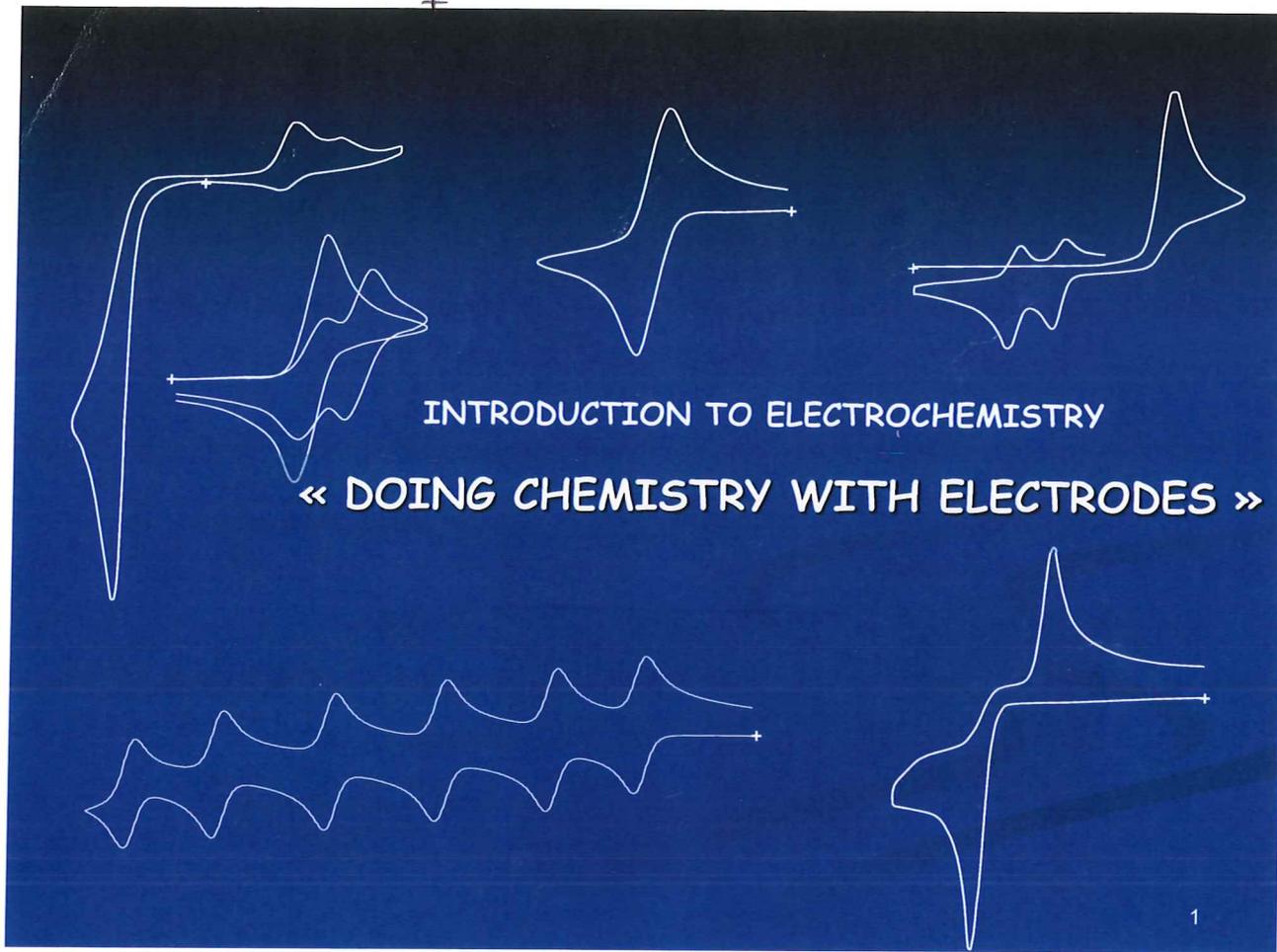
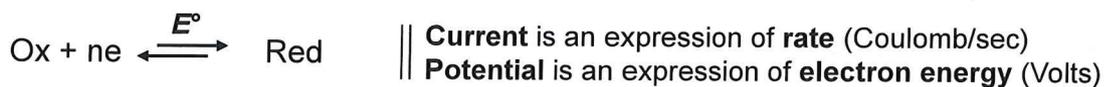


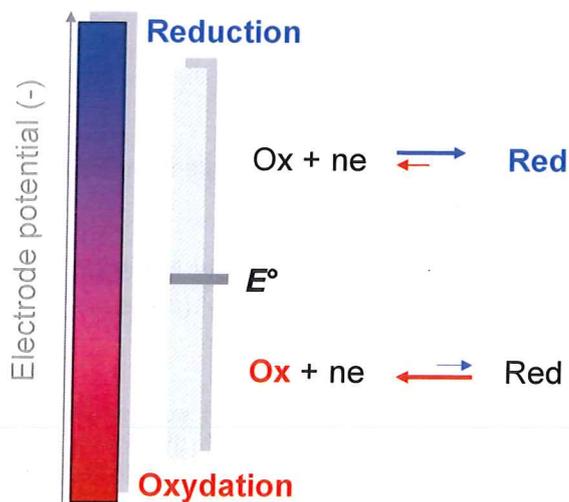
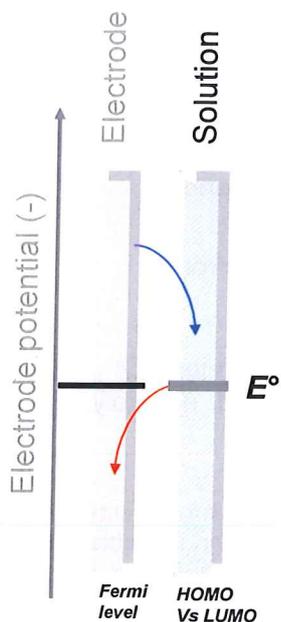
Cinetic 1



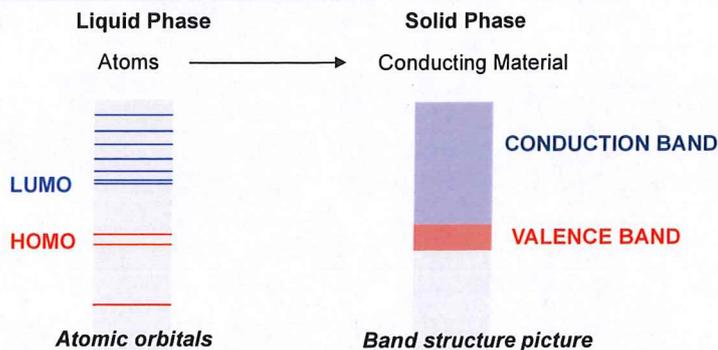
### Oxydation vs reduction – Potential vs current



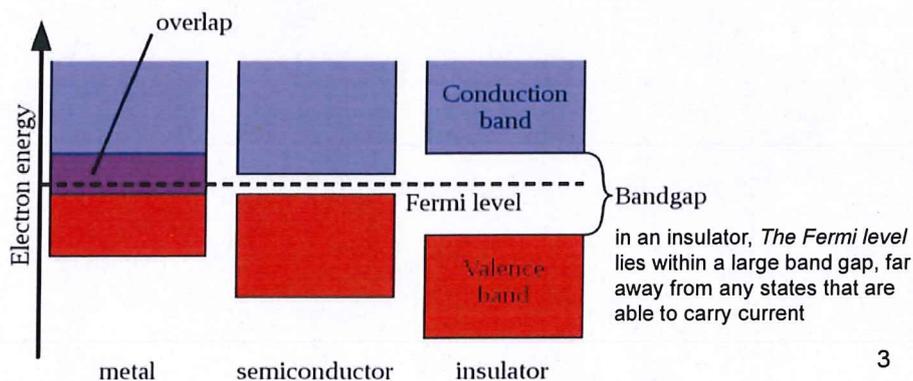
The electrochemical reaction proceeds at a rate (current flow) determined by the electrode potential



# From Atomic orbitals to Fermi Level: Understanding the electrode/molecule interphase



**Fermi Level in the band structure picture :**  
hypothetical energy level defined as with 50% probability of being occupied at any given time

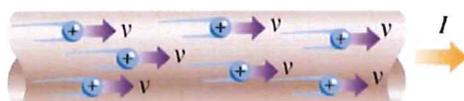


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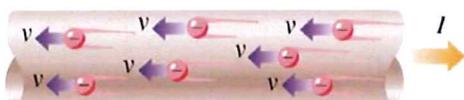
## Electric Current : Ordonnated flux of charges (positive or negative)

4

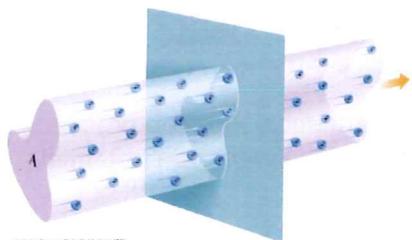
*The direction of current is defined as the movement of positive charges*



(a)



(b)



© 2001 Brooks/Cole Publishing ITP

$$I = \frac{\Delta q}{\Delta t} \quad \text{Ampere (coulomb/second)}$$

**In metallic wires**, the current is based on the movement of conduction electrons (Electronic conductor)

**In electrolyte solutions** the current is based on the movement of charged ions  $C^{x+}$ ;  $A^{y-}$  (ionic conductor); solvent + ions (aqueous/organic); ionic liquids, solid electrolytes, conducting polymers..



**Sign convention :** In europe (IUPAC recommendation) oxydation currents are positive (flowing from the solution to the electrode) and reduction currents are negative (from the electrode to the solution). (it is ≠ in brit and US manuels/papers)

# Basics of Electrochemistry

## Measuring potentials and currents from redox reactions

### STATIC TECHNIQUES ( $i = 0$ )

#### Potentiometric measurements

Measuring potentials of electrochemical cells **at Equilibrium** ( $i = 0$ )

$$E_{\text{cell}} = E_{\text{indicator}} - E_{\text{reference}} \quad (\text{at } i=0)$$

**Ex : Ion-Selective Electrode (ISE)** Based on the fact that the potential of one electrode is sensitive to the analyte's concentration

The most common ISE is the pH electrode, which contains a thin glass membrane that responds to the  $\text{H}^+$  concentration in a solution.

### DYNAMIC TECHNIQUES ( $i \neq 0$ ) allow current to flow

$I$  or  $E$  are imposed either by the electrochemical cell (discharge in battery mode) or by a potentiostat (electrolysis mode)

Remember that current and potential can not be simultaneously controlled ( controlled  $E$  or  $I$  )

☞ **Non-Equilibrium** processes ( $i \neq 0$ )

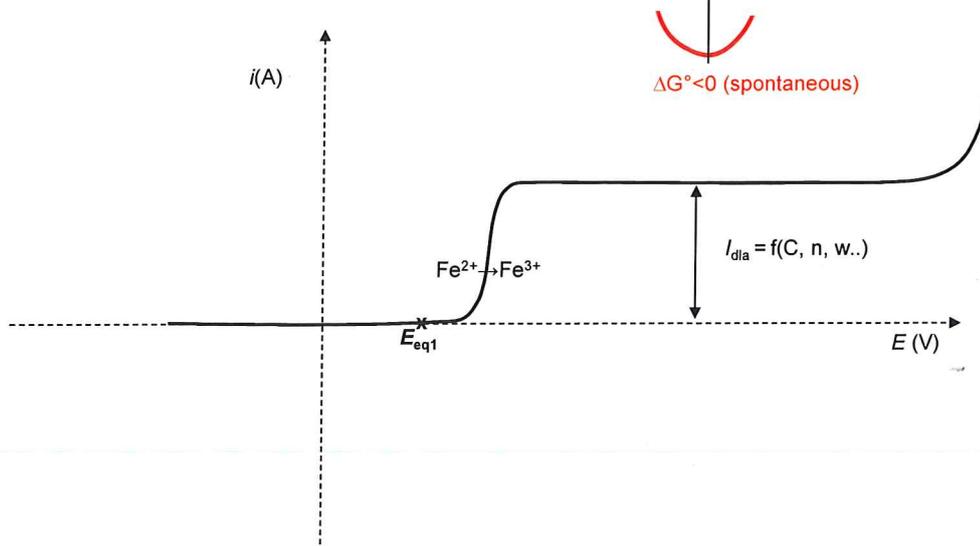
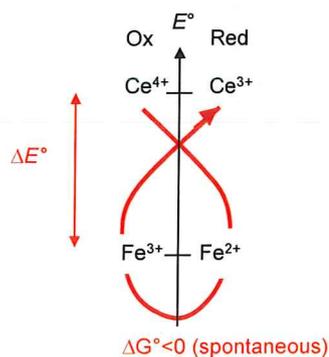
5

### STATIC TECHNIQUES : Recording Potential at $i = 0\text{V}$

#### Potentiometric Titration

Measure of potential at  $i = 0\text{ V}$

Titration of Iron(II) with cerium(IV)

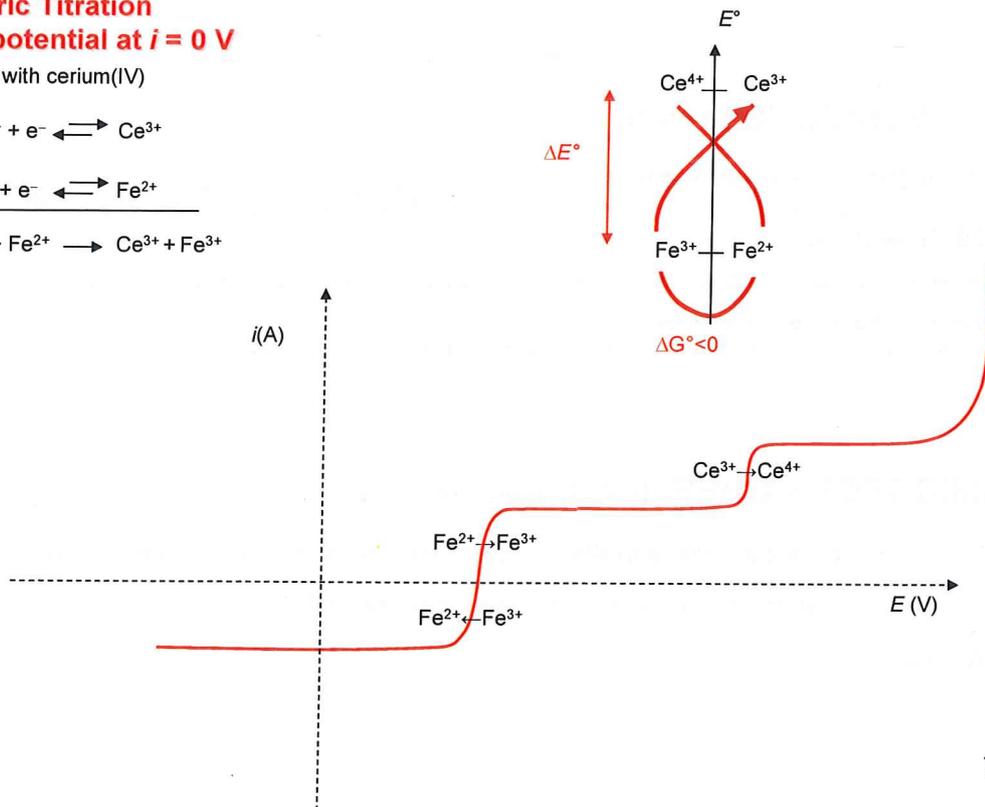


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## STATIC TECHNIQUES : Recording Potential at $i = 0V$

### Potentiometric Titration Measure of potential at $i = 0V$

Titration of Iron(II) with cerium(IV)

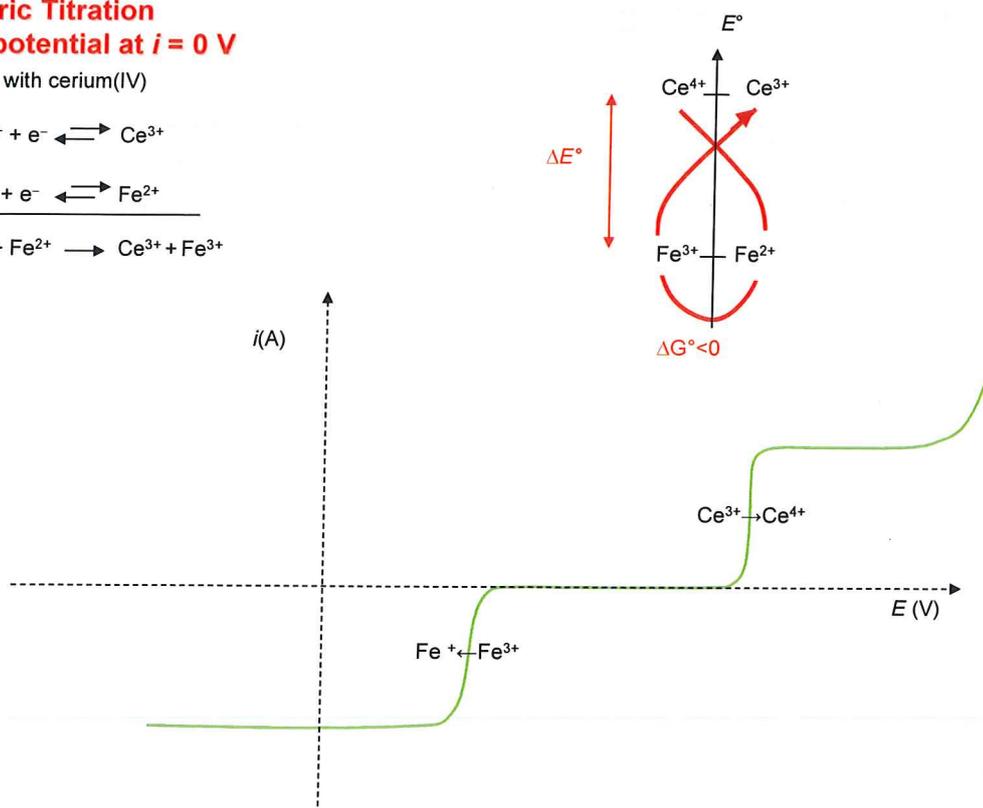


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## STATIC TECHNIQUES : Recording Potential at $i = 0V$

### Potentiometric Titration Measure of potential at $i = 0V$

Titration of Iron(II) with cerium(IV)

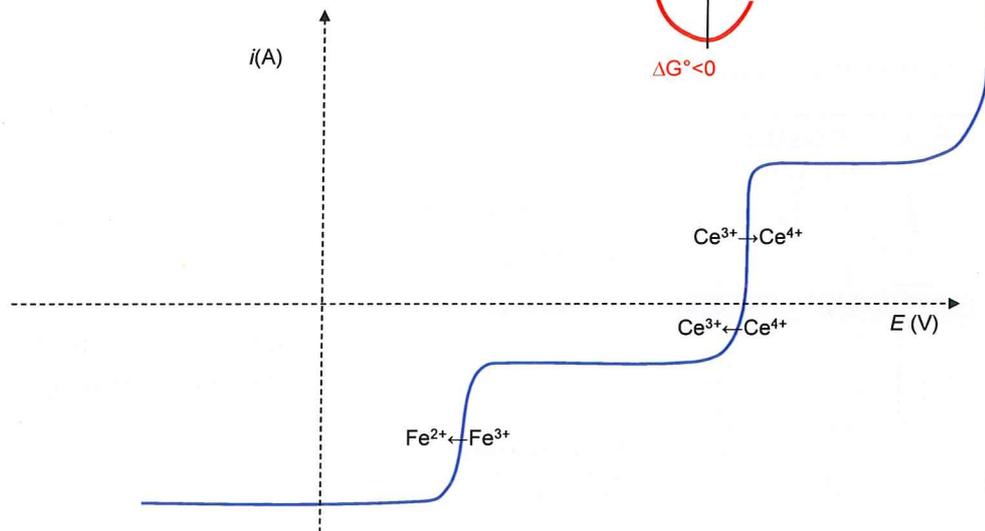
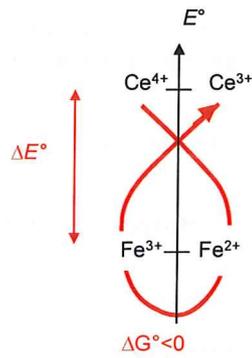
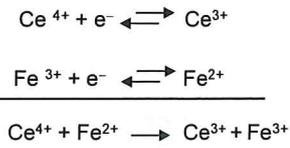


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## STATIC TECHNIQUES : Recording Potential at $i = 0V$

### Potentiometric Titration Measure of potential at $i = 0V$

Titration of Iron(II) with cerium(IV)

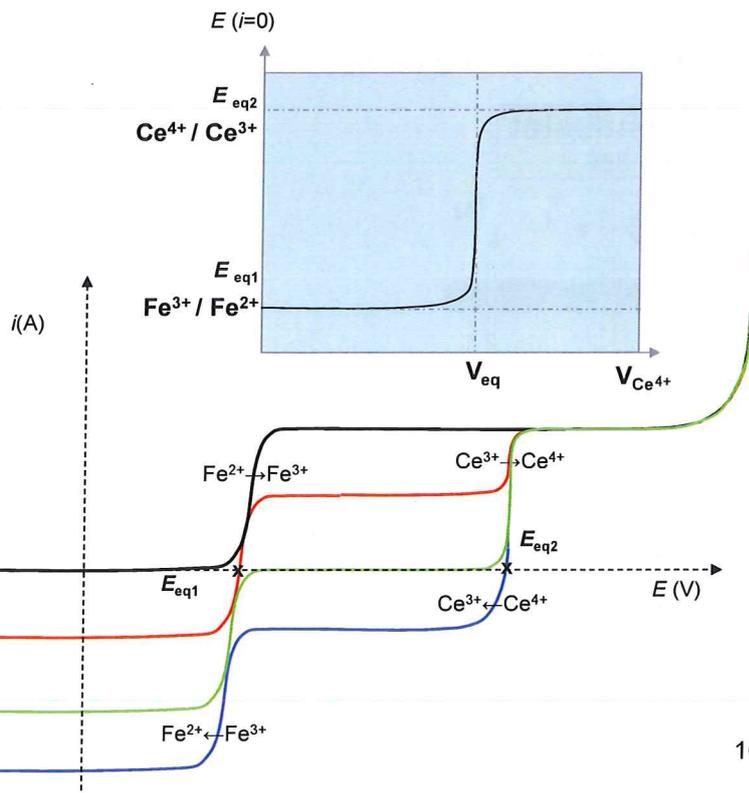
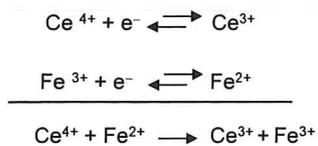


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## STATIC TECHNIQUES : Recording Potential at $i = 0V$

### Potentiometric Titration Measure of potential at $i = 0V$

Titration of Iron(II) with cerium(IV)



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# DYNAMIC TECHNIQS : The Electrochemical Cell

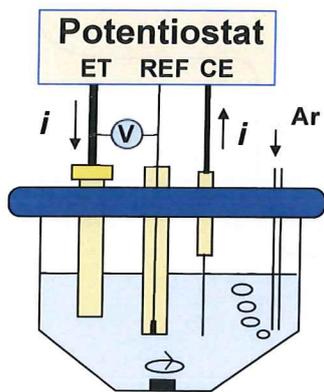
## Potential/current control at a « working » electrode

behaves either as an anode or a cathode, depending on the applied polarity.

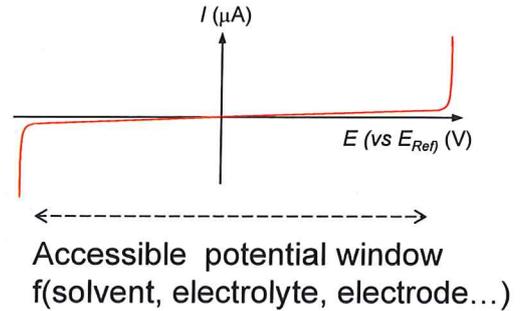
The auxiliary electrode allows current to flow through the cell

No current through the reference electrode (stable potential/fast kinetics)

### Three electrodes setting



Auxiliary electrode  
Reference electrode  
Working electrode

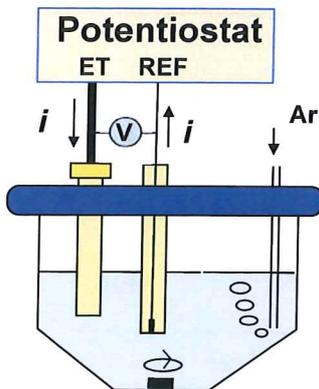


To be discussed :  
Surface of the electrodes  
Which reference electrode

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# The Electrochemical Cell

## Two electrodes setting (ET/ref or ET/CE)



If a ref electrode is used, large currents might flow through it  
► Degradation

Large potentials shifts might be observed due to ohmic drop

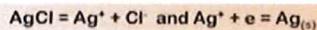
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# Standard Reference electrodes for aqueous solutions

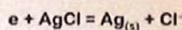
Stable potential (couple with fast kinetics)

ECS (chlorides might interfere)

◆ **Electrodes with a potential independent of solution composition**



end up with



$$E = E_o - 0.0592 \log \frac{a_{\text{Ag}} a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

$$E = E_o - 0.0592 \log a_{\text{Cl}^-}$$

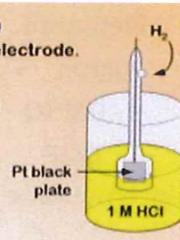
**Hydrogen electrode (SHE)**

The ultimate reference electrode. Difficult to work with.

H<sub>2</sub> is constantly bubbled into a 1 M HCl solution

Pt / H<sub>2</sub> (1atm), 1M H<sup>+</sup> //

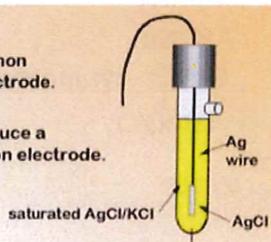
E° = 0.000000 V



**Ag/AgCl**

Another common reference electrode.

Easier to produce a combination electrode.

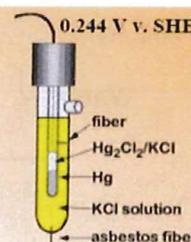


**Calomel electrode (SCE)**

A much more common reference electrode.

Hg / Hg<sub>2</sub>Cl<sub>2</sub>(sat), KCl //

Chloride is used to maintain constant ionic strength.



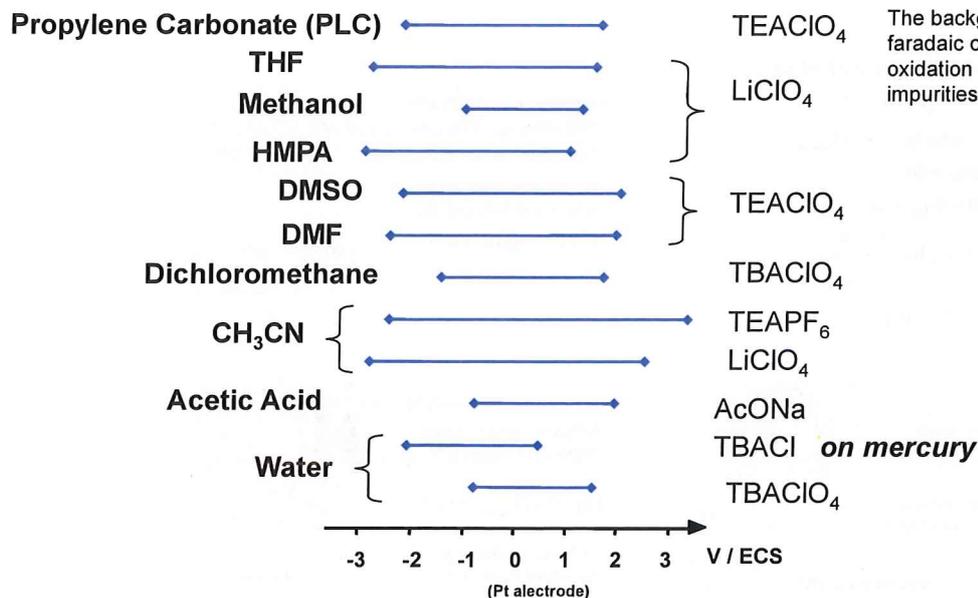
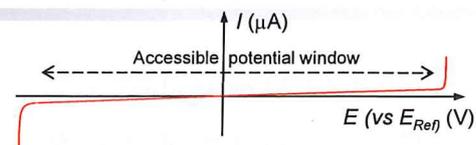
Electrode type	Electrode reaction	Potential at 25°C		Abbreviation	Electrode name
		vs.NHE	vs.SCE		
<b>Hydrogen</b>	(Pt)/H <sub>2</sub> , H <sup>+</sup> (a=1)	0	-0.2412	<b>NHE</b>	<b>Norm. Hyd. EI.</b>
<b>Silver / silver chloride</b>	Ag/AgCl, KCl (0.1 M)	0.2881	0.047		
	Ag/AgCl, KCl (3.5 M)	0.205	-0.036		
	Ag/AgCl, KCl (sat'd)	0.197	-0.045		
		0.1988	-0.042		
Ag/AgCl, NaCl (sat'd)	0.194	-0.047			
<b>Calomel</b>	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (0.1M)	0.3337	0.0925		
		0.336	0.095		
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (1 M)	0.2801	0.0389	<b>NCE</b>	<b>Norm. Cal. EI.</b>
		0.283	0.042		
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (3.5M)	0.250	0.009		
	Hg/Hg <sub>2</sub> Cl <sub>2</sub> , KCl (sat'd)	0.2412	0	<b>SCE</b>	<b>Sat. Cal. EI.</b>
0.244					
Hg/Hg <sub>2</sub> Cl <sub>2</sub> , NaCl (sat'd)	0.2360	-0.0052	<b>SSCE</b>	<b>Sod. Sat. Cal. EI.</b>	
<b>Mercury/ mercury oxide</b>	Hg/HgO, NaOH (0.1 M)	0.165	-0.076		
		0.926	0.685		
	Hg/HgO, NaOH (1 M)	0.14	-0.101		
<b>Mercury/ mercury sulfate</b>	Hg/Hg <sub>2</sub> SO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> (0.5 M)	0.68	0.44		
		0.682	0.441		
	Hg/Hg <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> (sat'd)	0.64	0.40		
0.65		0.41			
<b>Nonaqueous</b>	Ag/AgNO <sub>3</sub> (0.01 M) MeCN		0.3		
	Ag/AgNO <sub>3</sub> (0.1M) in MeCN		0.36		

Shaded, italics = calculated values; Bold = assumed standards. SCE assumed to be 0.2412V for conversions.

## Accessible potentials = f( solvents, electrodes, electrolytes)

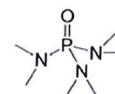
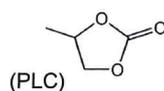
15

No reactivity/Weak electroactivity/High solubility



The background current is principally faradaic current arising from the oxidation (or reduction) of electroactive impurities in the mobile phase.

TBA = tetra-*n*-butylammonium  
TEA = tetra-*n*-ethylammonium



## MOBILE PHASE LIMITATIONS

### ELECTROLYTE MUST BE PRESENT :

- Usually at 0.01 M to 0.1 M concentrations, to convey charge through the electrochemical cell.

- The solvent must have a sufficiently high dielectric constant to permit IONIZATION OF THE ELECTROLYTE.

- The mobile phase (electrolyte + solvent) must be ELECTROCHEMICALLY INERT at the electrode surface; →the background current at the applied potential should be negligible, with no chemical deterioration of the surface.

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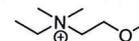
**IONIC LIQUIDS** : composed solely of anions and cations

- Liquid at ambient temperature
- Powerful solvents
- Non volatile, low vapor pressure /non toxic
- Nonflammable
- Thermally and hydrolytically stable
- Large electrochemical window

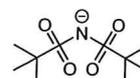
- High viscosity (slow diffusion of electroactive species)
- Synthetically demanding
- Expensive

**Applications in electrochemical cells and devices:**

- Li metal and Li ion batteries
- Ultracapacitors
- Electrochromic displays
- Fuel cell membranes..



N-ethyl-N,N-dimethyl-2-methoxyethylammonium



bis(trifluoromethane)sulfonimide (TFSI)

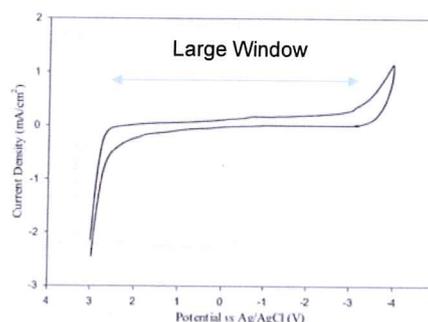


Fig. 3. CV of [N112.102][TFSI] using GC macro-electrode at sweep rate 100 mV/s and 25 °C.

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## Working electrodes

### Which Working electrodes ???

(Inert, high electronic conductivity, low price, well defined geometry, limited rugosity)

Planar disk electrodes → Conducting materials in insulating matrix {  
 -Diameter  
 -Noble metals, carbon, mercury, TiO<sub>2</sub>,...



#### Noble metals

platinum, palladium are not oxidized in water

Very high electronic conductivity

Catalytic properties which might reduce the electrochemical window



#### Carbon ≠ Diamond

Graphite (native crystalline allotrope of carbon), glass-like carbon (IUPAC for trademark vitreous® or glassy® carbon, 100% sp<sup>2</sup>, might be made of fullerenes), carbon fiber or carbon black, graphitic carbon (stacked graphene sheets), foam (high surface area) cheap

#### Mercury

Low oxidation potential

Liquid at room temperature allow an easy surface control

Not inert and might influence the electrochemical reactions

#### Metal Oxides

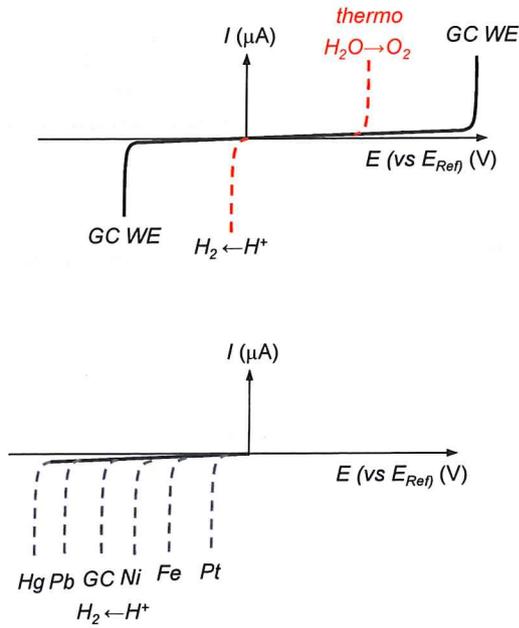
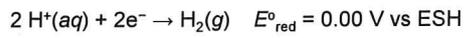
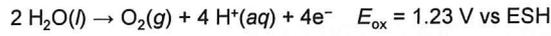
SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> (ITO) → transparent electrodes for spectroelectrochemistry

Usually 90% In<sub>2</sub>O<sub>3</sub>, 10% SnO<sub>2</sub>

TiO<sub>2</sub> → Photovoltaic cells

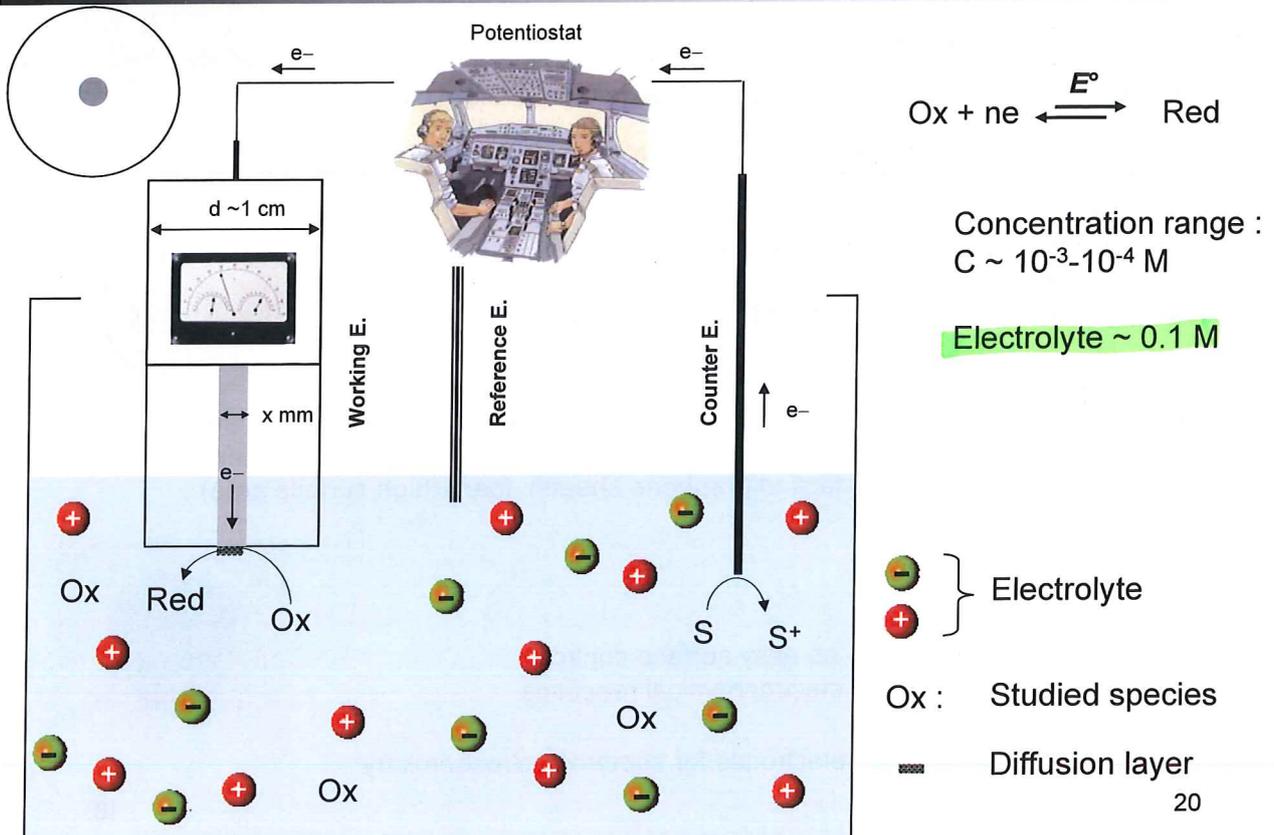


# Influence of the electrode material : evidencing kinetic effects



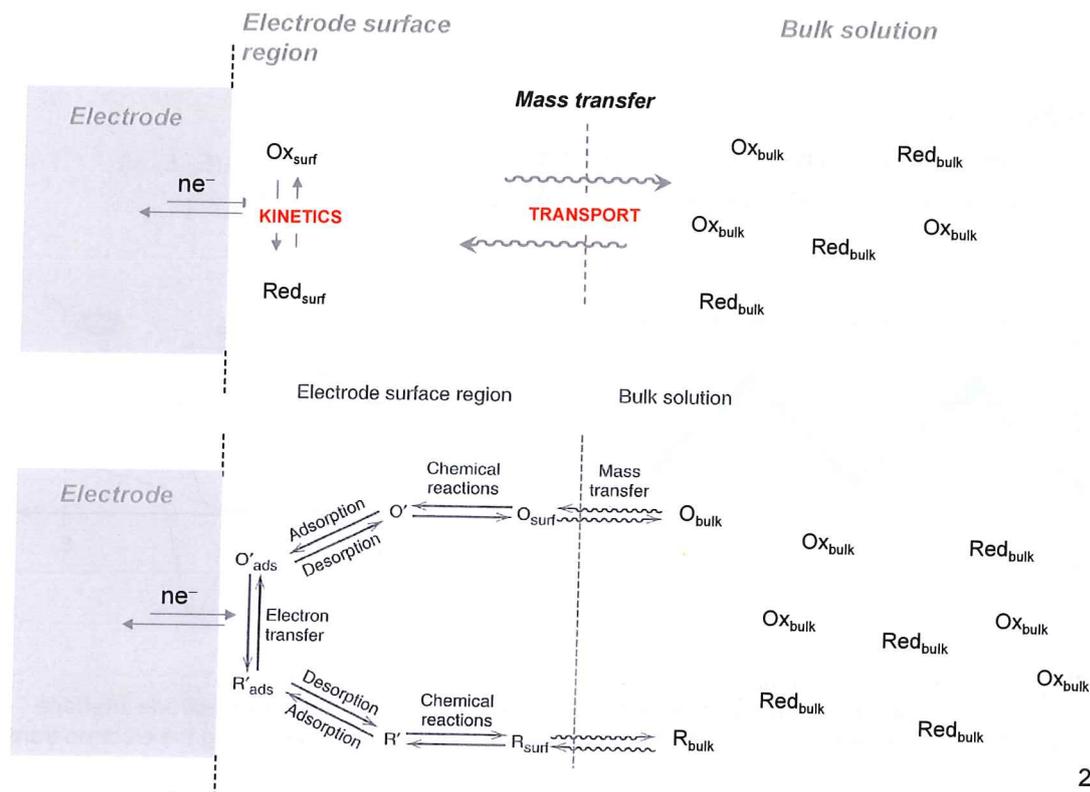
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## BASICS of electrochemistry measurements (three electrodes settings)



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## Pathway of a general electrode reaction : concept of diffusion layer



## Mass transport in electrochemical cells

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### Which species ??? Electroactive vs non electroactive species (faradic vs non-faradic )

**Faradic :** due to redox processes either from analyte or solvent impurities

**Non Faradic :** related to the charge and discharge of the electrode/solution interface (capacitive behavior): *not related to an oxidation/reduction reaction*. Investigation on NF processes requires the modelization of the interface (Helmoltz, gouy, stern...)

### Which transport modes ???

#### Convection

**Natural:** gradients of density, temperature, pressure in a fluidic media...

**Forced:** imposed by the experience. **Mecanic stirring** or **electrode rotation**

#### Diffusion

Movement of species induced by **concentration gradients**

Depend on the size, solvation, **mobility** of a given species and on the media (viscosity..)

#### Migration

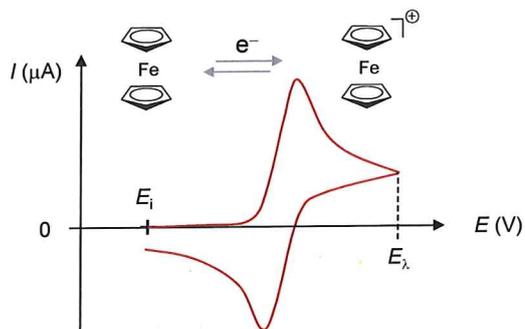
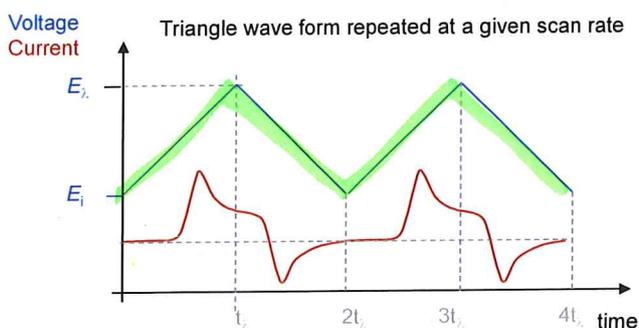
Movement of species induced by the **electric field**.

Only **Charged** species are concerned.

Depend on the size, solvation, **mobility** of a given species and on the media (viscosity..)

## Cyclic experiments

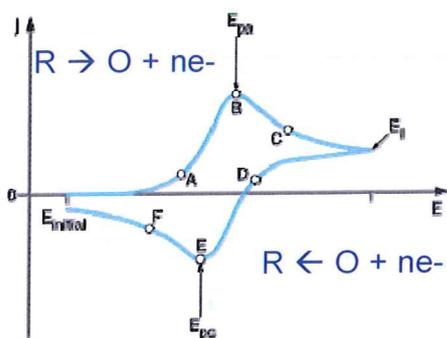
The working electrode potential is ramped linearly versus time  
 After reaching a set potential, the working electrode's potential ramp is inverted. }  $(E_i, E_\lambda, \nu)$



The  $i=f(E)$  curve gives important informations  
 -on the **thermodynamic and kinetics** of the electron transfer at the solution-electrode interface  
 -on the kinetics and **mechanisms of chemical reactions** following or preceding the electron transfer.

## Basics of Cyclic Voltametry : Concentration profiles

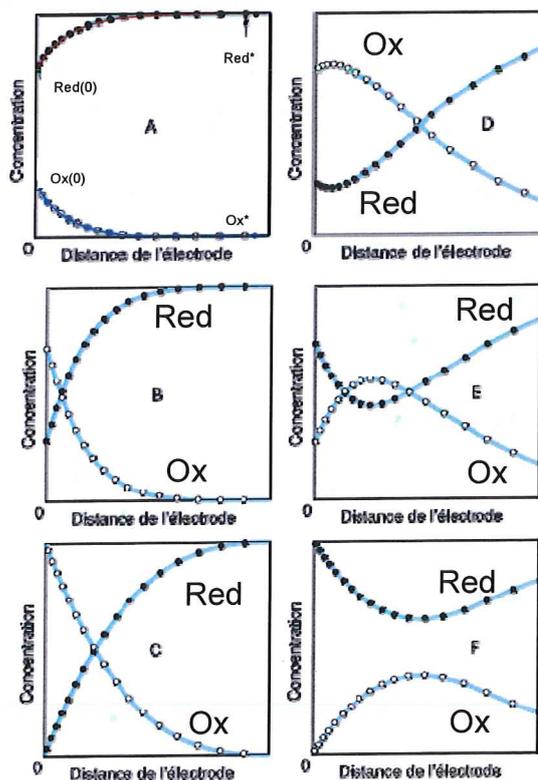
The shape of a cyclic voltammogram can be understood by considering the concentration gradients at the electrode-solution interface.



Diffusion layer thickness ( $\delta$ ) depends on time.

$$\delta \ll r$$

only a small part of the electrode surface is affected by the hemispherical diffusion at the electrode edges



# Basics of Cyclic Voltammetry : What is the capacitive current

When the potential of a working electrode is changed, two different types of current can flow: capacitive currents ( $i_c$ ) and faradaic currents ( $i_f$ ).

$$q = ACE; i_c = \frac{dq}{dt} = \frac{AE dC}{dt} + \frac{AC dE}{dt}$$

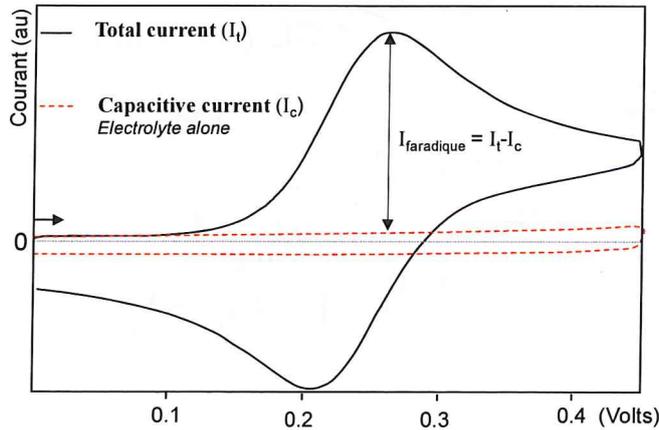
With  $E = E_r + vt \rightarrow i_c = ACv$

The capacitive current is related to the change in the electrode surface charge (double layer charging). It is not related to an oxidation/reduction reaction

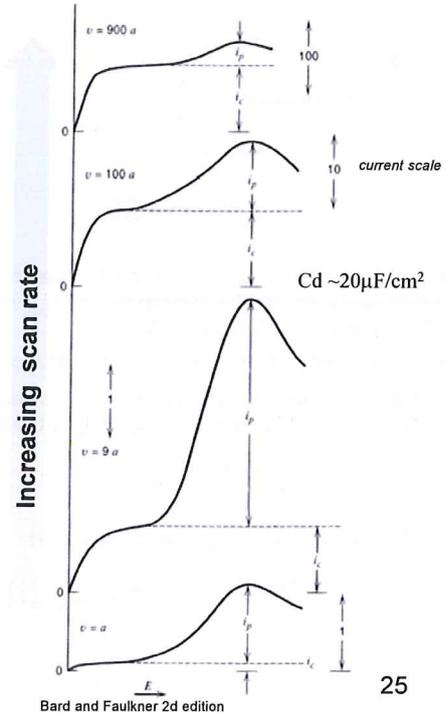
$i_p$  (CV peak current) varies with  $v^{1/2}$  for linear diffusion

$i_c = AC_d v$  (should be constant for a given exp if  $C_d$  does not vary with  $E$ .)

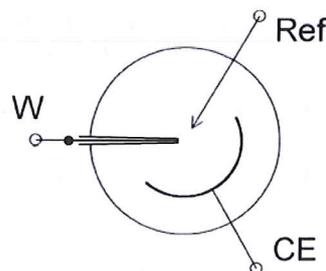
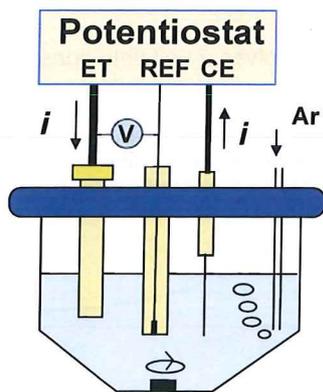
$i_c$  becomes relatively more important at faster scan rates  
Use of pulse voltammetry allows to lower the relative contribution of  $i_c$



Remember that low-level oxidation or reduction currents might also be observed (impurities) or slow, potential-dependent faradaic reactions centered on the electrode material or on the the solvent and supporting electrolyte



## Simple electrical equivalent of a three-electrode electrochemical cell



### Key features :

The potential is applied between the reference and working electrodes

Current Flows between the working (WE) and the counter electrodes (CE)

No current (pico Ampere) flows through the reference electrode (Ref). The potentiostat used to measure the potential difference between the working and reference electrodes has a high input impedance, so that a negligible current is drawn through the reference electrode. Its potential is thus constant and equal to its open-circuit value.

Each electrode interface can be modeled with an equivalent electric circuit involving capacitance and resistance elements