

## CHEY0016 Lecture 11 – Introduction to Interfacial Electrochemistry

### Surface Chemistry with extra Control: Electrochemistry

#### Introduction

So far, in this course in surface chemistry, all systems studied have been under equilibrium conditions e.g. a gas adsorbing on a surface with the only changes considered being properties of the gas and subsequent monolayer e.g. pressure, temperature, coverage.

The next 5 – 6 lectures are going to extend these ideas by considering the effect of changing the electronic properties of the surface itself – the electrode. This will be done by either supplying or withdrawing electrons via an external source (generally a *potentiostat*). Clearly, in any binary reaction, the properties (e.g. concentration, pressure, temperature) of both reactants can, in principle, effect the final reaction product and of course the rate of reaction. The same is true where one reactant is an electrode surface, with an important extra degree of controllability being available – the electron concentration controlled by the applied voltage on the electrode.

To supplement the lecture material, a number of external sources are available both in books and on the Web. Moreover, the electrochemistry experiment that you will all undertake in Phys. Chem labs should further help you.

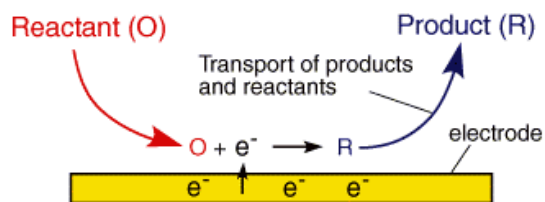
Finally, the following textbooks are recommended:

Electrode dynamics, by Adrian Fisher (Oxford Chemical Primers)  
Electrochemical Methods, by A.J. Bard and L. Faulkner.

#### Basic Concepts

##### ***Electrochemical reactions take place at the electrode surface***

A reactant moves towards an electrode, adsorbs, exchanges an electron, desorbs and moves away:



As in any reaction, the system can be affected by:

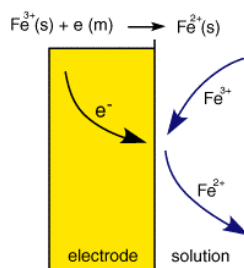
- The reactivity of the reactants (in this case the electrode and the surface). This means changes in the chemical potential, which are related to the change in free energy of the reactants: Thermodynamics.
- The temperature: Related via the Arrhenius equation to the rate constant.

But in addition, is crucially affected by:

- The applied voltage at the electrode. Change in voltage changes the energy of the electrode.
- The structure of the interfacial region where the electron transfer takes place.
- The nature of the electrode surface.

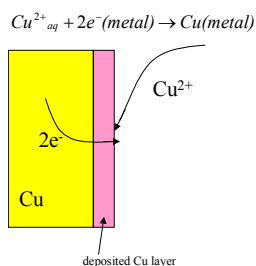
In order to illustrate this point, some examples are shown:

1. The reduction of Fe(III) to Fe(II) on a gold electrode:



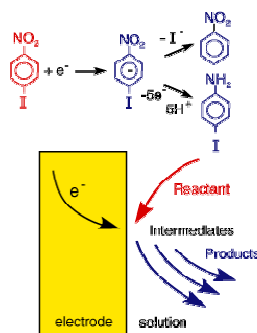
Since one electron is used up for each  $\text{Fe}^{3+}$  reduced at the electrode, the rate of reaction can be followed and moreover by controlling the availability of electrons on the electrode (via the applied voltage) the overall reaction can be controlled.

2. Electroplating - *Deposition of a metal layer on a metal electrode.*



$\text{Cu}^{2+}$  in solution is reduced to Cu metal by means of supplying 2 electrons to each  $\text{Cu}^{2+}$  that is reduced.

3. Oxidation / reduction of organic or inorganic molecules. In synthetic chemistry, a large amount of effort is frequently invested to oxidise or reduce molecules, often using dangerous / unpleasant reagents. In some cases, this can be done more easily using an electrochemical cell. The difficulty is that most organic compounds are only soluble in organic solvents (non-aqueous). Therefore, it is necessary to use an electrolyte that is soluble in organic solvent. A common electrolyte is  $\text{NaPh}_4\text{BO}_4$  (sodium tetraphenylborate). The need for such, so called background electrolyte is discussed in subsequent lectures.



An example is the reduction of iodo-nitrobenzene, with two possible products being formed from the unstable radical intermediate.

A large number of different electrochemical experiments can be carried out – as will be described and also illustrated in the text books and Web learning material which accompany this course.

However, in all case a number of fundamental processes take place in any electrochemical reaction:

- Reactants have to be transported to the surface and products (sometimes) removed (**mass transport**).
- An electron is transferred (**electrode kinetics**).

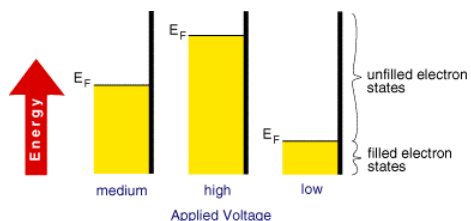
Understanding both mass transport and electrode kinetics are essential to get a proper understanding of interfacial electrochemical processes.

To start, some basic concepts will be considered:

The applied voltage at an electrode is simply the amount of energy supplied per coulomb of charge.

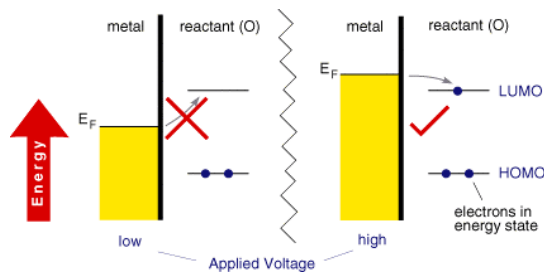
$$1V = 1 \text{ Joule} / \text{Coulomb}$$

A convenient way to consider the effect of applied voltage of electrons in a metal is to remember that in a metal, the highest occupied molecular orbital (HOMO), instead of being a discreet level containing just one or two electrons is made up of the interaction of the HOMO of many metal atoms together and is known as the Fermi level.



This figure illustrates the effect of the applied voltage on the energy of the Fermi level ( $E_F$ ) in the metal.

Since in electrochemistry one can control the applied voltage of an electrode, one can also control the Fermi level energy of the electrode as the next figure illustrates:

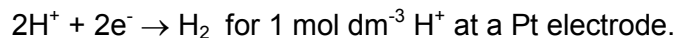


### Thermodynamics of Electrochemical Reactions

You'll be no doubt relieved to know that thermodynamics can be used to understand electrochemical reactions in the same way as for bulk chemical reactions.

#### Basic points:

The standard reduction potential is a measure of how easily a substance can gain an electron. Values are generally listed as being relative to the SHE (standard hydrogen electrode). This is arbitrarily defined as having a potential of 0.00V for the system:



The standard reduction potential (often referred to as the standard electrode potential) is related to the free energy of the reduction process by:

$$\Delta G^\circ = -nFE^\circ$$

So clearly, reduction reactions with a positive  $E^\circ$  will (if kinetically able) proceed spontaneously, those that have a negative  $E^\circ$  will not (though of course the reverse situation, an oxidation could then proceed spontaneously).

The slight complication is that reduction (or oxidation) reactions rarely take place in isolation. There is generally an associated oxidation reaction (liberating electrons) or reduction reaction (using up electrons) coupled to the system under study.

So, if considering whether a reaction will (or won't take place spontaneously), one should consider the total electrode potential difference between the oxidation and reduction reactions, which we can define as  $E_{\text{cell}}$ .

$E_{\text{cell}}$  is always defined (by convention) as the standard electrode potential of the reduction reaction – the standard electrode potential of the oxidation reaction:

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

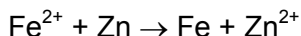
The terms refer to the standard **reduction** potentials of the system being reduced and the standard **reduction** potential of the system being oxidised.

**For example:**

In the manufacture of steel,  $\text{Fe}^{2+}$  is reduced to Fe. The standard reduction potential of this process (this half reaction) is  $-0.44 \text{ V}$  vs. SHE. For this reaction to be thermodynamically feasible, the standard reduction potential of the system doing the reduction (which is itself oxidised) must be positive to  $-0.44 \text{ V}$ .

Electrode reaction	$E^\circ$ vs. SHE
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00 V
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44 V
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76 V

So, considering the systems above.  $\text{Fe}^{2+}$  will not be reduced by  $\text{H}^+$  since the  $E_{\text{cell}}$  for this system is  $-0.44 \text{ V}$ , so the free energy of this system is  $+42 \text{ kJ mol}^{-1}$ . Since  $\Delta G$  is positive, the reaction is not feasible. However, the standard reduction potential of  $\text{Zn}^{2+}$  is negative of the  $\text{Fe}^{2+}$  reduction potential. Therefore  $E_{\text{cell}}$  for this system is  $+0.32 \text{ V}$ ,  $\Delta G = -31 \text{ kJ mol}^{-1}$ . Therefore, zinc can (by thermodynamics) reduce  $\text{Fe}^{2+}$ :



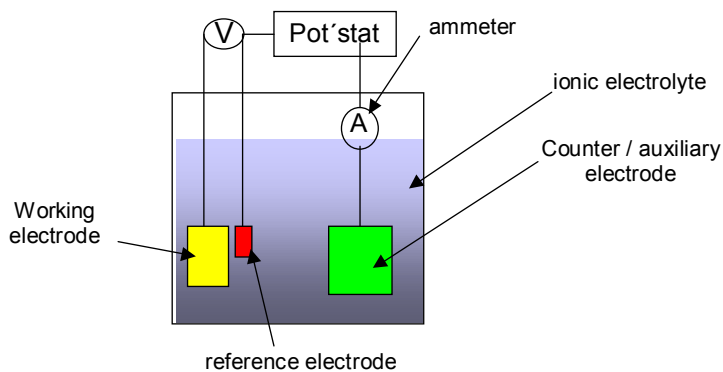
Of course in industry, using zinc is not economic, and coke (oxidised to CO) is used as the reductant.

Another important point from these considerations is that although  $\text{H}^+$  will not reduce  $\text{Fe}^{2+}$ , the reverse reaction is thermodynamically allowed: the oxidation of Fe to  $\text{Fe}^{2+}$ . This is important in corrosion systems and will be considered in lecture 15.

Don't forget: all these calculations assume activities of reactants is unity. When this is not the case, the Nernst equation must be used to correct the  $E^\circ$  for that system.

### Practical aspects of voltammetry – the 3 electrode cell

In experimental electrochemistry, the 3 electrode cell is one of the most common configurations used to study electrochemical reactions. It consists of a counter electrode (CE) which is used to polarise the electrode of interest, the working electrode. In order that the potential (voltage) on the working electrode is precisely known, a third electrode known as the reference electrode (RE) is held close to the surface of the WE and the potential difference measured. This is because the RE has no current passing through it, but merely maintains an invariant constant potential, no matter what is happening around it.



The potentiostat is used to supply a constant potential (potentiostatic mode) or current (galvanostatic mode) to the working electrode, regardless of the chemical changes taking place on the WE at that time – it is like a feedback circuit, constantly ensuring the potential or current is what the operator has set.

### Reference Electrodes

All electrode potentials are measured vs.  $\text{Pt}/\text{H}_2 \leftrightarrow 2\text{H}^+$ , the standard hydrogen electrode (SHE). This electrode couple is arbitrarily defined as 0.00 Volts. However, practically using this electrode is not at all easy – it requires a steady flow of hydrogen bubbling onto high surface area platinum. Much easier is to use an electrode couple that has a clearly defined potential relative to the SHE.

A commonly employed system is:

$\text{Ag} / \text{AgCl} = \text{Ag}^+ + \text{Cl}^-$  The potential of this system is determined by the concentration of  $\text{Cl}^-$  ions in the solution from the Nernst equation. By measuring relative to this electrode one can simply determine the potential relative to the SHE. This is why in electrochemistry, voltages must always be given relative to a known reference electrode.

### The Nernst Equation

The Nernst equation has already been introduced in courses in 1<sup>st</sup> year. It relates the concentrations (strictly activities) of ions taking part in an electrochemical reaction at equilibrium with the potential that the electrode takes up relative to the standard electrode potential of the system.

It can be written:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{\Pi a_{ox}}{\Pi a_{red}}$$

If we approximately define the activity of an ion as its concentration for the purpose of this argument, and consider the Ag/AgCl reference electrode then one can write:

$\text{AgCl} = \text{Ag}^+ + \text{Cl}^-$ , so:

$$E = E^{\circ} + \frac{RT}{F} \ln \left( \frac{1}{[\text{Cl}^-]} \right)$$

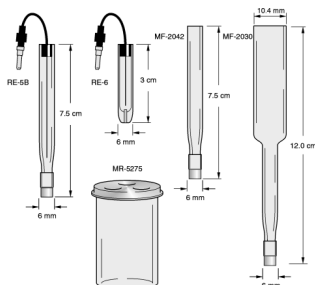
The concentrations of AgCl and  $\text{Ag}^+$  can be considered to be unity since they are in the solid phase.

So, for example, many Ag/AgCl reference electrode systems contain 3M NaCl. So their electrode potential vs.Pt/ $\text{H}_2$  is:

$$E^{\circ} = 0.222 \text{ V}$$

$$[\text{Cl}^-] = 3\text{M}$$

**So, E = 0.194 V in 3 M NaCl**



Typically reference electrodes come in self-contained vials, with a semi-permeable membrane.

Background reading on reference electrodes:

<http://www.currentseparations.com/issues/14-2/cs14-2d.pdf>

Other common reference electrodes include:

- Saturated Calomel electrode:  $\text{Hg}/\text{HgCl}_2 / \text{KCl}$
- $\text{Hg} / \text{HgSO}_4$