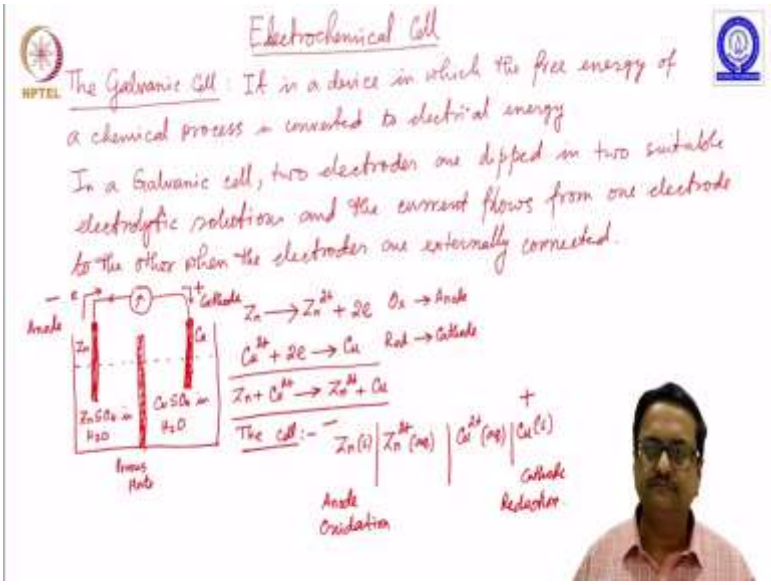
Elementary Electrochemistry
Professor Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali
Electrochemical/Galvanic Cell: Construction of Cell Reactions

Hello everyone. Welcome back to the course entitled Elementary Electrochemistry. In the previous class we discussed about the units of EMF measurement, Arrhenius theory of electrolyte dissociation, concepts of strong and weak electrolytes. So, in this class we are going to learn how to construct a couple of electrochemical cells and one of the important applications of electrolysis which has been running for more than 100 years since its introduction to the industry.

(Refer Slide Time: 01:08)



Today, we are going to first talk about the construction of an electrochemical cell and to start with we will first discuss about the galvanic cell. This galvanic cell is a device in which the free energy of a chemical process is converted to electrical energy. So, in a galvanic cell two electrodes are dipped in two suitable electrolytic solutions and the current flows from one electrode to the other when the electrodes are externally connected.

So, let us consider the Daniell cell as we have started discussing. So, let us first draw how the Daniell cell looks like. We have one electrolytic chamber which is divided into compartments using a semipermeable membrane or porous plate. On one side of the compartment you have a solution of ZnSO4 inverter and on the other side you have CuSO4 inverter. In these two compartments we have dipped two electrodes.

On the left hand side compartment we have a zinc electrode and on the right hand side compartment we have a copper electrode. So, when these two electrodes are externally connected using an emitter which measures the current we see that there is a flow of current in this direction in the outer cell and from zinc to copper in the inner cell which essentially indicates the flow of electron in the opposite direction which means that there is some reaction that is happening at zinc electrode which releases electrons at the electrode.

So, what reaction can happen? Zinc metal can get oxidized to Z n 2 plus and come to solution and release two electrons at the electrode. So, that means here it is oxidation that is taking place. On the other hand, on the right hand side this Cu 2 plus takes two electrons from the electrodes and gets converted to copper metal. So, this is a reduction process that is happening.

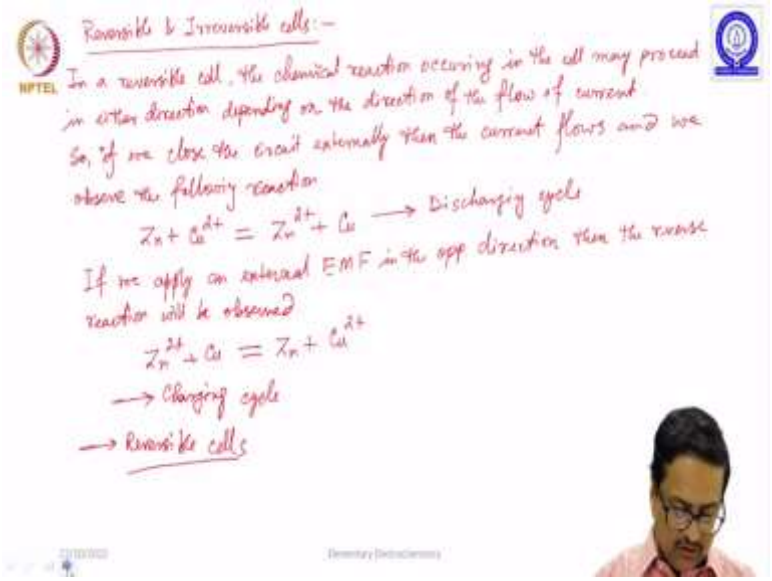
As we all know that the electrode at which oxidation is taking place is called or termed the anode and the electrode at which the reduction is taking place is called the cathode. So, this is besides where it is cathode and this is the anode; the negative side and the positive side of the cell. So, what is the overall cell reaction? Z n plus Cu 2 plus giving me Z n 2 plus plus Cu. So, what does it mean?

That with time this zinc electrode continuously reduces in amount, reduces in weight because zinc is coming in solution as Z n 2 plus and copper is getting deposited from copper sulfate solution as metallic copper by absorbing two electrons from the electrode. So, this is the overall cell reaction that is happening in this Daniell cell. So, instead of drawing this picture in your notebook one can write this cell in a simple one line way.

And this is how one should write the cell. On the left hand side you have zinc solid as electrodes. This zinc solid is in equilibrium with Z n 2 plus in aqueous medium then you have a porous membrane or porous plate which is designated here as a vertical straight line. On the other side you have Cu 2 plus in aqueous medium and then Cu solid as the corresponding electrode.

Remember that the right hand side electrode is plus and left hand side electrode is minus this right hand side is cathode and left hand side is anode as oxidation takes place at anode and reduction takes place at cathode. Hope you are able to understand this.

(Refer Slide Time: 10:08)



So, here we need to learn about a couple of terms which is like the reversible and irreversible cells and what does it mean? That means the some cell is such that if a cell reaction is happening in one direction by applying current in the opposite direction the reaction can be made to proceed in the opposite direction. So, one can state that in a reversible cell the chemical reaction occurring in the cell may proceed in either direction depending on the direction of the flow of current.

That means when you just connects the two electrodes from outside then there is a particular direction in which the current flows, but on the other hand if you connect this battery to a circuit where the current is made to flow in the other direction the opposite reaction happens. So, if we close the circuit externally then the current flows and we observe the following reaction, which reaction?

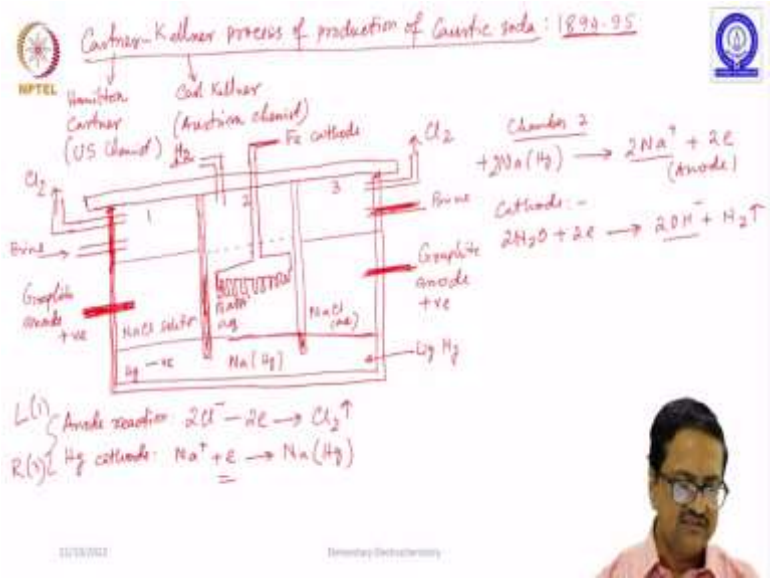
The same cell reaction that we had written in the previous slide that is Z n plus Cu 2 plus giving me Z n 2 plus plus Cu, but if we apply an external EMF. Suppose, we connect a battery or a source of electricity in the external circuit in the opposite direction then the reverse reaction will be observed. So, the reaction will be then Z n 2 plus plus copper we will get Z n plus Cu 2 plus.

So, when we are doing this reverse operation it is the charging cycle and the forward direction is discharging cycle. So, the batteries where this charging and discharging cycles are possible those batteries are called the reversible cells that is the case of various

rechargeable batteries that we use on our daily needs. So, those rechargeable batteries are having this charging and discharging cycles and those are called the reversible cells.

Then the other types of cells which cannot be recharged for example normal batteries that you encounter everyday those batteries cannot be recharged those can only be used only once. So, those kinds of cells in which the reaction cannot be reversed for various reasons are called the irreversible cells.

(Refer Slide Time: 16:30)



So, this method of electrolysis, the concept of electrolysis is a very well known and extremely old process. So, I would like to tell you about one of the very old process or very old applications of electrolysis which was commercialized in 1894-95.

So, this is called the Castner–Kellner process of production of caustic soda. This process was commercialized in 1894-95 in that period. So, here two scientists are involved Castner is Hamilton Castner, he is an US chemist and Kellner is Carl Kellner, an Austrian chemist. So, they established a plant in 1894-95 to produce sodium hydroxide in large scale. So, what did they do?

They set up a very nice electrolytic cell where of course this cell is a very primitive system. So, you can understand the original design if you look at is extremely primitive. So, they made a tank with non reactive stone so that when the chemical reaction is happening inside then the outer walls do not react. So, then they use the liquid mercury as one of the electrodes and then they built the lid in such a way that it is nearly airtight.

And from the lid two partitions are built such that the partitions do not touch the bottom, but it is dipped below the level of mercury. So, what is happening is this liquid mercury is acting as electrode between the chamber 1 and 2 and again between 2 and 3. So, in the chamber 1 they had the graphite anode that is positive on both side and filled the left hand side and the right hand side with solution of sodium chloride which is essentially solution of brine, saturated solution of sodium chloride in water is called brine solution.

So, they made this chamber filled with sodium chloride and the central chamber filled with a dilute solution of sodium hydroxide and then in the middle chamber they had placed one iron electrode which look like a comb, why like a comb? Because they wanted to have a very large surface area for the electrode to work. So, this is the iron cathode and then they made couple of vents or inlet lines.

So, this inlet line is for inlet of brine where as and when required this outlet is to let the gas come out which gas we will see very soon. So, this upper one is to let a gas out and the lower one is to fill brine here, but here one more outlet to take another gas out. So, we can understand that these reaction will take place and some gases will be released. So, what will be the gas that is released.

We have sodium chloride when they were trying to electrolyze sodium chloride the electrolysis, the anode reaction will be the release of chlorine gas 2 Cl minus releasing two electrons will become chlorine gas and will go out. So, on both the anode chamber chlorine gas will come out as a biproduct and in the process what will happen is this side this graphite is your positive electrode and mercury here acts as a negative electrode here.

So, at mercury what is happening is at the Hg cathode N a plus ions are taking up electrons and becoming sodium metal and you know when sodium metal comes in contact with mercury it becomes sodium amalgam. So, then this liquid mercury becomes sodium amalgam and being a liquid the entire places become sodium amalgam. So, this reaction is happening in the left and right side chambers that is chamber number 1 and chamber number 3.

What is happening at the central chamber; chamber number 2? Chamber 2 you have this iron as cathode and the mercury amalgam sodium amalgam N a Hg is your positive electrode be anode. So, at that point this sodium amalgam is getting converted to 2 N a plus and it is releasing two electrons which then is taken up on the other side by sodium to again form the amalgam.

This is happening at the anode and at cathode we are having the hydrolysis of water. 2 H 2 o taking up two electrons generating 2 O H minus and hydrogen gas. So, what is happening is in the central cell the sodium and O H minus ions are forming as a result the concentration of N O H increases drastically here and this produces a strong solution of N O H in this middle chamber.

So, one can tackle from time-to-time bring this especially produced sodium hydroxide from sodium chloride and use it for various applications and this hydrogen gas that is coming out comes out through the vent so that there is a biproduct of chlorine as hydrogen and your target compound that you are taking out is sodium hydroxide very useful chemical in the industry and on a daily application.

So, in this process they were able to produce sodium hydroxide in large quantities with the consumption of electricity. So, this was one of the very early applications of electrolysis in the industrial scale. It was initially developed by Hamilton Castner and it was brought to light that Carl Kellner also arrived at the same reaction in Austria. So, the scientists join hands to form the first industry to produce sodium hydroxide in large scale.

So, I would like to stop here in this lecture and in the next class we will discuss a couple of problems based on what we have discussed till now and then we will proceed for the next part of this course. Thank you.