Electrochemical Energy Storage
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Module - 01
Introduction to electrochemical energy storage and conversion
Lecture - 01
Fundamentals of Electrochemistry, Definition of Primary and Secondary Batteries

Welcome to my course on Electrochemical Energy Storage. And today, we are covering module number 1: Introduction to Electrochemical Energy Storage and Conversion. I will be giving lecture number 1 on Fundamentals of Electrochemistry: Definition of Primary and Secondary Batteries.

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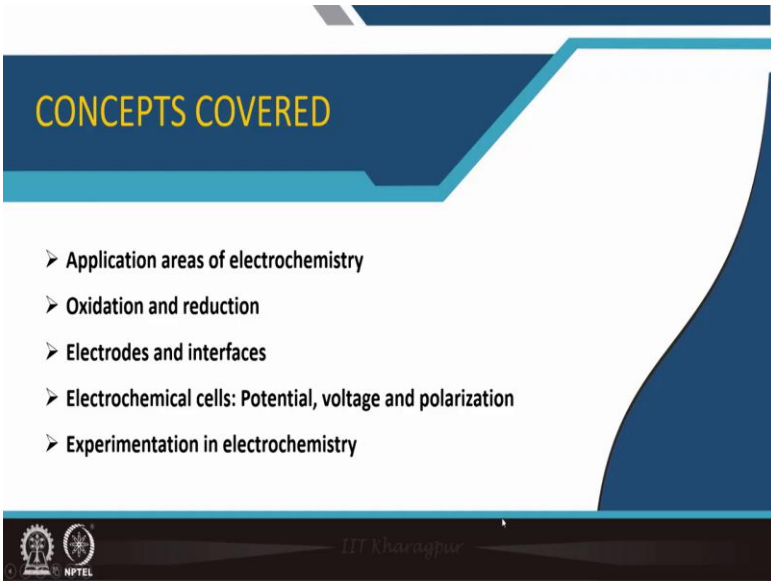

CONCEPTS COVERED

- Application areas of electrochemistry
- Oxidation and reduction
- Electrodes and interfaces
- Electrochemical cells: Potential, voltage and polarization
- Experimentation in electrochemistry

Now, electrochemistry as you might know is a vast chapter. I will try to cover the knowledge pertinent to the understanding of the storage material. We will elaborate certain important concepts as well in the later part of the lecture.

I will first start from the application areas of electrochemistry, where we will introduce the topic of oxidation and reduction (more importantly electrodes and interface). Then, we will introduce the electrochemical cells and the concept of potential, voltage and polarization. I will follow it up by introducing certain experimentation in electrochemistry.

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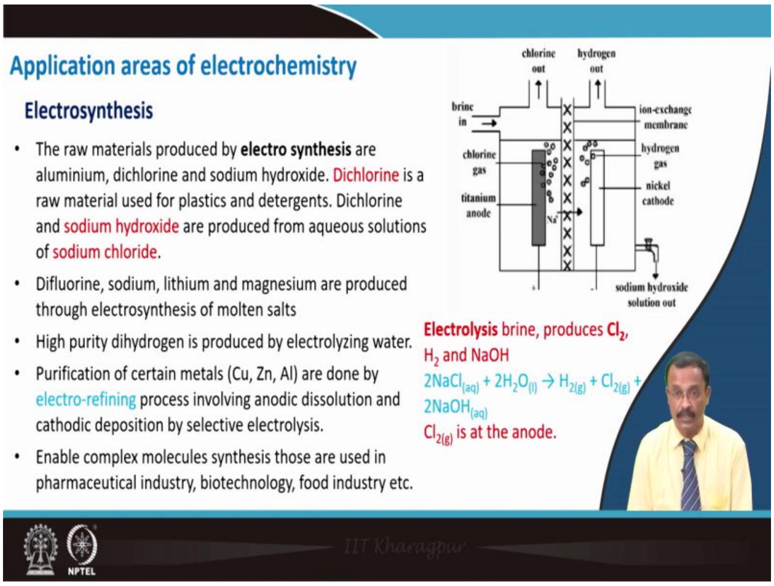

Application areas of electrochemistry

Electrosynthesis

- The raw materials produced by **electro synthesis** are aluminium, dichlorine and sodium hydroxide. Dichlorine is a raw material used for plastics and detergents. Dichlorine and sodium hydroxide are produced from aqueous solutions of sodium chloride.
- Difluorine, sodium, lithium and magnesium are produced through electrosynthesis of molten salts
- High purity dihydrogen is produced by electrolyzing water.
- Purification of certain metals (Cu, Zn, Al) are done by electro-refining process involving anodic dissolution and cathodic deposition by selective electrolysis.
- Enable complex molecules synthesis those are used in pharmaceutical industry, biotechnology, food industry etc.

Electrolysis brine, produces Cl_2, H_2 and NaOH

$2NaCl_{(aq)} + 2H_2O_{(l)} \rightarrow H_{2(g)} + Cl_{2(g)} + 2NaOH_{(aq)}$

$Cl_{2(g)}$ is at the anode.

So, we will first start with electrosynthesis, which is probably known to all of you. There are various raw materials that are produced by electrosynthesis. Examples can be cited as aluminium, dichlorine, sodium hydroxide. One of the examples I have shown here. And as you know, the dichlorine is a raw material used for plastics and detergents. Dichlorine and sodium hydroxides are produced from aqueous brine solution (sodium chloride solution).

And this kind of electrolyser is used where you can see two electrodes are there. One is made out of titanium, which we will call anode and another one is nickel, which is termed as cathode. We put positive potential to this anode and negative potential to the cathode. These two are separated by ion-selective or ion-exchange membrane, which will only pass sodium-ion from one side to another.

Now, in brine solution electrolysis takes place. It gets dissociated to produce hydrogen in cathode and chlorine gas, in anode. Sodium ions diffuse pass through this ionically conducting membrane and reacts with the hydroxyl ions to form sodium hydroxide. This is one way to make sodium hydroxide and dichlorine apart from hydrogen, and is one of the examples of electrosynthesis.

Several other examples can be cited: difluorine or sodium, lithium, and magnesium in metal form are produced through electrosynthesis of molten salts. High purity dihydrogen is produced by electrolyzing water, which produces oxygen as well. Today's concern is to make oxygen in this particular pandemic situation and that can be done by electrosynthesis.

Apart from that, purification of certain metal (in particular copper, zinc, aluminium) are also done by a process called electro refining, where one of the ores is used as anode and the purified metal is deposited on the cathode. By this process, you actually purify the material. And apart from that it enables complex molecules synthesis, and that is particularly useful for pharmaceutical industries, biotechnology, and food industry (as some of the examples).

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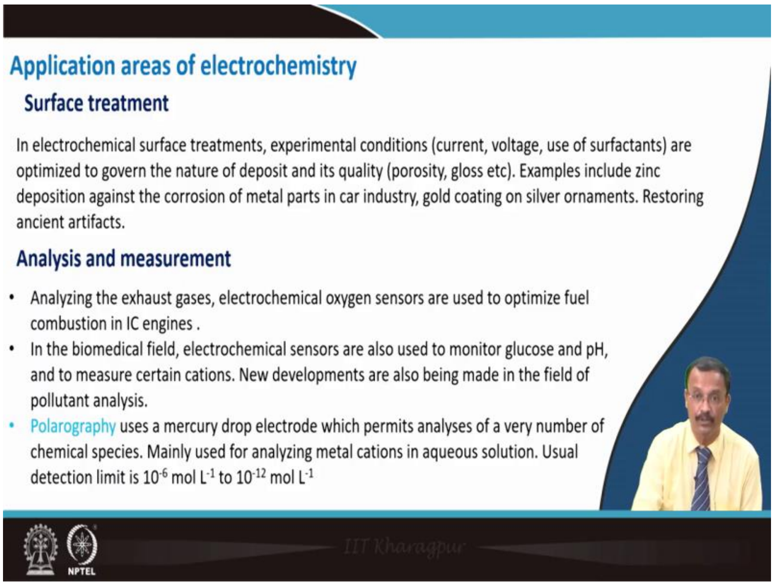

Application areas of electrochemistry

Surface treatment

In electrochemical surface treatments, experimental conditions (current, voltage, use of surfactants) are optimized to govern the nature of deposit and its quality (porosity, gloss etc). Examples include zinc deposition against the corrosion of metal parts in car industry, gold coating on silver ornaments. Restoring ancient artifacts.

Analysis and measurement

- Analyzing the exhaust gases, electrochemical oxygen sensors are used to optimize fuel combustion in IC engines .
- In the biomedical field, electrochemical sensors are also used to monitor glucose and pH, and to measure certain cations. New developments are also being made in the field of pollutant analysis.
- Polarography uses a mercury drop electrode which permits analyses of a very number of chemical species. Mainly used for analyzing metal cations in aqueous solution. Usual detection limit is 10^{-6} mol L^{-1} to 10^{-12} mol L^{-1}

Now, apart from this electrolyser, the electrochemistry is used for surface treatment as well. The common surface treatment that you know is where you can either impart porosity, or you can impart gloss in the material that is being prepared. Zinc deposition against the corrosive metal is one of the examples, and is particularly useful for car industries. And also for artificial jewellery, gold coating is done on silver ornaments and also to restore various ancient artifacts. There also surface treatment is important.

For various types of analysis and measurements too, electrochemistry is useful. One example I can cite: This is the exhaust gas. When you analyze it, it is important for you to know the oxygen content to determine whether the petrol has been fully under combustion. So, to optimize the fuel efficiency in the IC engine, we use oxygen sensor.

And in this part of the course, I will not talk about the oxygen sensor. But in one of my earlier lectures, we described at length their function, their operation principle, construction etc. In biomedical field as well, electrochemical sensors are used to monitor glucose and pH, and to also measure certain cations.

New developments are being made to identify the pollutants. Apart from that, polarography (that uses mercury drop electrode), eventually permits the analysis of a variety of chemical species at very low concentration, concentration as low as 10^{-12} mol/L, that kind of metal concentration can be detected in aqueous solution. So, they have variety of use.

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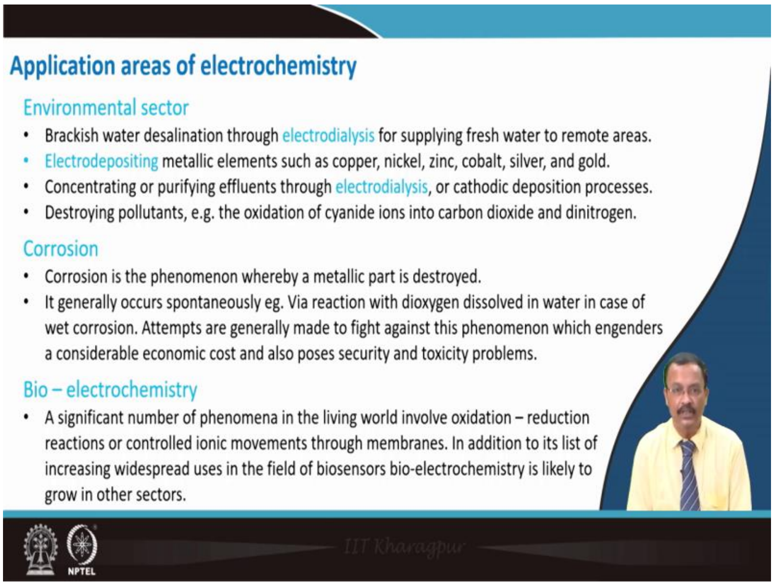

Application areas of electrochemistry

Environmental sector

- Brackish water desalination through electrodialysis for supplying fresh water to remote areas.
- Electrodepositing metallic elements such as copper, nickel, zinc, cobalt, silver, and gold.
- Concentrating or purifying effluents through electrodialysis, or cathodic deposition processes.
- Destroying pollutants, e.g. the oxidation of cyanide ions into carbon dioxide and dinitrogen.

Corrosion

- Corrosion is the phenomenon whereby a metallic part is destroyed.
- It generally occurs spontaneously eg. Via reaction with dioxygen dissolved in water in case of wet corrosion. Attempts are generally made to fight against this phenomenon which engenders a considerable economic cost and also poses security and toxicity problems.

Bio – electrochemistry

- A significant number of phenomena in the living world involve oxidation – reduction reactions or controlled ionic movements through membranes. In addition to its list of increasing widespread uses in the field of biosensors bio-electrochemistry is likely to grow in other sectors.

Environmental sector is also important. Desalination of Brackish Water is important which is done through electrodialysis for supplying fresh water to remote areas in our country. Electrodeposition, already I have talked about it metallic elements like copper and zinc, cobalt, silver, gold they are electro deposited on another metal surface.

Concentration or purifying effluents through electrodialysis is also another cathodic deposition process. Destroying the pollutants, particularly oxide oxidation of cyanides and carbon dioxide or dinitrogen, that is also important. Corrosion is another field, where metallic part is destroyed.

It generally occurs spontaneously where metal reacts with dioxygen dissolved in water, in case of wet corrosion. And the fight against corrosion is still on. And this actually incurs significant amount of losses, economic losses, particularly in the gas line; or the saline water, the ship etc, which are exposed to saline environment.

Biochemistry is another field. A significant number of phenomena of the living world is involved this oxidation and reduction, which I will be introducing in a while from now.

And apart from that, in biochemistry there are increasing field of other applications like biosensors, and this sector will certainly grow in near future. So, apart from the storage you have various applications for this so called electrochemistry principle.

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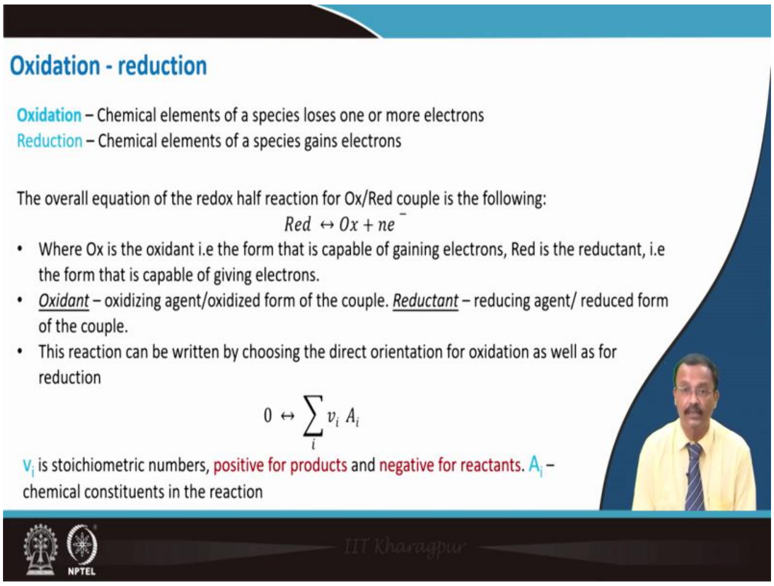

Oxidation - reduction

Oxidation – Chemical elements of a species loses one or more electrons
Reduction – Chemical elements of a species gains electrons

The overall equation of the redox half reaction for Ox/Red couple is the following:

$$Red \leftrightarrow Ox + ne^-$$

- Where Ox is the oxidant i.e the form that is capable of gaining electrons, Red is the reductant, i.e the form that is capable of giving electrons.
- *Oxidant* – oxidizing agent/oxidized form of the couple. *Reductant* – reducing agent/ reduced form of the couple.
- This reaction can be written by choosing the direct orientation for oxidation as well as for reduction

$$0 \leftrightarrow \sum_i v_i A_i$$

v_i is stoichiometric numbers, positive for products and negative for reactants. A_i – chemical constituents in the reaction

So, oxidation and reduction is an important part of it. In oxidation chemical elements of a species loses one or more electrons. And in contrary, in reduction, chemical elements of a species gains electron. So, the overall reaction if you take then we called this is a oxidation-reduction couple.

So, the term Ox is oxidant that is it is capable of gaining electrons, and the term Red is a reductant which is capable of giving electrons. We can use the term oxidant for oxidizing agent or oxidized form of the couple, and reductant is a reducing agent or reduced form of the couple.

So, in this particular reaction, you can either move the product part or the reactant part to one side and the left hand side is usually kept 0. And here the term v_i is a stoichiometric number, and it is usually positive for the product and negative for the reactant. I will cite certain examples. And A_i is a chemical constituents of the reaction that is being used.

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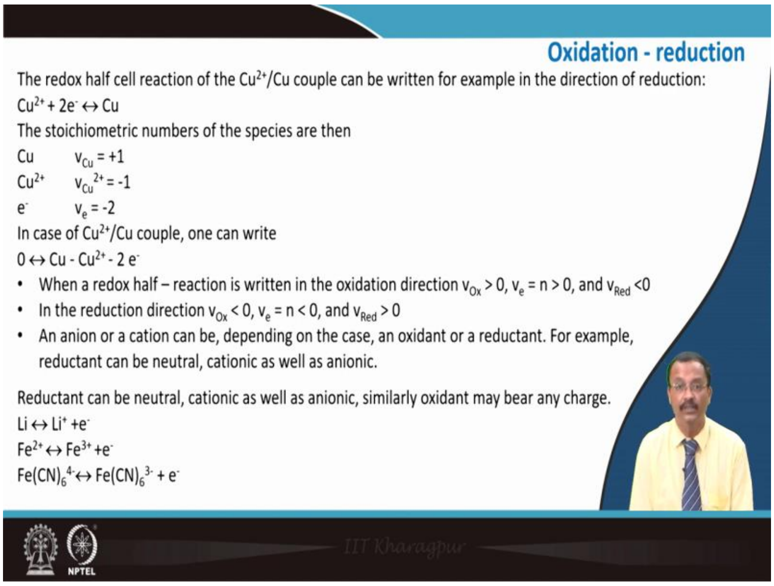

Oxidation - reduction

The redox half cell reaction of the Cu^{2+}/Cu couple can be written for example in the direction of reduction:

$Cu^{2+} + 2e^- \leftrightarrow Cu$

The stoichiometric numbers of the species are then

Cu	$v_{Cu} = +1$
Cu^{2+}	$v_{Cu}{}^{2+} = -1$
e^-	$v_e = -2$

In case of Cu^{2+}/Cu couple, one can write

$0 \leftrightarrow Cu - Cu^{2+} - 2\ e^-$

- When a redox half – reaction is written in the oxidation direction $v_{Ox} > 0$, $v_e = n > 0$, and $v_{Red} < 0$
- In the reduction direction $v_{Ox} < 0$, $v_e = n < 0$, and $v_{Red} > 0$
- An anion or a cation can be, depending on the case, an oxidant or a reductant. For example, reductant can be neutral, cationic as well as anionic.

Reductant can be neutral, cationic as well as anionic, similarly oxidant may bear any charge.

$Li \leftrightarrow Li^+ + e^-$

$Fe^{2+} \leftrightarrow Fe^{3+} + e^-$

$Fe(CN)_6{}^{4-} \leftrightarrow Fe(CN)_6{}^{3-} + e^-$

So, let us take an example. The redox half cell reaction of copper 2+ and copper couple can be written for example, in the direction of the reduction. As you can see that it is getting reduced because it is taking electron to form neutral copper. So, following a previous convention, for copper the stoichiometric value here I will take plus 1 because it is in the product side.

And reactant side copper 2 plus and electron we will take -1 and -2, respectively. So, following this relation, I take these values to the right hand side and here you can see it is charged balance because this is +1 and this oxidation state is 0. This is -1, so it will lead to -2 and electron is -1, so it will be +2, so as a whole it will be 0.

So, one can say that when redox half cell reaction is written in the oxidation direction then the stochiometric part for oxidation is positive for electron, whereas for the reductant it is negative and the reverse is true for the reduction direction, so the sign changes for anion and cation which can depend for the case it is an oxidant or reductant.

I can cite one example reductant can be neutral, it can be cationic or it can be anionic. So, for example, here you see the lithium is an electropositive material, it is oxidized and giving electron. So, this part is neutral, this part is cationic and this one is anionic. So, it can bear any charge, this, it can bear any charge depending on the reaction of interest.

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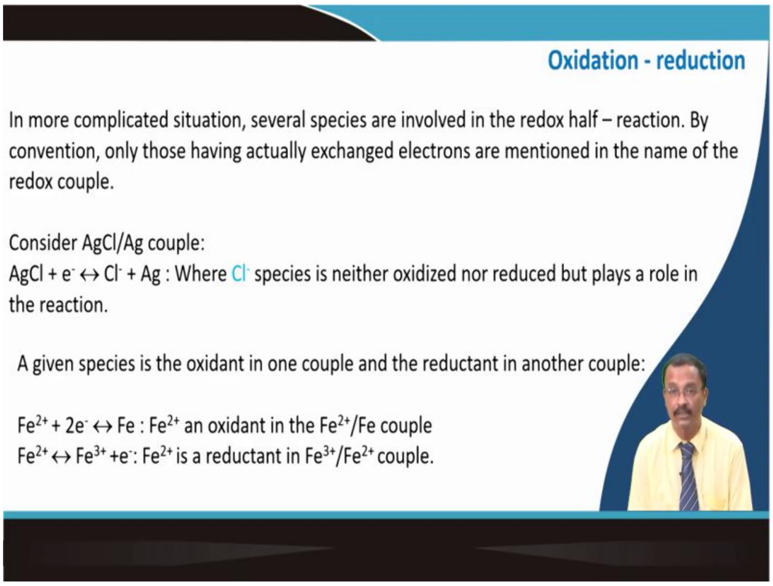

Oxidation - reduction

In more complicated situation, several species are involved in the redox half – reaction. By convention, only those having actually exchanged electrons are mentioned in the name of the redox couple.

Consider AgCl/Ag couple:

$AgCl + e^- \leftrightarrow Cl^- + Ag$: Where Cl^- species is neither oxidized nor reduced but plays a role in the reaction.

A given species is the oxidant in one couple and the reductant in another couple:

$Fe^{2+} + 2e^- \leftrightarrow Fe$: Fe^{2+} an oxidant in the Fe^{2+}/Fe couple

$Fe^{2+} \leftrightarrow Fe^{3+} + e^-$: Fe^{2+} is a reductant in Fe^{3+}/Fe^{2+} couple.

We can cite a more complicated situation where several species are involved in redox half cell. By convention only those who have actually exchanged electrons are mentioned in the name of the redox couple. So, if I consider this silver chloride and silver couple, so as you can see silver chloride is reacting this with this electron and chloride ion this species is neither oxidized nor reduced, but plays a major role in the reaction.

So, a given species may be the oxidant in one couple and the reductant in the other couple. So, this example is ferrous, Fe^{2+} that is an oxidant in this particular couple, Fe^{2+}/Fe couple. And if you consider this reaction then Fe^{2+} is the reductant when you considered Fe^{3+}/Fe^{2+} couple.

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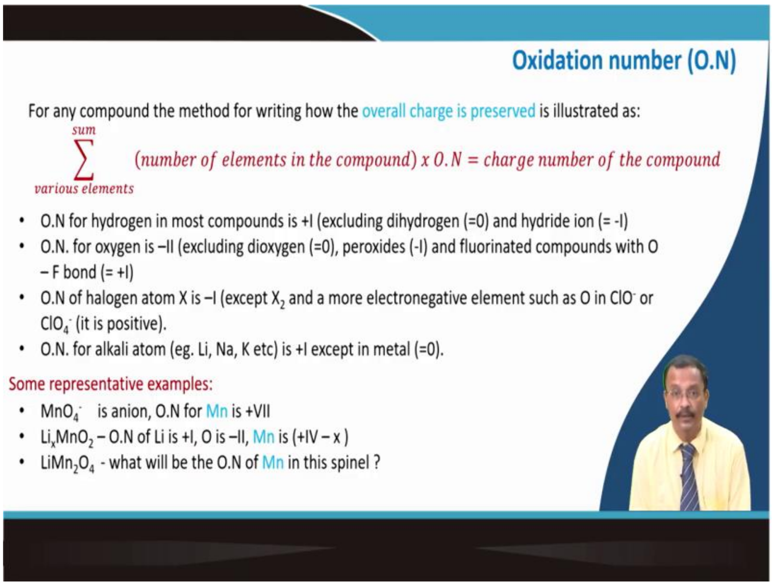

Oxidation number (O.N)

For any compound the method for writing how the overall charge is preserved is illustrated as:

$$\sum_{\text{various elements}}^{\text{sum}} (\text{number of elements in the compound}) \times O.N = \text{charge number of the compound}$$

- O.N for hydrogen in most compounds is +I (excluding dihydrogen (=0) and hydride ion (= -I)
- O.N. for oxygen is –II (excluding dioxygen (=0), peroxides (-I) and fluorinated compounds with O – F bond (= +I)
- O.N of halogen atom X is –I (except X_2 and a more electronegative element such as O in ClO^- or ClO_4^- (it is positive).
- O.N. for alkali atom (eg. Li, Na, K etc) is +I except in metal (=0).

Some representative examples:

- MnO_4^- is anion, O.N for Mn is +VII
- Li_xMnO_2 – O.N of Li is +I, O is –II, Mn is (+IV – x)
- $LiMn_2O_4$ - what will be the O.N of Mn in this spinel ?

So, now I will introduce the term oxidation number. For any compound, the method for writing how the overall charge is preserved is illustrated is this simple relation. It says that the summation of the number of elements in the compound into its oxidation number that will give you the charge number of the compound. So, there are certain rules, oxidation number for hydrogen and most of the component is +1, but excluding dihydrogen where it is 0 or hydride when it is -1.

Similarly, for oxygen usually is -2 excluding dioxygen where it is 0 or in peroxide H_2O_2 it is -1. And fluorinated compound with oxygen and fluorine bond this is +1. Oxidation number for halogen chlorine, bromine, fluorine, fluorine, iodine is -1 except X_2 where a more electronegative element such as oxygen in case of ClO^- or ClO_4^- it is positive. So, chlorine acts as a positive oxidation number. Oxidation number of alkali atom example lithium, sodium, potassium etce is +1 except in metal. In case of metal it is 0. So, cited some representative example MnO_4^-, this is an anion where oxidation number of manganese is +7 because you know oxygen is -2 as far as this, so this is coming to + 7.

When you consider Li_xMnO_2, one of the most prominent battery material these two oxidation number of lithium is +1, oxygen is -2, manganese here is plus 4 - x. And I will leave it on you to determine the oxidation state of manganese as you can see lithium is +1, oxygen is -8. So, manganese is coming +7/2. So, part of it is +3 state and part of it is in +4 state. So, that has important implication when I will be talking about the storage battery, we will talk more about it.

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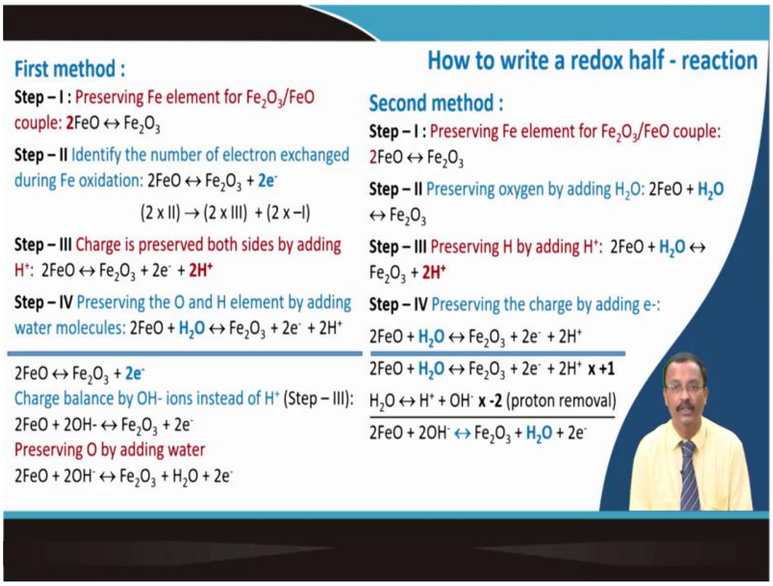

How to write a redox half - reaction

First method :

Step – I : Preserving Fe element for Fe_2O_3/FeO couple: $2FeO \leftrightarrow Fe_2O_3$

Step – II Identify the number of electron exchanged during Fe oxidation: $2FeO \leftrightarrow Fe_2O_3 + 2e^-$

$$(2 \times II) \rightarrow (2 \times III) + (2 \times -I)$$

Step – III Charge is preserved both sides by adding H^+: $2FeO \leftrightarrow Fe_2O_3 + 2e^- + 2H^+$

Step – IV Preserving the O and H element by adding water molecules: $2FeO + H_2O \leftrightarrow Fe_2O_3 + 2e^- + 2H^+$

$2FeO \leftrightarrow Fe_2O_3 + 2e^-$

Charge balance by OH- ions instead of H^+ (Step – III):

$2FeO + 2OH^- \leftrightarrow Fe_2O_3 + 2e^-$

Preserving O by adding water

$2FeO + 2OH^- \leftrightarrow Fe_2O_3 + H_2O + 2e^-$

Second method :

Step – I : Preserving Fe element for Fe_2O_3/FeO couple: $2FeO \leftrightarrow Fe_2O_3$

Step – II Preserving oxygen by adding H_2O: $2FeO + H_2O \leftrightarrow Fe_2O_3$

Step – III Preserving H by adding H^+: $2FeO + H_2O \leftrightarrow Fe_2O_3 + 2H^+$

Step – IV Preserving the charge by adding e-:

$2FeO + H_2O \leftrightarrow Fe_2O_3 + 2e^- + 2H^+$

$2FeO + H_2O \leftrightarrow Fe_2O_3 + 2e^- + 2H^+$ **x +1**

$H_2O \leftrightarrow H^+ + OH^-$ **x -2** (proton removal)

$2FeO + 2OH^- \leftrightarrow Fe_2O_3 + H_2O + 2e^-$

Now, you should know how to write a redox half cell reaction. There are certain steps. 1st step is preserving for example, Fe_2O_3 and FeO preserving the Fe element. So, here you will have to multiply FeO by 2 to get this one. 2nd step is to identify the number of electron that is exchanged, and you can easily calculate it. It is 2 oxidation state and this one is 3 oxidation state and this is -1, 2 into -1. So, the charge neutrality is maintained, so number of electron that is exchanged is 2.

Then charge is preserved both sides by adding a proton because here you have added electron, so you will have to add a proton to balance the charge. So, it is coming Fe_2O_3 plus $2e^-$ plus 2H+ and then preserving the oxygen and hydrogen by adding water molecules. So, 2 Fe plus H_2O equal to Fe_2O_3 plus 2 e^- plus 2H+. I am pretty sure that you are familiar with this kind of writing. So, this is just for a brush up of your knowledge.

There is the second method, which is slightly different initially preserving the Fe element for Fe_2O_3 and FeO couple. So, this is going like this. In step 2, preserving oxygen by adding H_2O. So, we get a 2 FeO plus H_2O is Fe_2O_3. Then, preserving hydrogen by adding H plus 2 Fe plus H_2O that will lead to Fe_2O_3 plus twice H+ and preserving as a step 4 preserving the charge by adding electron, so you come up with the same equation, which you got through the first method.

Charge balance also you can do by addition of hydroxyl ions instead of proton. So, in this first step, in step 3, instead of proton we can add a hydroxyl ion to get this to get this relation and again I will have to preserve oxygen by adding water, so I add water to get this relation.

Similarly, for this case also I can add H_2O and H_2O will dissociate and this is due to a proton removal. So, this reaction I can multiply by +1 and this one multiply by -2 and then we balance this one and we get the same relation as we got by hydroxyl ion addition.

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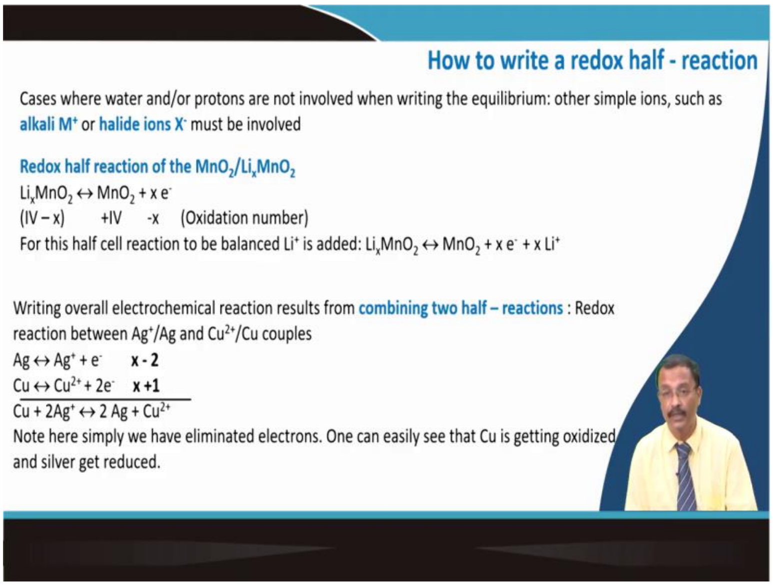

How to write a redox half - reaction

Cases where water and/or protons are not involved when writing the equilibrium: other simple ions, such as **alkali M^+** or **halide ions X^-** must be involved

Redox half reaction of the MnO_2/Li_xMnO_2

$Li_xMnO_2 \leftrightarrow MnO_2 + x\,e^-$

(IV – x)   +IV   -x   (Oxidation number)

For this half cell reaction to be balanced Li^+ is added: $Li_xMnO_2 \leftrightarrow MnO_2 + x\,e^- + x\,Li^+$

Writing overall electrochemical reaction results from **combining two half – reactions** : Redox reaction between Ag^+/Ag and Cu^{2+}/Cu couples

$Ag \leftrightarrow Ag^+ + e^-$ **x - 2**

$Cu \leftrightarrow Cu^{2+} + 2e^-$ **x +1**

$Cu + 2Ag^+ \leftrightarrow 2\,Ag + Cu^{2+}$

Note here simply we have eliminated electrons. One can easily see that Cu is getting oxidized and silver get reduced.

So, these are standard protocol that is followed while we write redox reaction. So, not everything is there where water and protons are involved. So, when writing the equilibrium other simple ions that also can be added, so one of the popular things are alkali metal ion or halide ion they are also involved.

So, one example is cited for the redox half cell reaction of manganese oxide and Li_x MnO_2. So, you can see that this one is oxidized like this. So, manganese part I put the oxidation number here and oxidation number here and here. So, for this half cell reaction to be balanced you must add lithium into it. So, you add lithium here and this is the redox, which is quite well balanced.

Writing overall electrochemical reaction from combining two half cell reaction that is also possible. So, redox reaction between Ag^+ to silver or Cu^{2+} to copper couples that example is cited here, and in order to maintain the balance we will have to multiply this by -2 and this one by +1.

So, here simply we have eliminated the electron as you can see. And one can see that the copper is getting oxidized and silver get reduced without even knowing the reduction potential of which we can determine that.

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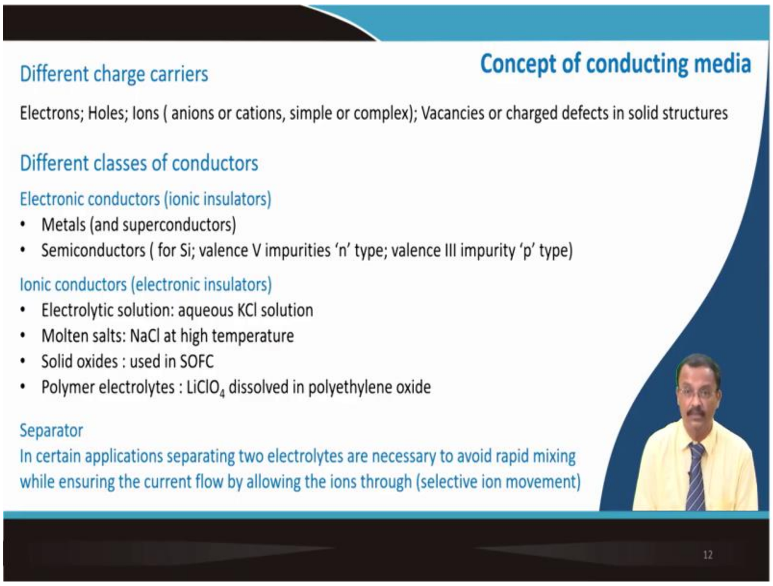

Concept of conducting media

Different charge carriers

Electrons; Holes; Ions (anions or cations, simple or complex); Vacancies or charged defects in solid structures

Different classes of conductors

Electronic conductors (ionic insulators)

- Metals (and superconductors)
- Semiconductors (for Si; valence V impurities 'n' type; valence III impurity 'p' type)

Ionic conductors (electronic insulators)

- Electrolytic solution: aqueous KCl solution
- Molten salts: NaCl at high temperature
- Solid oxides : used in SOFC
- Polymer electrolytes : $LiClO_4$ dissolved in polyethylene oxide

Separator

In certain applications separating two electrolytes are necessary to avoid rapid mixing while ensuring the current flow by allowing the ions through (selective ion movement)

So, different types of charged carriers, they may be involved in an electrochemical reactions, electron, holes, ions, ion could be anion or cations or simple complex ions. Vacancies could be involved. Charged defects in the solid structure, they all play important role in defining the electrochemical reactions. So, there are different classes of conductor. We will call electronic conductor (which are eventually ionic insulator) which are metal, and also super conductor and semiconductor.

For example in silicon, it is having valence V impurities for n type, and valence 3 type of impurity leads to p type of charge carrier. Similarly, ionic conductor are electronically insulator. So, electrolytic solution aqueous KCl solution is one example. Molten salts, sodium chloride at high temperature that is another example.

Solid oxides, which are eventually used in SOFC, and also polymer electrolyte like lithium based salt, lithium perchlorate that is dissolved in poly ethylene oxide, they are the examples of ionically conducting solids, which are used in electrochemistry. Apart from that we use separator. In certain applications, separating two electrolytes are necessary to avoid rapid mixing while it ensures the current flow by allowing ions through selective movement through the separator.

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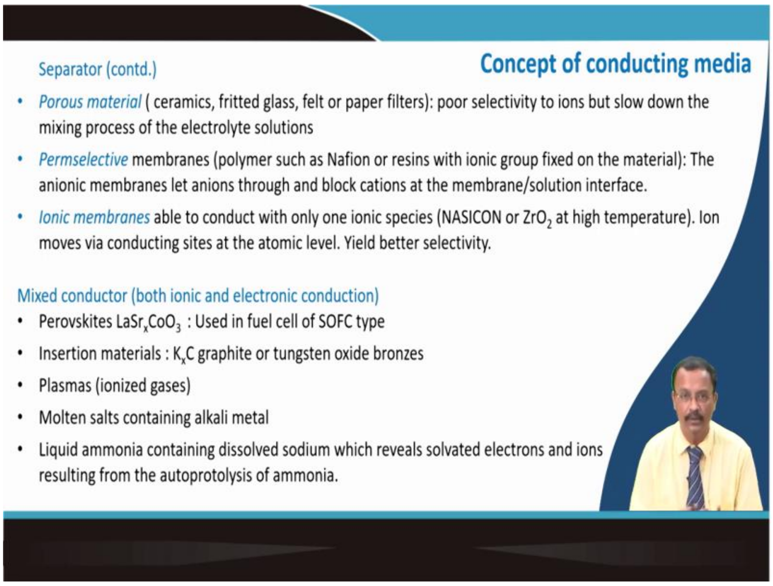

Concept of conducting media

Separator (contd.)

- *Porous material* (ceramics, fritted glass, felt or paper filters): poor selectivity to ions but slow down the mixing process of the electrolyte solutions
- *Permselective* membranes (polymer such as Nafion or resins with ionic group fixed on the material): The anionic membranes let anions through and block cations at the membrane/solution interface.
- *Ionic membranes* able to conduct with only one ionic species (NASICON or ZrO_2 at high temperature). Ion moves via conducting sites at the atomic level. Yield better selectivity.

Mixed conductor (both ionic and electronic conduction)

- Perovskites $LaSr_xCoO_3$: Used in fuel cell of SOFC type
- Insertion materials : K_xC graphite or tungsten oxide bronzes
- Plasmas (ionized gases)
- Molten salts containing alkali metal
- Liquid ammonia containing dissolved sodium which reveals solvated electrons and ions resulting from the autoprotolysis of ammonia.

There are types of separator. Usually porous material, ceramic, fitted glass, felt paper filters. They usually have poor selectivity, selectivity to ions, but slow down the mixing process of the electrolytic solutions. Then there are permselective membrane, which are basically polymer such as Nafion or resin with ionic group fixed on the material.

The anionic membrane let the anions through and blocks cations at the membrane solution interface. Then, we have ionic membrane which are able to conduct only specific ionic species for example, NASICON or ZrO_2 at high temperatures. ZrO_2 is a selective oxygen ion conductor.

The ion moves through conducting sites at atomic level and that yield better selectivity. The purpose of these separators for different applications will become clear when I will talk. I will proceed with the course and discuss various types of storage battery. Mixed conductor, which is both ionic and electronic type of conduction is prevailing here.

So, there are perovskite type oxides which are famous for that one. Example is lanthanum strontium cobalt oxide that is used in fuel cell or SOFC type cells. Insertion material which is potassium K x C graphite or tungsten oxide bronzes are again examples. Plasmas are one of the examples. Molten salts containing alkali metal that can be cited as example. Or liquid alumina containing dissolved sodium, which reveals solvated electrons, or ions resulting from autoprotolysis of ammonia. They are the examples of mixed conductor.

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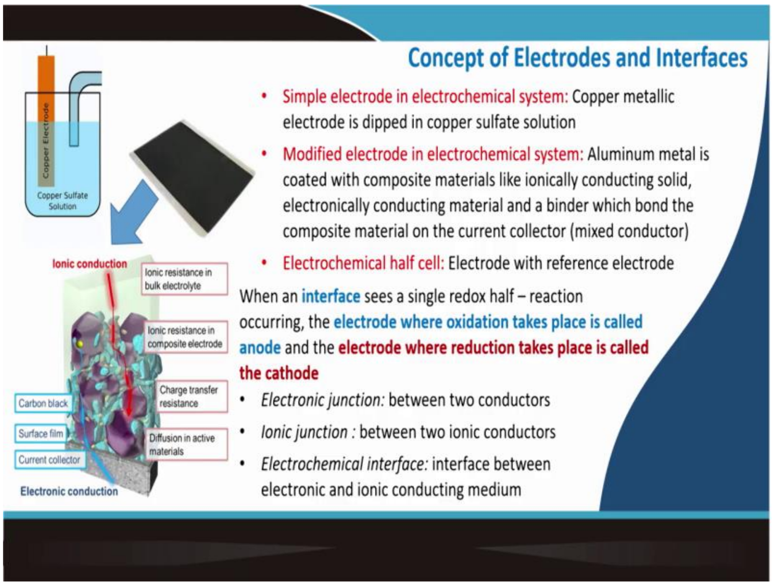

Concept of Electrodes and Interfaces

- Simple electrode in electrochemical system: Copper metallic electrode is dipped in copper sulfate solution
- Modified electrode in electrochemical system: Aluminum metal is coated with composite materials like ionically conducting solid, electronically conducting material and a binder which bond the composite material on the current collector (mixed conductor)
- Electrochemical half cell: Electrode with reference electrode

When an **interface** sees a single redox half – reaction occurring, the **electrode where oxidation takes place is called anode** and the **electrode where reduction takes place is called the cathode**

- *Electronic junction:* between two conductors
- *Ionic junction :* between two ionic conductors
- *Electrochemical interface:* interface between electronic and ionic conducting medium

Now, it is important that electrode and electrolyte. This interface that is important. So, you can use simple electrode in electrochemical system. For example, copper metallic electrode is dipped in copper sulphate solution. Or you can have modified electrode in electrochemical system.

For example, aluminium metal that is coated with a composite material like, ionically conducting solid plus electronically conducting solids, and a binder which bond this material on the current collector. So, they are the example of mixed conductors. So, that is also used for certain cases.

Electrochemical half cells, they are electrochemical half cells they have electrode with reference electrode. So, what an interface sees is a single redox half cell reactions occurring, the electrode where oxidation takes place is called anode and the electrode where the reduction takes place that is known as cathode.

Apart from that there are several electronic junctions between two conductors. Ionic junctions are also possible between two ionic conductor. Or electrochemical interface which is the interface between electronic and ionically conducting medium. So, I am just citing these examples and this is one of the examples of this so called a conducting composite electrode material where you can see the active material which is basically ionically conducting.

You have, it is intimately mixed with carbonaceous material, which is electronically conducting and a binder material which bind the whole mass, active mass plus electronically conducting material together with the current collector. So, we will come back again to this.

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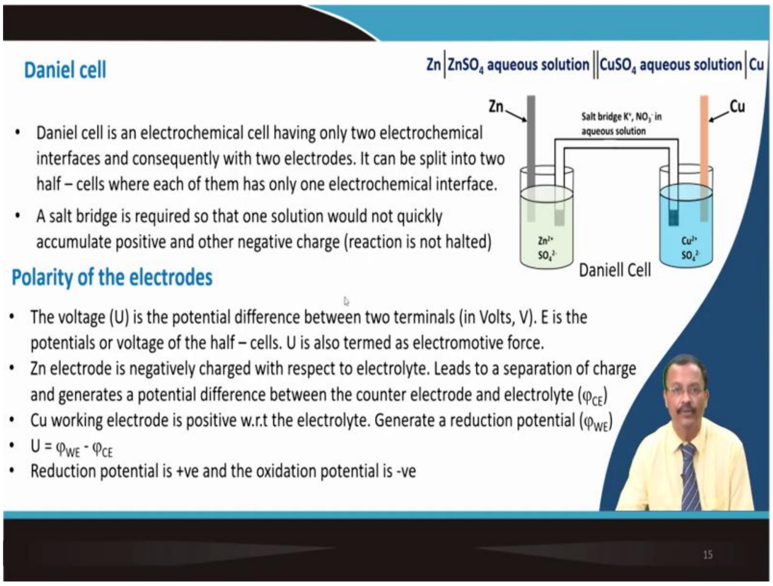

Daniel cell

Zn | $ZnSO_4$ aqueous solution || $CuSO_4$ aqueous solution | Cu

- Daniel cell is an electrochemical cell having only two electrochemical interfaces and consequently with two electrodes. It can be split into two half – cells where each of them has only one electrochemical interface.
- A salt bridge is required so that one solution would not quickly accumulate positive and other negative charge (reaction is not halted)

Polarity of the electrodes

- The voltage (U) is the potential difference between two terminals (in Volts, V). E is the potentials or voltage of the half – cells. U is also termed as electromotive force.
- Zn electrode is negatively charged with respect to electrolyte. Leads to a separation of charge and generates a potential difference between the counter electrode and electrolyte (φ_{CE})
- Cu working electrode is positive w.r.t the electrolyte. Generate a reduction potential (φ_{WE})
- $U = \varphi_{WE} - \varphi_{CE}$
- Reduction potential is +ve and the oxidation potential is -ve

Now, let us have a simple description of a so called Daniel cell. So, you have zinc as one of the electrode which is dipped in zinc sulphate aqueous solution and again copper is dipped in copper sulphate aqueous solution. So, that makes the Daniel cell. And you can see there is a salt bridge, which is basically potassium nitrate aqueous solution that connects these two.

So, this is an electrochemical cell having only two electrochemical interface and consequently with two electrodes. It can be split into two half cell where each of them has one electrochemical interface. A salt bridge that is shown here is required, so that one solution does not quickly accumulate positive another negative charges. So, reaction is not halted.

So, now, you can have the polarity of this electrode the voltage is a potential difference between two terminal, that is measured in volt and written as E sometimes. We use this as the potential or voltage of the half cell of one individual cell. U is also termed as a electromotive force when there is no load involved in the cell.

Zinc electrode is negatively charged with respect to the electrolyte. So, that leads to the separation of charge and generates a potential difference between the counter electrode and electrolyte and I have termed this as phi CE, CE stand stands for Counter Electrode.

And Cu is the working electrode that is positive with respect to the electrolyte. So, that generates a reduction potential. So your U is phi of working electrode minus phi of counter electrode. Usually reduction potential is positive and oxidation potential is treated as negative.

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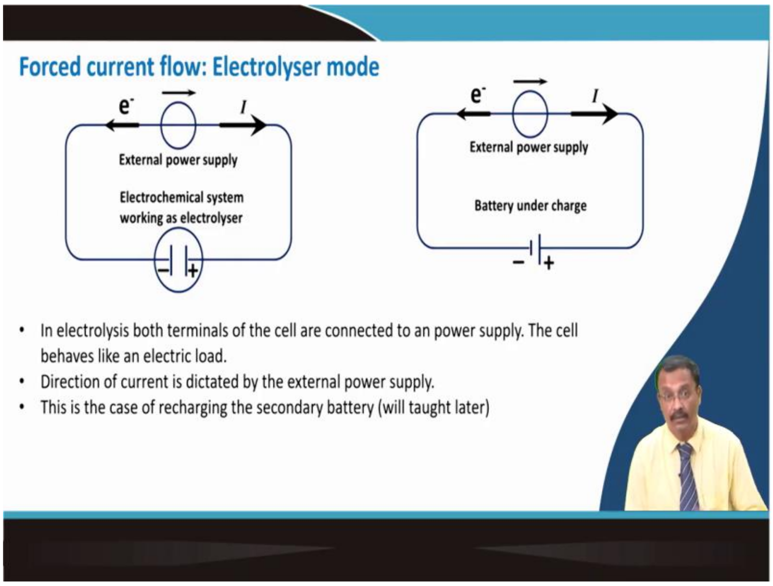

Forced current flow: Electrolyser mode

- In electrolysis both terminals of the cell are connected to an power supply. The cell behaves like an electric load.
- Direction of current is dictated by the external power supply.
- This is the case of recharging the secondary battery (will taught later)

So, you can pass current force fully and we call this is electrolyser mode. So, electrolysis both terminals of the cell are connected to a power supply that is very important. The cell behaves like an electric load and direction of the current is dictated by the external power supply which one is you put plus and which one you put minus. And this is exactly the case. Again I will come back to it when we will talk about rechargeable battery. So, during recharge of secondary battery, we use the force current mode.

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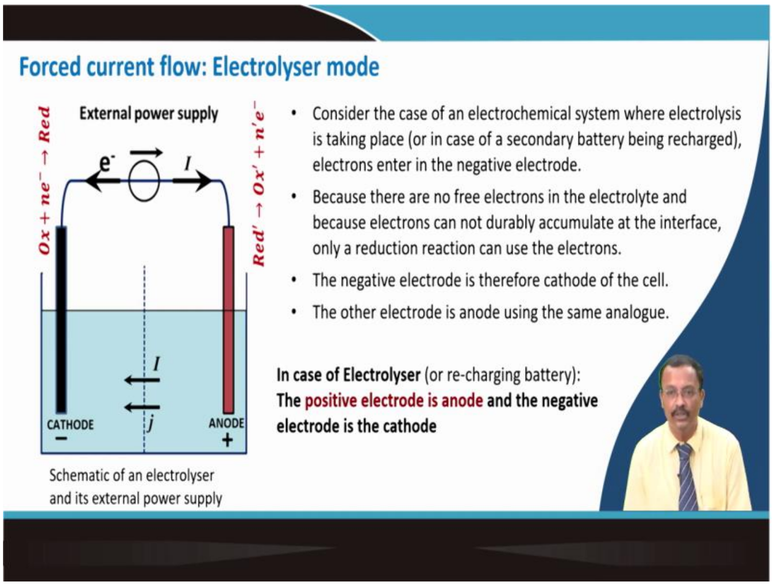

Forced current flow: Electrolyser mode

Schematic of an electrolyser and its external power supply

- Consider the case of an electrochemical system where electrolysis is taking place (or in case of a secondary battery being recharged), electrons enter in the negative electrode.
- Because there are no free electrons in the electrolyte and because electrons can not durably accumulate at the interface, only a reduction reaction can use the electrons.
- The negative electrode is therefore cathode of the cell.
- The other electrode is anode using the same analogue.

In case of Electrolyser (or re-charging battery):
The positive electrode is anode and the negative electrode is the cathode

So, in force current mode as you can see in an electrochemical system where electrolysis is taking place or in case of a secondary battery when it is being recharged, the electrons entered in the negative electrode. So, it is entered in the negative electrode. And there is no free electron here in the electrolyte, and because the electron cannot duly accumulate at the interface, only the reduction reaction can use these electrons.

The negative electrode is therefore, cathode of the cell and the other electrode is treated as anode in the cell. And this is different from the free mode or the discharged mode of the cell. So, in case of electrolyser or the recharging battery, the positive electrode is anode and the negative electrode is cathode.

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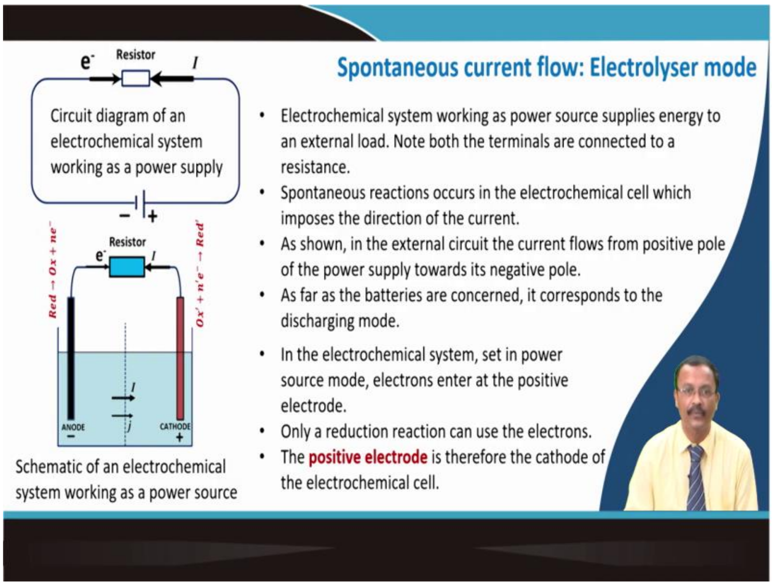

Spontaneous current flow: Electrolyser mode

Circuit diagram of an electrochemical system working as a power supply

Schematic of an electrochemical system working as a power source

- Electrochemical system working as power source supplies energy to an external load. Note both the terminals are connected to a resistance.
- Spontaneous reactions occurs in the electrochemical cell which imposes the direction of the current.
- As shown, in the external circuit the current flows from positive pole of the power supply towards its negative pole.
- As far as the batteries are concerned, it corresponds to the discharging mode.
- In the electrochemical system, set in power source mode, electrons enter at the positive electrode.
- Only a reduction reaction can use the electrons.
- The **positive electrode** is therefore the cathode of the electrochemical cell.

There are certain cases where spontaneous current flow electrolyser mode. So, this electrochemical system working as a power source supplying energy to the external load. So, this is actually the spontaneous current flow mode, not the electrolyser mode I am sorry. But this is a spontaneous electron flows. So, this reaction occurs in the electrochemical cell, which imposes the direction of the current by itself.

So, that is shown in this figure. The external circuit, the current flow from positive pole of the power supply towards a negative pole. In the electrochemical system, set in power source mode, electrons entered in the positive electrode. So, only a reduction reaction can use the electrons. The positive electrode is therefore cathode of the electrochemical cell.

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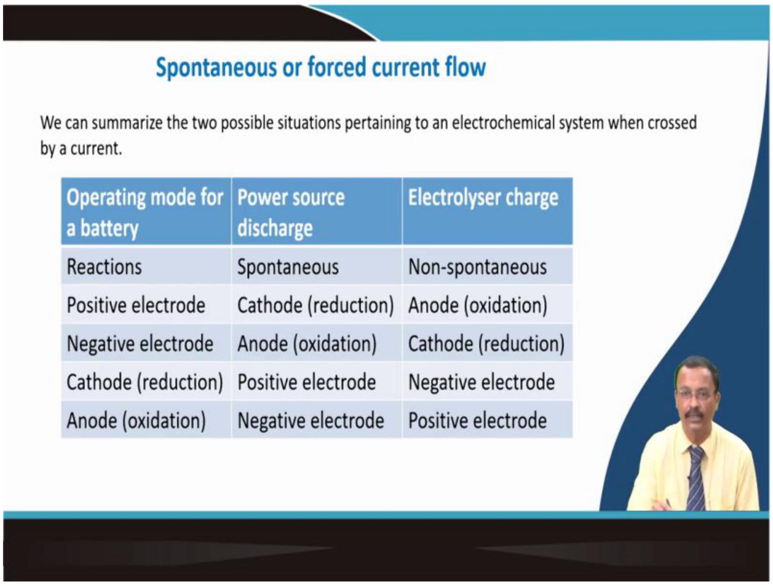

Spontaneous or forced current flow

We can summarize the two possible situations pertaining to an electrochemical system when crossed by a current.

Operating mode for a battery	Power source discharge	Electrolyser charge
Reactions	Spontaneous	Non-spontaneous
Positive electrode	Cathode (reduction)	Anode (oxidation)
Negative electrode	Anode (oxidation)	Cathode (reduction)
Cathode (reduction)	Positive electrode	Negative electrode
Anode (oxidation)	Negative electrode	Positive electrode

So, whether it is spontaneous or forced current flow, I have summarized it that operating mode in case of a battery, the reaction is spontaneous and electrolyser it is non-spontaneous. Here the positive electrode is cathode which is undergoing reduction. Electrolyser mode it is anode which is undergoing oxidation.

This is negative electrode anode which is oxidation this is cathode for reduction. Here also cathode for reduction for positive electrode and this one is termed as negative electrode. And when it is anode which is oxidation is taking place we call it is a negative electrode in case of power source mode and positive electrode in case of electrolyser mode, the one I just described few slides back.

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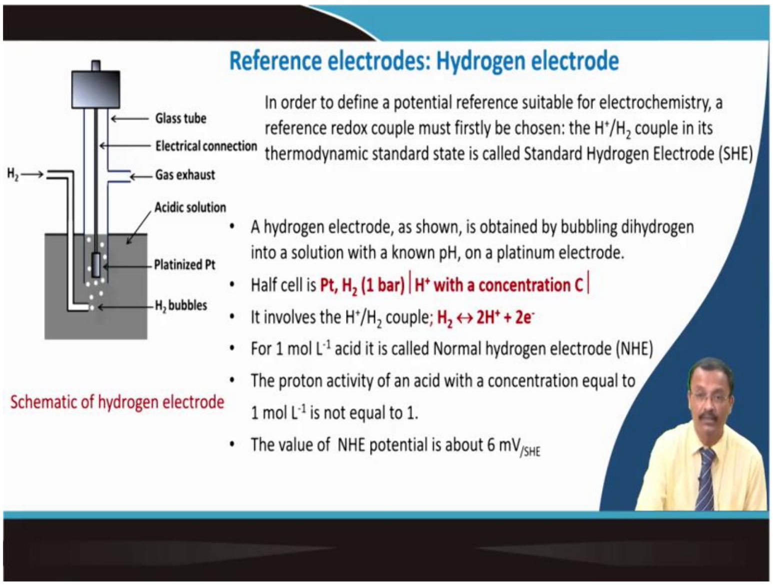

Reference electrodes: Hydrogen electrode

In order to define a potential reference suitable for electrochemistry, a reference redox couple must firstly be chosen: the H^+/H_2 couple in its thermodynamic standard state is called Standard Hydrogen Electrode (SHE)

Schematic of hydrogen electrode

- A hydrogen electrode, as shown, is obtained by bubbling dihydrogen into a solution with a known pH, on a platinum electrode.
- Half cell is **Pt, H_2 (1 bar) | H^+ with a concentration C |**
- It involves the H^+/H_2 couple; **$H_2 \leftrightarrow 2H^+ + 2e^-$**
- For 1 mol L^{-1} acid it is called Normal hydrogen electrode (NHE)
- The proton activity of an acid with a concentration equal to 1 mol L^{-1} is not equal to 1.
- The value of NHE potential is about 6 $mV_{/SHE}$

Now, a voltage that you measure, that is with respect to something. So, in order to define a potential difference suitable for electro chemistry, a reference redox couple must firstly, be chosen. The H^+/ H_2 couple is it is thermodynamically standard state. And this is called Standard Hydrogen Electrode and abbreviated as SHE.

The hydrogen electrode, as shown, is obtained by bubbling dihydrogen into a solution of a known pH, on a platinum electrode. So, half cell is platinum, then hydrogen in 1 bar, then H^+ with a concentration some kind of concentration C are not necessarily always it will be 1 mol.

It involves H^+/ H_2 couple. So, H_2 is given to H^+ plus $2e^-$. For 1 mol as it is called Normal Hydrogen Electrode, is abbreviated as NHE. The proton activity of an acid with concentration equal to 1 mol per litre is not really is equal to 1, so that the value of NHE potential is measured to be about 6 millivolt per standard hydrogen electrode.

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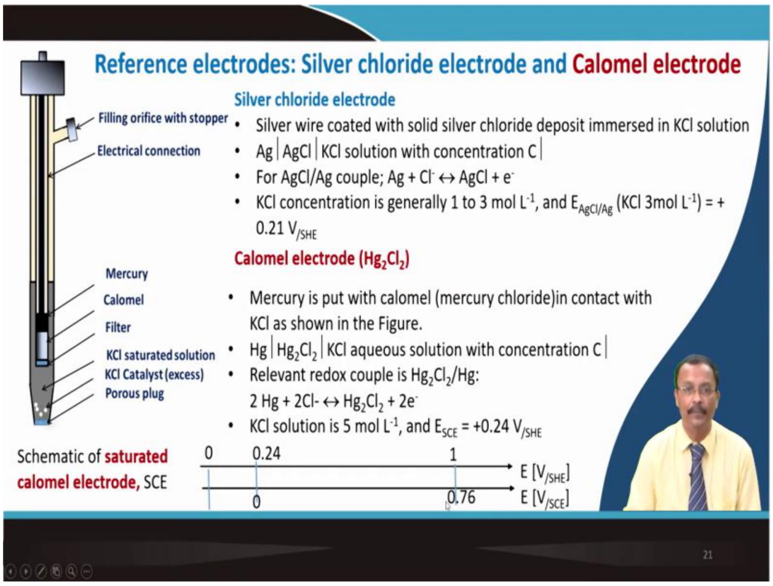

Reference electrodes: Silver chloride electrode and Calomel electrode

Silver chloride electrode

- Silver wire coated with solid silver chloride deposit immersed in KCl solution
- Ag | AgCl | KCl solution with concentration C |
- For AgCl/Ag couple; $Ag + Cl^- \leftrightarrow AgCl + e^-$
- KCl concentration is generally 1 to 3 mol L^{-1}, and $E_{AgCl/Ag}$ (KCl 3mol L^{-1}) = + 0.21 $V_{/SHE}$

Calomel electrode (Hg_2Cl_2)

- Mercury is put with calomel (mercury chloride)in contact with KCl as shown in the Figure.
- Hg | Hg_2Cl_2 | KCl aqueous solution with concentration C |
- Relevant redox couple is Hg_2Cl_2/Hg:
  $2\,Hg + 2Cl- \leftrightarrow Hg_2Cl_2 + 2e^-$
- KCl solution is 5 mol L^{-1}, and $E_{SCE} = +0.24\ V_{/SHE}$

Schematic of **saturated calomel electrode,** SCE

There are other reference electrode, one is silver chloride where silver silver chloride is used with KCl solution with a concentration C and the couple reaction is this one. And KCl concentration is taken 1 to 3 moles per litre. And the value is with respect to standard hydrogen electrode it is 0.21. We have mercury based calomel electrode.

So, mercury is put in the calomel that is mercury chloride it is in contact with KCl as shown in this accompanying figure. And the reaction is something like this and KCl solution is having a concentration 5 moles per litre around and this electrode the value of E for standard calomel electrode is about plus 0.24. So, you can convert it from SHE to calomel, and one example is given. So, you have 0.24 here in the full scale. So, for the calomel it will become 1 minus 0.24 that is about 0.76.

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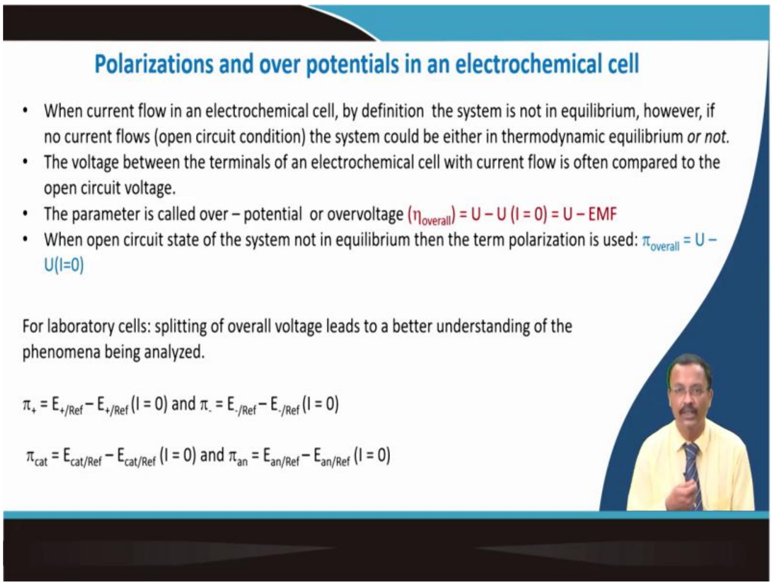

Polarizations and over potentials in an electrochemical cell

- When current flow in an electrochemical cell, by definition the system is not in equilibrium, however, if no current flows (open circuit condition) the system could be either in thermodynamic equilibrium *or not.*
- The voltage between the terminals of an electrochemical cell with current flow is often compared to the open circuit voltage.
- The parameter is called over – potential or overvoltage $(\eta_{overall}) = U - U\,(I = 0) = U - EMF$
- When open circuit state of the system not in equilibrium then the term polarization is used: $\pi_{overall} = U - U(I=0)$

For laboratory cells: splitting of overall voltage leads to a better understanding of the phenomena being analyzed.

$\pi_{+} = E_{+/Ref} - E_{+/Ref}\,(I = 0)$ and $\pi_{-} = E_{-/Ref} - E_{-/Ref}\,(I = 0)$

$\pi_{cat} = E_{cat/Ref} - E_{cat/Ref}\,(I = 0)$ and $\pi_{an} = E_{an/Ref} - E_{an/Ref}\,(I = 0)$

When current flow in a electrochemical cell by definition the system is not under equilibrium. However, if no current flows then it is an open circuit condition. The system could either be a thermodynamic equilibrium or not. The voltage between the terminals of the electrochemical cell with current flow is often compared with the open circuit voltage.

So, this particular parameter is called over potential or over voltage. So, this is defined as eta overall that is U minus U when no current is flowing. So, that is U minus EMF, so no current is flowing is EMF. So, open circuit state of the system is not in equilibrium then the term polarization is used.

So, overall polarization is same U minus U when I is not equal to 0. For laboratory cell, you can have a reference cell inserted in it. So, for better understanding you can do the same thing with respect to the reference electrode and estimate the respective polarization and over potential value the way it is shown.

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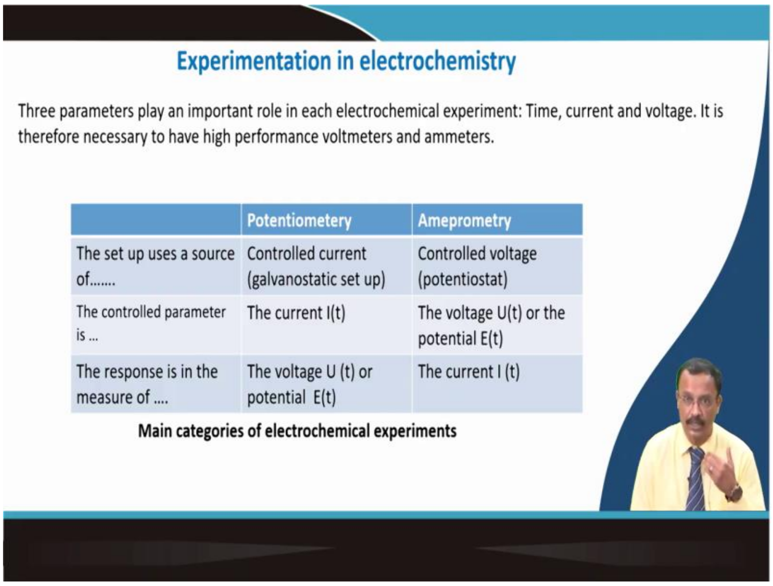

Experimentation in electrochemistry

Three parameters play an important role in each electrochemical experiment: Time, current and voltage. It is therefore necessary to have high performance voltmeters and ammeters.

	Potentiometery	Amepromety
The set up uses a source of…….	Controlled current (galvanostatic set up)	Controlled voltage (potentiostat)
The controlled parameter is …	The current I(t)	The voltage U(t) or the potential E(t)
The response is in the measure of ….	The voltage U (t) or potential E(t)	The current I (t)

Main categories of electrochemical experiments

So, when you set up the experimentation in an electrochemistry experiment, three parameters they play important role in each electrochemical experiments, one is time, current and voltage. It is therefore, necessary to have high performance volt meter and ammeter to have this kind of experimentation. To set up a source of controlled current, we call it is a galvanostatic set up.

The controlled parameter here is current as a function of time. And the response is the measure of voltage U or a potential E as a function of t. We call this is potentiometry. And when the setup source is control voltage that is potentiostat the controlled parameter is voltage or potential and the response is measured the current we call this is amperometry. So, this potentiometry, and the amperometry, they are the main category of electrochemical experiments. And we will come back to it in our future lecture.

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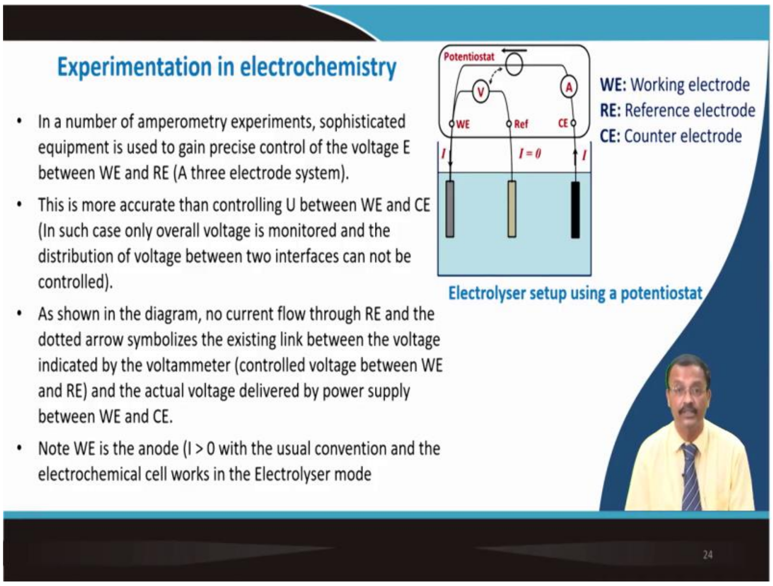

Experimentation in electrochemistry

- In a number of amperometry experiments, sophisticated equipment is used to gain precise control of the voltage E between WE and RE (A three electrode system).
- This is more accurate than controlling U between WE and CE (In such case only overall voltage is monitored and the distribution of voltage between two interfaces can not be controlled).
- As shown in the diagram, no current flow through RE and the dotted arrow symbolizes the existing link between the voltage indicated by the voltammeter (controlled voltage between WE and RE) and the actual voltage delivered by power supply between WE and CE.
- Note WE is the anode (I > 0 with the usual convention and the electrochemical cell works in the Electrolyser mode

WE: Working electrode
RE: Reference electrode
CE: Counter electrode

Electrolyser setup using a potentiostat

So, in a number of amperometry experiments, sophisticated equipments used to gain precise control over the voltage between working and the reference electrode when you are considering a 3 electrode system. This is more accurate than controlling the voltage between working electrode and counter electrode. So, in such case only overall voltage is monitored and the distribution of voltage between two interface cannot be controlled.

So, as you can see in the diagram, no current flow through this reference electrode and the dotted arrow that symbolize the existing link between the voltage, indicated by the volt meter that is a controlled voltage between the working electrode and reference electrode.

And the actual voltage delivered by the power supply between working electrode and counter electrode. So, working electrode is the anode with current is positive with the usual convention and the electrochemical cell works in the electrolyser mode.

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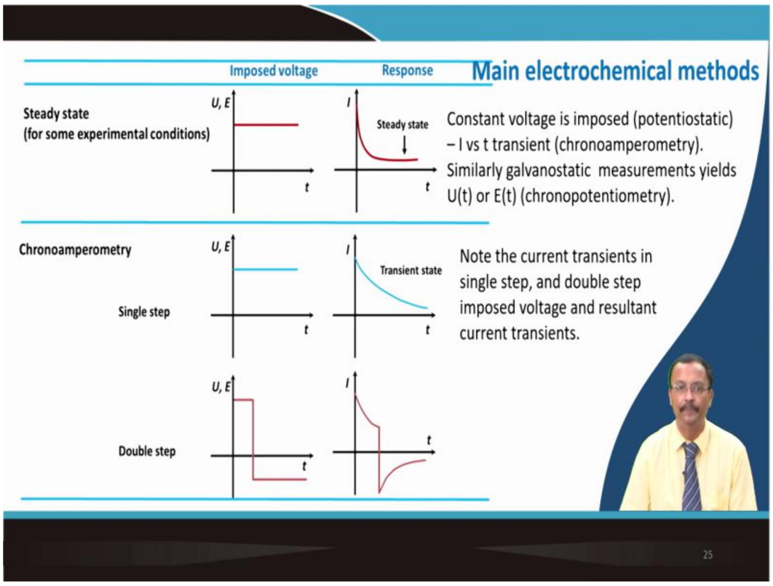

Main electrochemical methods

Steady state
(for some experimental conditions)

Constant voltage is imposed (potentiostatic) – I vs t transient (chronoamperometry). Similarly galvanostatic measurements yields U(t) or E(t) (chronopotentiometry).

Chronoamperometry

Single step

Note the current transients in single step, and double step imposed voltage and resultant current transients.

Double step

So, there are certain key electrochemical methods. So, you apply a constant voltage is imposed which is potentiostatic according to our definition. And I versus t the transient is measured and this is the steady state we call this is chronoamperometry. Similarly, galvanostatic measurement yields U as a function of t or E as a function of t, we call this is a chronopotentiometry.

Then in case of chronoamperometry, note that the current transient is in a single step, and double step imposed voltage and resultant currents transient. So, this is this will be the voltage transient that is either in the single step or in the double step and the current transient, which is a measurable parameter that shows this kind of feature and this is termed as chronoamperometry.

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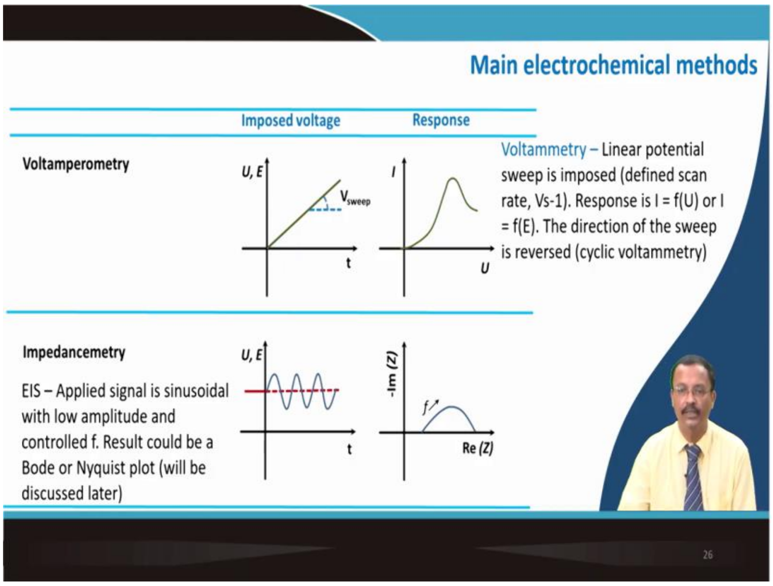

Main electrochemical methods

	Imposed voltage	Response
Voltamperometry		
Impedancemetry EIS – Applied signal is sinusoidal with low amplitude and controlled f. Result could be a Bode or Nyquist plot (will be discussed later)		

Voltammetry – Linear potential sweep is imposed (defined scan rate, Vs-1). Response is I = f(U) or I = f(E). The direction of the sweep is reversed (cyclic voltammetry)

Then, we have volt amperometry or voltammetry. Here a linear potential sweep is imposed defined as a scan wrecked volt per second and response is I that is a function of U of course, and the direction of the switch is reversed in case of cycling voltammetry.

So, this is also a useful measurement for understanding the electrochemical reactions. In case of impedancemetry, applied signal is usually sinusoidal with low amplitude and controlled frequency and result could be either a Bode plot or a Nyquist plot. And this particular thing I will discuss in details in the later part of the course.

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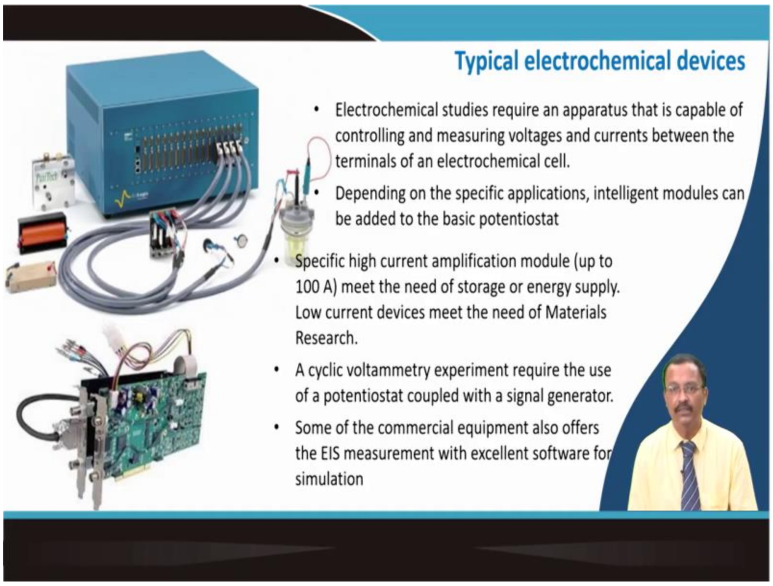

Typical electrochemical devices

- Electrochemical studies require an apparatus that is capable of controlling and measuring voltages and currents between the terminals of an electrochemical cell.
- Depending on the specific applications, intelligent modules can be added to the basic potentiostat
- Specific high current amplification module (up to 100 A) meet the need of storage or energy supply. Low current devices meet the need of Materials Research.
- A cyclic voltammetry experiment require the use of a potentiostat coupled with a signal generator.
- Some of the commercial equipment also offers the EIS measurement with excellent software for simulation

So, typical electrochemical device, this electrochemical studies required an apparatus that is capable of controlling and measuring the voltage and current between the terminals of the electrochemical cell. So, depending on the specific application intelligent modules can be added to the basic potentiostat. Specific current high current application module up to 100 ampere that can meet the need of the storage or energy supply and low current device meet the need of material research.

So, various modular systems are available. A cyclic voltammetry experiments required a potentiostat that is coupled with a signal generator. And some of the commercial equipment also offers the EIS measurement with excellent software for simulation. So, these are the actual equipment that is available in the market to do this various electrochemical measurements.

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REFERENCES

- **C. Lefrou, P. Fabry, J-C. Poignet** Electrochemistry: The basics, with examples, Springer, page 1 – 46 (2012) (Study materials)
- **J.S. Newman** Electrochemical systems, Prentice Hall Inc. (Englewood Cliffs, New Jersey), 2nd Edn. (1991)
- **A.J. Bard, L.R. Faulkner, Electrochemical methods. Fundamentals and applications, John Wiley and Sons (New York) 2nd Edn. 2001**

So, that ends the lecture 1. And the red marked one is your study material, a book by Poignet et al, Electrochemistry: The basics, with examples by Springer, page 1 to 46. And apart from that the book by Newman and A. J. Bard, they are bibles of electrochemistry and you can consider to clarify your fundamental ideas.

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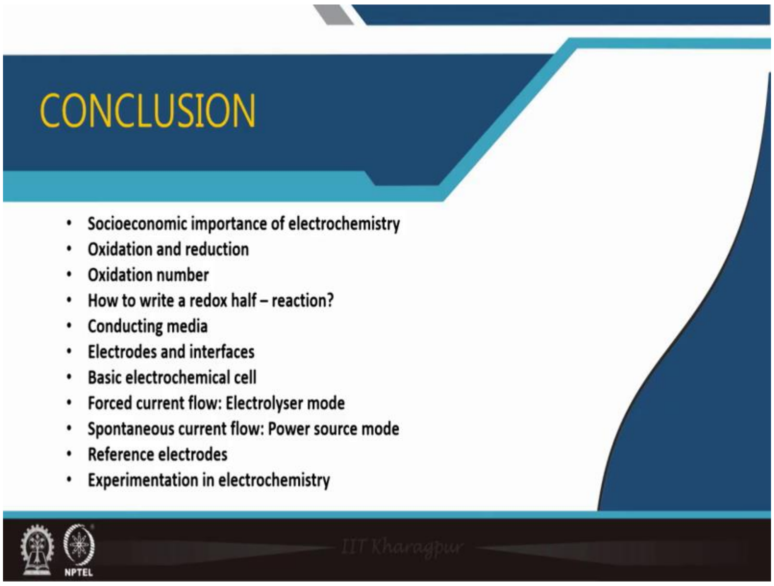

CONCLUSION

- Socioeconomic importance of electrochemistry
- Oxidation and reduction
- Oxidation number
- How to write a redox half – reaction?
- Conducting media
- Electrodes and interfaces
- Basic electrochemical cell
- Forced current flow: Electrolyser mode
- Spontaneous current flow: Power source mode
- Reference electrodes
- Experimentation in electrochemistry

IIT Kharagpur

So, in this particular lecture we covered socioeconomic importance of electrochemistry. Then, we talked about oxidation reduction, then oxidation number, then how to write a redox half reaction, then the concept of conducting media, electrode and interface, then we talked about the basic Daniel electrochemical cell, then we introduce the concept of the force current flow in the electrolyser mode of spontaneous current flow, in the power source mode.

And the reference electrodes, we define three types, major types of reference electrodes and experimentation in electrochemistry we covered.

Thank you for your attention.