Electrochimie

Cours d'introduction

Jules Schleinitz

22 Septembre 2021

Plan du Cours

1. **Le Module**

2. **Introduction Historique**
   - Thermodynamique
   - Cinétique Chimique
   - Hydrodynamique

3. **Applications contemporaines**
   - Accumulateurs
   - Cellules photovoltaïques
   - Detection de nanoparticules
   - Etude mécanistique

4. **L’Electrochimie à l’ENS**

5. **Bibliographie**

Le Module

COURS

(~15h)



Laurent THOUIN

TP

2 à 3 séances



Eric LABBE



Emile ESCOUDE

TD

(~12h)

Le Module

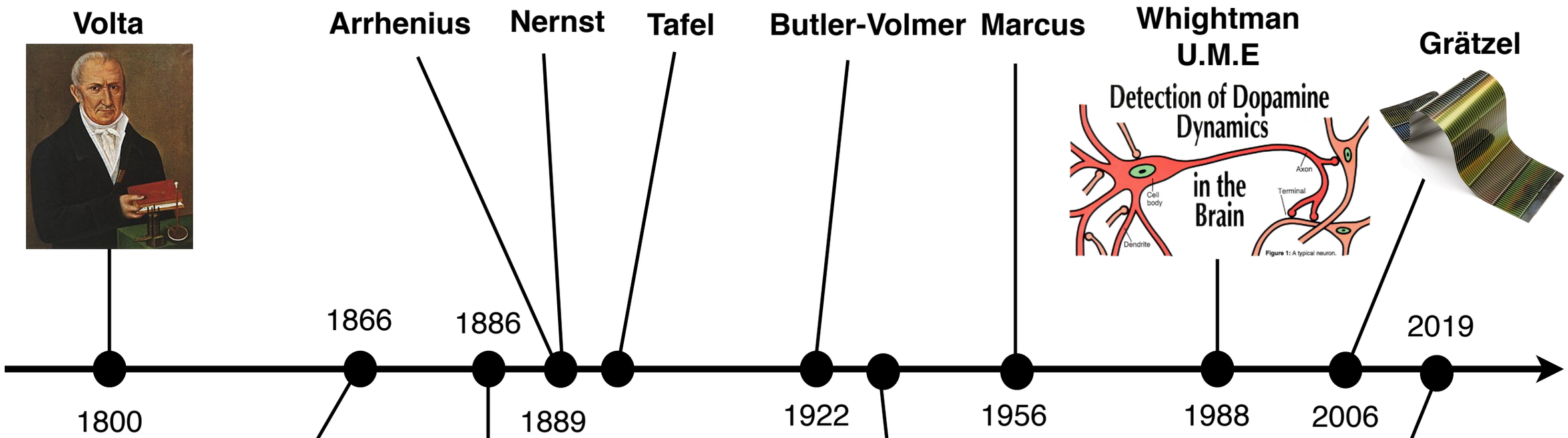
Évaluation

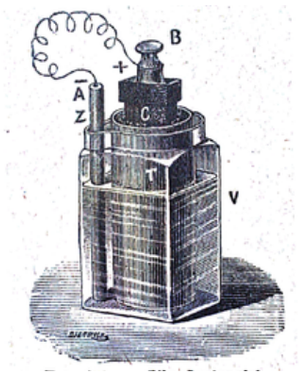
TP

Oral mi-semestre

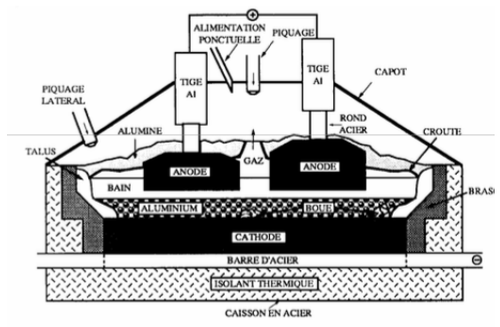
Partiel

Petit point historique

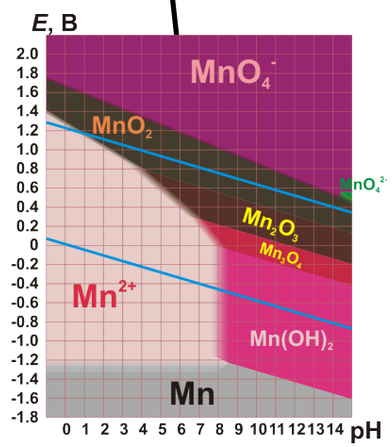




Leclanché



Hall - Héroult

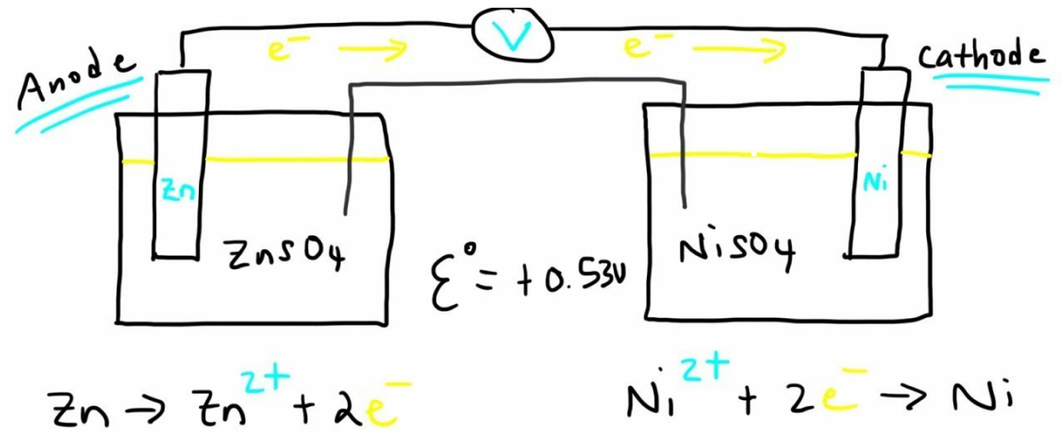


Pourbaix



R. Mark Wightman et al., *Anal. Chem.* **1988**, 60, 13, 769A–793A

Loi de Nernst



- **Réaction :**

$$Ni^{2+}_{aq} + Zn_{(s)} \rightarrow Ni_{(s)} + Zn^{2+}_{aq}$$

- **Nernst :**

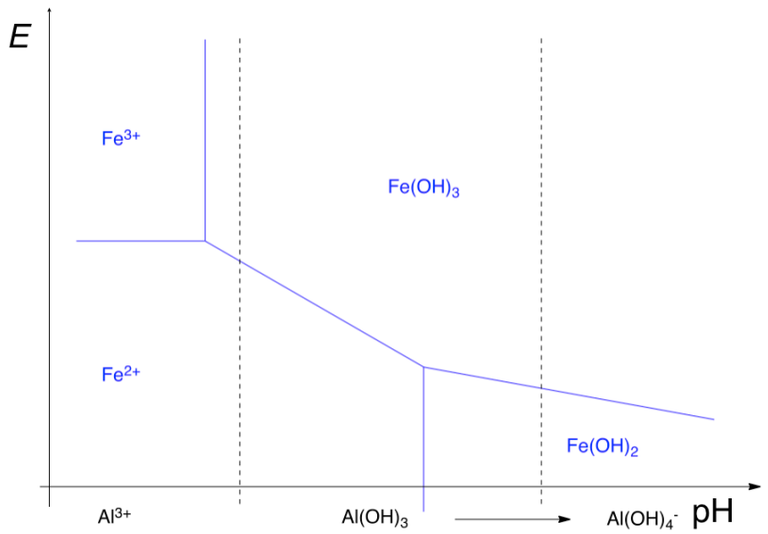
$$E = E^0 + \frac{RT}{nF} ln(\frac{a_{Ox}}{a_{Red}})$$

- **Calcul de la force électromotrice :**

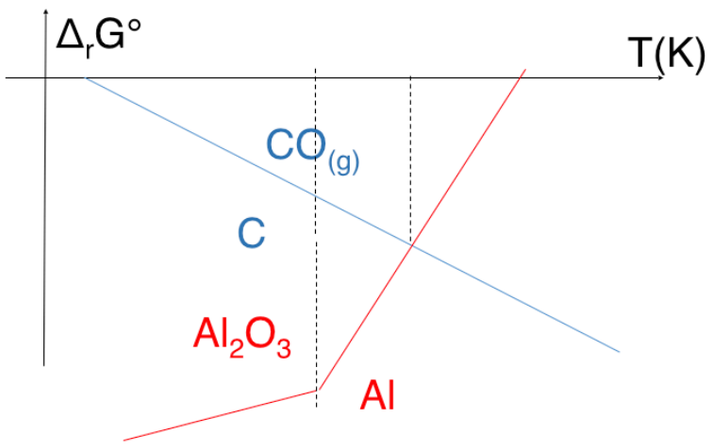
$$\Delta E_{pile} = E_{couple_1} - E_{couple_2}$$

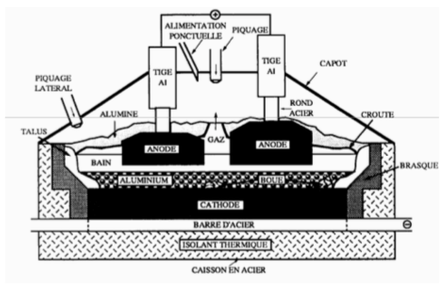
https://www.khanacademy.org/science/chemistry/oxidation-reduction

Potentiel Electrique









- **Thermo et potentiel électrique :**

$$Ox + ne^- = Red$$

$$\Delta_r G^0 = -nFE^0_{Ox/Red}$$

- **Pourbaix :**

$$\Delta_r G = f(E, pH)$$

- **Ellingham :**

$$\Delta_r G = f(E, T)$$

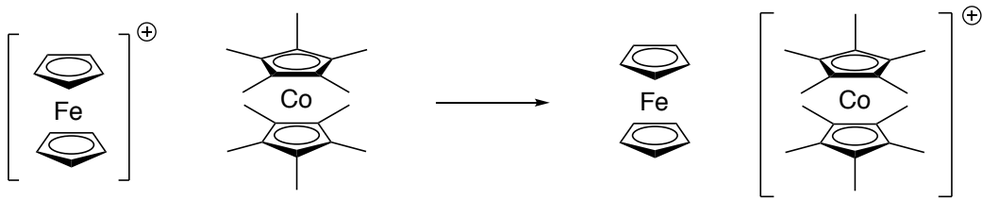
Potentiel Electrique

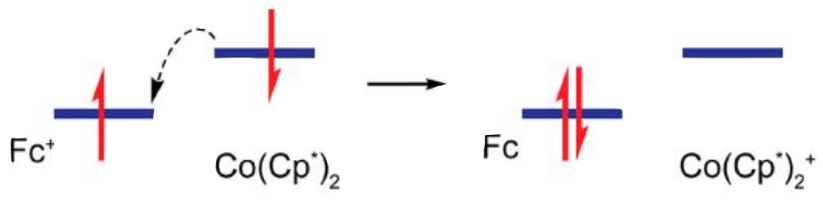
- **Thermo et potentiel électrique :**

$$Ox + ne^- = Red$$

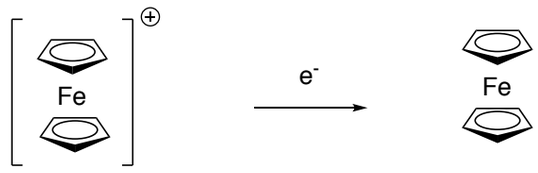
$$\Delta_r G^0 = -nFE^0_{Ox/Red}$$

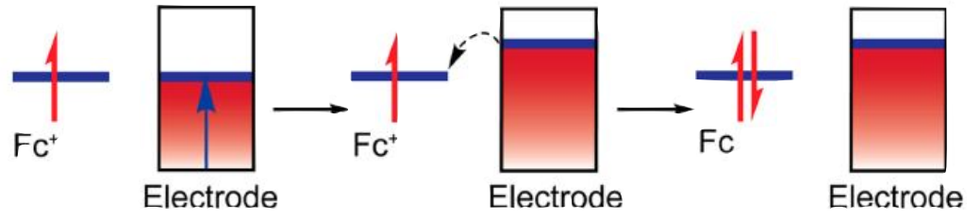
Réaction homogène





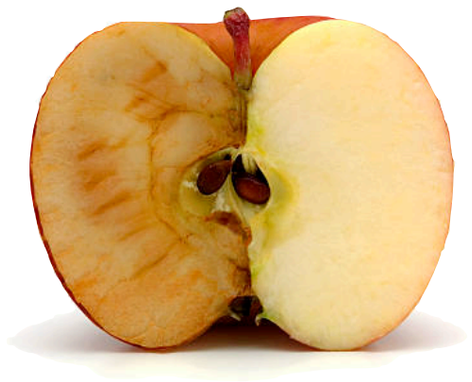
Réaction à l'électrode





Noémie Elgrishi et al. *J. Chem. Educ.* **2018**, 95, 2, 197–206

La Corrosion





“An irreversible interfacial reaction of a material [...] with its environment which results in consumption of the material or in <u>dissolution</u> into the material of a component of the environment. [...]”

“En France la dégradation des matériaux sous l’effet de l’environnement a coûté en 2019 plus de 80 milliards d’euros, et plus de 2500 milliards de dollars dans le monde.”

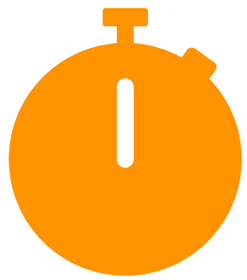
- https://goldbook.iupac.org/terms/view/C01351
- https://www.cefracor.org/fr/actualites/pour-un-monde-durable-journee-mondiale-de-la-corrosion-24-avril-2020

Thermo vs Cinétique



$$E^0_{O_2/H_2O} \simeq 1{,}3\ \mathbf{V}_{vs.ENH}$$

$$E^0_{phenol/quinone} \simeq 0{,}7\ \mathbf{V}_{vs.ENH}$$



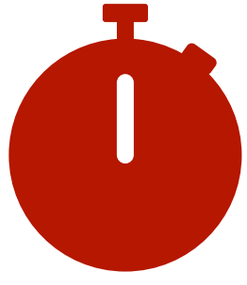
10 min

$$\Delta_r G = -\,nF(E_{O_2/H_2O} - E_{ol/one}) < 0$$

$$E^0_{Fe^{II}/Fe} \simeq -\,0{,}45\ \mathbf{V}_{vs.ENH}$$

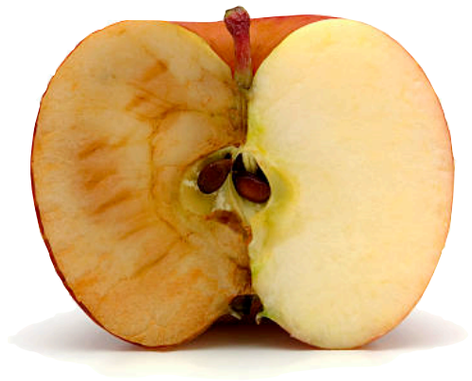
$$\Delta_r G = -\,nF(E_{O_2/H_2O} - E_{Fe^{II}/Fe}) < 0$$

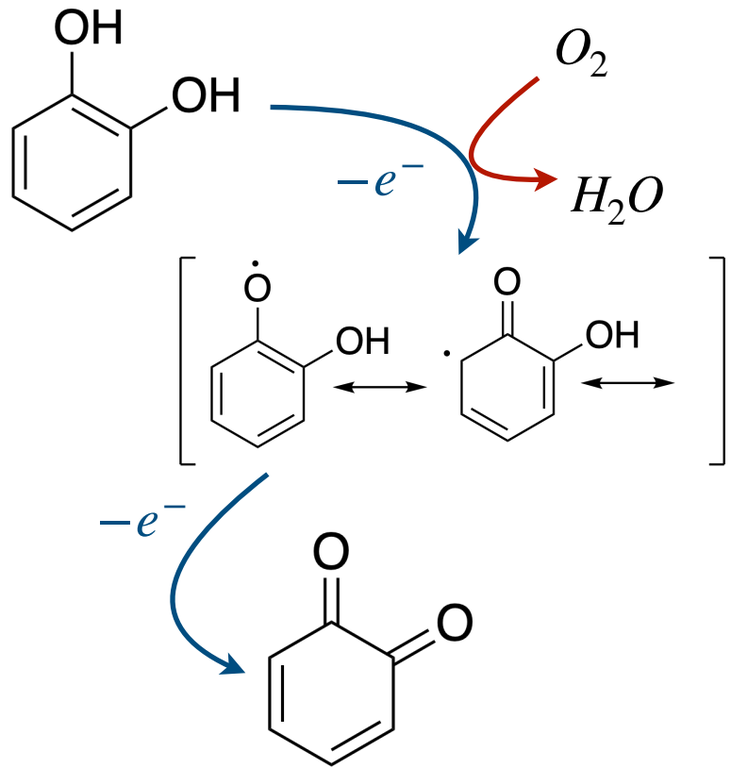


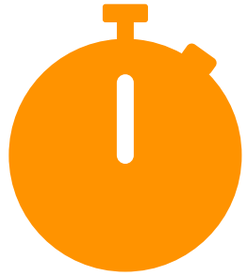


10 ans

Thermo vs Cinétique

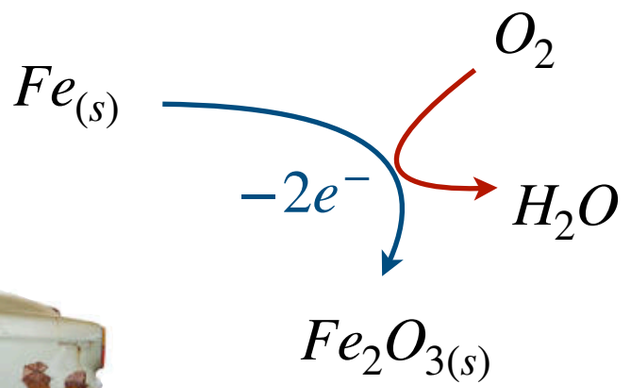


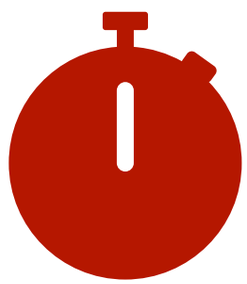




10 min

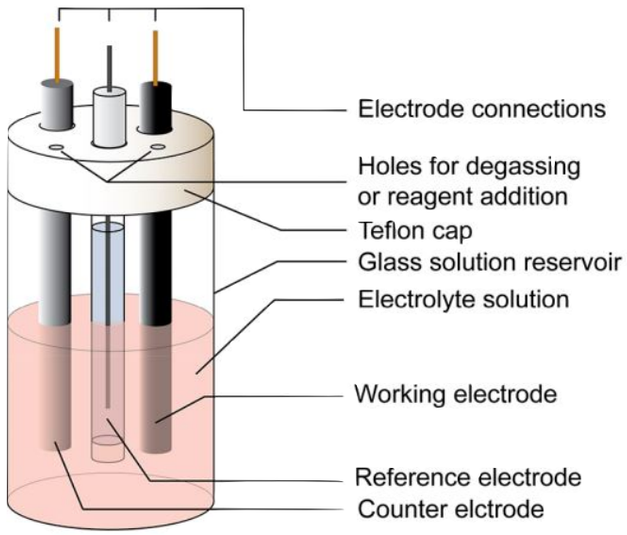


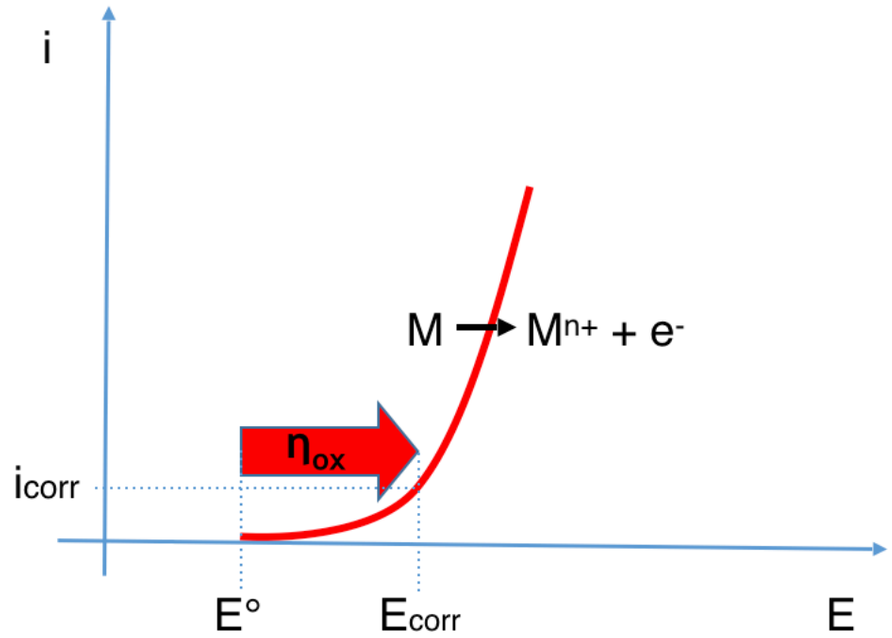




10 ans

Surtensions

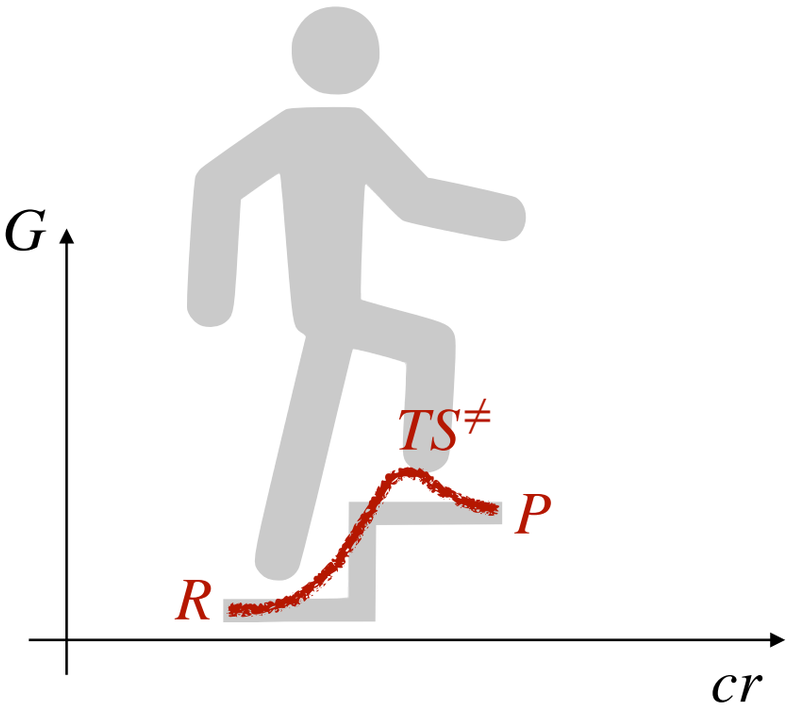




Définition empirique :
la surtension dépend de la surface et est déterminée pour un courant donné.

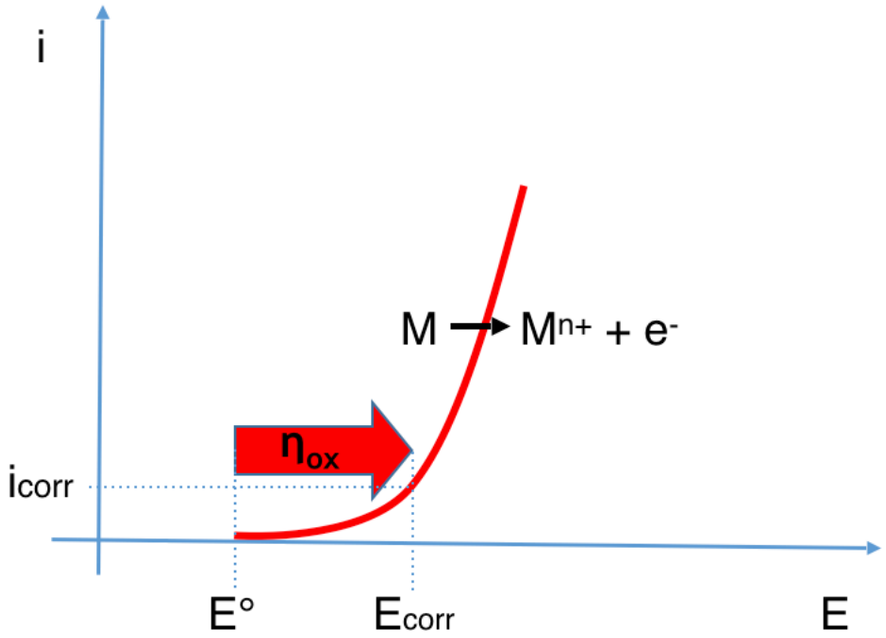
Noémie Elgrishi et al. *J. Chem. Educ.* **2018**, 95, 2, 197–206

Surtensions



$$\Delta G^{\neq} > \Delta G$$

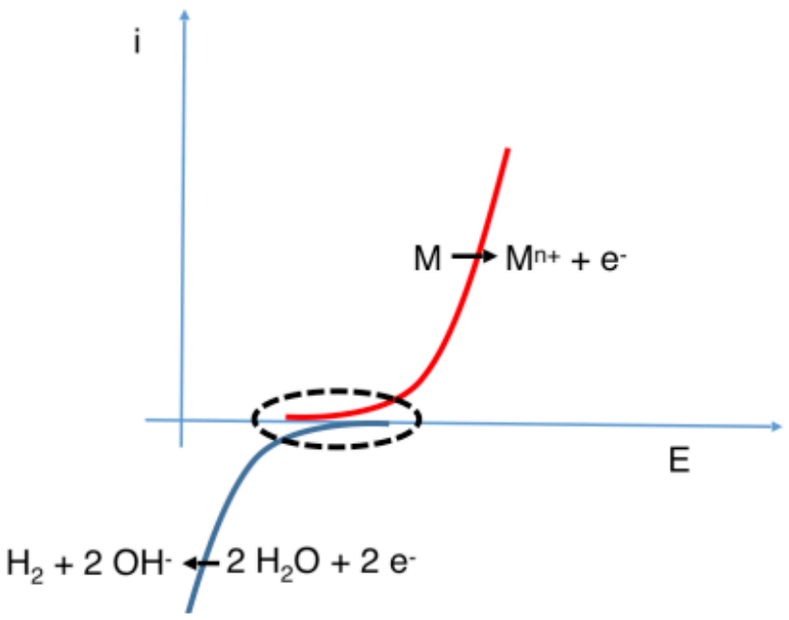
L'énergie d'activation dépend du système chimique et de la nature de l'electrode de travail

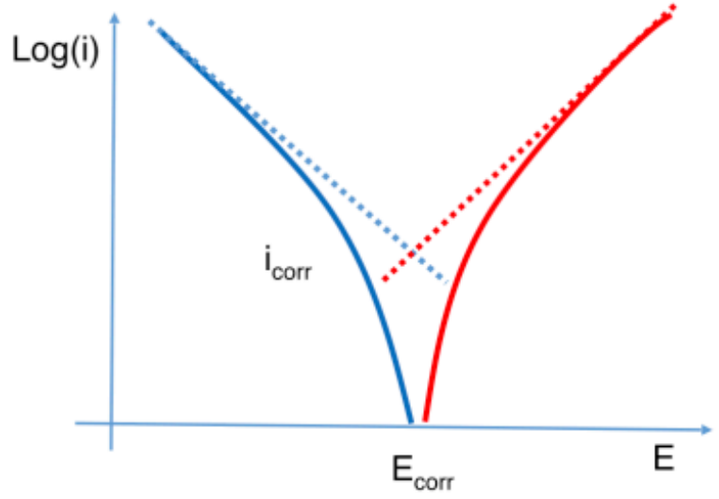


Courant de Corrosion : Tafel

1. i = f(E) est du **type Arrhenius**
2. Linéarisation

   $k = Ae^{-Ea/RT}$ on peut modeliser i tel que :$i = Be^{\gamma(E-E^{\circ})}$





Courant de Corrosion : Tafel

- Idée à retenir : pour rationaliser ces surtensions nécessite de modéliser : deux grands noms de l'électrochimie pour expliquer ce que l'on appelle le **transfert de charge**

1. Butler-Volmer :

$k = Ae^{-Ea/RT}$ on peut modéliser i tel que : $i = Be^{\gamma(E-E^\circ)}$

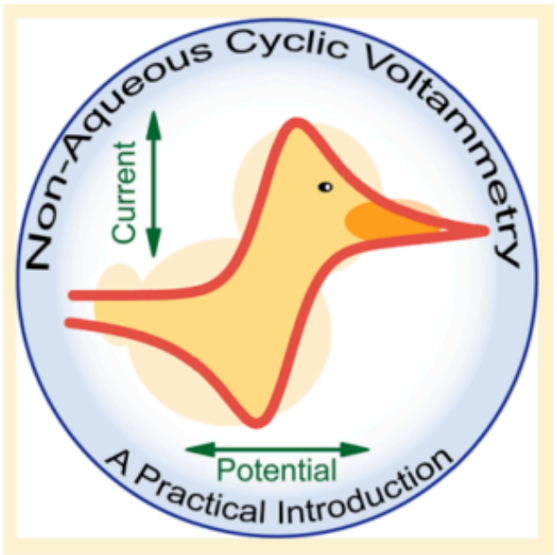
2. Marcus :

Explication à l'ordre supérieur :

E_a *n'est pas toujours proportionnel à* $E - E^\circ$

Limitations physique

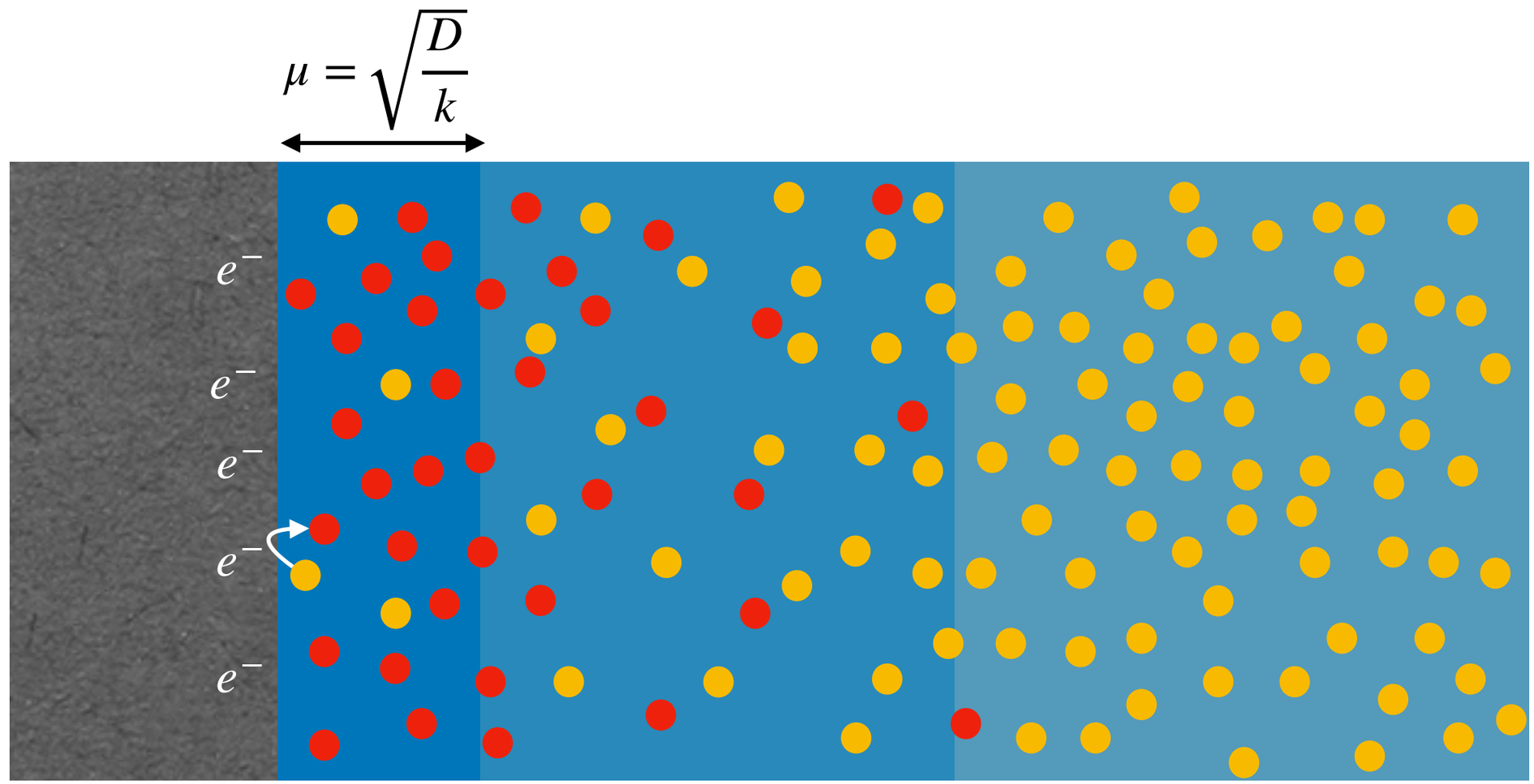
- Il y a cependant toujours une limite à ce transfert de charge : réalisation expérimentale d'une courbe i=f(E)



- Cette limitation est due au **transfert de masse**

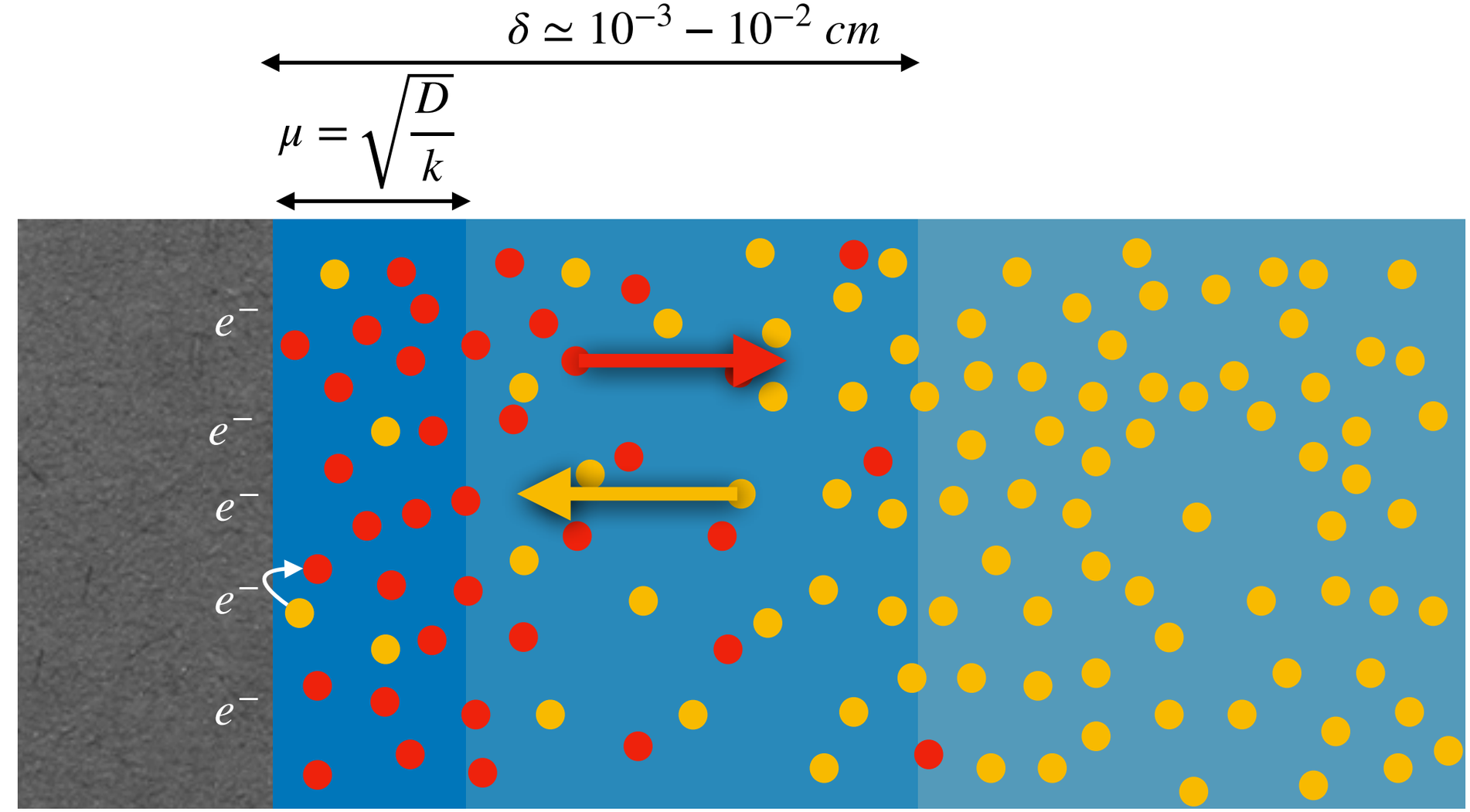
Noémie Elgrishi et al. *J. Chem. Educ.* **2018**, 95, 2, 197–206

Transfert de masse



Limitations Physiques

Diffusion

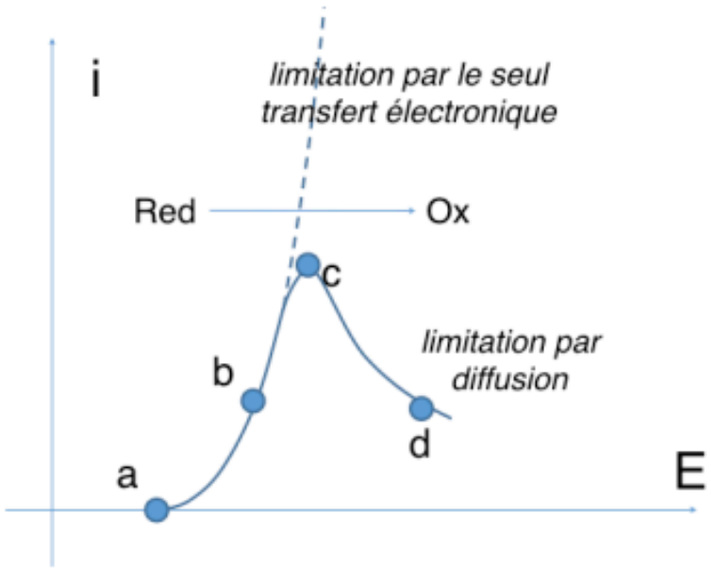


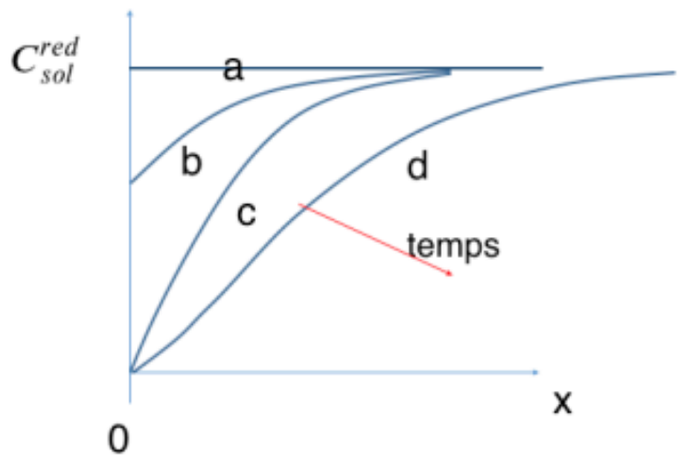
Cyrille Costentin and Jean-Michel Savéant, ***PNAS*, 2019**, 116 (23) 11147-11152

Diffusion

- Le transfert de masse est en partie régit par la **diffusion**

$$J = -D\nabla C$$

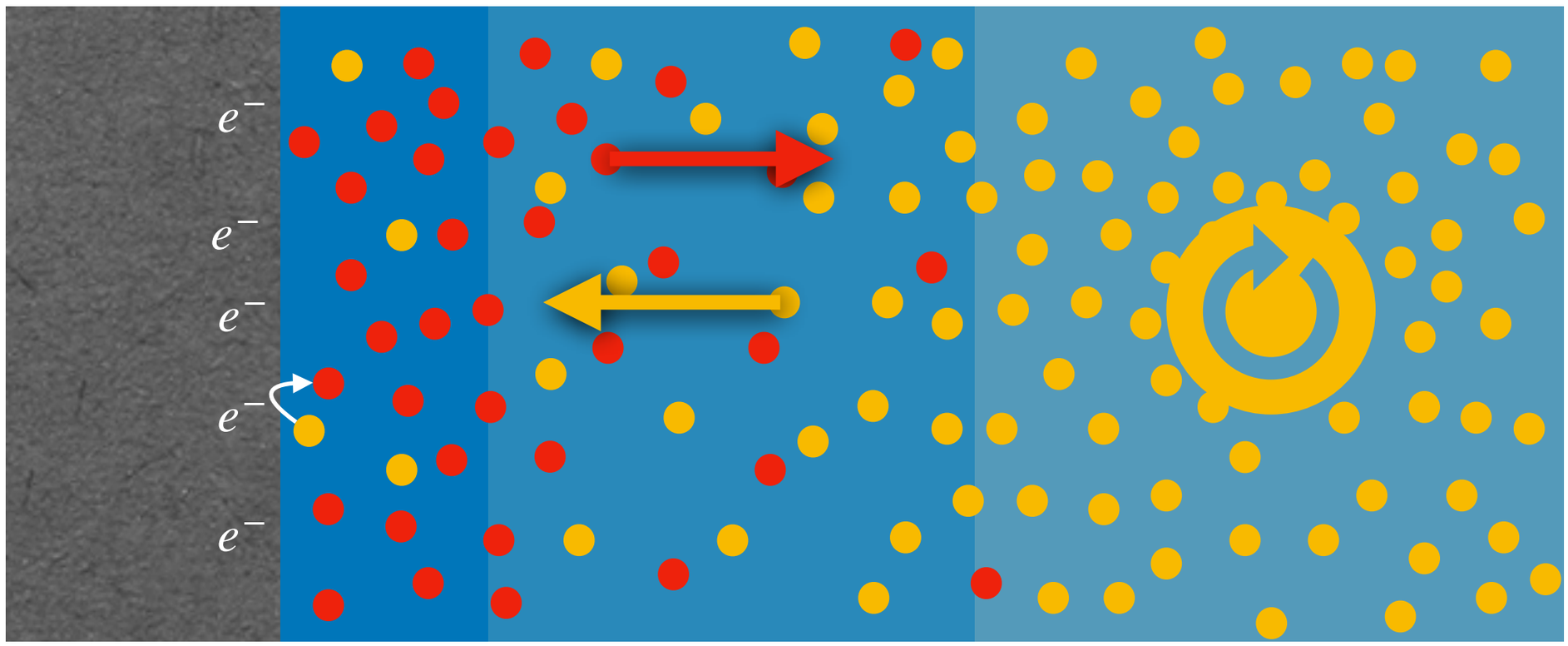




Diffusion

$$\delta \simeq 10^{-3} - 10^{-2}\ cm$$

$$\mu = \sqrt{\frac{D}{k}}$$



Electrode

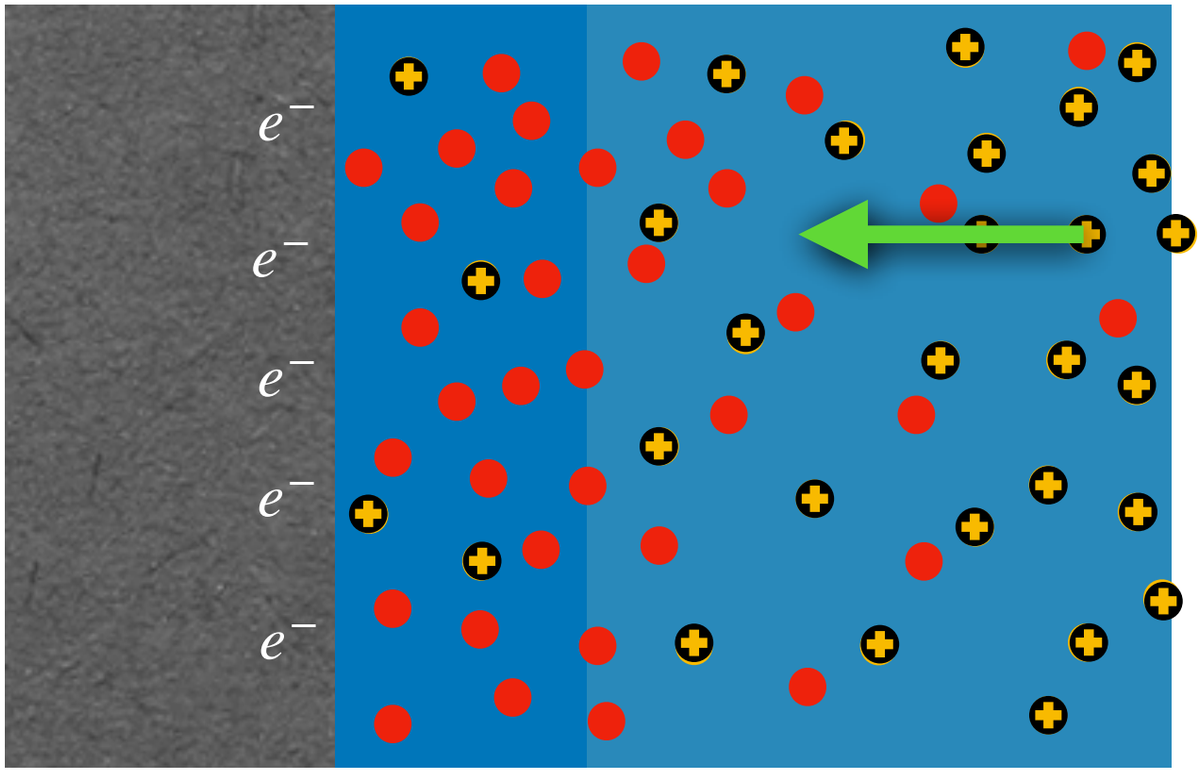
Couche de Réaction Diffusion

Couche de Diffusion

Solution

Limitations Physiques

Migration



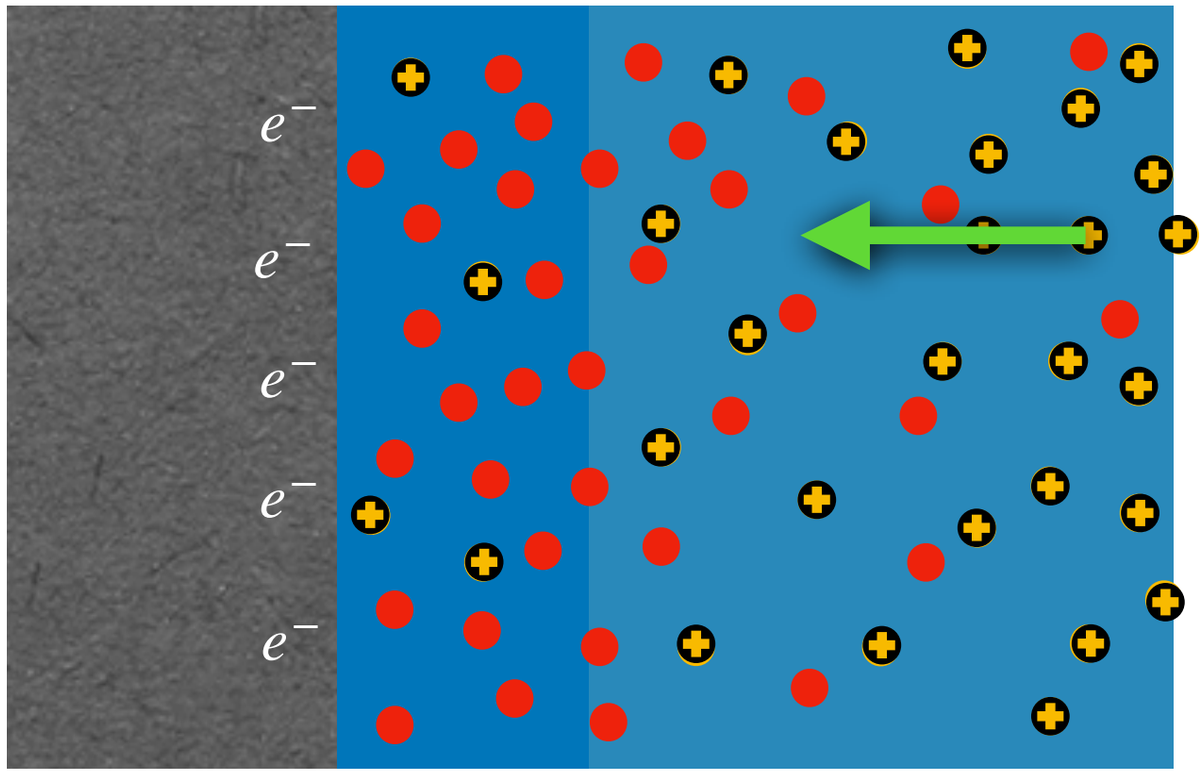
Electrode

Couche de Réaction Diffusion

Couche de Diffusion

Limitations Physiques

Migration



Electrode

Couche de Réaction Diffusion

Couche de Diffusion

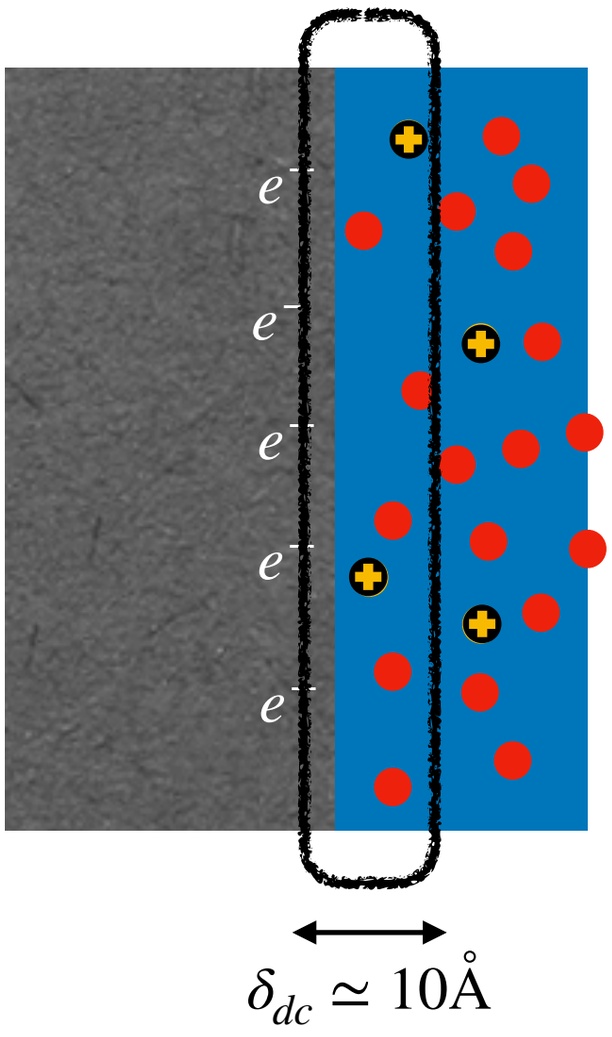
Migration

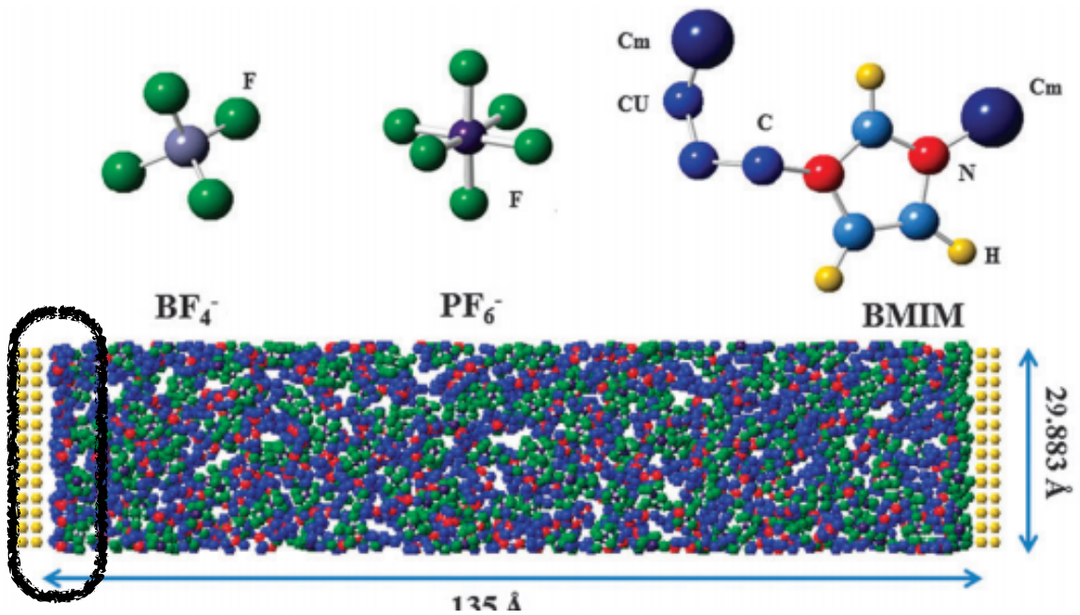
- Le transfert de masse est en partie régit par la **migration** : mouvement des charges sous l'action d'un champ électrique

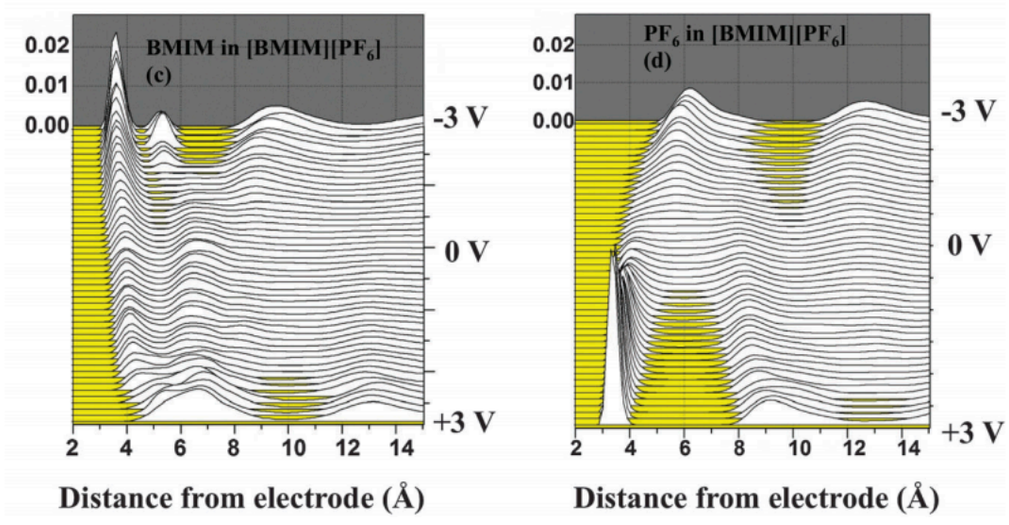
Généralement on s'affranchit de la migration grâce à l'utilisation d'un sel de fond.

- Cependant des phénomènes dus au champs électriques s'exerçant sur les charges à l'électrode ont tout de même lieu.

Phénomènes de Surface







Ion center-of-mass density profiles

Zongzhi Hu et al, ***Phys. Chem. Chem. Phys.***, 2013,**15**, 14234-14247

Synthèse

Modes de **transport** des espèces en solution :

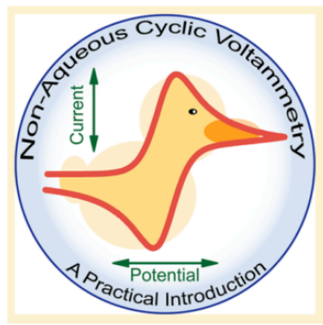
- **Diffusion** (sous l'effet d'un gradient de C°) : toutes les espèces dissoutes
- **Convection** (sous l'effet d'un gradient de densité = mouvement de la solution)
- **Migration** (sous l'effet d'un gradient de champ électrique) : espèces chargées

En absence d'intervention spécifique de l'opérateur, le mode de transport au voisinage s'effectue par **diffusion**.

Courbes Intensité-Potentiel

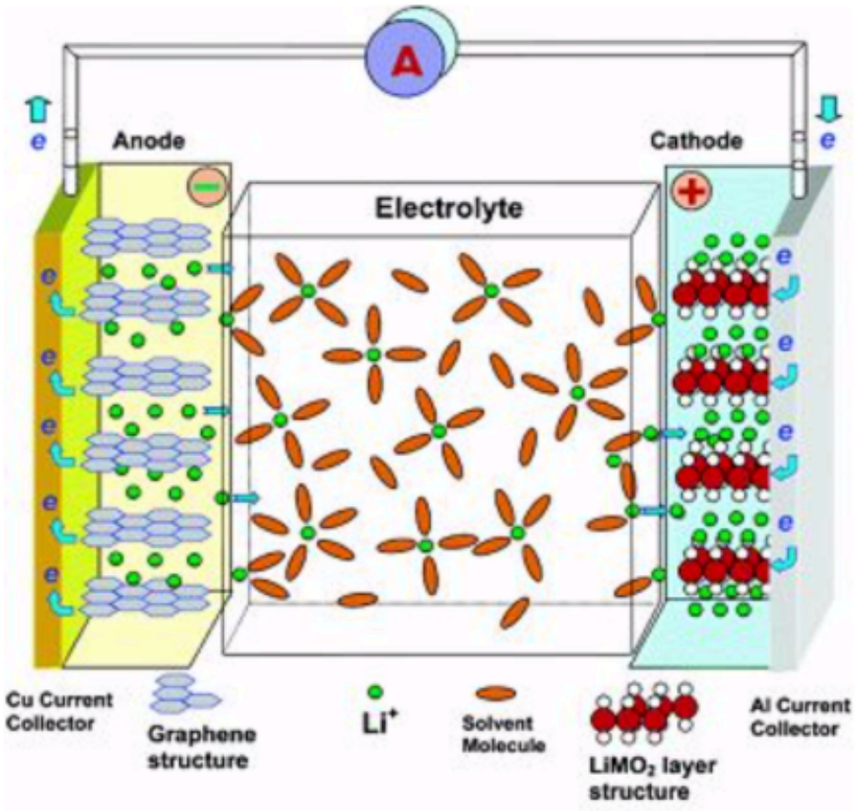
La mesure de courbes i=f(E) permet de :

- mesurer des constantes cinétiques de transfert d'électrons
- mesurer des potentiels de réduction
- et bien plus à découvrir...



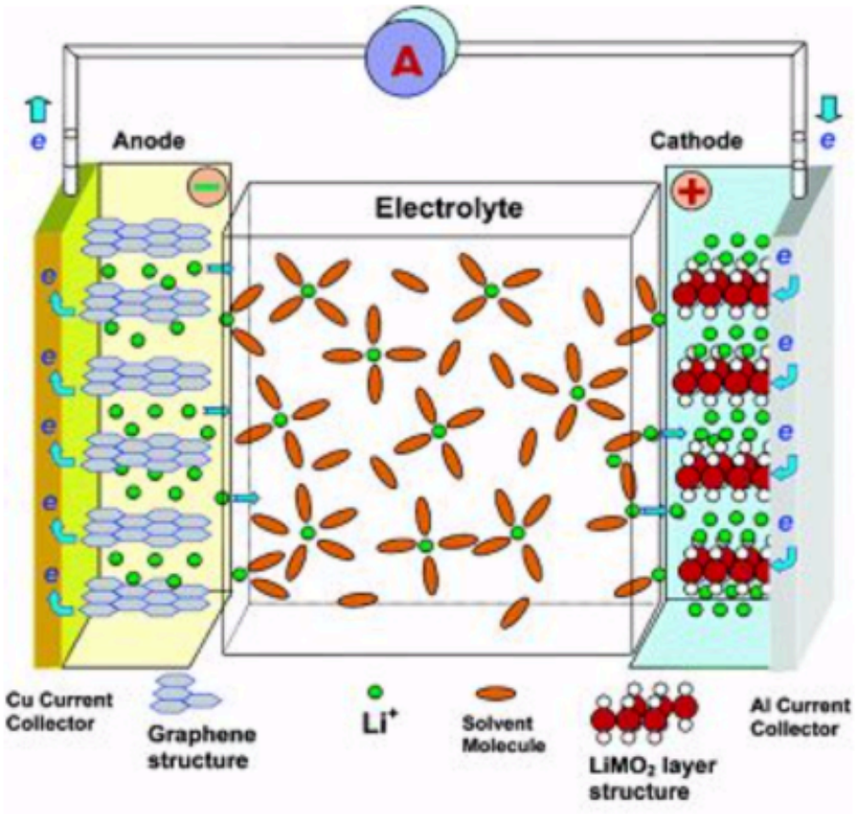
Noémie Elgrishi et al. *J. Chem. Educ.* **2018**, 95, 2, 197–206

Accumulateurs



Piles électriques - Piles au lithium, C. Sarrazin, *Technique de l'ingénieur*, **2002**
https ://www.encyclopedie-energie.org/accumulateurs-lefutur-du-stockage-denergie/
https ://lejournal.cnrs.fr/articles/batterie-sodium-ion-une-revolution-en-marche

Accumulateurs

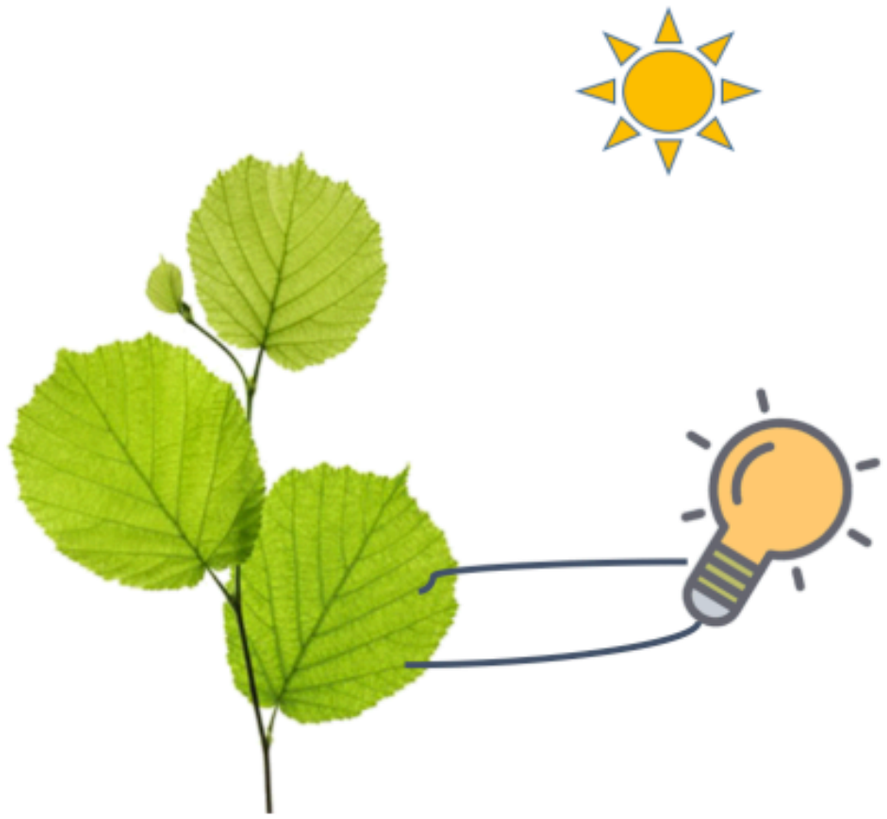


- Choix du potentiel de Nernst
- Capacité massique
- Abondance correcte
- Ampérage

Piles électriques - Piles au lithium, C. Sarrazin, *Technique de l'ingénieur*, **2002**
https ://www.encyclopedie-energie.org/accumulateurs-lefutur-du-stockage-denergie/
https ://lejournal.cnrs.fr/articles/batterie-sodium-ion-une-revolution-en-marche

Cellules de Grätzel





Cellules de Grätzel

Il existe de nombreux complexes métalliques qui permettent de réaliser un transfert mono-électronique lorsqu'ils sont sous irradiation

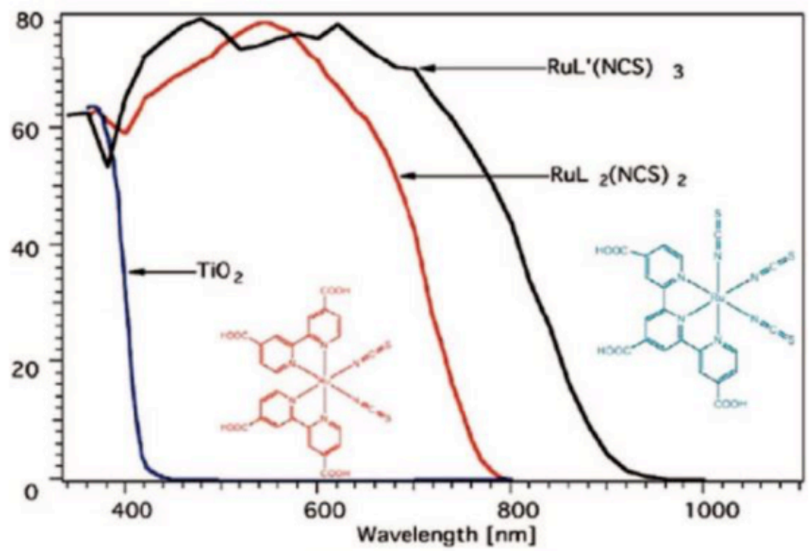


Figure 3. Incident photon to current conversion efficiency as a function of the wavelength for the standard ruthenium sensitizers N3 (red line), the black dye N749 (black curve), and the blank nanocrystalline TiO_2 film (blue curve). The chemical structures of the sensitizers are shown as insets. Reprinted with permission from ref 22. Copyright 2009 American Chemical Society.

Hagfeldt et al., *Chem. Rev.*, **2010**, 110 (11), 6595–6663.

Cellules de Grätzel

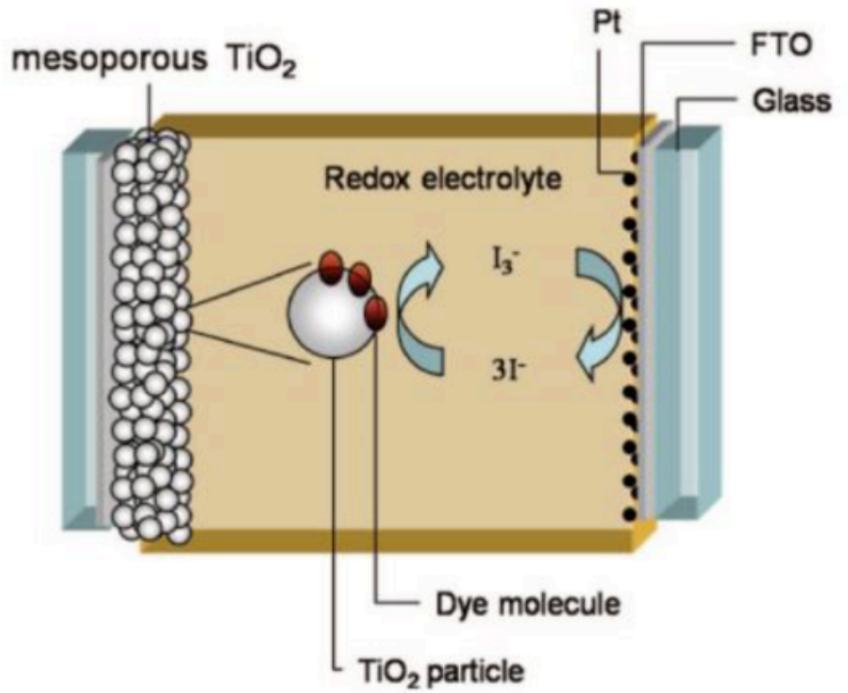
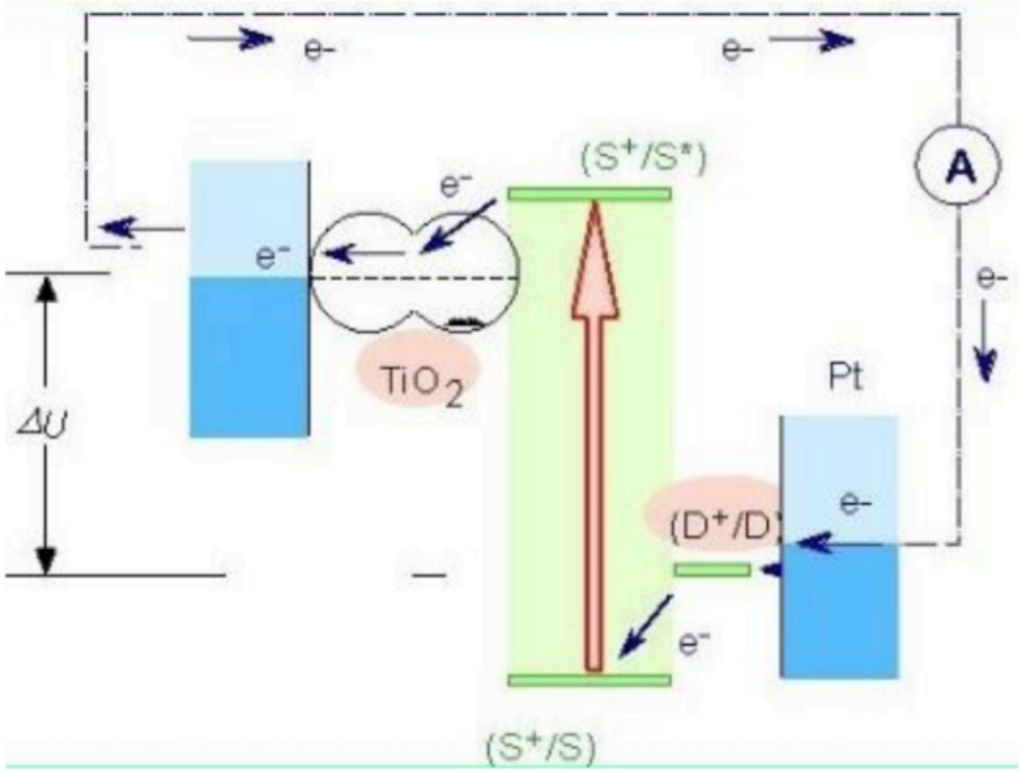


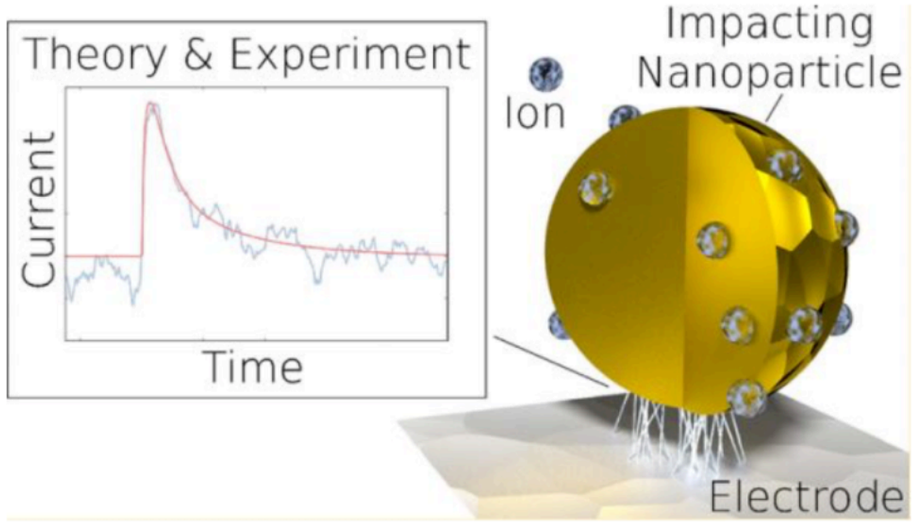
Figure 4. Schematic overview of a dye-sensitized solar cell.



Hagfeldt et al., *Chem. Rev.*, **2010**, 110 (11), 6595–6663.

NanoImpact

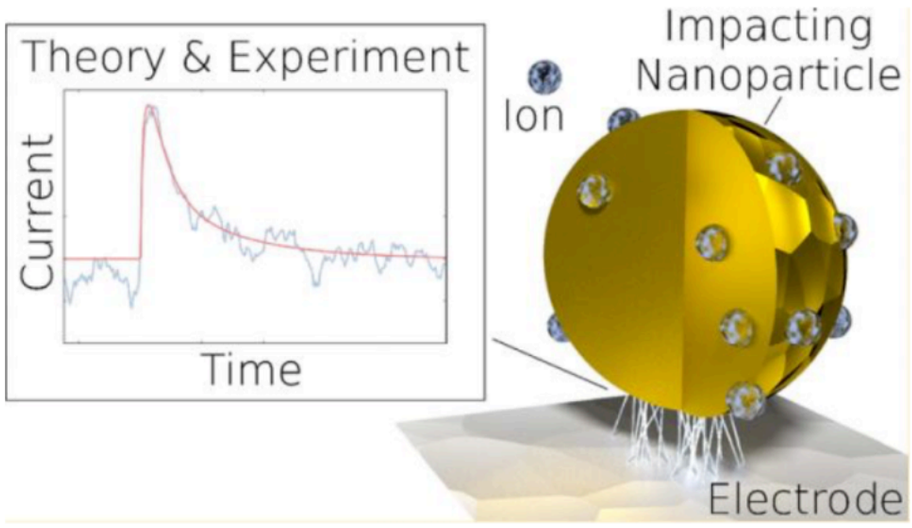
Nanoparticules jouent des rôles catalytiques important parfois à la place de certains complexes.
Le **NanoImpact** permet de détecter les nanoparticules voir de remonter à leur tailles. On peut meme remonter a la distribution de nanoparticules en solution !



Enno Kätelhön et al., *J.Phys. Chem. C*, **2016**, 120, 30, 1, 7029-17034.

NanoImpact

Pics d'oxydation de 0,1 à 1nA !



Enno Kätelhön et al., *J.Phys. Chem. C*, **2016**, 120, 30, 1, 7029-17034.

Chimie Physique Biologie de la Matière Vivante

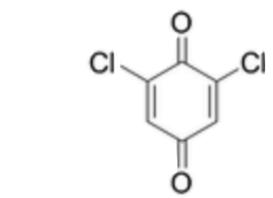
Production d'électricité à partir de suspension de microalgues photosynthétiques et de quinones

Pr. F. Lemaître



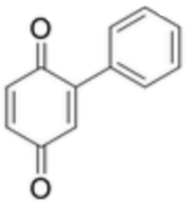






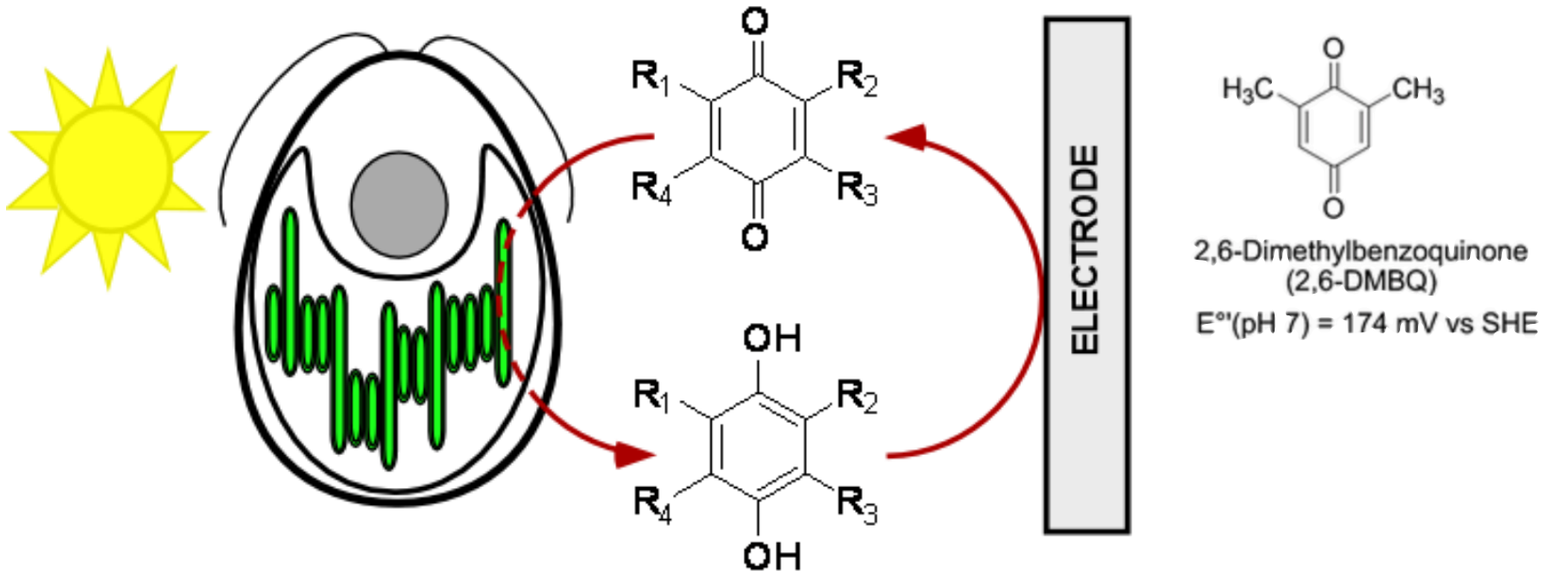
2,6-Dichlorobenzoquinone
(2,6-DCBQ)

$E^{\circ\prime}$(pH 7) = 315 mV vs SHE



p-phenylbenzoquinone
(PPBQ)

$E^{\circ\prime}$(pH 7) = 277 mV vs SHE



2,6-Dimethylbenzoquinone
(2,6-DMBQ)

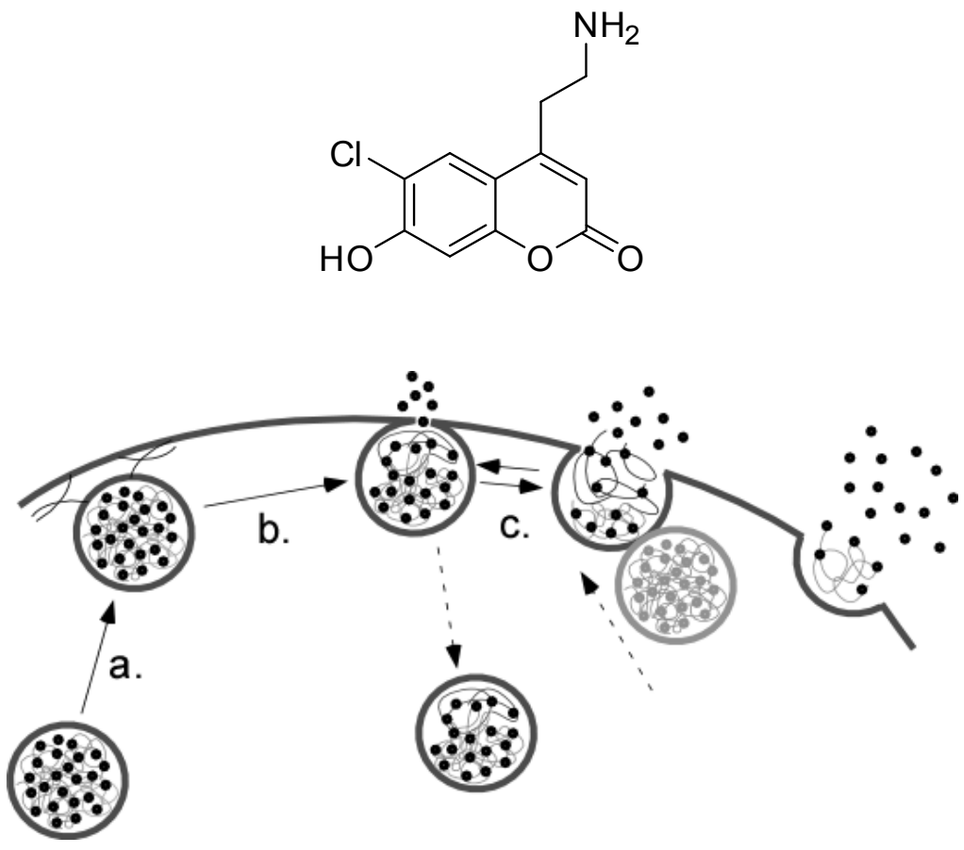
$E^{\circ\prime}$(pH 7) = 174 mV vs SHE

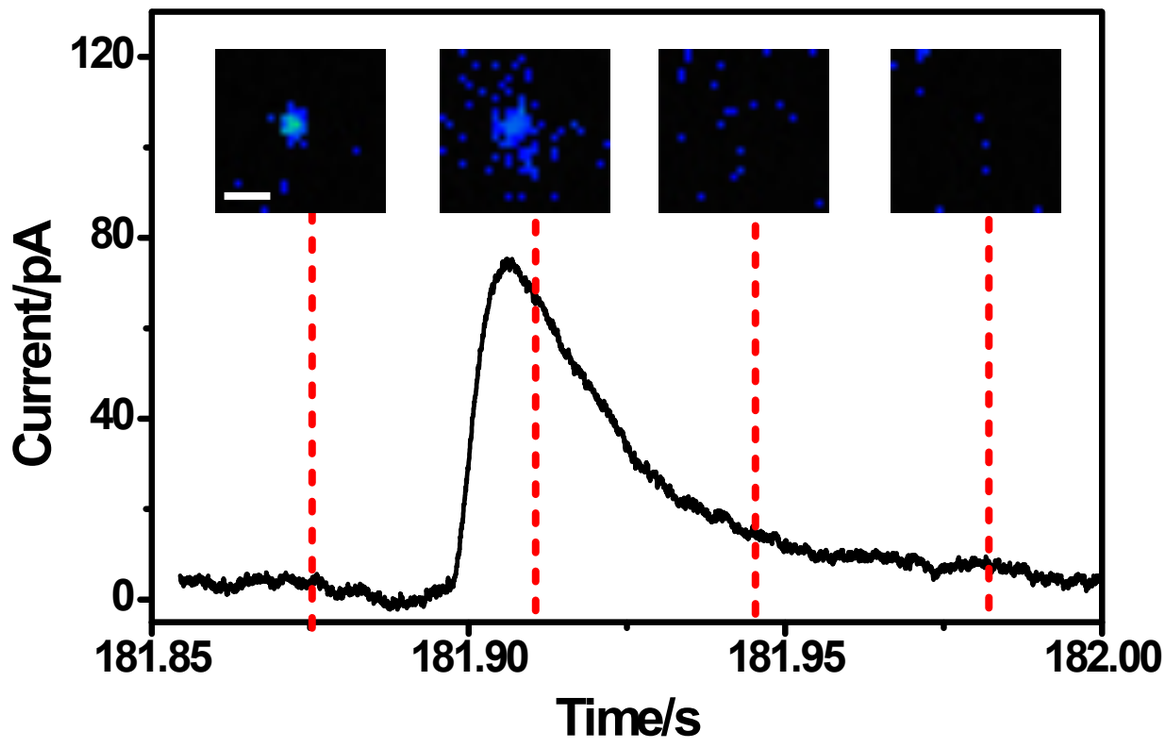
Longatte et al. ***Chem. Sci.***, 2018, **9**, 8271-8281

Chimie Physique Biologie de la Matière Vivante

Etude l'exocytose par couplage électrochimie-fluorescence et utilisation de sondes duales

Dr. M. Guille-Collignon



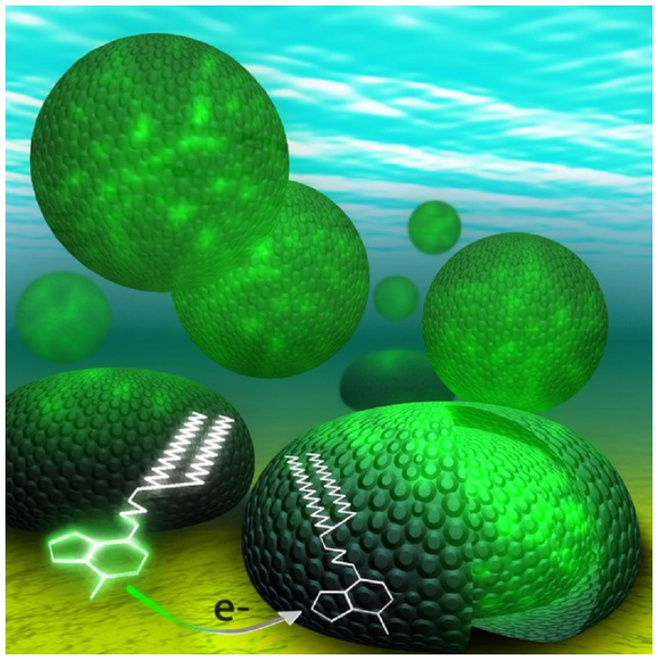


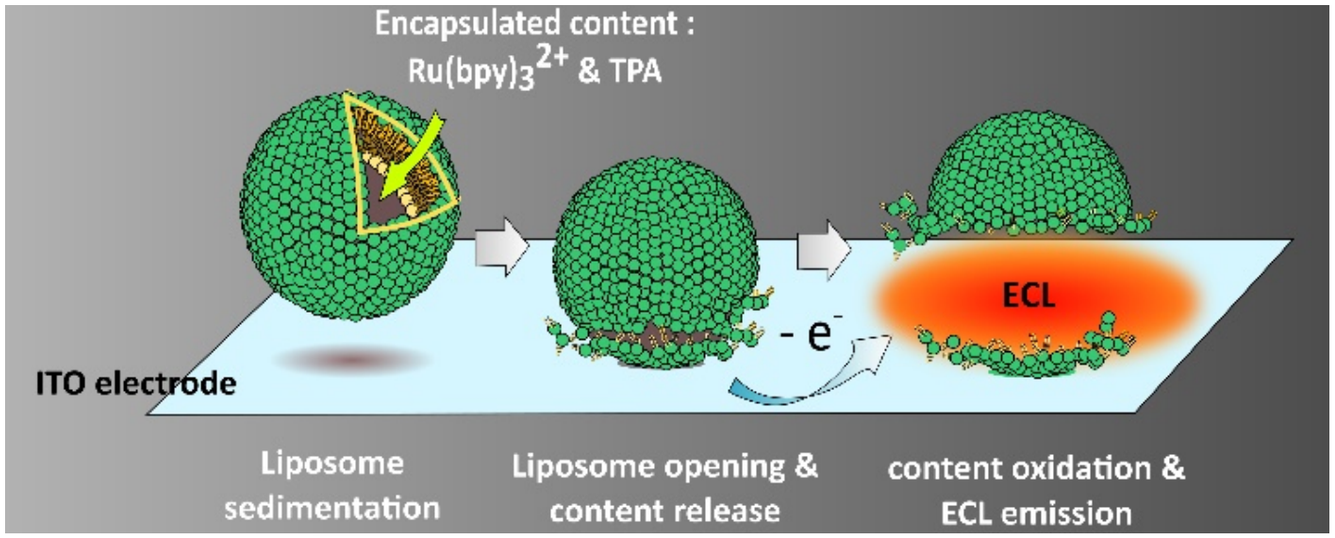
Pandard et al., ***ChemPlusChem***, **2019**, 84, 10

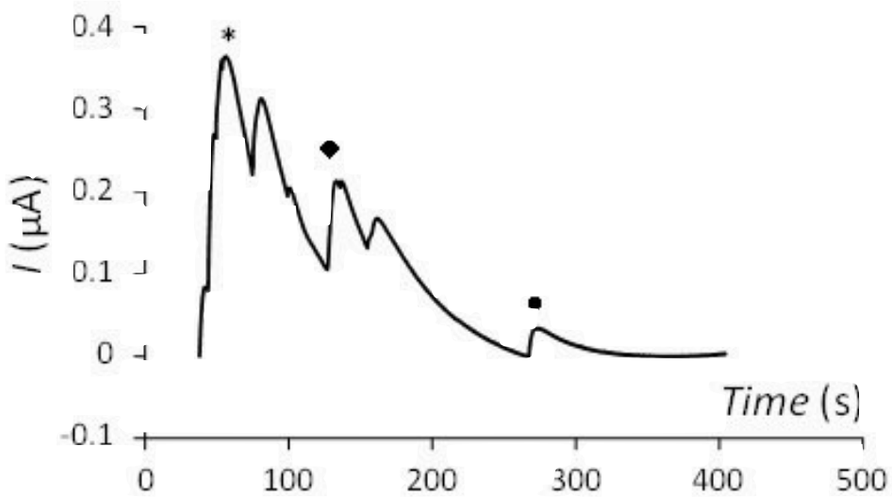
Chimie Physique Biologie de la Matière Vivante

Etude des interactions entre peptides pénétrants et membrane par extinction de fluorescence électro-induite ou électrochimiluminescence

Dr. O. Buriez, Pr. E. Labbé



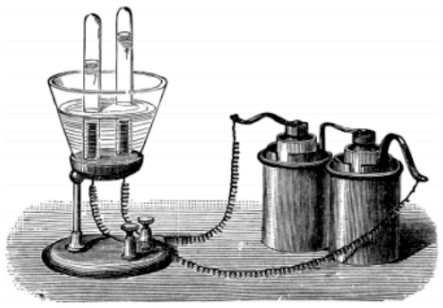




A. Sayegh et al. *Electrochim. Acta*. **2019**, *304*, 465-473

A. Sayegh et al. Submitted to *ChemElectroChem*

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Nicholson & Carlisle

1800

Faraday Kolbe

1834

Petersen et al.
(Shono et al. 1975)



1966



IKA Electrasyn 2.0®

2016



Petersen et al. *JACS* **1966**, *88*, *4657*.
Petersen et al. *JOC* **1966**, *88*, *128*.
Shono et al. JACS **1975**, *97*, 4264,



Baran et al. *Nature* **2016**, *533*, 77.



- **Green** (electron as reagents)
- **Predictive** (Electroanalytical studies)
- **Selective** (Potentiostatic conditions)
- **Safe** (on/off control of the reaction)



???

For reviews, see:

Baran et al. *Chem. Rev.* **2017**, *117*, 13230.
Kärkäs et al. *Chem. Soc. Rev.* **2018**, *47*, 5786
Waldvogel et al. *ACIE* **2018**, *57*, 5594.

https://www.chimie.ens.fr/grimaud/

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Maxime Vitale

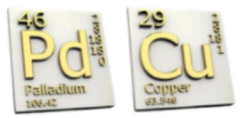


Laurence Grimaud

Team's research interests

Methods

Metal catalysis



- Rearrangement of cyclopropanes (Pd)
  - (3+2) cycloadditions (Pd,Cu)
  - Dearomatizations (Pd, Cu)

Electrocatalysis



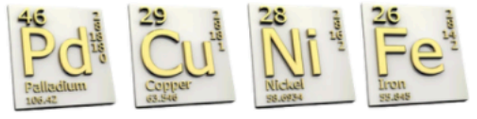


Mechanisms





Kinetic analyses
& Identification of catalytic intermediates

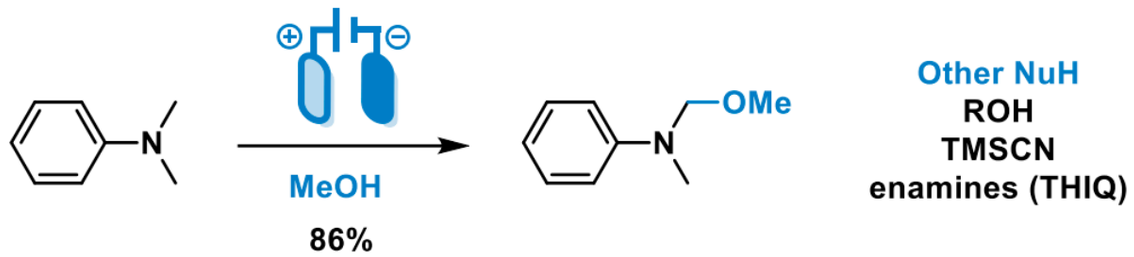


- Suzuki couplings (Pd, Ni)
- (3+2) cycloadditions (Cu)
- Electrophilic activation of allenes (Cu)
- Oxyamination/aziridination (Fe)

https://www.chimie.ens.fr/grimaud/

Anodic oxydation of amines

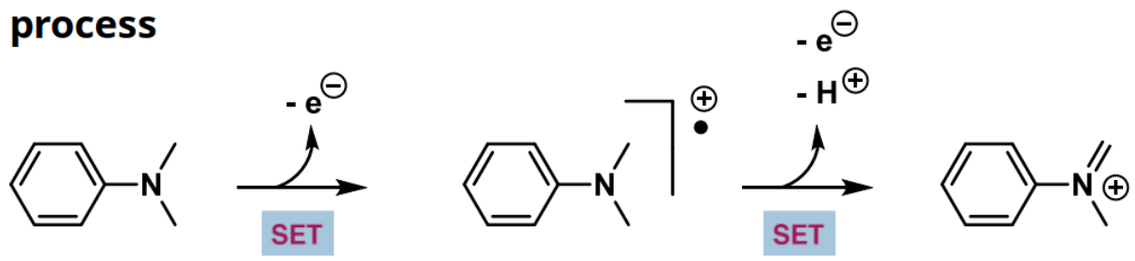
Direct oxydation



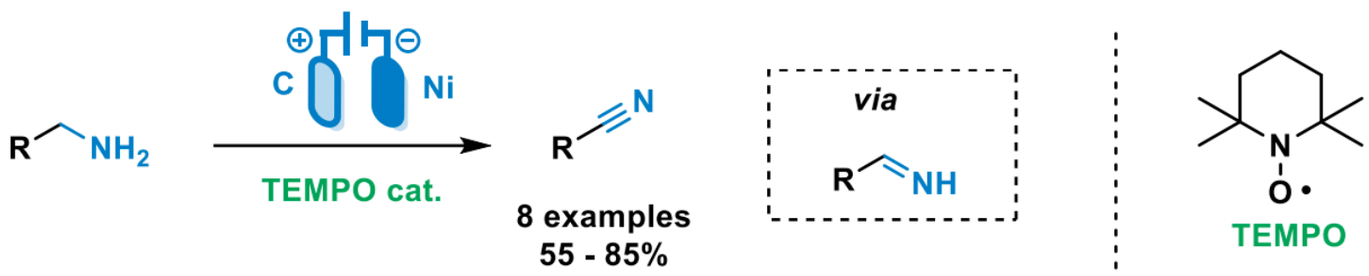
Weinberg & Brown *J OC* **1966**, *31*, 4058.

For a review, see: Kärkäs et al. *Chem. Soc. Rev.* **2018**, *47*, 5786,

consecutive SET oxidation process

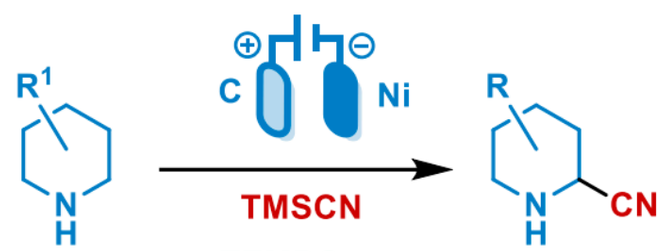


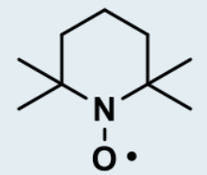
Indirect oxidation – Redox mediator

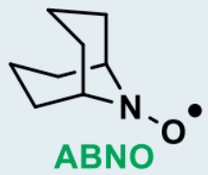


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Indirect oxidation – Redox mediator

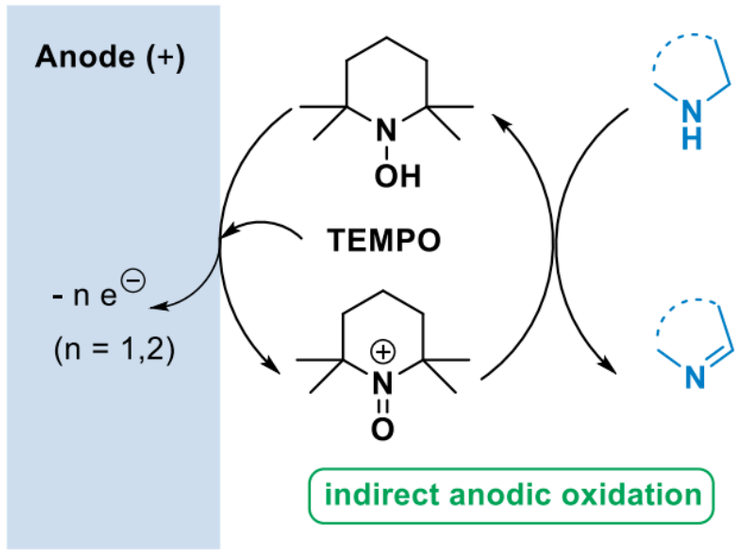






Chiba et al. *JOC* **1977**, *42*, 2973.
Stahl et al. *JACS* **2018**, *140*, 11227.

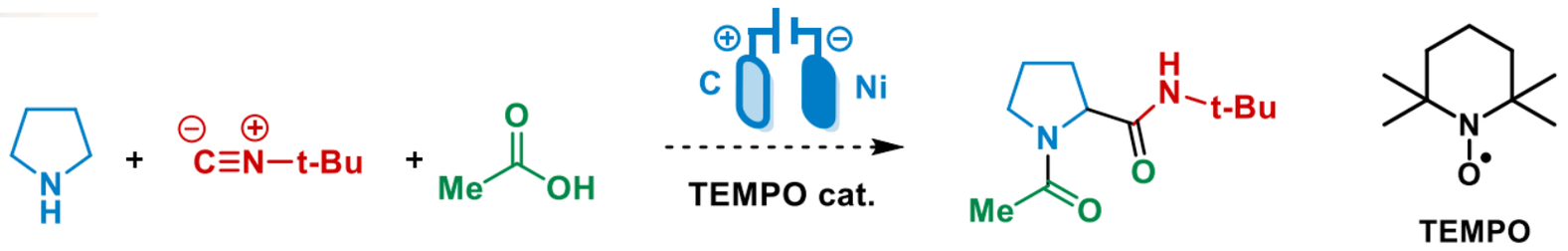
Catalytic process : 2 $e^{\ominus}$ oxydation (formal hydride transfert)



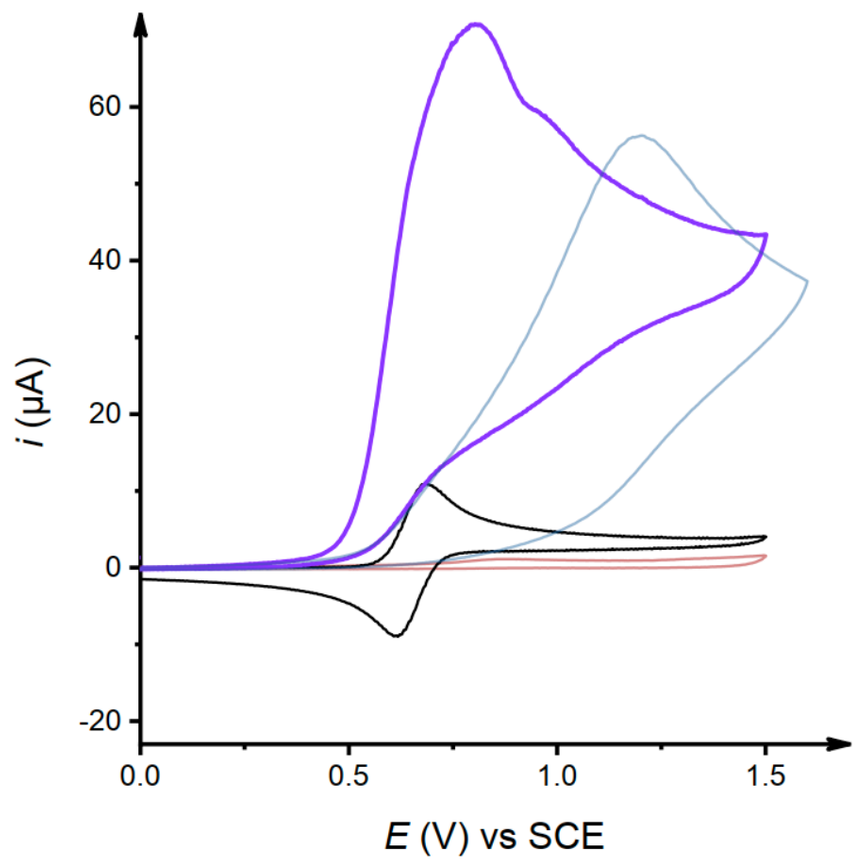
For reviews on indirect electrolysis, see:
Franke & Little *Chem. Soc. Rev.* **2014**, *43*, 2492.
Stahl et al. *Chem. Rev.* **2018**, *118*, 4834.

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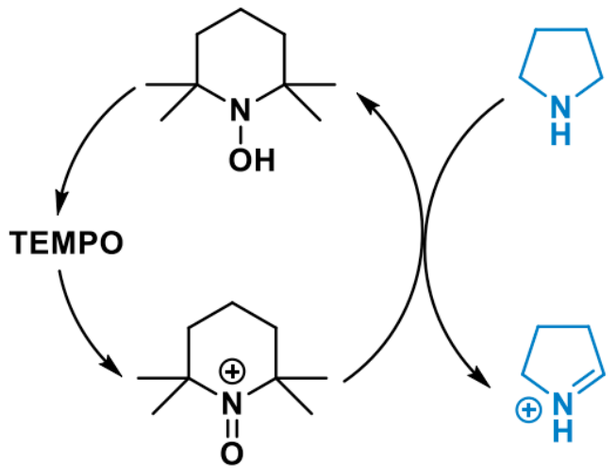
Cyclic voltammetry



0.3 M of *n*-Bu_4NBF_4 in MeCN performed at 20C,
(0.1 V/s, GC (Ø = 3 mm) as WE, Pt wire as CE and SCE as RE).







TEMPO⊕ is consumed **and** regenerated

Electrocatalytic effect

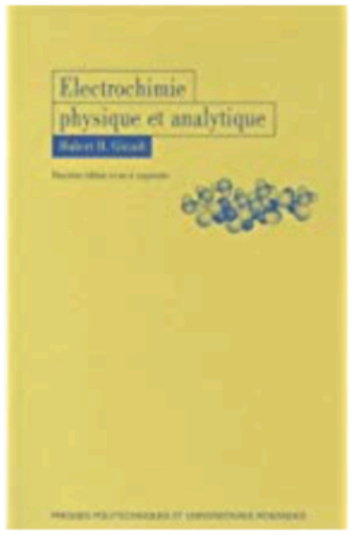
Références Bibliographiques



Y. Verchier
F. Lemaitre



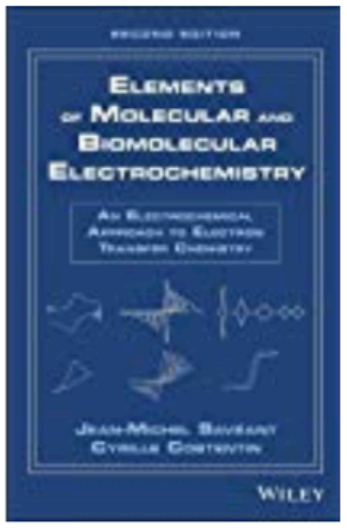
F. Miomandre



H. Girault



A. Bard



J.M. Savéant