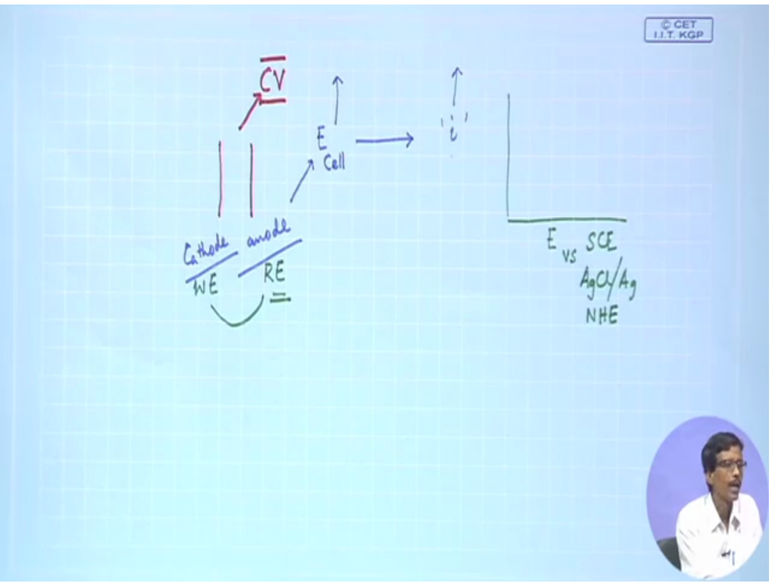
Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module 11
Lecture No 52
Electrochemical Methods 3(Contd)

Hello welcome back where we are discussing the technique which can be abbreviated as CV which is cyclic voltammetry, it is typically known as cyclic process because we scan one potential and then we come back to the original potential that means the 0 potential if we start from the 0th level. So how we measure this thing and 2 already we have defined, one is your working electrode, another is your reference electrode and as we all know that when we construct a half cell and that if we consider that consideration of this half cell we need one electrode and when we get the other electrode so you have the corresponding values for the cathode and anode.

(Refer Slide Time: 1:17)

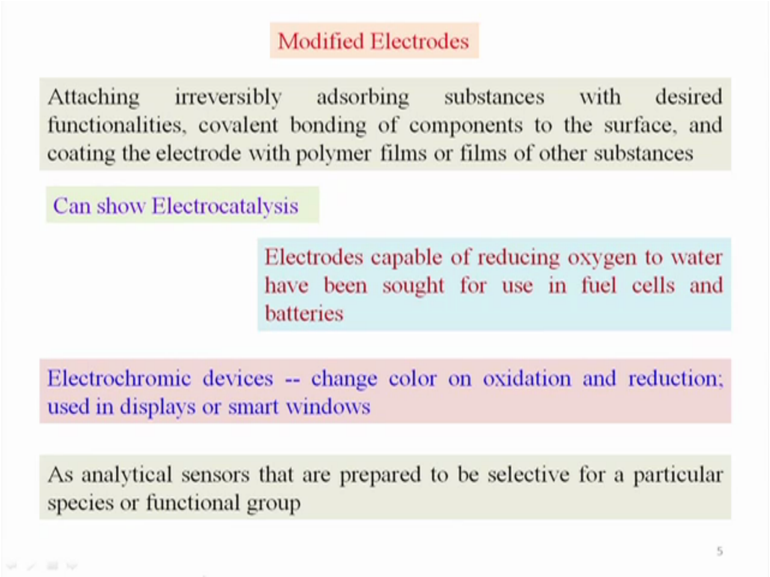


So one is cathode and one is anode and we all know from the corresponding difference that means the E right – E left will give you the corresponding potential for the E cell so these were all very much useful for your potentiometric measurement for many measures the E values. Now we are trying to measure the ‘i’ values, the current we are measuring and this current also not at constant potential what we have seen for the corresponding one for the charge transfer that charge is being carried out for your coulometric estimation also which is potentiostatic that means it will have the fixed potential. Now this will vary, this will vary so it is typically a continuous process that is why this technique is very useful that your potential will vary and with respect to that variation in the potential how we can determine the corresponding change in your current.

So that the change in the current is very much required to have that particular type of plot, so current versus potential we will be plotting so these 2 electrodes we have so cathode and anode. And if we consider that okay fine we have 2 electrode system and we know that it can be within the cell, you have the cell outside and if you consider that one of them will be working electrode and another will be your reference electrode. But to do so to know that corresponding potential of the working electrode should be monitored because whatever we flawed and whatever we get as the plot because this particular plot we will be getting and your E will be there.

And E is basically the corresponding potential versus something, it can be respect to your (()) (3:14) electrode or the corresponding silver chloride silver electrode or you can directly consider it for normal hydrogen electrode. So you have to scan this potential with respect to this that means these 2 are engaged so working electrode is engaged with RE to get this particular potential of this E,. And one of the conditions we imposed in our previous class that we should not pass current to this reference electrode, so how to short-circuit the situation how to pass the entire current through the cell without taking the help of your reference electrode and these 2 electrode combination.

(Refer Slide Time: 4:20)



Modified Electrodes

Attaching irreversibly adsorbing substances with desired functionalities, covalent bonding of components to the surface, and coating the electrode with polymer films or films of other substances

Can show Electrocatalysis

Electrodes capable of reducing oxygen to water have been sought for use in fuel cells and batteries

Electrochromic devices -- change color on oxidation and reduction; used in displays or smart windows

As analytical sensors that are prepared to be selective for a particular species or functional group

So we have to have something that means we can whether we can bring another electrode or some other arrangement that we will see. Before seeing all these things what we can see also that how we can modify these electrodes for your cyclic voltammetric measurements. So modification of electrodes can be done in all different ways, one such modification is there based on the miniaturisation that means making electrodes to a very small one like a needle like electrode.

If we can have a needle and that the size of the needle is only several micrometres or nanometres or picometers so that needle can be inserted on your hand also and it can reach to your blood level also and is you can monitor externally with something so that can be your typical needle like microelectrodes which can be useful for handling your biological samples like serum or blood. So that we will discuss when we will talk in terms of your bioelectric chemistry but here we will see that how we can modify the surfaces, the electrode is small it can be your microelectrode but still we can go for the modification on the surface.

So irresistibly the absorbing substances with desired functionalities so you have the absorption and you attach something such that your absorption will be more or sometimes bonding of component to the substance that means the substance the molecule what we are looking for their electro-activity can be attached covalently to the electrode surface. And we know that we can have a gold electrode also, the gold surface is very much known for its attachment to the thiols the sulphur groups, so you can have a monolayer of molecules sulphur bearing compounds on the gold surface that we call sometime as self assembled monolayer that is a very small or thin layer and we call it as a monolayer which we can consider as SAM.

So self assembled mono-layering is possible on the surface and sometimes we can coat the electrodes also with polymer film when is your electrode is dipped into the polymer and with some times with some other substances. That means you can have any Teflon bid or any carbon bid or a carbon disc and you can modify the surfaces with some absorption or molecules or some other good species like what we try to measure for that electro activity because what we require is that this particular attachment of the molecules, the molecule itself is not as functioning as a catalyst but it can source on electron transfer catalyst through a mediator like arrangement or a mediator like behaviour.

That means through this attachment and if you put some potential to the electrode that molecule which is attaching to this particular electrode can so either oxidation or reduction that means it can go for electron transfer reaction and as a result it can show sometime the electro catalysis that means the catalytic cycle which is attached to the particular molecule or other species which is attached to the electrode through some polymer film or anything else. So there are also that is why some electrodes that we will see also that sensors because this designing this electrodes are very much useful and you can have some good electrodes because we just now discussed that hanging marker electrode on the dropping electrode.

So the dropping marker or your hanging marker electrodes have been discarded from the very inception by the corresponding polarographic technique has been modified to go for carbon type electrodes solid electrodes, solid state electrodes, carbon electrodes, platinum electrode, graphite electrode and all this. So if you have electrode which can be useful for reducing oxygen to water can be used in fuel cells and batteries also. So one challenge is that how you produce oxygen from water but this is a reversible one where we can have oxygen from air any other source and that oxygen can be reduced for a 4 electron reduction state to get water molecule and that particular one can be useful for the methodology is that we will see that fuel cells or in batteries.

And extension of that we will also see that the microbes can be useful, the microbes can give rise to the energy which can be termed as microbial fuel cells MFS microbial fuel cell that we will see afterwards in our next class probably that how we can use this as fuel cell and sometimes that batteries and all because these microbes what is formed in water can be river water, can be seawater or any stagnant water and that microbes or this microorganisms can be given you the corresponding energy in terms of electron transfer giving rise to burning of the carbonaceous matter to carbon dioxide and water and cap give energy to your fuel cell.

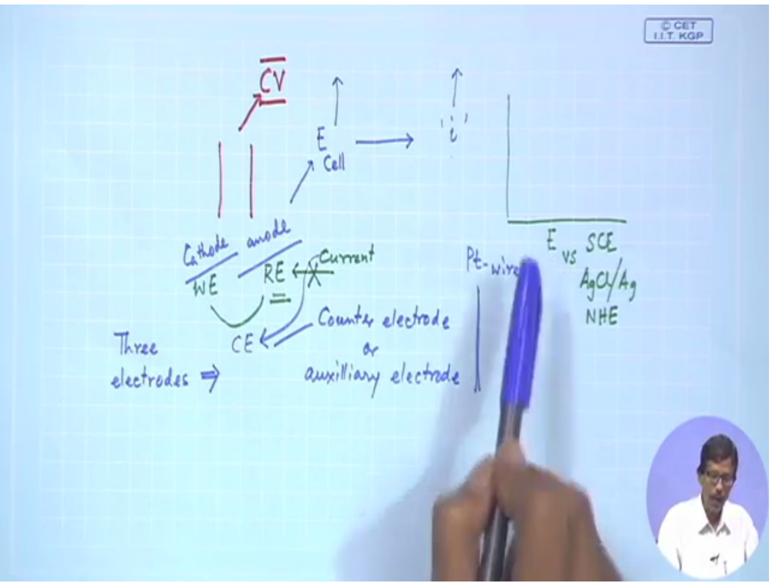
And sometimes these electrodes can be also useful for making Electrochromic devices, what electrochromic? The chrome we know that is the change in colour due to electron transfer so electron + chrome chroming that means the colour change, so electrochromic devices are nothing but it can give rise to the change in colour due to oxidation or reduction of the material and we can have some displays that means if you change the corresponding potential of that particular display it changes its colour that we see nowadays that electronic display boards or billboards we call, so those change colour depending upon the corresponding electron transfer reaction whether it is going for oxidation or reduction and some smart windows that means darkening of the window when you have to seal the typical entry of the daylights.

So this will be very much useful but there within that particular window or the Billboard you have the typical electrodes and because all these are has been miniaturised that electrodes you have in terms of your working electrodes or in terms of some filament that we get in light. So these electrodes can be charged with the corresponding potential and we see some change in terms of its colour or in terms of its darkening. So we try to develop the these electrodes also analytical sensors, sometimes this can also be considered as bioanalytical sensor, how we can prepare those? For particular specimen or functional groups we can attach and this can be very much useful for sensing some analyte.

Suppose we try to develop a glucose sensor so how we develop that particular glucose sensor so we must have attachment for something a particular species or functional group or sometimes enzyme. It is the enzyme which we know as the glucose oxidised so if you are able to attach that glucose oxidised to this particular electrode that will be functional in terms of electron transfer to the glucose molecule such that the glucose molecule can be oxidised to gluconic acid and we can have something that if we use oxygen for its oxidation that oxygen that means that the oxygen molecule here we have seen the electrodes capable of reducing oxygen. So this thing here (())(12:17) sensors which is your glucose sensor, so here we are reducing oxygen it can be sensing oxygen that we know that the oxygen sensors are also available.

So for one point it is oxygen sensor and another point it is a corresponding glucose sensor so we can develop these analytical sensors in that way that glucose can be sensed by the electrodes where you have the corresponding glucose oxidising enzymes is present and we will be producing here not water, we will be producing here hydrogen peroxide H2O2. So production of that hydrogen peroxide can be sensed by this electrochemical technique.

(Refer Slide Time: 13:06)

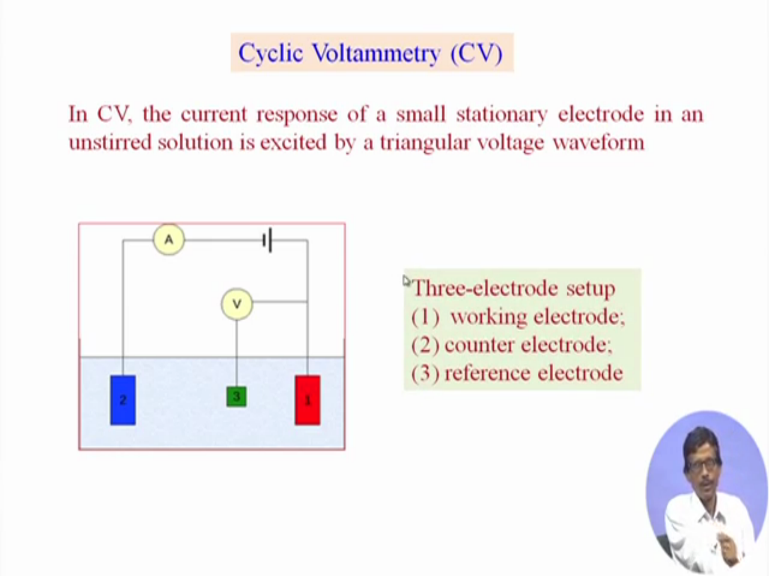


So what we see now that how we get the CV that means the cyclic voltammetry how we measure, how we record and what are the corresponding cell arrangement for this. So as we were started our discussion there are 2 electrodes, one is working electrode and the reference electrode is not sufficient so we must bring something over here for getting CV, we need 3 electrodes so you will have a system which is having 3 electrodes. So already we have working electrodes, the reference electrode now will bring the third one as your counter electrode or auxiliary electrode.

So it will be counter electrode or auxiliary electrode as we basically what we discuss that and we promised that we will not allow to pass any electron or any charge or any current to pass through the reference electrode because that way it will not be if we pass current through reference electrode the meaning of using reference electrode to monitor the working electrode potential would be meaningless. So we will not allow any current, now we are bringing counter electrode so this will be the (())(14:37) basically to allow this particular current to pass through this electrode. So this auxiliary electrode or counter electrode it can be a simple platinum wire sometime a simple platinum wire which is dipped inside the particular cell or the electrochemical cell.

So the entire current will be passed through your counter electrode for this type of measurement so we can measure the current as well as we can measure the potential, now we will see how we can plot that and how the arrangement is in terms of the corresponding placement of the electrodes what is written in the different books and all the information about we gathered from any other sources.

(Refer Slide Time: 15:26)



Cyclic Voltammetry (CV)

In CV, the current response of a small stationary electrode in an unstirred solution is excited by a triangular voltage waveform

Three-electrode setup
(1) working electrode;
(2) counter electrode;
(3) reference electrode

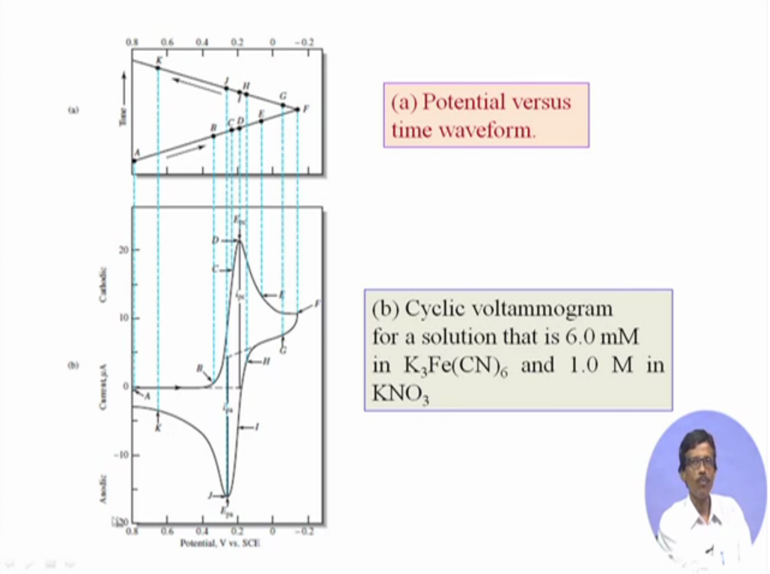
So CV is nothing but a current response of small stationary electrode in an unstirred solution, so these are the basic conditions that solution should not be stirred is not agitated whatever they are in the rest state that means unstirred solution, initially you can stir the solution we will stir basically we will stir for half a minute or a minute then we stop the stirring then we switch on the thing for measurement. So unstirred solution is that and is getting the corresponding excitation from the waveform as we have discussed already, we categorise the thing as triangular voltage waveform. So the triangular waveform is required and this is the connection we have, what we have? We have electrode 1, electrode 2 and electrode 3.

So that gives rise to the corresponding to electrode system for cyclic voltammetric measurement so this is most important thing that you can given this typical block diagram for that also and you can be asked to level the different parts which is A, which is V and what are the 3 electrodes and where the corresponding external source for the measurement is available because everything is your electrochemical cell that means you require the voltage from here from external source. So as the diagram tells this is A and V and basically what we will be looking for also do not forget this also that current is nothing but your A and V is your potential.

So sometimes not only we consider is as the current voltage plot or current potential plot you can consider as the current voltage plot, also we can consider as A-V plot or also we can consider as i-E plot so these are the names for your CV we can have for these plots anything can be asked to you, you should be very much careful at this point that it is the current potential plot, current voltage plot, A-V plot this corresponding i-E plot. So what we get therefore that 3 electrodes and 2 measurements. So is typically a 3 electrodes setup you have where number 1 is your working electrode so working electrode is directly attaching to your source but is also giving rise to the connection for your measurement or your potential, so you have the corresponding one is your 3.

So as I told you that the working electrode is measuring your potential A is being measured or V is being measured so V is being measured. So as I just say that working electrode is responsible for the measurement of V so this is one such circuit then we require this third one is for your reference electrode so reference electrode and working electrode is measuring your potential and the counter electrode and your working electrode and this is also connected so this is one circuit and this is another circuit, this is your solution. So within the solution you dip 1, you dip 2 and you dip 3 so all 3 electrodes are inserted within the solution which is electroactive in nature and you have 2 electrical circuits.

(Refer Slide Time: 19:34)



(a) Potential versus time waveform.

(b) Cyclic voltammogram for a solution that is 6.0 mM in $K_3Fe(CN)_6$ and 1.0 M in KNO_3

So 3 electrodes and 2 electrical circuit you require, one circuit is measuring your potential that means the voltage V and another circuit is measuring your current A or i so that is the most important technique what we can have and output what we get is like this and any standard textbook have this sort of plot because this is well-known plot for your cyclic voltammetric measurements and this typical cyclic voltammetric measurement what you can have is very important because point wise we can have, is not that you recorded the data like your potentiometric titration because this is also you can consider as some sort of titrimetric method when you have only linear sweep you get up to this point F only so up to this point you get only one sided thing that means whether your system is oxidised or your system is reduced.

So this particular waveform which is not a triangular one, it is a linear waveform can give rise to a response from A to F, so is A to F so this is your linear sweep linear scan, you get A, B, C, D, E and F. So what you see? You see that corresponding one that means with respect to the time what basically the instrument is looking for us, instrument is measuring for us instrument is measuring for us is nothing but your corresponding measurement of your potential with respect to time because what instrument is giving we get the corresponding one we know that the Potentiostat as well as the Galvanostat is in there in the current. So the combination of these things based on complicated not much complicated nowadays, we will say very basic electronic parts on operational amplifiers.

So operational amplifiers are making our life easy such that we have automated instruments and these automated instruments are also giving advantage by measuring all these in computers, so computer terminal is fine to record this (())(21:39) earlier we were using X-Y recorders or oscilloscopes for those measurements. So here what we find that this typical measurement so when we move from A to B, that the linear switch is like that, so when you move from A to B is not changing much. So the potential what we are going from B to C because A to B is a very long scan but B to C is not very much but you see the current is increasing like anything, B to C and C to D so this particular range, the whole current is increasing but your waveform or potential is changing linearly.

So if we get this for this particular type of scan A to D we will be getting so D will at D will be reaching the maxima. So the maximum what we are reaching for the plot is D then as it is scanning tell F your current is decreasing so is basically the corresponding thing that some electrode processes are taking place that means the available concentration on the electrodes surface which is electroactive as all will reduce if we consider or all will oxidise. So if we consider that this is the corresponding potential for your oxidation or the reduction but if it is a corresponding one for your value what we see is your cathodic peak potential so cathodic peak potential is for your reduction.

So if you get that as reduction potential so you get the immediate reduction so everything will be exhausted so no more reduction so your current will decrease in this fashion that means a typical Gaussian step of decaying is there till you reach the endpoint F where we automatically the machine will switch off to go for a cyclic process that means A to F is the maximum one, maximum 1 is nothing but + 0.8 to – 0.14, this is – 0.14. So as your potentially scanning + 0.8 to – 0.14 we get the response so the upper part of the plot we get, so as we go back again to again that starting potential of 0.8 volts.

So going to the starting potential of 0.8 volt what we get that your thing will not change and again we have the points but now the points are marked differently, one is as G so when it is G the time potential plot will give you the corresponding time, the potential current plot G will come over here then you have H, I, J and then K. So the whole cyclic process is completed and we get this particular plot and how we use to extract of the information out of this plot that we will see and this one the plot has we have discussed that what sort of waveform you put to the electrodes system is a 3 electrodes system and the corresponding potential watt is being applied to all these electrodes particularly the working electrode.

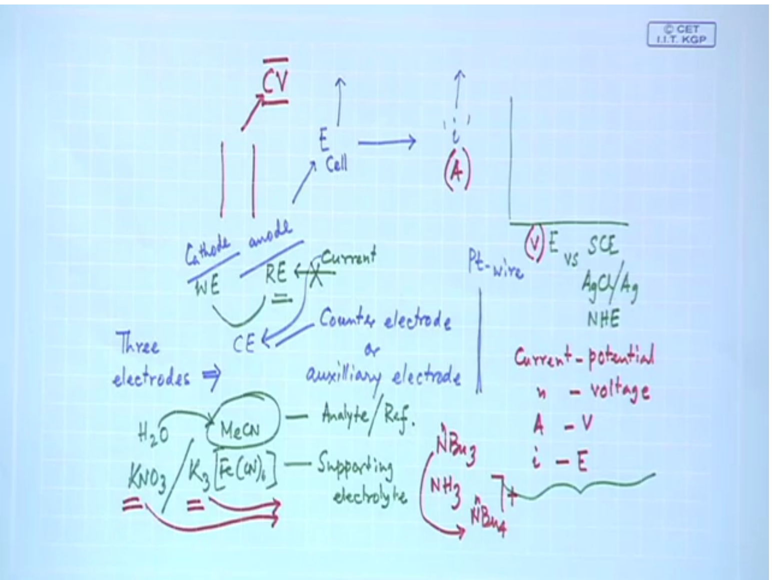
Now this potential is applied to your working electrode with respect to the reference electrode so potential versus time waveform is looked like this and we have the cyclic voltammogram. So this is the typical cyclic voltammogram of a very small concentration of potassium ferricyanide, so this is a 6 millimolar concentration of potassium ferricyanide what you have in your hand and that 6 millimolar solution that means 6 into 10 to the power – 3 molar solution and usually we go for simply the millimolar concentration so you see that millimolar concentration and the cell volume is also very less because we require a very small concentration of this material because the cell volume is only 10ml sometimes it can go down to 5 ml even 1ml.

So solution volume of 10 ml is fine so then your required concentration to get this concentration of 6 millimolar you can find out so how small concentration of potassium ferricyanide you require to get this response and all this information related to a very electroactive species because ferricyanide is a standard material for our reference material. Once instrument is installed, if you install a new instrument the first thing what your will ask you that you give me some amount of some reference material. So this material is available for any lab for any school lab any college lab or university lab or any other institutional lab ferricyanide is a cheap molecule, you have this particular lab materials. So this is your say standard material that is no need to have any costly material to standardise their thing.

But thing is that initially what you are establishing is that we are establishing everything whatever is written over there one thing is missing is not written over them is your medium of measurement, what is the solvent. So since it is a potassium salt as we all know that most of the potassium and sodium salts are highly soluble in water, so definitely it will be in water. So the measurement is taken in water and you should always be careful about all this information all this very small information because the voltammogram is shown is levelled with nicely with the material and is other thing which is attached to that and one thing is missing sometimes it can be deliberately missed to test your eyes, test your information, test your understanding that whether you can see that a voltammogram is doing only on the solution because it can be done on the solid-state also.

But right now what we are doing in solution is so the solution technique and we are inserting everything in solution in the electrochemical cell in starting these 3 electrodes. So one is in the many molar range of 6 concentration millimolar 6 millimolar concentration of your electroactive species which is potassium ferricyanide. Along with that we add one molar of potassium nitrate so you see the times of concentration what you require to add for the measurement is your potassium nitrate concentration so this potassium nitrate concentration is known as supporting electrolyte when you go for your measurement in water medium or aqua medium.

(Refer Slide Time: 30:13)



So not that the entire thing that means the electrolyte you require because the medium should be sufficiently conducting electro-conducting so that is why we being this one as supporting electrolyte to carry the electronic charge entirely by this, not by your electroactive species potassium ferricyanide. So always we require a supporting electrolyte and the analyte so what you have the supporting electrolyte and the analyte concentration but if you go since the medium is not told to you so what you do that if you go from water and if I want to measure this in some non-aqua medium which is acetonitrile MeCN. So in MeCN also you can have some compound which is your analyte or the reference material to test the machine to see the corresponding response and the supporting electrolyte.

So since it was K3 efficient whole 6 and we all know this is soluble in water because this is potassium salt and the supporting electrolyte is KNO3. So what synthetic manipulation you can understand, you can think of to go for similar type of compounds which can be soluble in your non-aqua medium which is acetonitrile. So very simple thing that as I told you as I was mentioning that it is the potassium salt, the solubility of these salts in water medium is responsible for your potassium salt. So if you are able to change these potassium salts by cationic part organic cationic part, it should be soluble in MeCN.

So what organic part we can think of, we can think of the typical organic base like NBu is the motile group so N instead of NH3 we have NH, so NR so NR3 is tributylamine like ammonia then you can make some cation of it which is NBu4 which is normal Butyle and which is definitely a cationic so tetra butyl ammonium ion. What you require is your tetra butyl ammonium ion and that tetra butyl ammonium ion can replace these potassium ions so you get the corresponding tetra butyl ammonium salt of ferricyanide and the tetra futile ammonium salt of nitrate that can be very easily useful for your analyte or the reference material or your supporting electrolyte for your cyclic voltammetric measurement.

So we measure all this and the potential waveform we can correlate with all these points and what we see that this can be very much useful for your understanding of the medium as well as the relative concentration of the material or the analyte as well as the supporting material. So anywhere you can apply this particular thing it should be able to indicate that this is the corresponding process of cyclic voltamatric measurement and you start from here A you start from year so that is why this arrow is shown to you so this is your scan direction so you have to give the arrow all the time not only the forward direction but also sometimes give the backward direction so we are ending.

So we start from A and we end to K with respect to the time it is A and we are ending K to again 2 0 so that gives rise to a typical cyclic process but is electroactive so next day we will be considering from here basically that what are these IPC IPA and how we measure how we get the right information what we are looking for the most important information is your E 0 value or the E r value for the process for the electroactive species which is undergoing oxidation or the reduction, thank you very much.