example: Direct Methanol Fuel Cell



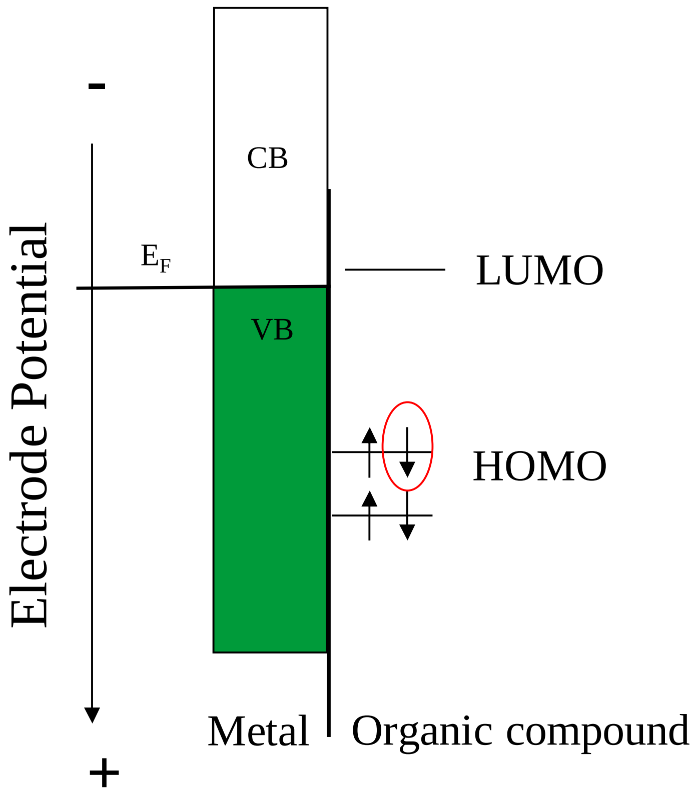
Total: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$

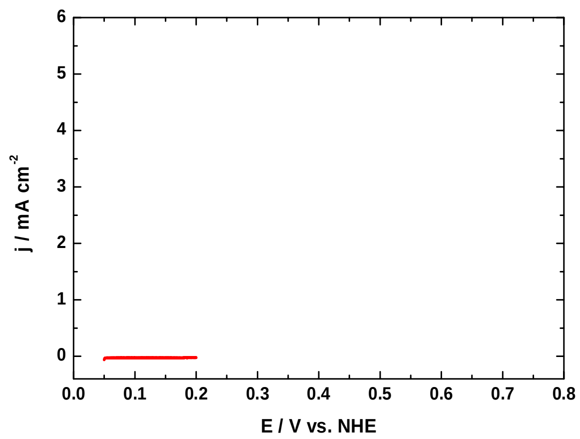
Example: Direct Methanol Fuel Cell



Total: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2 H_2O$

Electro-oxidation of methanol





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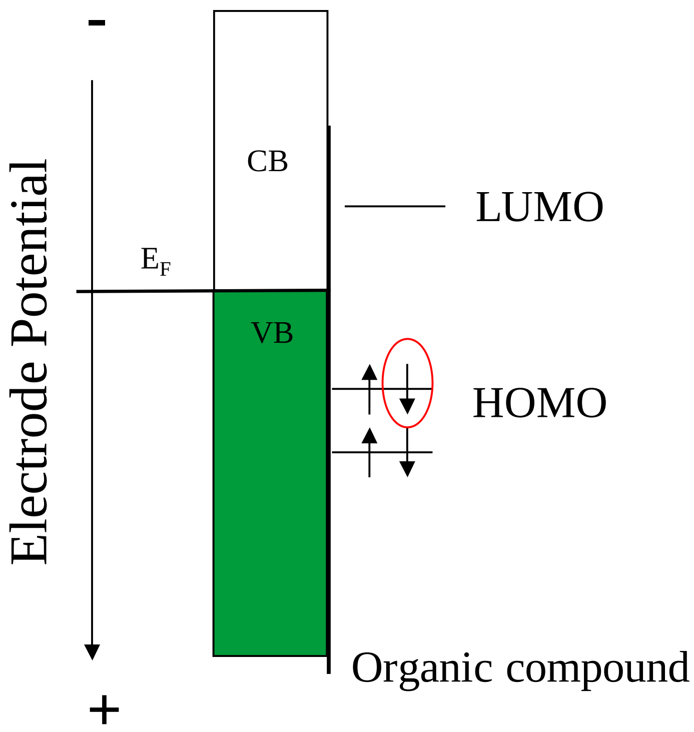
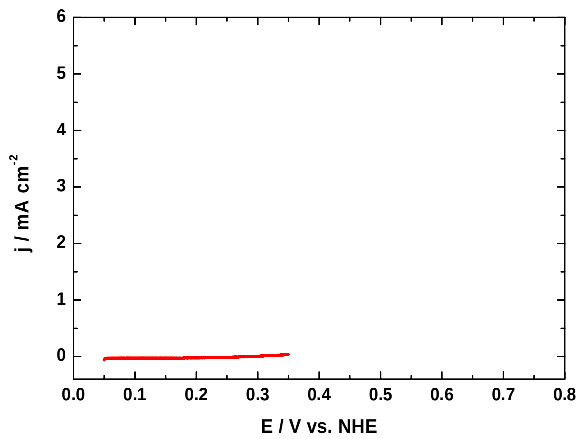
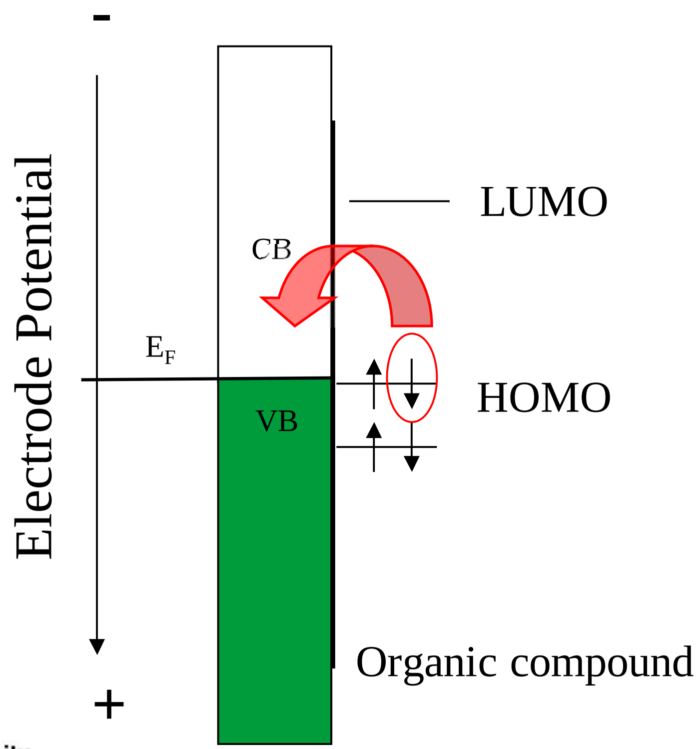
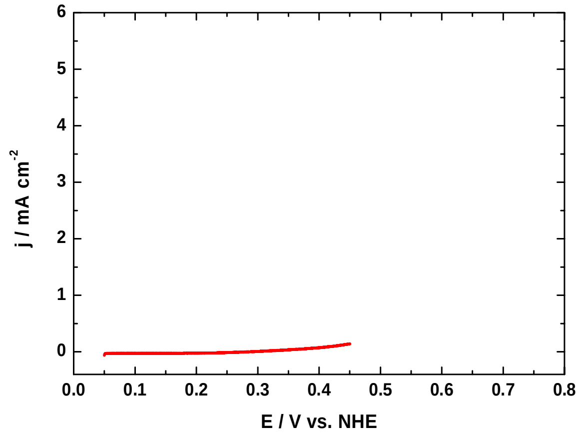
Electro-oxidation of methanol



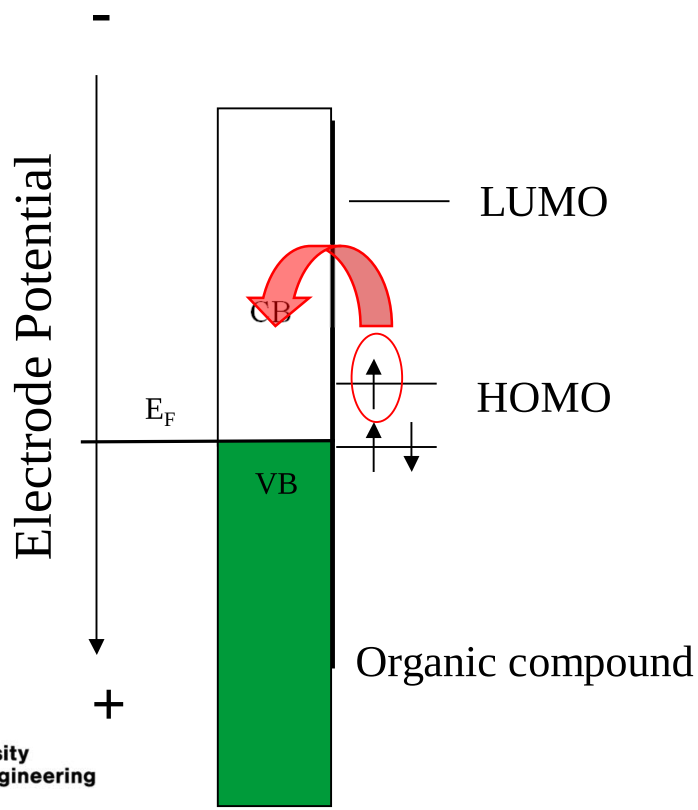


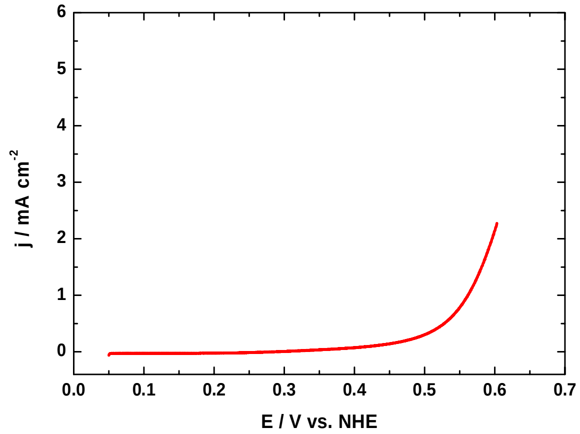
Electro-oxidation of methanol



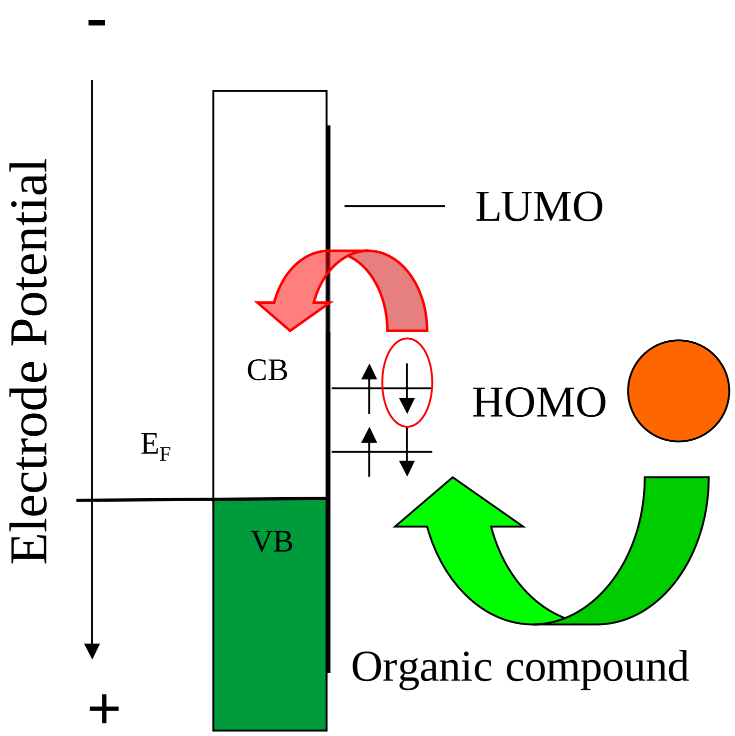


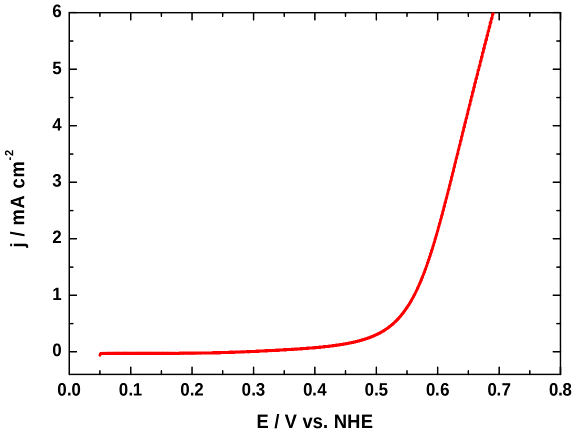
Electro-oxidation of methanol





Electro-oxidation of methanol





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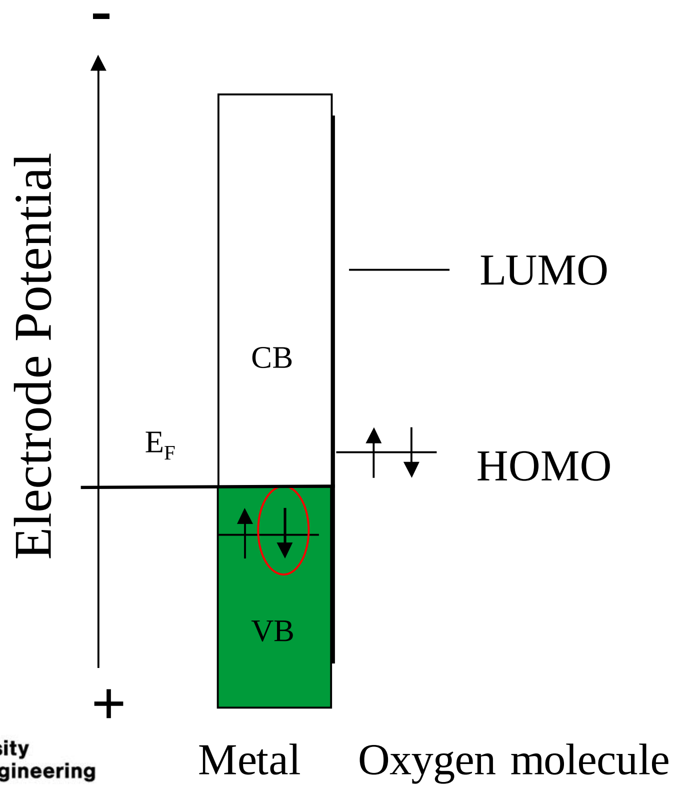
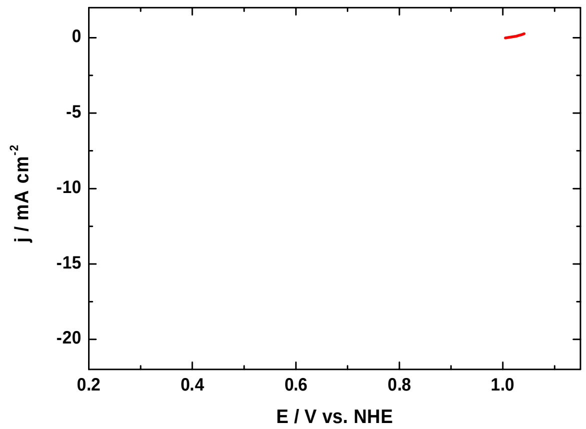
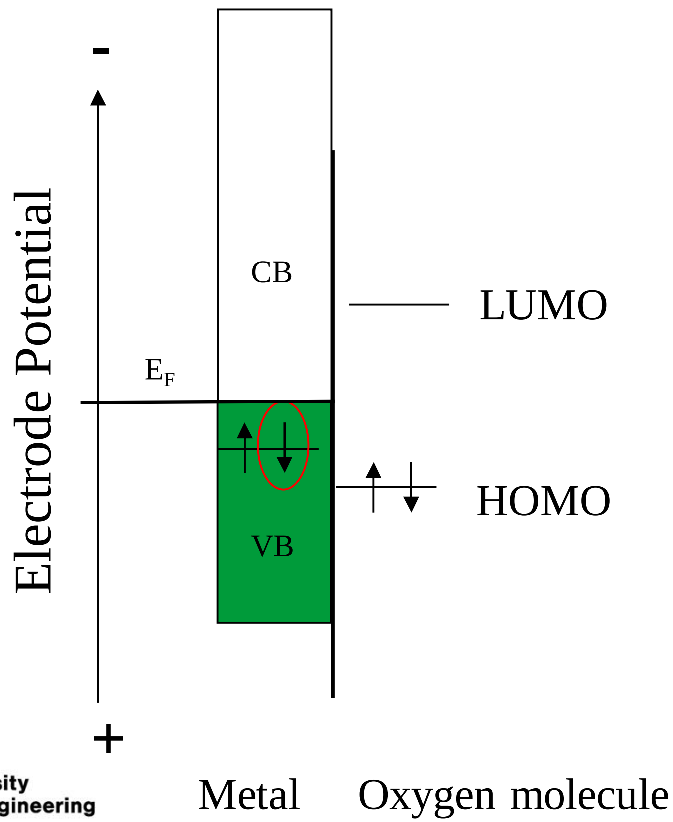
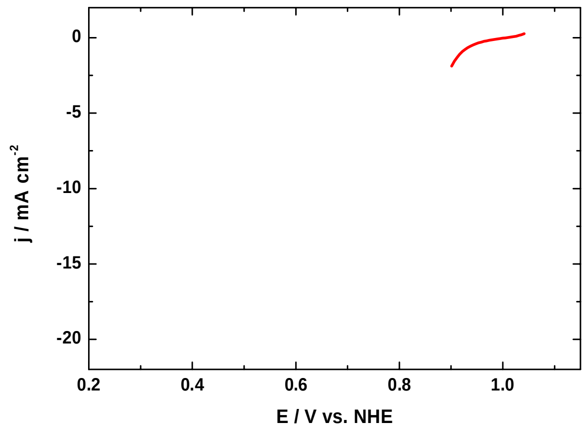
Oxygen reduction



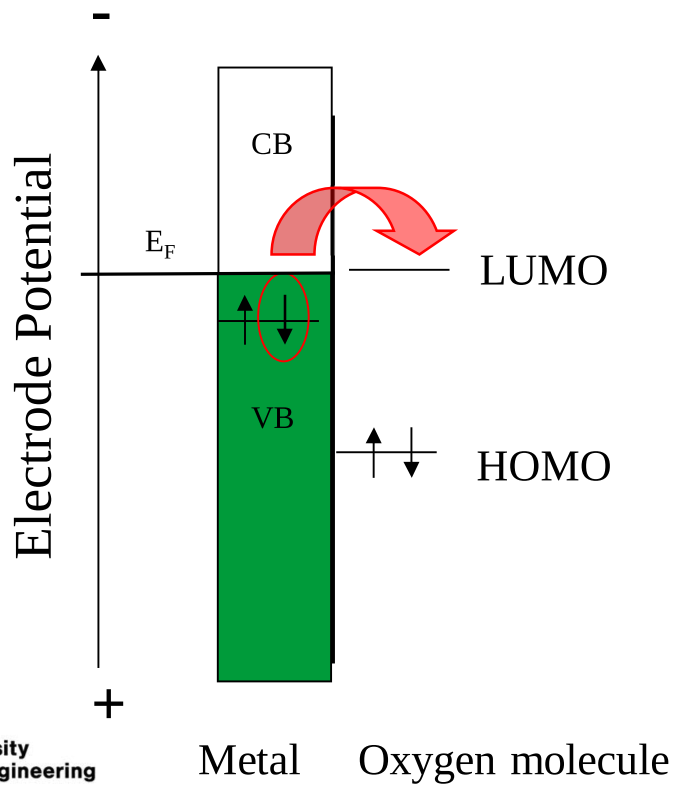


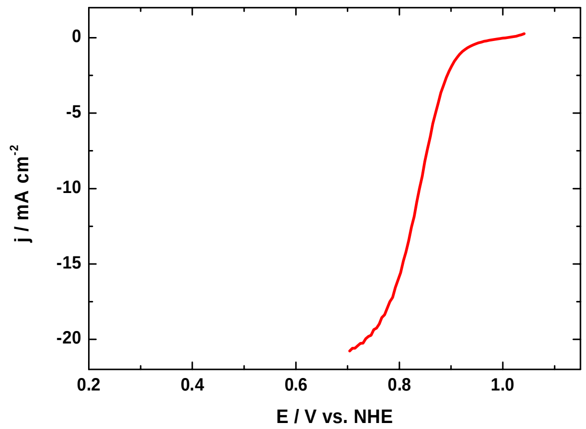
Oxygen reduction





Oxygen reduction





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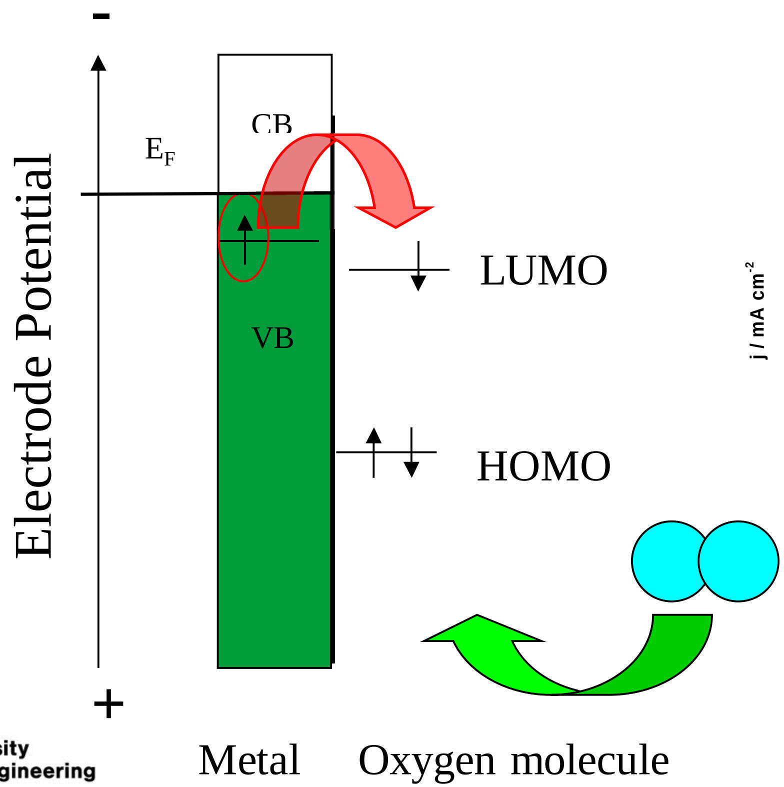
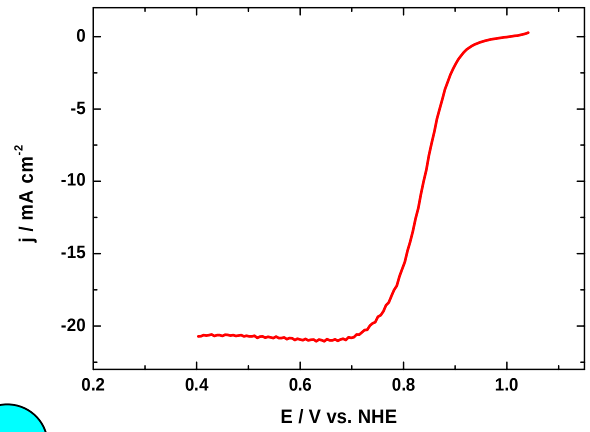
Oxygen reduction





Energy Levels - Batteries

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Different voltages and chemistries
Lithium ion battery (LIB)

Positive electrode

Discharge ->

$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$ $E^0 \sim 3.8$ V

<- Charge

Negative electrode

$LiC_6 + \leftrightarrow C_6 + Li^+ + e^-$ $E^0 \sim 0.1$ V

Full reaction

$CoO_2 + LiC_6 \leftrightarrow LiCoO_2 + C_6$ $E^0 \sim 3.7$ V

Different voltages and chemistries
Lead (Pb) acid battery

Positive electrode

Discharge ->

$PbO_2 + 3H^+ + HSO_4^- + 2\ e^- \leftrightarrow PbSO_4 + 2\ H_2O$ $E^0 \sim 1.7\ V$

<- Charge

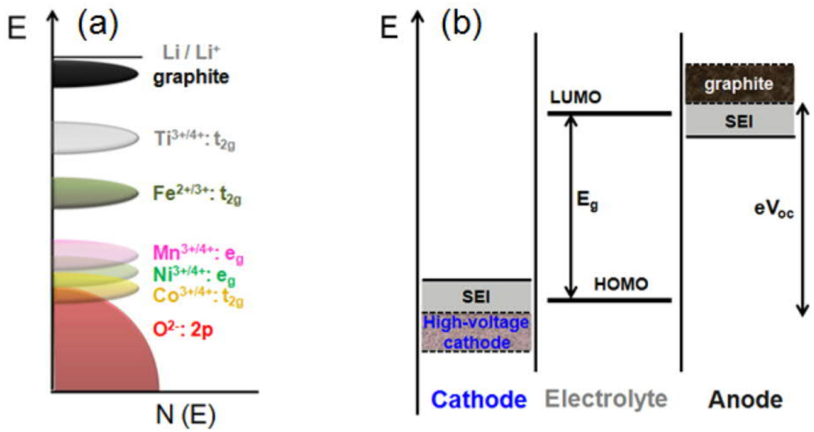
Negative electrode

$Pb + HSO_4^- \leftrightarrow PbSO_4 + H^+ + 2e^-$ $E^0 \sim 0.4\ V$

Full reaction

$PbO_2 + Pb + 2H_2SO_4 \leftrightarrow 2\ PbSO_4 + H_2O$ $E^0 \sim 2.1\ V$

How different electrode materials effect on battery voltage



Similarly, the materials of the positive and negative electrodes ->

effect on the battery voltage

A. Manthiram, An Outlook on Lithium Ion Battery Technology – ASC Central Science
DOI: 10.1021/acscentsci.7b00288

Take a home message

From active materials to achieve

HIGH performance,

we must understand their impact on the electrode reaction.

This possess limitations to entirely change the materials.

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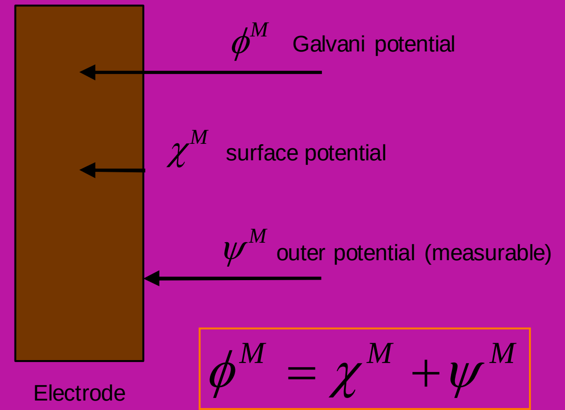
Energy Material – Electrochemical Potential

(how to derive)



$$\phi^M = \chi^M + \psi^M$$

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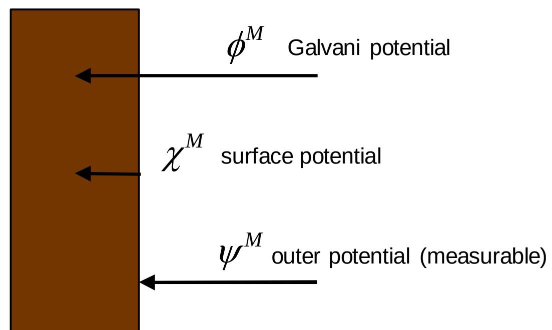
Electrochemical potential

Electrochemical potential (in general)

$$\tilde{\mu}_i^a = \mu_i^a + z_i F \phi^a$$

For an electron in a metal phase?



$$\phi^M = \chi^M + \psi^M$$

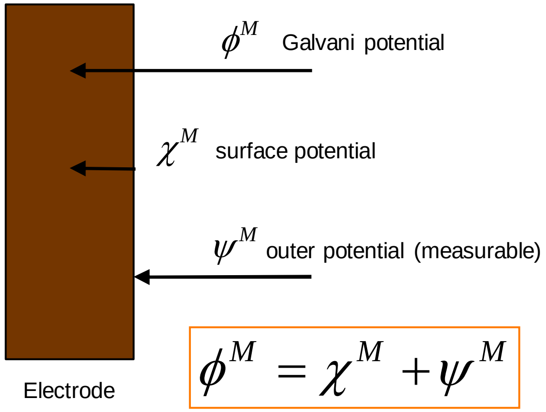
Electrochemical potential

Electrochemical potential (in general)

$$\tilde{\mu}_i^a = \mu_i^a + z_i F \phi^a$$

For an electron in a metal phase

$$\tilde{\mu}_e^M = \mu_e^M - F\phi^M$$



$$\phi^M = \chi^M + \psi^M$$

Electrochemical potential

Electrochemical potential (in general)

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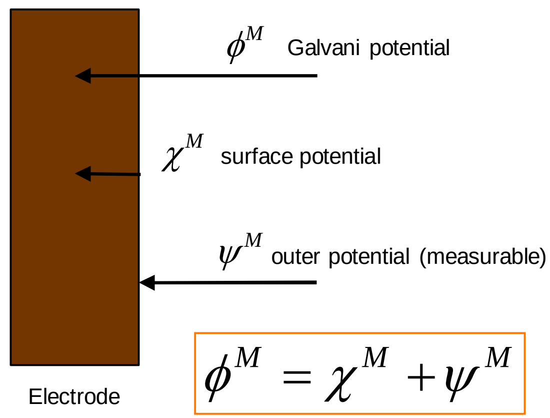
Surface and outer potential?



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Aalto University
School of Engineering

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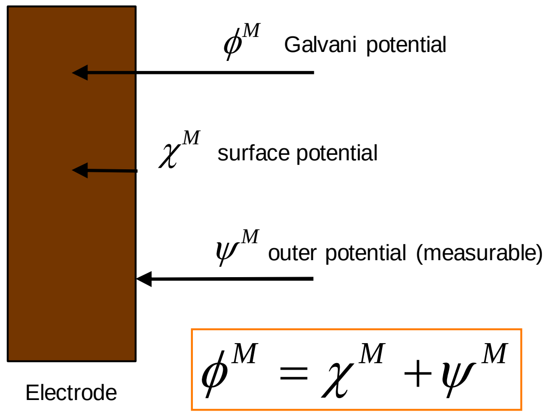

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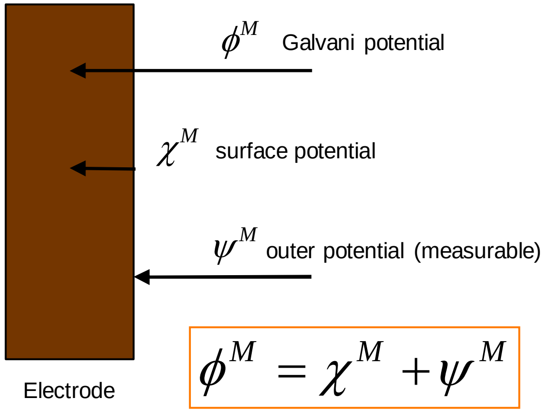

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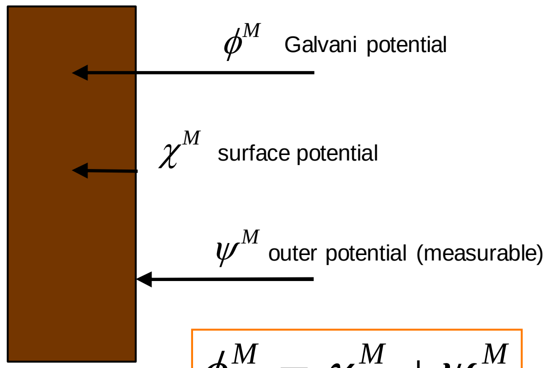

Electrode

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