

CH5715

Energy Conversion and Storage

Part 2: Ionic Conduction, Electrochemistry, Batteries and Other Applications

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For lecture notes: <http://koruk.wp.st-andrews.ac.uk>

Lectures 6-9

Electrode Reactions

Charge Transfer

Impedance Spectroscopy

Some other applications *Supercaps, HT
batteries, OTMs*

Texts

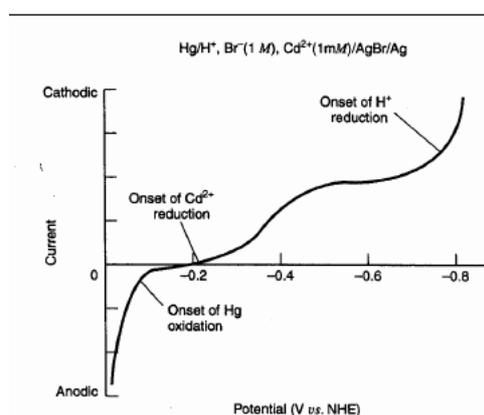
Solid State Electrochemistry

Cambridge - P. G. Bruce

A First Course in Electrode Processes

Electrochemical Consultancy - D Pletcher

A typical electrochemical measurement



Electrochemical Cells and Reactions

There are two types of current flow:

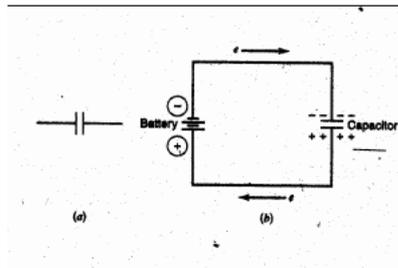
1. Faradaic – charge transferred across the electrified interface as a result of an electrochemical reaction.
2. Non-faradaic – charge associated with movement of electrolyte ions, reorientation of solvent dipoles, adsorption/desorption, etc. at the electrode-electrolyte interface. This is the background current in voltammetric measurements.

Useful presentation

- <http://www.cheng.cam.ac.uk/research/groups/electrochem/JAVA/electrochemistry/ELEC/11html/intro01.html>

Ideally polarizable electrode (IPE) – no charge transfer across the interface. Ions move in and out of the interfacial region in response to potential changes. The interface behaves as a capacitor (charge storage device).

Excess electrons on one plate and a deficiency on the other.



Changing the potential, E , causes the charge stored, Q , to change according to the relationship:

$$Q(\text{Coulombs}) = C(\text{Farads}) \times E(\text{Volts})$$

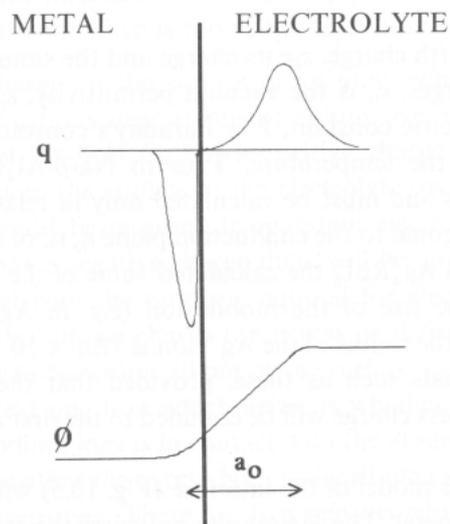
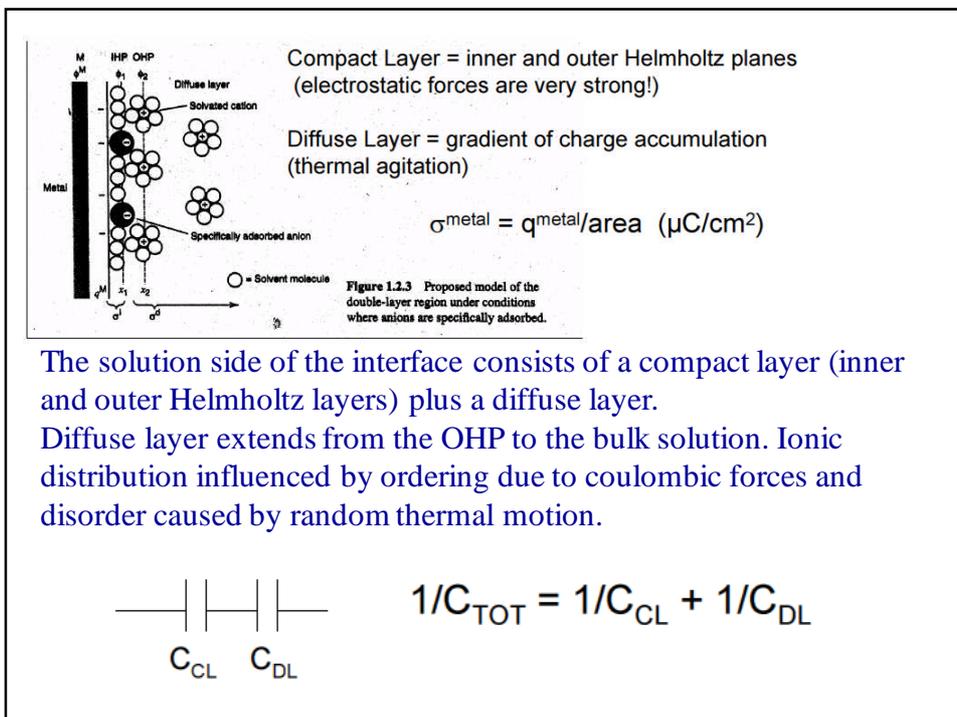
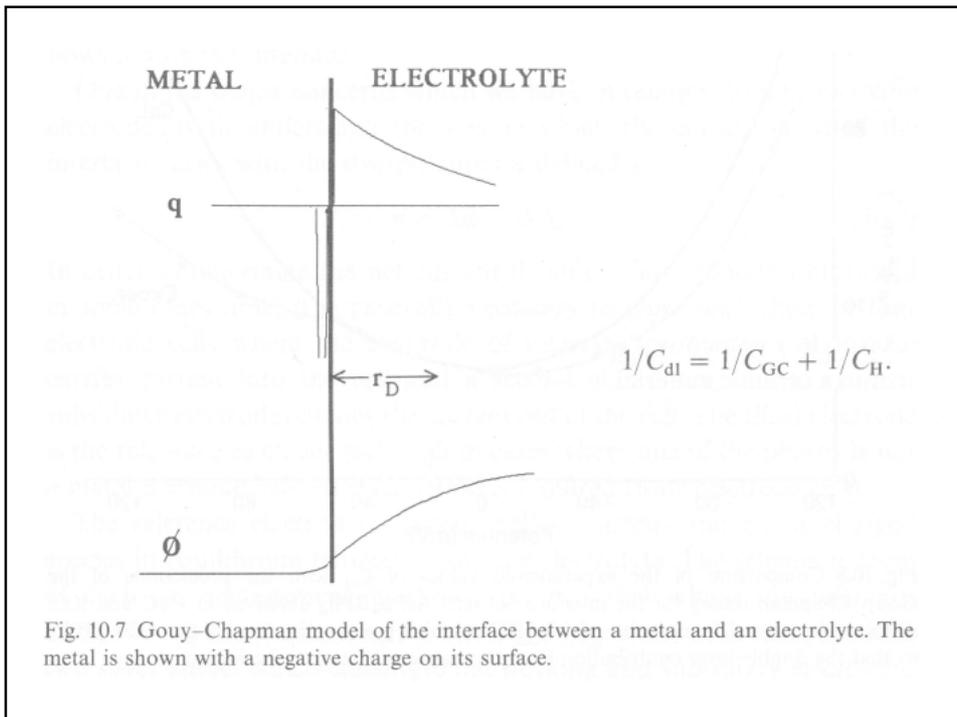


Fig. 10.5 Helmholtz model of the interface between a metal and an electrolyte. The metal is shown with a negative charge (excess of electrons) which is balanced by an excess of mobile cations, the centres of which are one atomic radius from the surface.



Non-Polarisable Interfaces

Exhibit charge transfer

Divide electrodes into 3 types:

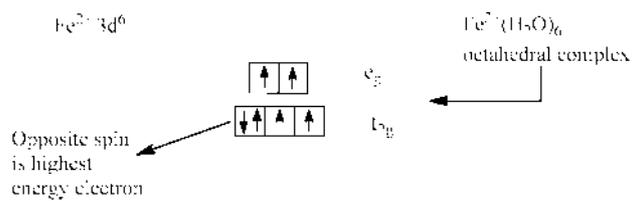
Redox	1st Kind	2nd Kind
$\text{Fe}^{3+/2+}$ at Pt electrode	Ag^+/Ag	$\text{AgCl, Cl}/\text{Ag}$
e transfer	e + ion transfer	e + ion transfer

Redox Electrodes, $\text{Fe}^{3+/2+}$

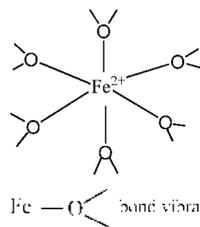
The electrode reaction involves e tunnelling between the ions in solution within 30\AA from the electrode, and with the electrode itself.

We will consider $\text{Fe}^{2+/3+}$, i.e. a one electron transfer

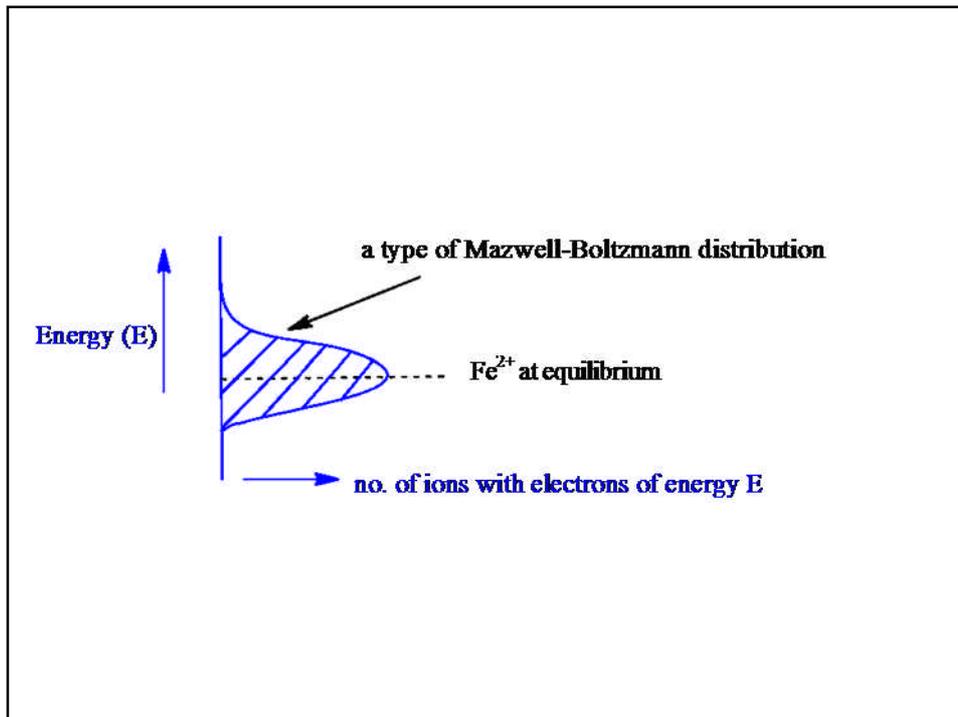
Electron energy levels on ions



Since 1e⁻ transfer ($\text{Fe}^{3+/2+}$) only need to consider the highest energy electron.

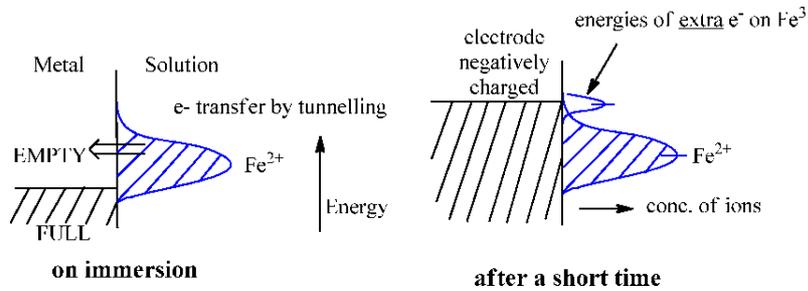


$\text{Fe}-\text{O}$ bond vibrations shift the energy of the e_g up and down

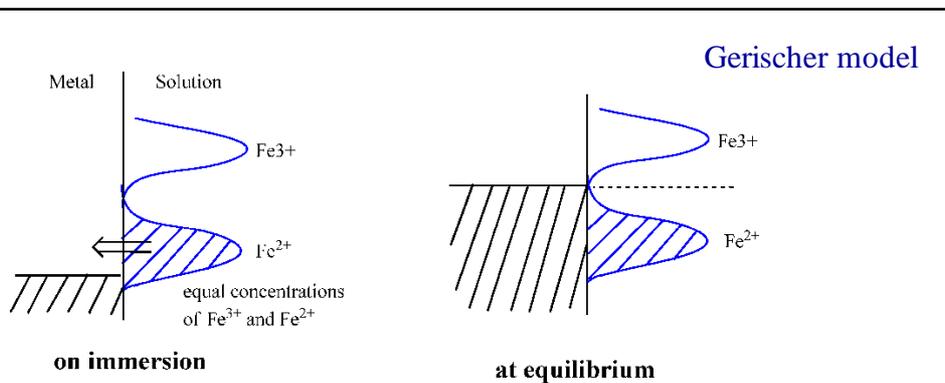


- Introduce Pt electrode into aqueous solution of $\text{Fe}(\text{NO}_3)_2$
- e^- transfer very fast 10^{-16}s - solution vib. and rot. frozen during e^- transfer.
- Tunnelling only occurs between levels of equal energy on the metal and the ion.
- If only Fe^{2+} in solution to begin with, then at equilibrium e^- transfer very slow.
- few levels on metal for $\text{Fe}^{2+} - \text{Fe}^{3+} + e^-$
- few Fe^{3+} ions

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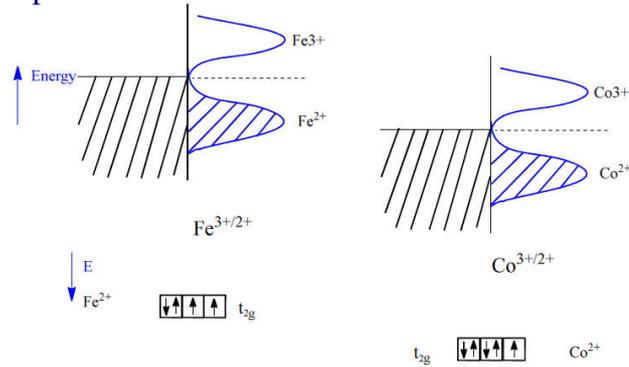


Position of e^- energy level in metal determined by ions in solution. Increase $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ pushes e^- level down i.e. more +ve potentials. Compare with Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

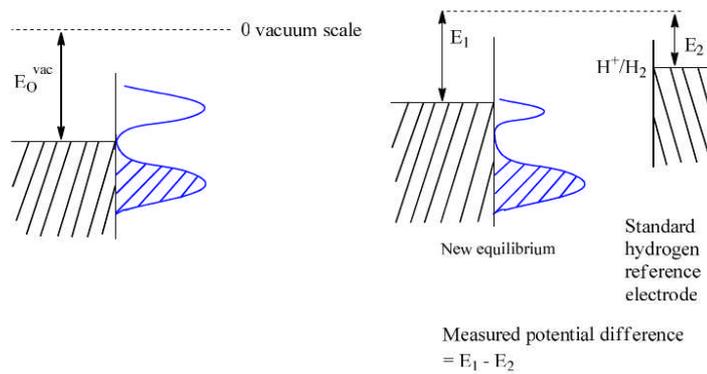
The Electrochemical Series

Position of e (and hence voltage) depends on ions in solution.
 When you have equal concentrations of reduced and oxidised forms then position of electron energy level in metal depends on ion type i.e. redox couple

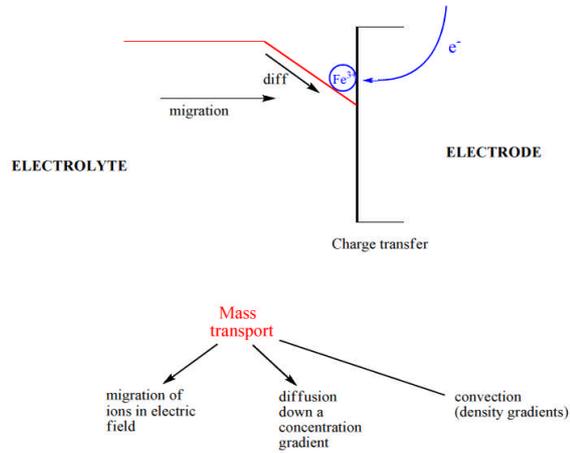


Co has higher effective nuclear charge than Fe, therefore e on Co ion which transfers to/from metal lower in energy than e on Fe lower F_{e^+} level (more positive potential EO)

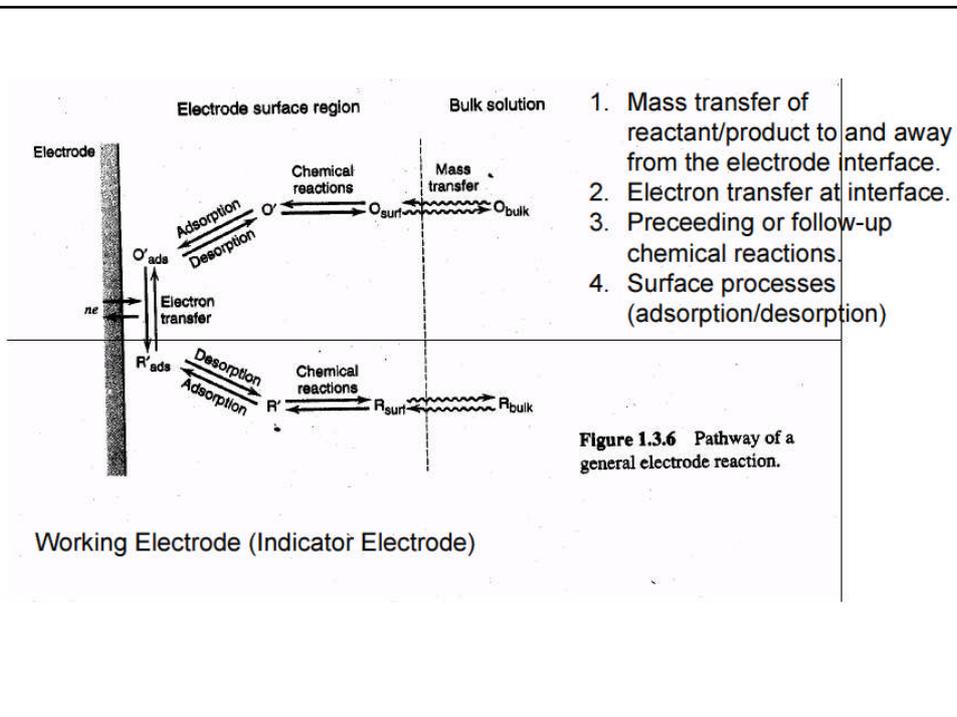
Influence of Potential



Electrode Reactions



Rate of electrode reaction depends on mass transport to the electrode and charge transfer. Often transport dominates.



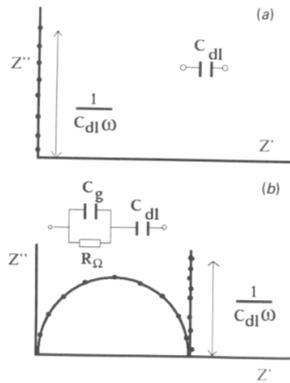


Fig. 10.3 Impedance diagrams for: (a) a blocking interface; (b) a blocking interface when the associated bulk impedance is taken into account.

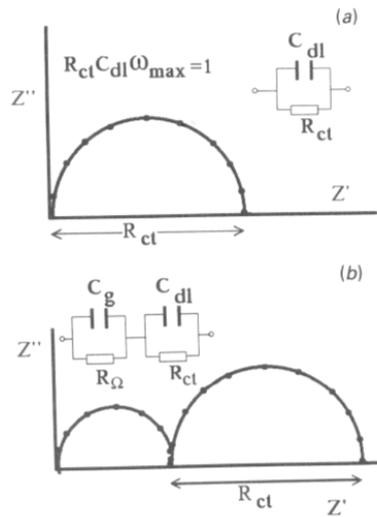


Fig. 10.4 Impedance diagrams for a non-blocking interface when: (a) bulk effects are neglected; (b) bulk effects are taken into account. The impedance diagrams are different if diffusional effects are significant.